

JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN
INSTITUT FÜR ANORGANISCHE UND ANALYTISCHE CHEMIE



**SYNTHETIC AND MECHANISTIC INVESTIGATIONS OF DIOXYGEN
ACTIVATION ON COBALT-COMPLEXES**

Inaugural-Dissertation

zur Erlangung des Doktorgrades der Naturwissenschaften im Fachbereich Biologie
und Chemie der Justus-Liebig-Universität Gießen

vorgelegt von

Jörg Müller

aus

Gießen

Erstgutachter:	Prof. Dr. S. Schindler
Zweitgutachter:	Prof. Dr. R. Göttlich
Abgabe der Dissertation im Prüfungsamt:	31.01.2011
Tag der mündlichen Prüfung:	04.03.2011

***Die Natur ist so gemacht, daß sie verstanden werden kann.
Oder vielleicht sollte ich richtiger sagen, unser Denken ist so gemacht,
daß es die Natur verstehen kann.***

Werner Heisenberg

(1901 - 1976)

For my family

Acknowledgements

The work described in this doctoral thesis has been carried out between October 2005 and November 2010 at the Institute of Inorganic and Analytical Chemistry at the Justus Liebig University Gießen under the supervision of Prof. Dr. Siegfried Schindler.

At this place I would like to thank my supervisor Prof. Dr. Siegfried Schindler for his support, his patience and guidance during these years.

Furthermore, I wish to thank my colleagues and lab mates Dr. Anja Henss, Dr. Sabrina Turba, Sandra Kisslinger, Alexander Beitat, Dr. Thomas Nebe, Dr. Christian Würtele, Tobias Hoppe, Lars Valentin, Prof. Dr. Jing-Yuan Xu, Dr. Ildikó Kerezsi, Dr. Jörg Astner, Jenny Blank, Melanie Jopp, Sabrina Schäfer, Janine Will, Janine Cappell, Janina Heck, Natascha Kempf, Sabine Löw, Jonathan Becker, Cornelius Brombach, and Stefan Schaub for their friendship and encouragement.

I would like to express my gratitude to Dipl. Chem. A. Beitat, Dr. C. Würtele, Dr. O. Walter and Dr. M. Serafin for their kindly support with the X-ray crystallographic studies.

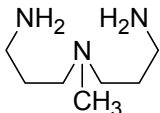
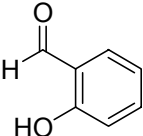
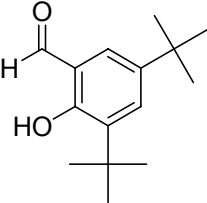
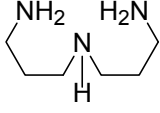
Furthermore, I would like to thank the people of the Institute of Inorganic and Analytic Chemistry, and the people of the Institute of Organic Chemistry at the Justus Liebig University Gießen for their support of my work.

My warmest thanks go to my friends and colleagues in our research group. You made the laboratory more than just a working place.

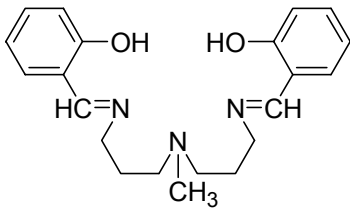
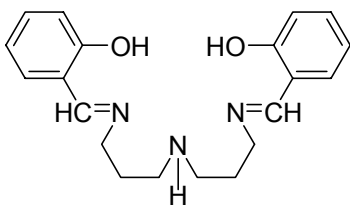
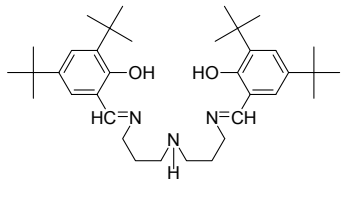
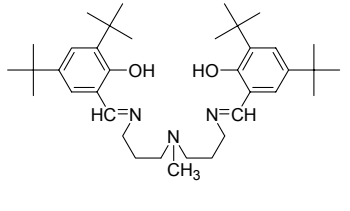
I would like to thank my close friends outside the university.

Surely, I would also like to thank my family for their support during all these years.

Used Precursors, Ligands and Complexes

Name	Formula	Structure	Molar Mass [g/mol]
<i>N</i> -methyl- <i>N,N'</i> -bis(3-aminopropyl)-amine	C₇H₁₉N₃		145.25
2-Hydroxy-benzaldehyde (Salicylaldehyde)	C₇H₆O₂		122.12
3,5-Di- <i>tert</i> -butyl-2-hydroxy-benzaldehyde	C₁₅H₂₂O₂		234.33
<i>N,N'</i> -bis(3-aminopropyl)-amine	C₆H₁₇N₃		131.22

USED PRECURSORS AND LIGANDS

<p>Bis[3-(salicylideneimino)-propyl]methylamine</p> <p>salmdptH₂</p>	<p>C₂₁H₂₇N₃O₂</p>		<p>353.46</p>
<p>Bis[3-(salicylideneimino)-propyl]amine</p> <p>saldptH₂</p>	<p>C₂₀H₂₅N₃O₂</p>		<p>339.43</p>
<p>Bis[3-(3,5-Di-<i>tert</i>-butyl-salicylideneimino)-propyl]amine</p> <p>3,5-Di-<i>tert</i>-butyl-saldptH₂</p>	<p>C₃₆H₅₇N₃O₂</p>		<p>563.86</p>
<p>Bis[3-(3,5-Di-<i>tert</i>-butyl-salicylideneimino)-propyl]methylamine</p> <p>3,5-Di-<i>tert</i>-butyl-salmdptH₂</p>	<p>C₃₇H₅₉N₃O₂</p>		<p>577.88</p>

Abbreviations

d	Doublet (NMR)
δ	chemical shift in ppm (NMR)
THF	Tetrahydrofuran
e. g.	for example (Latin: <i>exempli gratia</i>)
IR	Infrared
m	Multiplet
MeOH	Methanol
CH ₂ Cl ₂	Dichloromethane
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
RT	Room temperature
s	Singlet (NMR)
t	Triplet (NMR)
UV/Vis	Ultraviolet-visible

Table of Contents

Acknowledgements	I
Used Precursors, Ligands and Complexes	II
Abbreviations.....	IV
Table of Contents	V
Table of Figures	X
Tables	XV
Table of Schemes	XVIII
1 Introduction	1
1.1 Motivation	1
1.2 The Element Cobalt	2
1.3 Cobalt in Biology	2
1.4 Hemoglobin.....	4
1.5 Cobalt-Oxygen Complexes	5
1.5.1 Dioxygen	5
1.5.2 Cobalt Salen	6
1.6 Properties and Reactivity of the Cobalt(II) and Cobalt(III) Complexes of [Co(saldpt)] and its Derivatives	7
1.6.1 Crystal Structure of the Cobalt(III) Peroxido Complex of [Co(saldpt)]	8
1.6.2 Crystal Structure of the Cobalt(II) Complex [Co(salmdpt)]	9
1.6.3 Crystal Structure of the Cobalt(III) Superoxido Complex of [Co(salmdpt)]	10
1.6.4 Crystal Structure of the Cobalt(III) Superoxido Complex of [Co(saSiMedpt)O ₂].	11
1.6.5 Further Cobalt “Dioxygen Adduct” Complexes.....	12

TABLE OF CONTENTS

1.7	Nitrogen Monoxide Complexes	13
1.7.1	Nitrogen Monoxide	13
1.7.2	Crystal and Molecular Structure of <i>N,N</i> -Ethylene-bis-(salicylideneiminato)-nitrosylcobalt(III) [Co(salen)NO]	14
1.8	Projects	15
1.8.1	Cobalt Complexes with Schiff Base Ligands	16
2	Cobalt Superoxido Complexes	17
2.1	Crystal Structures of [Co(salmdpt)] from Nitrile Solvents	17
2.1.1	Crystal Structure of [Co(salmdpt)] from Acetonitrile	17
2.1.2	Crystal Structure of [Co(salmdpt)] from Butyronitrile	20
2.1.3	Benzonitrile as Solvent in an Attempt to Prepare the Superoxido Complex of [Co(salmdpt)]	22
2.2	Crystal Structure of [Co(salmdpt)] from Dichloromethane	24
2.3	Crystal Structure of [Co(salmdpt)] from Toluene	26
2.4	Synthesis of [Co(salmdpt)O ₂] from Benzene	30
2.4.1	Results of the IR Spectroscopic Analysis of [Co(salmdpt)O ₂] from Benzene ..	30
2.5	Cobalt(II) Complexes with Derivatives of SaldptH ₂ and a SalmdptH ₂ as Ligands	33
2.5.1	Results of the X-ray Crystallographic Analysis of [Co(3,5-Di- <i>tert</i> -butyl-saldpt)O ₂] from Acetonitrile	33
2.5.2	Results of the X-ray Crystallographic Analysis of [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone	37
2.6	Experimental Section	41
2.6.1	Materials and Techniques	41
2.6.2	Physical Measurements	41
2.6.3	Syntheses	42

TABLE OF CONTENTS

3	Synthesis and Properties of a Cobalt Cyanido Complex	45
3.1	Transformation of Nitrile to Cyanide and Aldehyde Using a Cobalt(II) Complex and Dioxygen	45
3.1.1	Experimental Section	48
3.2	Selected Parts of Supporting Information and Unpublished Results for Chapter 3.1	50
3.2.1	Results of the ^1H NMR Analysis of Propionaldehyde	50
3.2.2	Results of the GC-MS Analysis of Butyronitrile and Propionaldehyde	50
3.2.3	Results of the X-ray Crystallographic Analysis of $[\text{Co}(\text{salmcpt})\text{CN}]$ from Acetonitrile	52
3.2.4	Results of the X-ray Crystallographic Analysis of $[\text{Co}(\text{salmcpt})\text{OH}]$ from Toluene	54
3.3	Experimental Section	57
3.3.1	Materials and Techniques	57
3.3.2	Physical Measurements	57
4	End-on Cobalt Superoxido Complexes in Organic Synthesis	58
4.1	Introduction	58
4.2	Results	60
4.2.1	Reaction of Butyronitrile with $[\text{Co}(\text{salmcpt})]$ in Toluene	60
4.2.2	Experiments with Hydrogen Peroxide as Oxidant	61
4.2.3	Reactions of 3-Adamantane-1-yl-propionitrile with $[\text{Co}(\text{salmcpt})]$ in Toluene..	61
4.2.4	Reactions of 3-[3-(2-Cyano-ethyl)-adamantane-1-yl]-propionitrile with $[\text{Co}(\text{salmcpt})]$ in Toluene	62
4.3	Experimental Section	62
4.3.1	Materials and Techniques	62
4.3.2	Physical Measurements	63

TABLE OF CONTENTS

4.3.3	Syntheses	63
5	Cobalt Nitrogen Oxide Complexes	65
5.1	Crystal Structure of [Co(salmdpt)NO] from Dichloromethane	65
5.1.1	IR Spectra of [Co(salmdpt)NO] from Dichloromethane	68
5.2	Experimental Section	70
5.2.1	Materials and Techniques	70
5.2.2	Physical Measurements	70
5.2.3	Syntheses	70
6	Attempts to Isolate and Characterize a Cobalt Oxido Complex.....	72
6.1	Crystal Structure of [Co(salmdpt)NO ₂] from Acetonitrile	72
6.1.1	IR Spectra of [Co(salmdpt)NO ₂] from Acetonitrile	75
6.2	Crystal Structure of [Co(salmdpt)NO ₂] from Methanol	76
6.2.1	IR Spectra of [Co(salmdpt)NO ₂] from Methanol	80
6.3	Nitrate Complexes of [Co(salmdpt)]	81
6.4	Ozonolysis	85
6.4.1	Reactions of [Co(salmdpt)] with Ozone.....	85
6.5	Experimental Section	87
6.5.1	Materials and Techniques	87
6.5.2	Physical Measurements	87
6.5.3	Syntheses	88
7	Summary.....	90
8	Zusammenfassung	95
	List of Crystal Structures.....	101

TABLE OF CONTENTS

Publication	104
Presentations	104
9 Curriculum Vitae	105
10 Bibliography	107

Table of Figures

Chapter 1

Figure 1-1: Structure of Cobalamines Coenzyme B12 R = 5'-Desoxyadenosyl; Cyanidocobalamine R = CN; Hydroxycobalamine R = OH; Methylcobalamine R = CH ₃	3
Figure 1-2: Oxygen Binding on Ironporphyrine (Desoxy-Form and Oxy-Form) ^[2]	4
Figure 1-3: The Cobalt Salen Complex ^[35]	6
Figure 1-4: ChemDraw Plot of the Ligands saldpH ₂ /salmdpH ₂ and their Cobalt(II) . Complexes.....	8
Figure 1-5: Coordination of the Cobalt Atoms Stereoscopic of [Co(saldpt)O ₂]	8
Figure 1-6: Stereoscopic View of the Structure of [Co(saldpt)O ₂].....	9
Figure 1-7: Ortep Plot of [Co(salmdpt)] in Benzene (Monoclinic Crystal Symmetry)	9
Figure 1-8: Ortep Plot of the Oxygenated and Non-Oxygenated Molecule.....	10
Figure 1-9: Crystal Package of [Co(salmdpt)] ₂ ·O ₂ ·2C ₆ H ₆	11
Figure 1-10 Crystal Structure of [Co(salSiMedpt)O ₂].....	12
Figure 1-11: Samples of Characterized Cobalt Oxygen Adduct Complexes	13
Figure 1-12: Illustration of Limiting Cases of NO Binding to a Metalloporphyrin Center as (a) the Nitrosyl Cation (NO ⁺) or (b) the Nitroxyl Anion (NO ⁻)	14
Figure 1-13: Ortep Plot of <i>N,N</i> -Ethylene-bis-(salicylideneiminato)-nitrosylcobalt(II) [Co(salen)NO].....	15

Chapter 2

Figure 2-1: Ortep Plot of [Co(salmdpt)] from Acetonitrile.....	18
Figure 2-2: Ortep Plot of [Co(salmdpt)] from Butyronitrile.....	20
Figure 2-3: ¹ H NMR (200 MHz, CDCl ₃) of Benzamide.....	22
Figure 2-4: IR Spectrum (ATR-technique) of Benzamide	23

TABLE OF FIGURES

Figure 2-5: Ortep Plot of Benzamide ^[88]	23
Figure 2-6: Ortep Plot of [Co(salmdpt)] from Dichloromethane.....	24
Figure 2-7 Ortep Plot of [Co(salmdpt)] from Benzene (Monoclinic Crystal Symmetry) ^[44]	27
Figure 2-8 Ortep Plot of [Co(salmdpt)] from Toluene.....	27
Figure 2-9 a) Crystal Packing of [Co(salmdpt)] and Benzene Molecules. The View is Approximately down the 100 Direction b) Crystal Packing of [Co(salmdpt)] and Toluene Molecules. The View is Approximately down the 001 Direction.....	29
Figure 2-10: IR Spectrum of [Co(salmdpt)] from Acetonitrile	31
Figure 2-11: IR Spectrum of [Co(salmdpt)O ₂] from Benzene.....	31
Figure 2-12: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)O ₂] ..	32
Figure 2-13: Selected Area for the Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)O ₂]	32
Figure 2-14 ChemDraw Plot of [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] and [Co(3,5-Di- <i>tert</i> - butyl-salmdpt)]	33
Figure 2-15: Ortep Plot of [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)O ₂] with Necessary Distances and Angles.....	34
Figure 2-16 Ortep Plot of [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone (Structure 1)	37
Figure 2-17 Ortep Plot of [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone (Structure 2)	39
 Chapter 3	
Figure 3-1: Molecular Structure of [Co(salmdpt)CN] (3)	46
Figure 3-2: Molecular Structure of [Co(salmdpt)OH] (5)	48

TABLE OF FIGURES

Figure 3-3: ^1H NMR (400 MHz, CDCl_3) of Propionaldehyde	50
Figure 3-4: a) GC-MS Spectrum of the Reaction Mixture Before Reaction. b) GC-MS Spectrum of the Reaction Mixture After Reaction.	51

Chapter 4

Figure 4-1: Receptor-Ligand-Model.....	58
Figure 4-2: Substitution Archetypes of Adamantane and Synthesized Biologically Active Derivatives ^[121-124]	59
Figure 4-3: Expected Reactions of Adamantane Derivatives and the Complex [Co(salmdpt)]	60
Figure 4-4: Reaction of [Co(salmdpt)] and Butyronitrile with Dioxygen in Toluene .	60
Figure 4-5: Reaction of [Co(salmdpt)] and Butyronitrile with Hydrogenperoxide in Toluene.....	61

Chapter 5

Figure 5-1: Ortep Plot of [Co(salmdpt)NO] from Dichloromethane	65
Figure 5-2: IR Spectrum of [Co(salmdpt)NO] from Dichloromethane	69
Figure 5-3: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)NO] from Dichloromethane	69

Chapter 6

Figure 6-1: Ortep Plot of [Co(salmdpt)NO ₂] from Acetonitrile	73
Figure 6-2: Ortep Plot of Nitro-(<i>N,N'</i> -4-Azaheptane-1,7-diylbis-(salicylal- iminato)cobalt(III) [Co(salmdpt)NO ₂] ^[130]	74
Figure 6-3: IR Spectrum of [Co(salmdpt)NO ₂] from Acetonitrile	76
Figure 6-4: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)NO ₂] from Acetonitrile	76

TABLE OF FIGURES

Figure 6-5: Ortep Plot of [Co(salmdpt)NO ₂] from Methanol	77
Figure 6-6: IR Spectrum of [Co(salmdpt)NO ₂] from Methanol	81
Figure 6-7: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)NO ₂] from Methanol.....	81
Figure 6-8: IR Spectrum of the Cobalt(II) Complex [Co(salmdpt)]	83
Figure 6-9: IR Spectrum of the Cobalt(III) Complex [Co(salmdpt)ONO ₂].....	83
Figure 6-10: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)ONO ₂]	84
Figure 6-11: Generation of an Iron(IV) Oxido Species by Oxidation with O ₃	85
Figure 6-12: UV/Vis Spectrum of the Reaction of [Co(salmdpt)] with Ozone at -96°C	86
Figure 6-13: UV/Vis Spectrum of the Reaction of [Co(salmdpt)] with Ozone at -40°C	86

7 Summary

Figure 7-1: Reversible Reaction of [Co(salmdpt)] with Air or Dioxygen	90
Figure 7-2: The Ligand salmdptH ₂ and its Derivatives Reviewed in the Present Work	90
Figure 7-3: Reaction of [Co(salmdpt)] and Butyronitrile with Dioxygen in Toluene	91
Figure 7-4: Expected Reactions of Adamantane Derivatives and the Complex [Co(salmdpt)]	91
Figure 7-5: Comparison of the Ortep Plots of a) [Co(salmdpt)NO] and b) [Co(salmdpt)O ₂].....	93
Figure 7-6: ChemDraw Plot of the Expected [Co ^{IV} (salmdpt)O] Complex.....	93
Figure 7-7: ChemDraw Plot of the Expected [Co(salmdpt)ONO ₂] Complex	94

TABLE OF FIGURES

Figure 7-8: UV/Vis Spectrum of the Reaction of [Co(salmdpt)] with Ozone at -96°C	
.....	94
8 Zusammenfassung	
Abb. 8-1: Reversible Reaktion von [Co(salmdpt)] mit Luft oder Sauerstoff.....	95
Abb. 8-2: Der in dieser Arbeit untersuchte Ligand salmdptH ₂ und seine Derivate.	95
Abb. 8-3: Reaktion von [Co(salmdpt)] und Butyronitril mit Sauerstoff in Toluol ..	96
Abb. 8-4: Erwartete Reaktionen der Adamantan Derivate mit dem Komplex [Co(salmdpt)]	97
Abb. 8-5: Vergleich der Ortep Bilder von a) [Co(salmdpt)NO] und b) [Co(salmdpt)O ₂].....	98
Abb. 8-6: ChemDraw Zeichnung des vermuteten [Co ^{IV} (salmdpt)O] Komplexes.	99
Abb. 8-7: ChemDraw Zeichnung des [Co(salmdpt)ONO ₂] Komplexes	99
Abb. 8-8: UV/Vis-Spektren der Reaktion von [Co(salmdpt)] mit Ozon bei -96°C	
.....	100

Tables

Chapter 1

Table 1-1: Stretching Bands and Bond Length of Dioxygen and its Derivatives ^[2] ...	5
--	---

Chapter 2

Table 2-1: Crystal Data and Structure Refinement for [Co(salmdpt)] from Acetonitrile	19
Table 2-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Acetonitrile	19
Table 2-3: Crystal Data and Structure Refinement for [Co(salmdpt)] from Butyronitrile	21
Table 2-4: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Butyronitrile	21
Table 2-5: Crystal Data and Structure Refinement for [Co(salmdpt)] from Dichloromethane	25
Table 2-6: Comparison of the Unit Cell Parameters of the Structures Described in Chapter 2.1.1, 2.1.2 and 2.2	26
Table 2-7: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Dichloromethane	26
Table 2-8: Crystal Data and Structure Refinement for [Co(salmdpt)] from Toluene	28
Table 2-9: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Toluene	29
Table 2-10: Crystal Data and Structure Refinement for [Co(3,5-Di- <i>tert</i> -butyl-saldpt)O ₂] from Acetonitrile	35

TABLES

Table 2-11: Selected Bond Lengths [Å] and Angles [°] for [Co(3,5-Di- <i>tert</i> -butyl-saldpt)O ₂] from Acetonitrile	36
Table 2-12: Cell Parameters of [Co(saldpt)O ₂] and [Co(3,5-Di- <i>tert</i> -butyl-saldpt)O ₂] .	36
Table 2-13: Crystal Data and Structure Refinement for [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone (Structure 1)	38
Table 2-14: Selected Bond Lengths [Å] and Angles [°] for [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone (Structure 1).....	39
Table 2-15: Crystal Data and Structure Refinement for [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone (Structure 2)	40
Table 2-16: Selected Bond Lengths [Å] and Angles [°] for [Co(3,5-Di- <i>tert</i> -butyl-salmdpt)] from Acetone (Structure 2).....	41

Chapter 3

Table 3-1: Crystal Data and Structure Refinement for [Co(salmdpt)CN] from Acetonitrile	53
Table 3-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)CN] from Acetonitrile	54
Table 3-3: Crystal Data and Structure Refinement for [Co(salmdpt)OH] from Toluene.....	55
Table 3-4: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)OH] from Toluene.....	56

Chapter 5

Table 5-1: Crystal Data and Structure Refinement for [Co(salmdpt)NO] from Dichloromethane.....	66
Table 5-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)NO] from Dichloromethane.....	67

TABLES

Table 5-3:	Comparison of the Cell Parameters, some Selected Bond Lengths and Angles of [Co(salen)NO] ^[73] [Co(saldpt)NO] and [Co(saldpt)O ₂] ^[48-49] ...	68
------------	---	----

Chapter 6

Table 6-1:	Crystal Data and Structure Refinement for [Co(salmdpt)NO ₂] from Acetonitrile	73
Table 6-2:	Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)NO ₂] from Acetonitrile	74
Table 6-3:	Crystal Data and Structure Refinement for [Co(salmdpt)NO ₂] from Methanol.....	78
Table 6-4:	Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)NO ₂] from Methanol.....	79
Table 6-5:	Strong, Moderate, and Weak Hydrogen Bonds following the Classification of Jeffrey ^[134-135]	80

Table of Schemes

Chapter 1

Scheme 1-1 Formation of the Bis- μ -Peroxido-Complex of Cobalt Salen	7
--	---

Chapter 2

Scheme 2-1: ChemDraw Plot of the Reaction of Benzonitrile to Benzamide using [Co(salmdpt)]	24
---	----

Chapter 3

Scheme 3-1: Postulated Reaction Mechanism (L=Salmdpt)	47
Scheme 3-2: Schematic Depiction of the Possible Oxidation of [Co ^{II} (salmdpt)] in Toluene.....	56

7 Summary

Scheme 7-1: ChemDraw Plot of the Reaction of Benzonitrile to Benzamide using [Co(salmdpt)]	92
---	----

8 Zusammenfassung

Schema 8-1: ChemDraw Zeichnung der Reaktion von Benzonitril zu Benzamid unter Verwendung des Komplexes [Co(salmdpt)].....	97
--	----

1 Introduction

1.1 Motivation

Bioinorganic chemistry is a combination of inorganic chemistry and biology in which molecules are investigated that contain metal ions that are related to biological systems. An important study object are metalloenzymes, a sub-class of metalloproteins, which are responsible for many different essential processes in biology, such as dioxygen uptake and oxidation of organic substrates.^[1-2]

Binding and activation of small molecules such as dioxygen or nitrogen oxide takes place at the so-called active site of the enzyme. In about half of the known proteins responsible for this are the metal cations bound to the active site, coordinated through donor atoms of the amino acid chains. In order to understand such processes and their implications on binding and activation of substrate molecules, numerous model complexes are synthesized and studied instead.

Investigations of model complexes can offer a less complicated approach compared to the biological molecules. It is particularly interesting to model the reactivity of the metalloenzymes in regard to finding new catalysts for selective oxidation reactions under mild conditions. One of the most studied metalloproteins is hemoglobin. The first model compound for hemoglobin was cobalt salen (see 1.5.2) because of its ability to bind dioxygen reversibly.

So far, cobalt ions have not been observed in oxygen activating enzymes. However in biology the element cobalt plays an important role as a trace element. It is part of the active center of co-enzymes. The reactivity of cobalt complexes towards dioxygen makes them excellent model compounds for dioxygen activation. At present the activation of dioxygen on cobalt complexes is a major topic in research and development.^[3-5] Synthesis and characterization of dioxygen complexes as well as investigations of their reactivity are an important contribution to the search for homogenous catalysts for selective oxidations of organic substrates. Some of these cobalt complexes could also be of high interest in medicinal chemistry.^[6]

1.2 The Element Cobalt

The wonderful blue color of cobalt compounds has been known for more than 4000 years. However even more in the Middle Ages the existence of the iron-like element was identified. The oldest cobalt-containing artifact known today is a Persian necklace with blue-glazed pearls (2250 BC).^[7]

Cobalt-containing minerals have been mined in the Saxon Erzgebirge since the 14th century. Tin or silver ore are relatively similar to these. Therefore, it is likely that the mining of cobalt ore occurred unknowingly. During this time it was not possible to get useful metal from the cobalt containing ore. Furthermore, toxic arsenic was formed upon roasting of the ore, in form of a nebular aerosol. In that time the miners thought that all this must be the work of evil kobolds. This fact gave the element cobalt its name.^[7]

The ferromagnetic metal cobalt does not occur in its elemental form in nature. In its minerals it is frequently associated with nickel.^[8] Today, cobalt is used in many respects like hard metal, permanent magnets, in the video technology or in the nuclear technology. Since the beginning of the last century cobalt-complexes have been known in research.^[9-11]

1.3 Cobalt in Biology

In biology, the element cobalt plays an important role as a trace element. It is part of the active center of coenzymes, which are called cobalamines. These coenzymes can be found in all multicell organisms. For mammals the cobalamine vitamin B12 (see Figure 1-1) is essential.^[2]

The history of vitamin B12 originated in 1925 with the descriptions by Whipple and Minot & Murphy.^[12-13] A hunt spanning two decades led to the independent isolation of the cofactor by Smith & Folkers in 1948.^[14-17]

The crystal structure of vitamin B12 was obtained by Dorothy Crowfoot Hodgkin. In 1956, she produced a three-dimensional analysis of vitamin B12, and became so the first scientist to determine the chemical structure of a substance solely by X-ray analysis.^[18-20] In 1964, she was awarded the Nobel Prize in Chemistry for her work on vitamin B12, the third woman ever to receive the Nobel Prize in Chemistry.

Vitamin B12 is a tetrapyrrolic cofactor in which the central cobalt atom is coordinated by four equatorial nitrogen ligands donated by the pyrroles A-D of the corrin ring. B12 is partly and, unlike other tetrapyrroles, has a built-in axial ligand appended from the periphery of ring D of the corrin macrocycle (cf. Figure 1-1).^[17] The identity of the base at the terminus of the propanolamine moiety varies in different organisms and is the unusual ribonucleoside, dimethylbenzimidazole, found in cobalamins. Diversity is also present at the upper axial ligand where cyanido-, methyl-, and deoxyadenosyl-groups are coordinated in the vitamin B12, methylcobalamin (MeCbl1), and AdoCbl or coenzyme B12, respectively.^[17]

Presently, three classes of B12 enzymes are known, isomerases, methyltransferases, and reductive dehalogenases.^[17]

Today, a large number of books, papers and reviews report on vitamin B12.^[2, 21-27]

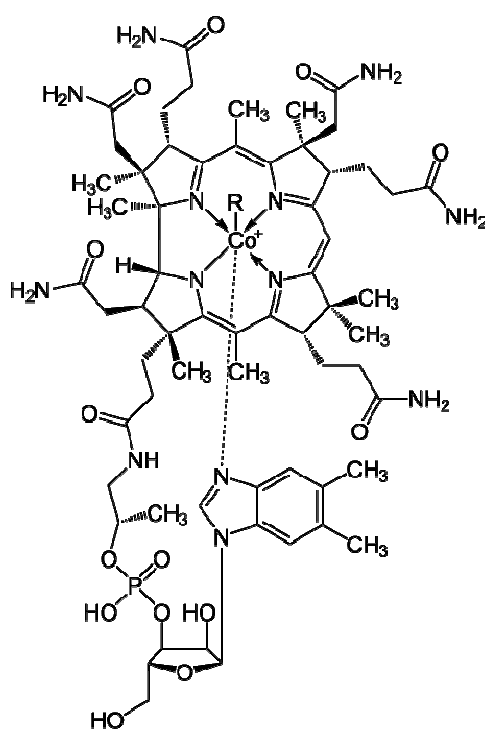


Figure 1-1: Structure of Cobalamines Coenzyme B12 R = 5'-Desoxyadenosyl; Cyanidocobalamine R = CN; Hydroxycobalamin R = OH; Methylcobalamin R = CH₃

The central corrin ring of vitamin B12 is related to the porphyrin ring just like in hemoglobin. In difference to porphyrin the carbon bridge, which links the pyrrole A with the pyrrole D, is absent. Based on this relationship, hemoglobin will be described in the following.

1.4 Hemoglobin

Hemoglobin acts as a dioxygen carrier in blood. Therefore, hemoglobin gathers O_2 in the lungs and hands it over to myoglobin in the tissue. Hemoglobin consists of multiple subunits, two α - and β -polypeptide chains. Both polypeptide chains contain an ironporphyrin-IX-group, which is retained by a histidin-imidazole moiety. The reduced, oxygen free form is called desoxy-hemoglobin and the oxidized form oxy-hemoglobin. In the deoxygenated form, the iron is 0.36 – 0.40 Å out of the porphyrin ring plane. During oxygen-binding the iron atom moves about 0.12 Å towards the plane.

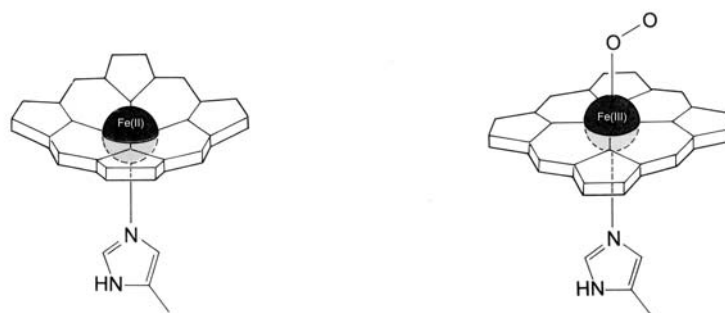


Figure 1-2: Oxygen Binding on Ironporphyrine (Desoxy-Form and Oxy-Form)^[2]

X-ray diffraction indicates the formation of a hydrogen bond between the NH-group, the histidine residue and the coordinated dioxygen molecule. This Fe-O₂- -HN-unit inserts well into the hemoglobin structure. Thermodynamic, kinetic and spectroscopic measurements of the coordinated dioxygen molecule show that the iron atom in the hemoglobin-oxygen-adduct is an iron(III) ion. Coordination of dioxygen takes place as a superoxido ion (see Chapter 1.5.2), stabilized by the hydrogen bond. This was confirmed by IR measurements. They show an O-O-stretching vibration at $\sim 1105\text{ cm}^{-1}$ for the coordinated dioxygen molecule. Therefore, the band is located in the range of superoxido-ions (Table 1-1).^[2]

Many model complexes exist for hemoglobin and myoglobin. Most importantly are natural iron-porphyrin complexes which show similar characteristics to proteins. However, these models will not be discussed in detail, as they only play an indirect role for this work. In the following, the cobalt salen complex, a first model for the reversible binding of dioxygen in hemoglobin, will be mentioned briefly.^[2]

Species	$\nu_{\text{O-O}}$ [cm^{-1}]	$d_{\text{O-O}}$ [\AA]
O_2^+	1950	1.12
O_2	1580	1.21
O_2^-	1097	1.33
O_2^{2-}	802	1.49

Table 1-1: Stretching Bands and Bond Length of Dioxygen and its Derivatives^[2]

1.5 Cobalt-Oxygen Complexes

So far, cobalt ions have not been observed in oxygen-activating enzymes, but the reactivity of cobalt complexes towards dioxygen makes them excellent model compounds for dioxygen activation. Therefore, cobalt complexes and their reaction with dioxygen are of great interest for coordination chemists. They have a high potential as oxygen carriers^[28] and also as oxidation catalysts.^[6, 29-32]

1.5.1 Dioxygen

Dioxygen is a colorless, odorless, tasteless gas with a spin triplet electron configuration (ground state). Molecular dioxygen is essential for most animals and plants, as it generates energy by photosynthesis and cellular respiration in all aerobic organisms. Moreover, oxygen is the most abundant chemical element in our biosphere.

Dioxygen was almost not existent until photosynthetic processes of archaea and bacteria developed. Today, green algae and cyanobacteria in marine environments provide about 70% of the free oxygen produced on earth. The rest is produced by terrestrial plants. The present atmosphere consists of 21% O_2 .

Dioxygen is a very strong oxidant with the second highest electronegativity of all elements. However, usually reactions between O_2 and metal complexes proceed irreversibly by cleavage of the oxygen-oxygen bond, leading to oxides, hydroxides or water. With appropriate ligand configurations, the reversible binding of dioxygen with transition metal complexes is possible.^[33]

Reversible binding of dioxygen on cobalt complexes is well known in inorganic chemistry (see 1.5 and 1.6). But it seems that this reaction does not occur in

biological systems. Here, solely iron- and copper proteins take this role. A distinction can be drawn between three species of dioxygen transport and dioxygen storage systems. The dioxygen carriers are hemoglobin, hemocyanin and hemerythrin. Hemoglobin is rife in vertebrates and in various invertebrate organisms. Hemocyanin can be found in arthropods and mollusks, and hemerythrin in some marine invertebrates.^[2] Hemoglobin contains an iron porphyrin group (heme), hemocyanin two copper atoms in its active site and hemerythrin two non-heme iron atoms.^[2]

1.5.2 Cobalt Salen

The fact that specific cobalt(II) complexes activate dioxygen and yield it reversibly, has been well-known for a long time.^[34-37] Pfeiffer, Breith, Lübke & Tsumaki reported in 1933 about the preparation of salicylaldehyde ethylendiimine cobalt(II) (cobalt salen, Figure 1-3). Thereby they observed that the complex changed slowly its color from red to brown, when it was exposed to air.^[34] In 1938 Tsumaki picked upon this issue. He recognized that it was a matter of an oxidation by aerial oxygen. Furthermore, he found out that upon heating of the brown compound dioxygen was emitted reversibly, and that the complex regained its original color.^[35]

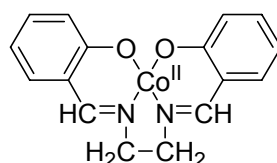


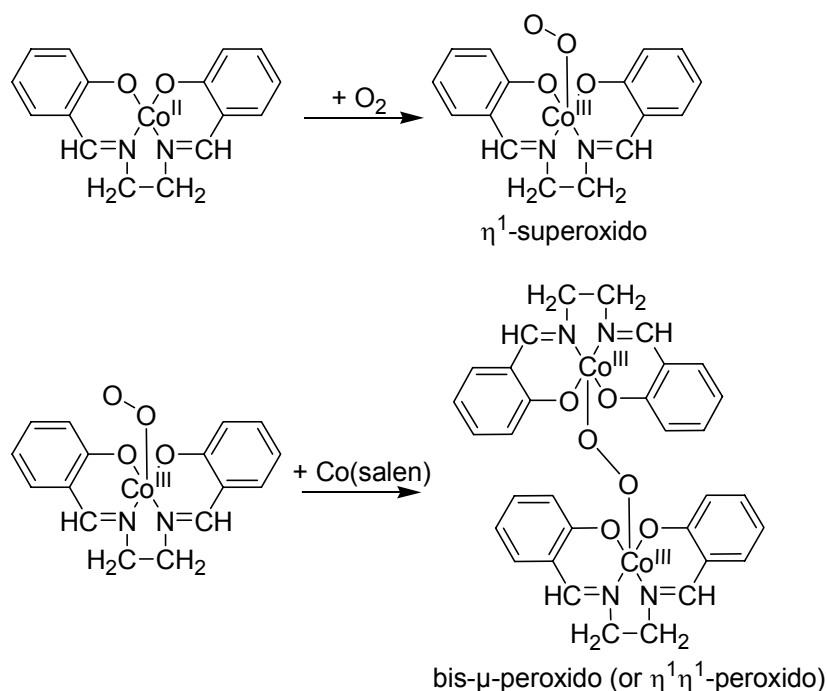
Figure 1-3: The Cobalt Salen Complex^[35]

Therefore, cobalt salen was one of the first model compounds for hemoglobin that could bind dioxygen reversibly according to the natural model. Studies were directed towards military applications, as a system for oxygen storage in submarines.^[36, 38-40]

Scheme 1-1 shows the reaction of cobalt salen with dioxygen. Herein, cobalt salen forms a dimer μ -peroxido-species, in which the formation proceeds over a not isolatable superoxido intermediate (Scheme 1-1).^[40-41]

Through addition of a solvent molecule (e.g. pyridine), the reversible dioxygen uptake associated with the oxidation of cobalt salen can be enhanced.^[8, 41] The same effect can be achieved in non coordinating solvents (e.g. toluene) in presence of

coordinating ligands (e.g. pyridine).^[41] Through coordination of a solvent molecule or an additional ligand, the vacant fifth coordination site of cobalt salen is occupied. Salen derivatives which offer additional donor atoms and / or sterical hindrance can stabilize the initial superoxido species.



Scheme 1-1: Formation of the Bis-μ-Peroxido-Complex of Cobalt Salen

1.6 Properties and Reactivity of the Cobalt(II) and Cobalt(III) Complexes of [Co(saldpt)] and its Derivatives

As described above, cobalt salen needs a fifth coordinating group (solvent or ligand) to optimize the reversible oxygen binding. For this purpose, the salen ligand was modified, by inserting a fifth donor atom. This ligand is bis[3-(salicylideneimino)propylamine] (saldptH₂). The cobalt(II) complex of this ligand is [N,N'-(3,3'-dipropylamine)bis(salicylideneiminato)cobalt(II)] ([Co(saldpt)], Figure 1-4). Herein, another amine nitrogen atom can coordinate to the Co^{II} ion. The proton on the amine nitrogen can be easily replaced by organic groups (e.g. CH₃). With an additional methyl group, the ligand is bis[3-(salicylideneimino)propyl]methylamine (salmdptH₂). The cobalt(II) complex of this ligand is called [N,N'-(3,3'-dipropylmethylamine)-bis(salicylideneiminato)cobalt(II)] ([Co(salmdpt)], Figure 1-4).

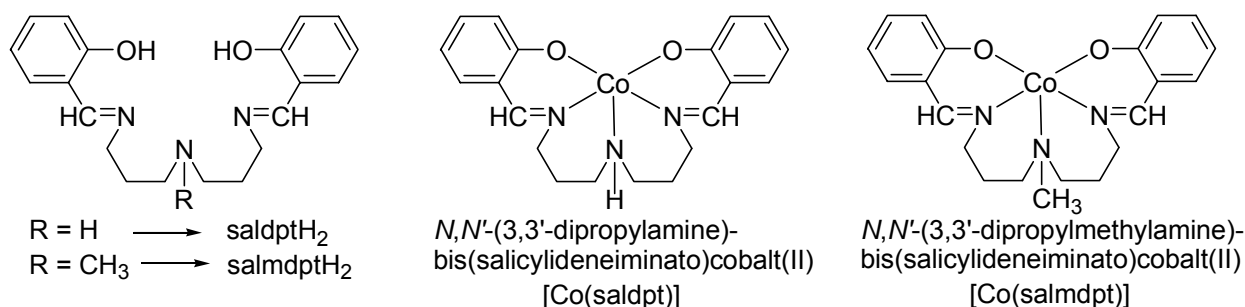


Figure 1-4: ChemDraw Plot of the Ligands saldptH₂/salmdptH₂ and their Cobalt(II) Complexes

1.6.1 Crystal Structure of the Cobalt(III) Peroxido Complex of [Co(saldpt)]

The peroxido complex of $[\text{Co}(\text{saldpt})\text{O}_2]$ has been described previously and its dimeric structure in which the two cobalt atoms are bridged by an O-O group has been reported. The bond length between the two oxygen atoms averages 1.45 Å and the angle of torsion Co-O-O-Co averages 149° (Figure 1-6). This is typical for peroxido groups.^[42-43] The octahedral environment of the cobalt atom includes three oxygen and three nitrogen atoms. Both oxygen atoms of the salicylaldehyde groups are in cis-position, whereas the imine nitrogen atoms are in trans-position (Figure 1-5 and Figure 1-6).^[43]

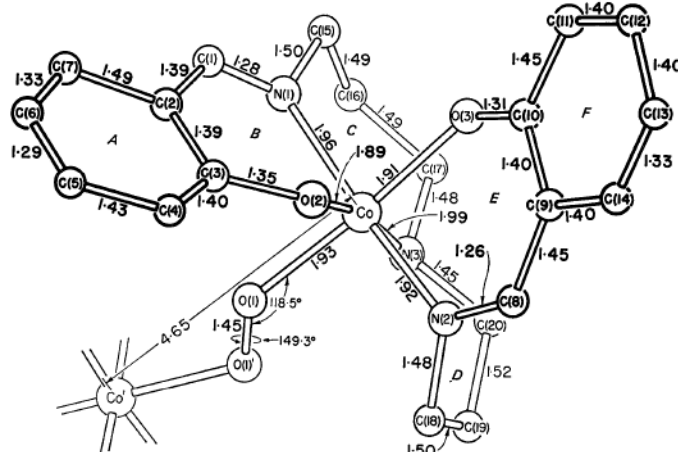


Figure 1-5: Coordination of the Cobalt Atoms Stereoscopic of $[\text{Co}(\text{saldpt})\text{O}_2]$

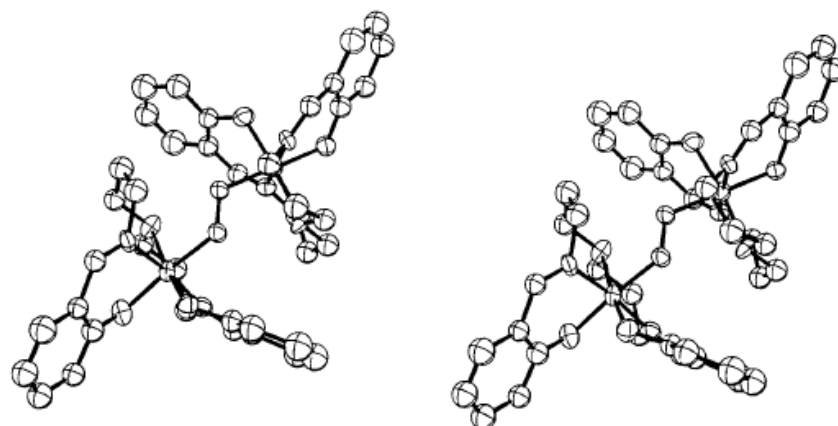


Figure 1-6: Stereoscopic View of the Structure of [Co(saldpt)O₂]

1.6.2 Crystal Structure of the Cobalt(II) Complex [Co(salmdpt)]

In contrast to [Co(saldpt)] that forms a peroxido complex, [Co(salmdpt)] reacts with dioxygen to form a superoxido complex. Isolation and characterization of the cobalt(II) complex, [Co(salmdpt)], prior to oxidation has been reported previously in the literature.^[44-45] Crystal structure analysis shows that the cobalt atom is coordinated by three nitrogen and two oxygen atoms of the ligand salmdptH₂ (Figure 1-4) in a distorted trigonal bipyramidal arrangement. The expected five-fold coordination arrangement is visible. Thereby, O(1), O(2), and N(3) are located almost in the equatorial plane, and N(2) and N(1) occupy the axial positions (Figure 1-7).^[44-45]

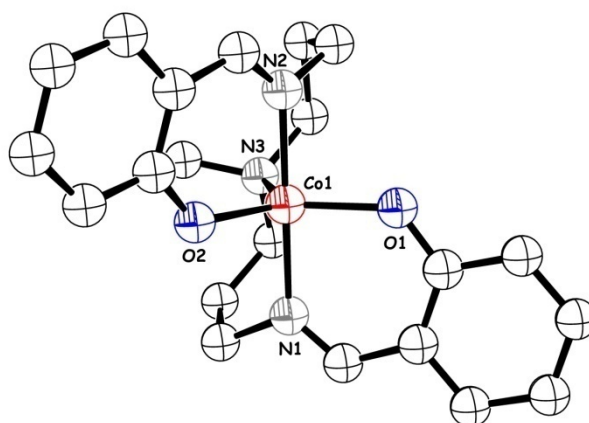


Figure 1-7: Ortep Plot of [Co(salmdpt)] in Benzene (Monoclinic Crystal Symmetry)

1.6.3 Crystal Structure of the Cobalt(III) Superoxido Complex of [Co(salmdpt)]

The reversible oxygen uptake of the cobalt(II) complex with the ligand salmdptH₂ has already been described in the literature.^[46-47] Herein, Niswander postulated the presence of a cobalt(III) superoxido complex and a high-spin five-coordinated precursor compound, based on spectral and magnetic properties. Based on chemical analysis, the formula [Co(salmdpt)]₂·O₂·2C₆H₆ of the compound crystallized from benzene solution could be confirmed.^[48] However, in contrast to these analytical data crystallographic analysis showed that a mixture of the non-oxygenated cobalt(II) complex and the according superoxido complex had formed (Figure 1-8).^[48-49]

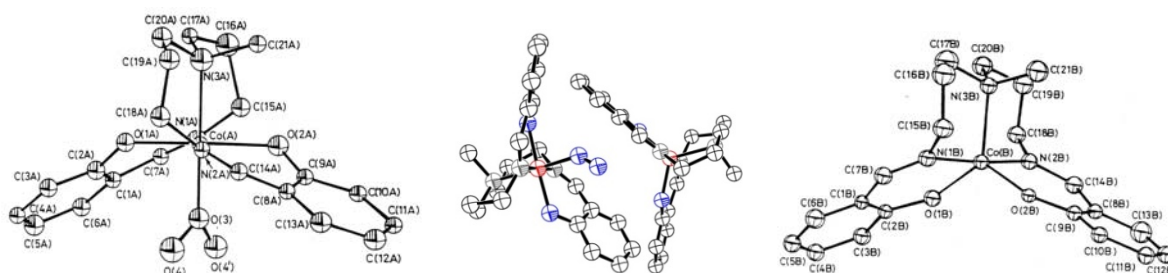


Figure 1-8: Ortep Plot of the Oxygenated and Non-Oxygenated Molecule

The metal atom showed a pseudo-octahedral coordination in the oxidized form of the complex. The Atoms O(1A), O(2A), N(1A) and N(2A) are co-planar. The atoms (N1A), C(7A), and N(2A), C(14A) are displaced a slightly out of plane. The dihedral angle between the two salicylaldehyde groups averages 115.3°.^[49] The unit cell of the crystal includes four benzene solvent molecules. These benzene molecules fill up cavities in the crystal structure. The coordinated oxygen atom is stabilized by two of the benzene rings by weak interactions (Figure 1-9).^[49]

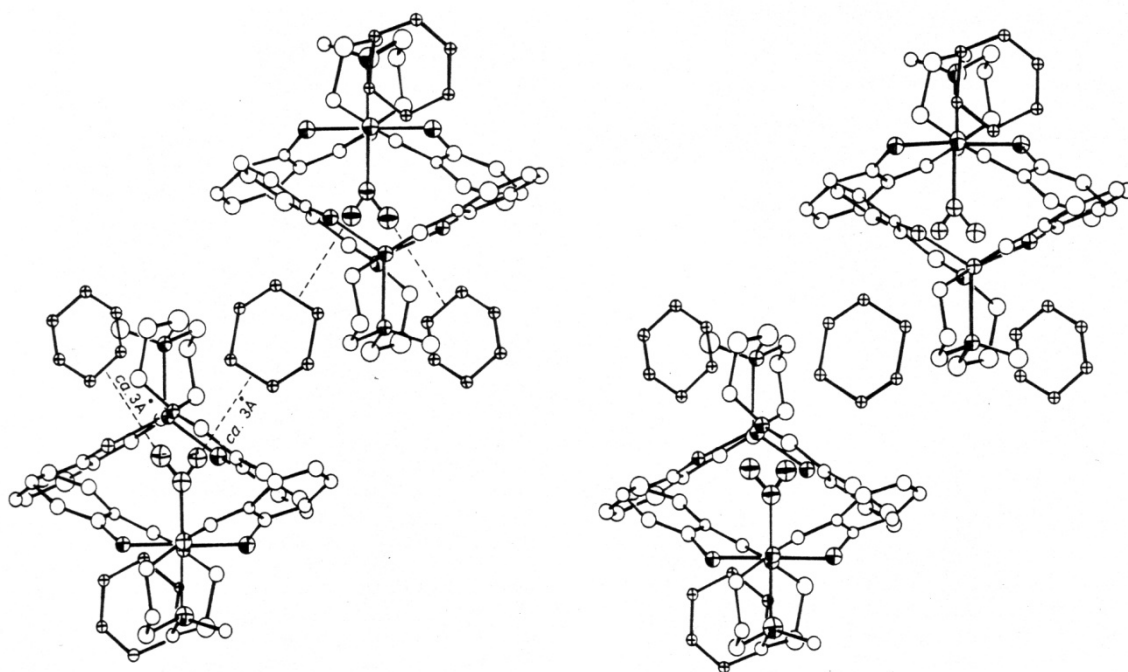


Figure 1-9: Crystal Package of $[\text{Co}(\text{salmdpt})]_2 \cdot \text{O}_2 \cdot 2\text{C}_6\text{H}_6$

1.6.4 Crystal Structure of the Cobalt(III) Superoxido Complex of $[\text{Co}(\text{saSiMedpt})\text{O}_2]$

Since it was observed that a five-coordinated Schiff base ligand is necessary for binding dioxygen^[43, 45, 47-48, 50-52] (see 1.6.3 and 1.6.1), it was important to know if further modification of the amino group has a strong influence on the coordination of the nitrogen donor atom to the metal atom.

It is worth noting that only a few single crystal X-ray analyses of pentadentate Schiff base complexes have been reported in the literature.^[43, 45, 48, 50] Carré et al. substituted the methyl group in salmdpt with a silyl group in their efforts to support metal complexes of this ligand on silica.^[53] During their synthetic procedures they recrystallized the obtained cobalt complex in presence of air. Crystallographic analysis of the crystals formed from benzonitrile solution showed that a superoxido complex was obtained. The crystal structure of $[N,N'-(3,3'\text{-dipropyltrimethylsilylamine})\text{-bis}(\text{salicylideniminato})\text{-cobalt(III)}\text{O}_2]$ ($[\text{Co}(\text{saSiMedpt})\text{O}_2]$) is shown in Figure 1-10. However, the resolution of this structure is not very good. Described angles and bond lengths disagreed with the data released in the supporting cif-file. Still due to the significance of this data for this work, the depiction of the crystal structure should not be omitted.

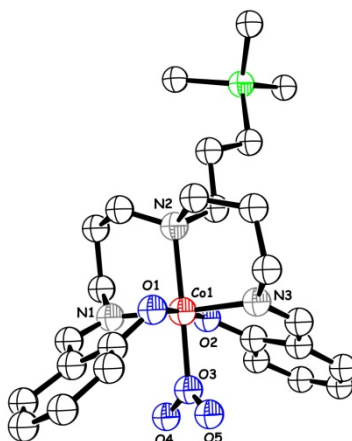


Figure 1-10: Crystal Structure of [Co(salSiMedpt)O₂]

The arrangement around the cobalt ion can be described as octahedral. The five coordinating positions are occupied by three nitrogen atoms and two oxygen atoms. The sixth position, opposite to the tertiary amino group, is occupied by a dioxygen molecule (N(2)-Co(1)-O(3) 178.8°), which is bound in a bent end-on fashion. The O(3)-O(4)-O(5) plane almost bisects the angles N(1)-Co(1)-O(1) (89.3(8)°) and N(3)-Co(1)-O(2) (93.1(8)°). The dioxygen O(3)-O(4) distance is in the same range (average 1.20 Å) as in the dioxygen molecule (1.216 Å).^[53] Therefore, this structure is very similar to that of [Co(salmdpt)O₂].^[48] Indeed, in this complex, the bond length between the cobalt atom and the tertiary amino group is 2.09 Å, whereas it is 2.119 Å for [Co(salSiMedpt)O₂] (Co(1)-N(2) 2.119 Å). The structure of [Co(salSiMedpt)O₂] is furthermore similar to [Co(bzacn)-(pyridine)O₂], another octahedral superoxido complex.^[50]

1.6.5 Further Cobalt “Dioxygen Adduct” Complexes

As described above, cobalt(II) complexes can react with dioxygen to form cobalt(III) superoxido and peroxido complexes. However, further binding modes of dioxygen have been observed in general for metal complexes.^[54] Figure 1-11 shows examples of the different binding modes of oxygen in structurally characterized cobalt complexes.^[55] Today, there is a large number of well-characterized cobalt oxygen complexes.^[6, 28, 48, 56-72]

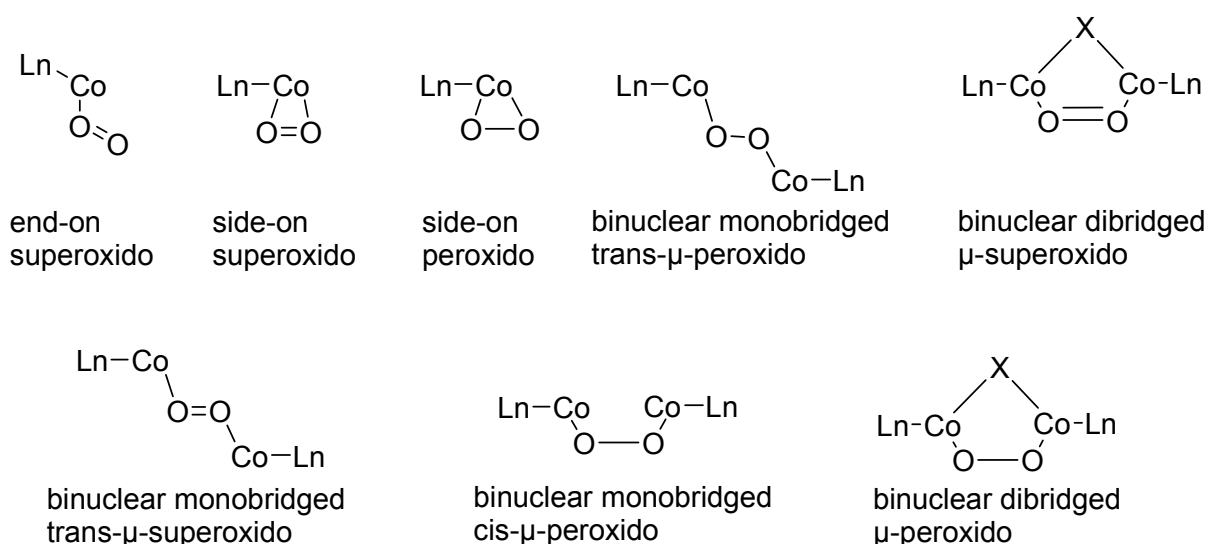


Figure 1-11: Samples of Characterized Cobalt Oxygen Adduct Complexes

1.7 Nitrogen Monoxide Complexes

As described above, intensive studies have been performed on the reactivity of dioxygen towards cobalt salen as described already by Tsumaki in 1938 (Chapter 1.5.2).^[73] During these investigations it was observed that the stability of these dioxygen adduct complexes was highly dependent on the nature of the Schiff base ligand and on crystal-packing effects.^[74] In contrast, only more recently investigations on the binding of nitrogen monoxide, NO, with these complexes have been performed.

1.7.1 Nitrogen Monoxide

It is now well established that nitrogen monoxide (NO) plays several fundamental roles in biochemical processes. Early concerns with the biology of NO were largely focused on the known toxicity of NO. However, natural physiological activities are now known to include roles in blood pressure control, neurotransmission, and immune response. Such observations have stimulated extensive research activity into the chemistry, biology, and pharmacology of NO.^[75]

Nitrogen monoxide (NO) is a colorless gas, only slightly soluble in water. NO contains an unpaired electron and is therefore one of the simplest free radicals. However its affinity to dimerize to N_2O_2 is very low (only at low temperatures or high pressures it is significant). Reason for this is the delocalization of the electron over

the whole molecule, and thereby the dimerization does not accomplish the bonding order.^[8, 75]

NO is an interesting molecule in comparison with dinitrogen or dioxygen. Compared with N₂, NO exhibits an additional electron in one of the anti-binding π^* -orbitals. Due to the strong effect of the additional electron, NO is able to donate an electron easily. In comparison with dioxygen it is missing an electron with an electronic structure analogous to the dioxygen cation O₂⁺. Therefore, it can be interesting to compare binding of NO with coordination of dioxygen with a metal complex. NO reacts rapidly with other free radicals, and substitution labile redox active metals, but it is neither a strong one-electron oxidant nor a strong one electron reductant. Many articles and reviews about NO and its metal complexes have been published in the last 30 years. Therefore, only a few selected examples are given in the references.^[76-86]

In a complex with a metal atom, the character of the NO ligand can range from that of a nitrosyl cation (NO⁺), which binds to the metal with a M-NO angle of ~180°, or to that of a nitroxyl anion (NO⁻), for which a bond angle of ~120° can be anticipated (Figure 1-12).^[75]

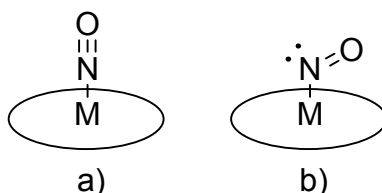


Figure 1-12: Illustration of Limiting Cases of NO Binding to a Metalloporphyrin Center as (a) the Nitrosyl Cation (NO⁺) or (b) the Nitroxyl Anion (NO⁻)

1.7.2 Crystal and Molecular Structure of *N,N*-Ethylene-bis-(salicylideneiminato)-nitrosylcobalt(III) [Co(salen)NO]

The crystal and molecular structure of [Co(salen)NO], was determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group P2₁/c, with eight molecules in a cell of the dimensions $a = 14.417(7) \text{ \AA}$, $b = 11.982(7) \text{ \AA}$, $c = 17.481(9) \text{ \AA}$, and $\beta = 100.39(4)^\circ$ and a volume of 2970.23 \AA^3 .^[73]

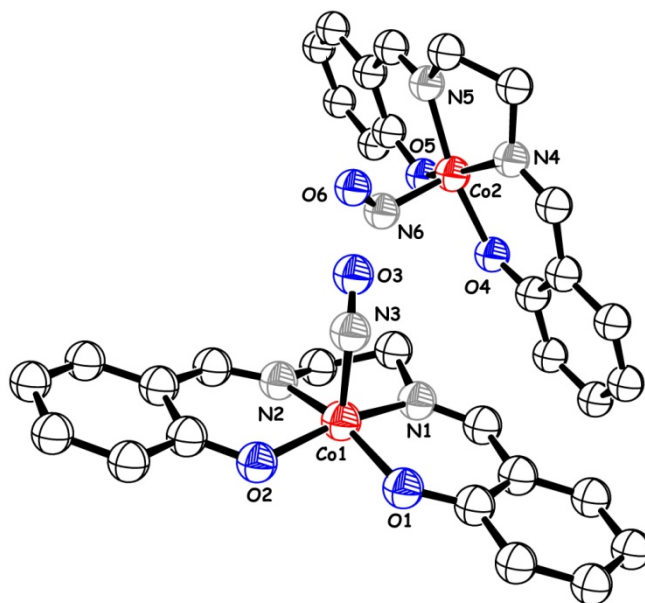


Figure 1-13: Ortep Plot of *N,N'*-Ethylene-bis-(salicylideneiminato)-nitrosylcobalt(II) [Co(salen)NO]

The crystal structure consists of two separated molecules of [Co(salen)NO]. Perspective views of the two molecules are presented in Figure 1-13. Both independent molecules have a five-coordinate tetragonal pyramidal coordination sphere around the Co atoms, with the nitrosyl group in the axial position. The average nitrosyl bond length is 1.155(11) Å, and the average Co-N-O angle is 127.0(4)°.^[73]

1.8 Projects

As discussed in the introduction dioxygen and nitrogen monoxide complexes of cobalt can play an important role in the better understanding of the reactivity of small molecules such as dioxygen and nitrogen oxide towards metal complexes. Reactions of this type are relevant in biological systems, homogeneous catalytic oxidation processes and medical applications. Therefore, the topic of this thesis is a detailed study of the activation of small molecules on cobalt complexes. Investigations on the following projects were performed and are described in this work.

1.8.1 Cobalt Complexes with Schiff Base Ligands

As described in Chapter 1.6 [Co(saldpt)] complexes are interesting compounds in regard to their behavior towards dioxygen. Previous reports have shown that [Co(salmdpt)] can form an end-on superoxido complex, a species that is quite important in selective oxidation reactions. Therefore, the following two projects have been investigated in this thesis.

1. Synthetic and reactivity studies on the interaction of [Co(saldpt)] and derivatives with dioxygen and hydrogen peroxide as well as studies on the reactivity of the superoxido cobalt complex [Co(salmdpt)].
2. As described in Chapter 1.7, it is quite interesting to compare dioxygen binding with NO coordination to a metal complex. Therefore, synthetic and reactivity studies were performed on the reaction of NO with [Co(salmdpt)].

2 Cobalt Superoxido Complexes

As described in the introduction several cobalt “dioxygen” adduct complexes were prepared and characterized in the past. Very interesting are compounds that include the ligand salmdptH₂ and derivatives described previously by Orioli and co-workers. They postulated that the cobalt superoxido complex of [Co(salmdpt)] can only be obtained from a benzene solution.^[49] In contrast, Carré et al. reported that they obtained a cobalt superoxido complex from [Co(salSiMedpt)] in benzonitrile which could be structurally characterized.^[53] [Co(salSiMedpt)] is a derivative of [Co(salmdpt)] (Figure 1-7 and Figure 1-10). Based on these findings, it was likely that it should be possible to synthesize the superoxido complex of [Co(salmdpt)] in other solvents such as e. g. nitriles, toluene or dichloromethane as well.

In 1.6.3, the crystal structure of [Co(salmdpt)O₂], obtained by Orioli and co-workers, is described. It shows the dioxygen-active species (in solid state) of the complex obtained from benzene.^[45] Furthermore, Orioli and co-workers described two dioxygen-inactive forms (in solid state) of [Co(salmdpt)],^[44] which were obtained from benzene and acetone solutions. The dioxygen-active species shows monoclinic crystal symmetry just as the dioxygen-inactive species from acetone. For the one obtained from benzene, an orthorhombic symmetry was found.

2.1 Crystal Structures of [Co(salmdpt)] from Nitrile Solvents

In a first effort to prepare the superoxido complex of [Co(salmdpt)], crystals of the unreacted complex were obtained with a crystal structure similar to the one reported previously by Cini and Orioli.^[44]

2.1.1 Crystal Structure of [Co(salmdpt)] from Acetonitrile

The molecular structure depicted in Figure 2-1 shows a distorted trigonal bipyramidal arrangement, just like the dioxygen-inactive (in solid state) structure from acetone.^[44] The cobalt atom is located exactly in the middle of the equatorial plane in which the angles O(1)-Co(1)-O(2), O(1)-Co(1)-N(1) and O(2)-Co(1)-N(1) are 128.18(6), 115.74(6) and 116.08(6)°. The structure shows the expected five-fold coordination of the cobalt(II) atom. These coordinating positions are occupied by three nitrogen and two oxygen atoms. The atoms N(1), O(1) and O(2) are located in the equatorial plane

and the atoms N(2) and N(3) occupy the axial positions. The oxygen-active species (in solid state) shows here the same properties.^[44]

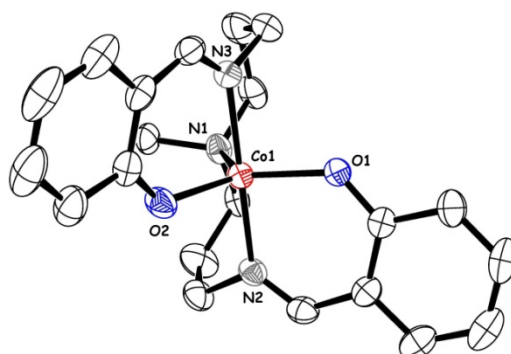


Figure 2-1: Ortep Plot of [Co(salmdpt)] from Acetonitrile

The unit cell for the determined complex shows the same dimensions as the dioxygen-inactive form (in solid state) obtained from acetone. The two structures only distinguish in the space group. For the structure described in this work the space group is $P2_1/c$ and for the structure published by Orioli and co-workers, the space group is $P2_1/a$. The structure described here, is most likely a dioxygen-inactive form (in solid state) of the [Co(salmdpt)] complex. Crystallographic data are presented in Table 2-1 and Table 2-2.

Table 2-1: Crystal Data and Structure Refinement for [Co(salmdpt)] from Acetonitrile

Habitus	quadrate stick		
Color	brown		
Crystal size	0.40 x 0.40 x 0.25 mm		
Temperature	200(2) K		
Diffractionmeter type	SIEMENS		
	SMART 5000 CCD		
Wavelength	0.71073 Å		
Empirical formula	C ₂₁ H ₂₅ CoN ₃ O ₂		
Formula weight	410.37 g/mol		
Crystal system, space group	monoclinic, P2 ₁ /c (Nr. 14)		
Unit cell dimensions	a = 6.7627(6) Å	α = 90°	
	b = 13.7463(12) Å	β = 92.6030(10)°	
	c = 20.8444(18) Å	γ = 90°	
Volume	1935.7(3) Å ³		
Z, calculated density	4, 1.408 Mg/m ³		
Absorption coefficient	0.907 mm ⁻¹		
F(000)	860		
Theta range for data collection	1.78 to 28.30		
Limiting indices	-8 ≤ h ≤ 8, -18 ≤ k ≤ 17, -27 ≤ l ≤ 27		
Reflections collected / unique	22290 / 4712 [R (int) = 0,0274]		
Completeness to theta = 28.30	94.3 %		
Absorption correction	Multi-scan (SADABS)		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	4712 / 0 / 276		
Goodness-of-fit on F ²	1.035		
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0813		
R indices (all data)	R1 = 0.0432, wR2 = 0.0849		
Largest diff. peak and hole	0.278 and -0.297 eÅ ⁻³		

Table 2-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Acetonitrile

Co(1)-N1	2.1383(14)	Co(1)-O1	1.9464(12)
Co(1)-N2	2.00651(15)	Co(1)-O2	1.9484(12)
Co(1)-N3	2.0556(15)		
N1-Co(1)-N2	90.32(6)	O1-Co(1)-N3	90.52(6)
N1-Co(1)-N3	89.59(6)	O2-Co(1)-N1	116.08(6)
N2-Co(1)-N3	179.91(6)	O2-Co(1)-N2	90.46(6)
O1-Co(1)-N1	115.74(6)	O2-Co(1)-N3	89.58(6)
O1-Co(1)-N2	89.52(6)	O1-Co(1)-O2	128.18(6)

2.1.2 Crystal Structure of [Co(salmdpt)] from Butyronitrile

Apart from acetonitrile, butyronitrile was also used as a solvent to synthesize the superoxido complex of [Co(salmdpt)O₂]. Again only the starting material the cobalt(II) complex was crystallized.

The molecular structure depicted in Figure 2-2 is very similar to the one obtained from acetonitrile. The cobalt atom is five-fold coordinated and the structure shows a slightly distorted trigonal bipyramidal arrangement. The cobalt atom is almost located in the middle of the equatorial plane, spanned by the atoms O(1), O(2) and N(3), whereas N(1) and N(2) fill the axial positions. The bond angles O(1)-Co(1)-O(2), (O1)-Co(1)-N(3) and (O2)-Co(1)-N(3) are 127.85(10), 115.99(10), and 116.16(10). The bond lengths are in the range 1.9 to 2.2 Å.

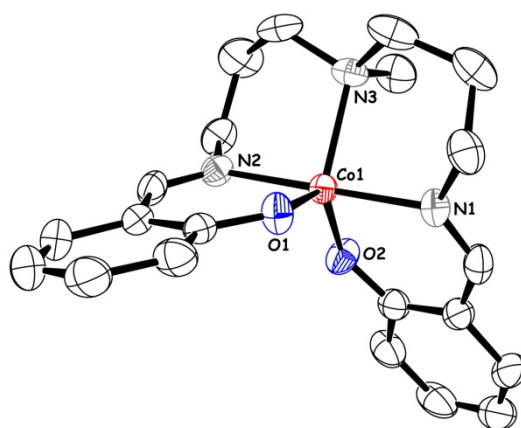


Figure 2-2: Ortep Plot of [Co(salmdpt)] from Butyronitrile

The unit cell for the determined complex shows the same dimensions as the complex described in Chapter 2.1. The structure described here, is probably a dioxygen-inactive form (in solid state) of the [Co(salmdpt)] complex. Crystallographic data are presented in Table 2-3 and Table 2-4.

Table 2-3: Crystal Data and Structure Refinement for [Co(salmdpt)] from Butyronitrile

Habitus	block-shaped
Color	brown
Crystal size	0.36 x 0.20 x 0.20 mm
Temperature	193(2) K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₂₁ H ₂₅ CoN ₃ O ₂
Formula weight	410.37 g/mol
Crystal system, space group	monoclinic, P2 ₁ /c (Nr. 14)
Unit cell dimensions	a = 6.7560(14) Å α = 90° b = 13.767(3) Å β = 92.50(3)° c = 20.801(4) Å γ = 90°
Volume	1932.9(7) Å ³
Z, calculated density	4, 1.410 Mg/m ³
Absorption coefficient	0.909 mm ⁻¹
F(000)	860
Theta range for data collection	2.46 to 27.01
Limiting indices	-8 ≤ h ≤ 8, -17 ≤ k ≤ 17, -26 ≤ l ≤ 24
Reflections collected / unique	15345 / 4198 [R (int) = 0.0702]
Completeness to theta = 27.01	99.2 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4198 / 0 / 274
Goodness-of-fit on F ²	0.931
Final R indices [I > 2σ(I)]	R1 = 0.0430, wR2 = 0.1093
R indices (all data)	R1 = 0.0700, wR2 = 0.1214
Largest diff. peak and hole	0.685 and -0.589 eÅ ⁻³

Table 2-4: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Butyronitrile

Co(1)-N1	2.053(2)	Co(1)-O1	1.99418(19)
Co(1)-N2	2.165(2)	Co(1)-O2	1.946(2)
Co(1)-N3	2.140(2)		
N2-Co(1)-N1	179.62(11)	O1-Co(1)-N3	115.99(10)
N1-Co(1)-N3	90.09(10)	O2-Co(1)-N1	89.53(9)
N2-Co(1)-N3	89.54(10)	O2-Co(1)-N2	90.58(9)
O1-Co(1)-N1	90.46(9)	O2-Co(1)-N3	116.16(10)
O1-Co(1)-N2	89.76(9)	O1-Co(1)-O2	127.85(10)

2.1.3 Benzonitrile as Solvent in an Attempt to Prepare the Superoxido Complex of [Co(salmdpt)]

In accordance with the literature, a silane derivative of [Co(salmdpt)] forms the cobalt superoxido complex in benzonitrile. Due to the fact that all previous experiments trying to get the cobalt superoxido complex failed, benzonitrile was used as a solvent for the reaction with dioxygen. Once the reaction was finished, colorless crystals suitable for X-ray crystallographic analysis formed.^[87] As expected from the missing color of the crystals a different reaction must have occurred. A ^1H NMR spectrum (see Figure 2-3) and an IR spectrum (see Figure 2-4) indicated the formation of benzamide as a product. These results were further confirmed by X-ray analysis of the crystals. The Ortep plot of benzamide is shown in Figure 2-5. The observed unit cell parameters are $a = 5.022(4) \text{ \AA}$, $b = 5.579(5) \text{ \AA}$, $c = 21.779(22) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ and a volume of 610.3 \AA^3 . The described unit cell is analog to the cell of benzamide.

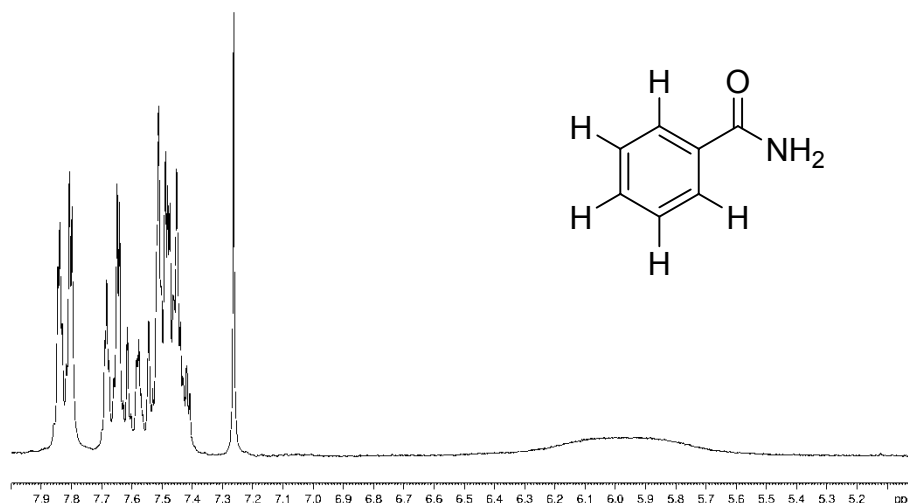


Figure 2-3: ^1H NMR (200 MHz, CDCl_3) of Benzamide: [ppm] = 7.9 – 7.4 (m, 5 H, ArH); 7.26 (s, CDCl_3); 6 (br, 2H, NH_2)

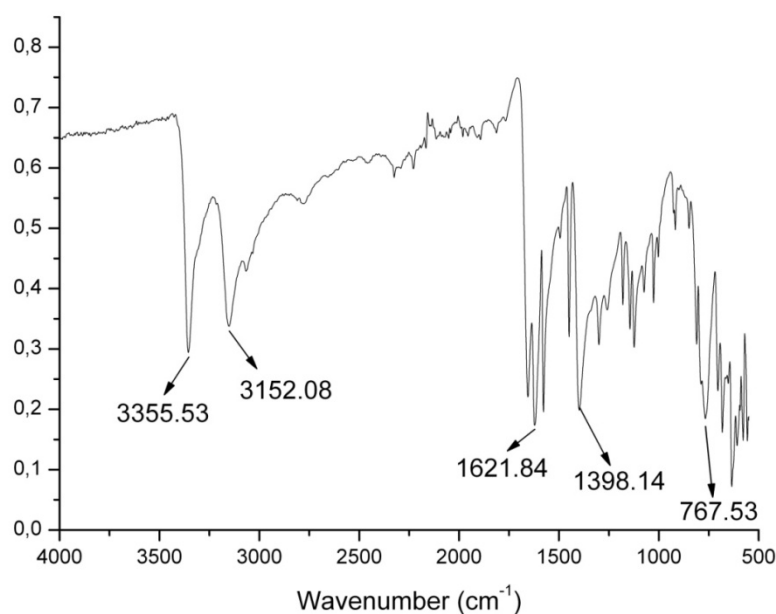


Figure 2-4: IR Spectrum (ATR-technique) of Benzamide: 3355.53 cm⁻¹ N-H-Valency; 3152.08 cm⁻¹ C-H (Ar-H); 1621.84 cm⁻¹ C=O-Valency; 1398.14 cm⁻¹ C=C-Valency (Aryl); 767.53 cm⁻¹ C-H-Valency (Ar-H)

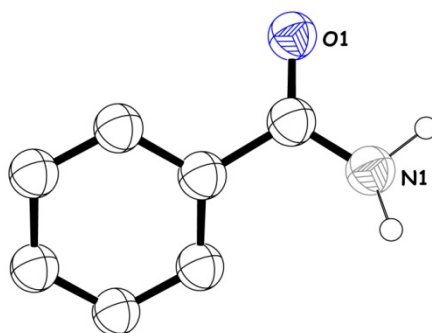
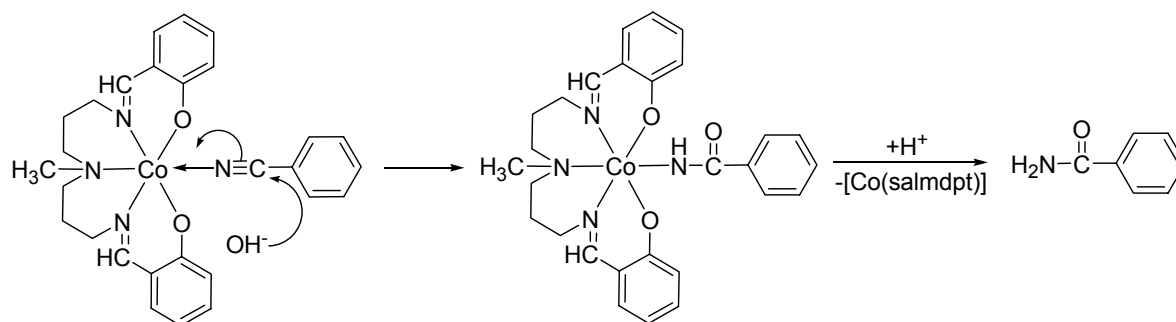


Figure 2-5: Ortep Plot of Benzamide^[88]

The hydrolysis of nitriles has been investigated in detail. Numerous metal salts have been shown to be effective in promoting the hydrolysis of nitriles to amides. The attack has been shown in some cases to be caused by coordinated hydroxide ion, whereas in other cases the hydroxide is acting as an external nucleophile.^[89]

The results obtained for the reaction of [Co(salmdpt)] in benzonitrile indicate that this complex reacts in a similar way.^[89] The proposed mechanism for this reaction is shown in Scheme 2-1.



Scheme 2-1: ChemDraw Plot of the Reaction of Benzonitrile to Benzamide using [Co(salmdpt)]

2.2 Crystal Structure of [Co(salmdpt)] from Dichloromethane

Furthermore it was tried to use dichloromethane in order to prepare the superoxido complex of [Co(salmdpt)]. Still, once more the crystal structure of the Co^{II} complex was obtained. However, different to the other two structures in acetonitrile and butyronitrile, are the crystal symmetry, the space group and the unit cell dimensions (Table 2-6).

The molecular structure depicted in Figure 2-6 shows a five-fold coordination of the cobalt atom in a slightly distorted trigonal bipyramidal arrangement. The cobalt atom is located almost exactly in the middle of the equatorial plane and is surrounded by the atoms O(1), O(2) and N(2). The atoms N(1) and N(3) fill the axial positions. In contrast to the structures described in Chapter 2.1.1 and 2.1.2, the structure described here shows orthorhombic crystal symmetry.

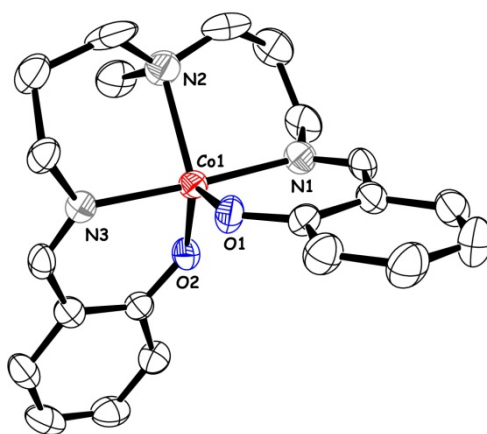


Figure 2-6: Ortep Plot of [Co(salmdpt)] from Dichloromethane

Table 2-5: Crystal Data and Structure Refinement for [Co(salmdpt)] from Dichloromethane

Habitus	block-shaped
Color	brown
Crystal size	0.36 x 0.32 x 0.12 mm
Temperature	193(2) K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₂₂ H ₂₇ Cl ₂ CoN ₃ O ₂
Formula weight	495.30 g/mol
Crystal system, space group	orthorhombic, Pna2 ₁ (Nr. 33)
Unit cell dimensions	a = 13.097(3) Å α = 90° b = 15.280(3) Å β = 90° c = 11.524(2) Å γ = 90°
Volume	2306.2(8) Å ³
Z, calculated density	4, 1.4278 Mg/m ³
Absorption coefficient	0.999 mm ⁻¹
F(000)	1028
Theta range for data collection	2.67 to 28.31
Limiting indices	-15 ≤ h ≤ 17, -20 ≤ k ≤ 20, -15 ≤ l ≤ 15
Reflections collected / unique	20081 / 5504 [R (int) = 0.0908]
Completeness to theta = 28.31	96.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5504 / 1 / 301
Goodness-of-fit on F ²	0.872
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1128
R indices (all data)	R1 = 0.0882, wR2 = 0.1273
Largest diff. peak and hole	1.106 and -1.005 eÅ ⁻³

The space group is Pna2₁, whereas the structures from acetonitrile and butyronitrile crystallize in the space group P2₁/c with a monoclinic crystal symmetry. The crystal cell dimension is also different to those of the two other structures.

The bond angles are different to those of the structures from acetonitrile and butyronitrile as well. In the structure described here, the angles O(1)-Co(1)-O(2), (O1)-Co(1)-N(2) and (O2)-Co(1)-N(2) are 123.40(15), 116.41(18) and 120.19(17). The bond lengths are in the range 1.9 to 2.1 Å, respectively. Therefore, they are similar to those in the other two structures. Crystallographic data are presented in Table 2-5 and Table 2-7.

Table 2-6: Comparison of the Unit Cell Parameters of the Structures Described in Chapter 2.1.1, 2.1.2 and 2.2

	[Co(salmdpt)] from CH ₃ CN	[Co(salmdpt)] from C ₃ H ₇ CN	[Co(salmdpt)] from CH ₂ Cl ₂
Crystal system, space group	monoclinic, P2 ₁ /c	monoclinic, P2 ₁ /c	orthorombic, Pna2 ₁
Unit cell dimensions	a = 6.7627(6) Å α = 90°	a = 6.7560(14) Å α = 90	a = 13.097(3) Å α = 90°
	b = 13.7463(12) Å β = 92.6030(10)°	b = 13.767(3) Å β = 92.50(3)°	b = 15.280(3) Å β = 90°
	c = 20.8444(18) Å γ = 90°	c = 20.801(4) Å γ = 90°	c = 11.524(2) Å γ = 90°
Volume	1935.7(3) Å ³	1932.9(7) Å ³	2306.2(8) Å ³

Table 2-7: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Dichloromethane

Co(1)-N1	2.035(4)	Co(1)-O1	1.954(3)
Co(1)-N2	2.165(4)	Co(1)-O2	1.9459(3)
Co(1)-N3	2.043(4)		
N1-Co(1)-N2	88.51(16)	O1-Co(1)-N3	90.82(14)
N1-Co(1)-N3	176.88(16)	O2-Co(1)-N1	92.03(15)
N3-Co(1)-N2	88.47(16)	O2-Co(1)-N2	120.19(17)
O1-Co(1)-N1	89.83(16)	O2-Co(1)-N3	90.16(14)
O1-Co(1)-N2	116.41(18)	O1-Co(1)-O2	123.40(15)

2.3 Crystal Structure of [Co(salmdpt)] from Toluene

According to the literature, the cobalt superoxido complex has only been obtained from benzene so far.^[49] In the publication reporting on the silane derivatives of [Co(salmdpt)], benzonitrile was used as solvent for the recrystallization.^[53] Given that all experiments with nitrile solvents did not result in the formation of the superoxido complex of [Co(salmdpt)], another solvent should be used in the next experiment. Therefore, toluene was used as a solvent because of its similarity to benzene and in order to avoid the toxicity of benzene.

However, analysis of the crystals obtained from the toluene solution did not show the expected superoxido complex. Instead, the cobalt(II) complex [Co(salmdpt)] was formed. Its crystal structure consists of separate molecules of the complex and of toluene in a 1:1 ratio (Figure 2-8). Crystallographic data are presented in Table 2-8 and Table 2-9.

The structure depicted in Figure 2-8 is similar to the monoclinic structure of the crystals from benzene, described by Orioli and co-workers (Figure 2-7).^[45] The structure obtained from toluene also shows a distorted trigonal bipyramidal arrangement. This is clearly visible from the equatorial angles O(1)-Co(1)-O(2), O(1)-Co(1)-N(1) and O(2)-Co(1)-N(1), which are 132.95(9), 111.73(10) and 115.32(9)°.

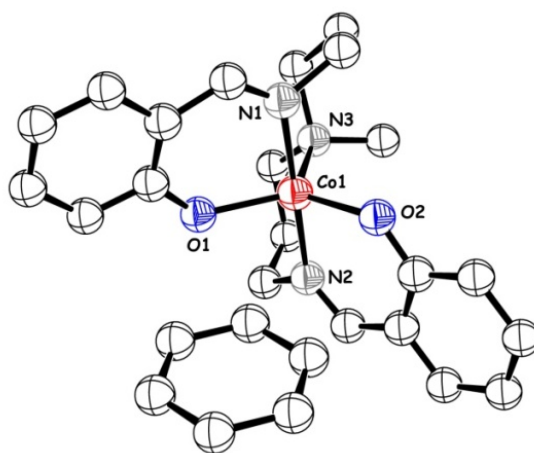


Figure 2-7: Ortep Plot of [Co(salmdpt)] from Benzene (Monoclinic Crystal Symmetry)^[44]

The arrangement around the cobalt atom is roughly identical with that found in the structures of the two oxygen-inactive forms.^[44]

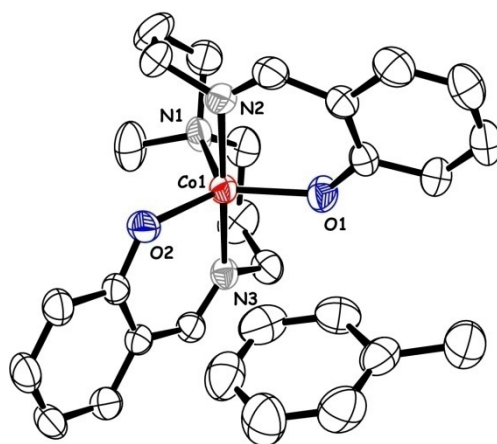


Figure 2-8 Ortep Plot of [Co(salmdpt)] from Toluene

Table 2-8: Crystal Data and Structure Refinement for [Co(salmdpt)] from Toluene

Habitus	prism
Color	brown
Crystal size	0.32 x 0.32 x 0.19 mm
Temperature	193 K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₂₈ H ₃₃ CoN ₃ O ₂
Formula weight	502.50 g/mol
Crystal system, space group	monoclinic, P2 ₁ /c (Nr. 14)
Unit cell dimensions	a = 11.4552(15) Å α = 90° b = 16.6517(15) Å β = 94.567(16)° c = 13.3868(18) Å γ = 90°
Volume	2545.4(5) Å ³
Z, calculated density	4, 1.311 Mg/m ³
Absorption coefficient	0.703 mm ⁻¹
F(000)	1060
Theta range for data collection	2.56 to 28.09
Limiting indices	-15 ≤ h ≤ 15, -20 ≤ k ≤ 21, -17 ≤ l ≤ 17
Reflections collected / unique	22443 / 6124 [R (int) = 0.0892]
Completeness to theta = 28.09	98.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6124 / 0 / 342
Goodness-of-fit on F ²	0.877
Final R indices [I > 2σ(I)]	R1 = 0.0453, wR2 = 0.0845
R indices (all data)	R1 = 0.1147, wR2 = 0.1017
Largest diff. peak and hole	0.355 and -0.267 eÅ ⁻³

The toluene molecules are located in close proximity of the cobalt atom on the side of the wide O(1)-Co(1)-O(2) angle and are almost co-planar with the equatorial plane of the trigonal bipyramid (Figure 2-8). The distance between the two salicylaldehyde groups is 9.8 Å compared to 9.1 Å in the oxygen-inactive form (in solid state) from acetonitrile. The toluene molecule is 4 Å away from the cobalt atom. In addition, it is worth mentioning the O(1)-Co(1)-O(2) angle is wider than the other two equatorial angles in all three forms as a consequence of an in-plane d-electron-ligand repulsion. It reaches a value of 132.95(9)° in this structure compared to 129.8(4)° of the

monoclinic form from benzene and 126.9(3) and 127.9(3)° in the other two forms of [Co(salmdpt)].^[44]

Table 2-9: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)] from Toluene

Co(1)-N1	2.1143(2)	Co(1)-O1	1.958(2)
Co(1)-N2	2.048(3)	Co(1)-O2	1.9551(19)
Co(1)-N3	2.050(2)	N(1)-C21	1.476(7)
N1-Co(1)-N2	89.71(10)	O2-Co(1)-N2	91.09(9)
N1-Co(1)-N3	89.36(10)	O2-Co(1)-N3	88.96(9)
N2-Co(1)-N3	179.00(10)	O1-Co(1)-O2	132.95(9)
O1-Co(1)-N1	111.73(10)	C10-N(1)-C11	106.4(4)
O1-Co(1)-N2	89.18(9)	C10-N(1)-C21	106.3(5)
O1-Co(1)-N3	91.51(9)	C11-N(1)-C21	115.0(5)
O2-Co(1)-N1	115.32(9)		

The cobalt atom is also five-fold coordinated and is located exactly in the middle of the equatorial plane, which is spanned by O(1), O(2) and N(1). N(2) and N(3) fill the axial positions. Probably, this structure is another dioxygen-active species (in solid state) like the one from benzene.^[45] This becomes clear when the crystal packing of the two complexes are compared (Figure 2-9). The crystal data for the determined complex is very similar to the one from benzene. Both crystal structures show monoclinic crystal symmetry and the crystal sizes are nearly identical.

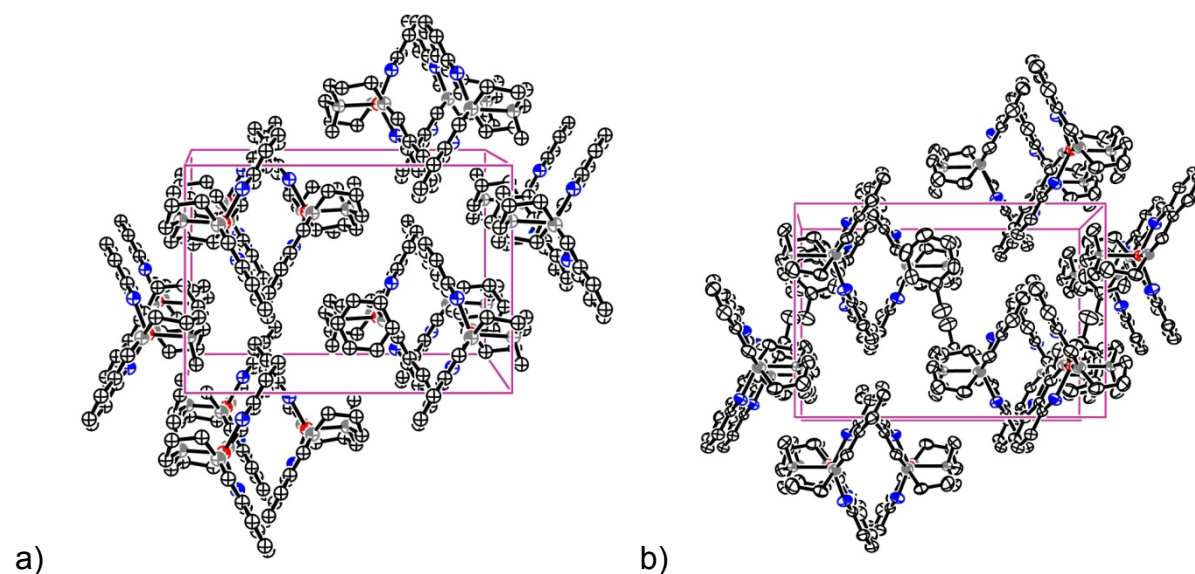


Figure 2-9: a) Crystal Packing of [Co(salmdpt)] and Benzene Molecules. The View is Approximately down the 100 Direction b) Crystal Packing of [Co(salmdpt)] and Toluene Molecules. The View is Approximately down the 001 Direction.

To verify these findings, a lot of experiments in toluene were carried out. However, so far it was not possible to obtain crystals of a superoxido complex of [Co(salmdpt)] from toluene. Therefore, it is not clear if a superoxido complex forms in toluene.

2.4 Synthesis of [Co(salmdpt)O₂] from Benzene

According to the literature, the cobalt(III) superoxido complex has only been obtained from benzene so far. Given that all previous experiments did not show the expected results, the superoxido complex should be prepared strictly according to the literature. The structure of the cobalt(III) superoxido complex is shown in Figure 1-8. To synthesize the depicted complex, a solution of the cobalt(II) complex in dry benzene under inert conditions was generated. This solution was flushed with pure dioxygen. The dioxygen flask was stored in a fridge. However, no crystals for X-ray crystallographic analysis, but a black powder of the product could be obtained. Nevertheless, the color of the obtained powder, and the IR spectra described below, indicated that the [Co(salmdpt)O₂] complex was formed.

2.4.1 Results of the IR Spectroscopic Analysis of [Co(salmdpt)O₂] from Benzene

IR spectra of the crystals from the dioxygen-free [Co(salmdpt)] complex were obtained and described in Chapter 2.1.1, as well as from the powder obtained from the desired [Co(salmdpt)O₂] complex in benzene. In Figure 2-10 and Figure 2-11 the IR spectra are depicted. The comparison of the IR spectra is depicted in Figure 2-12 and Figure 2-13. It is clearly visible, that the spectrum of the oxidized complex shows a different band located at 683.7 cm⁻¹, which does not occur in the spectrum of the dioxygen-free complex (Figure 2-10). This is probably the cobalt dioxygen band (Co-O₂), which occurs in the spectrum of the oxidized complex.

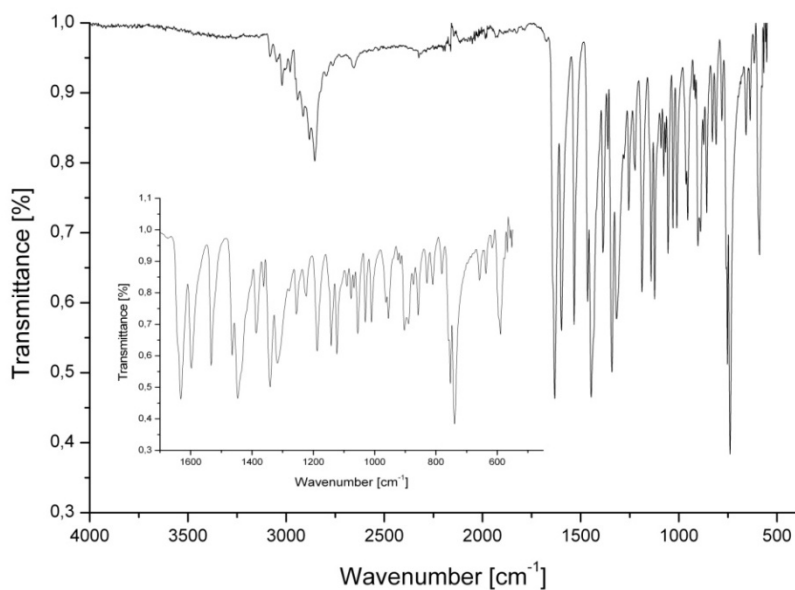


Figure 2-10: IR Spectrum of [Co(salmdpt)] from Acetonitrile

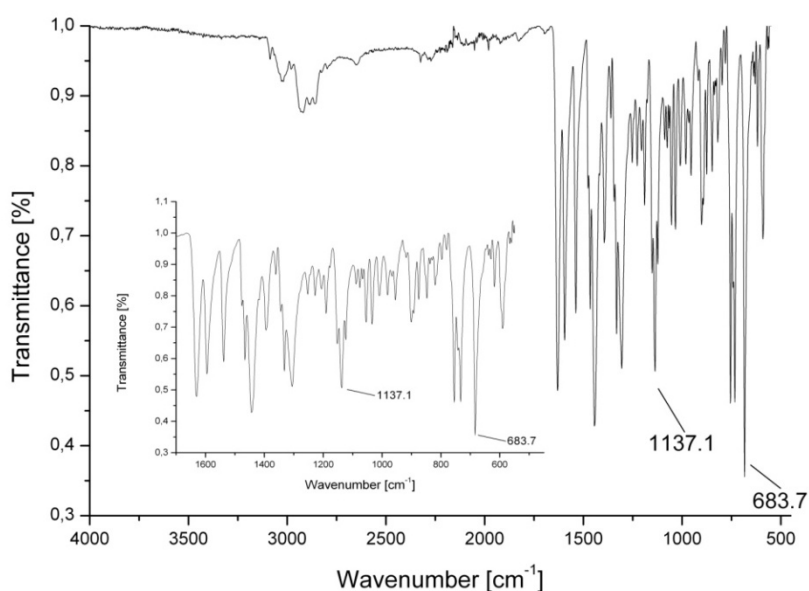


Figure 2-11: IR Spectrum of [Co(salmdpt)O₂] from Benzene

Next to this band, another band of the bound dioxygen is visible in the spectrum of the oxidized complex. This must be the band of the superoxido ion (O_2^-). It has to be located in the range of 1120 to 1150 cm^{-1} .^[90] A band is located in this area (1137 cm^{-1}) but it is also detectable in the spectrum of the dioxygen-free complex.

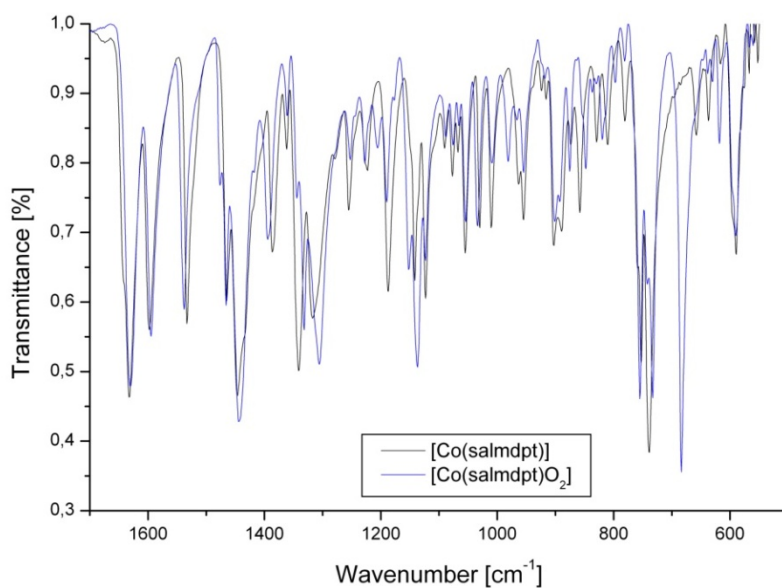


Figure 2-12: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)O₂]

On closer inspection, it is obvious that the band at 1137 cm⁻¹ has become more intense. Therefore, we gathered that the band of the superoxido ion is located on top of the band which is already present in the spectrum of the dioxygen-free complex (Figure 2-13).

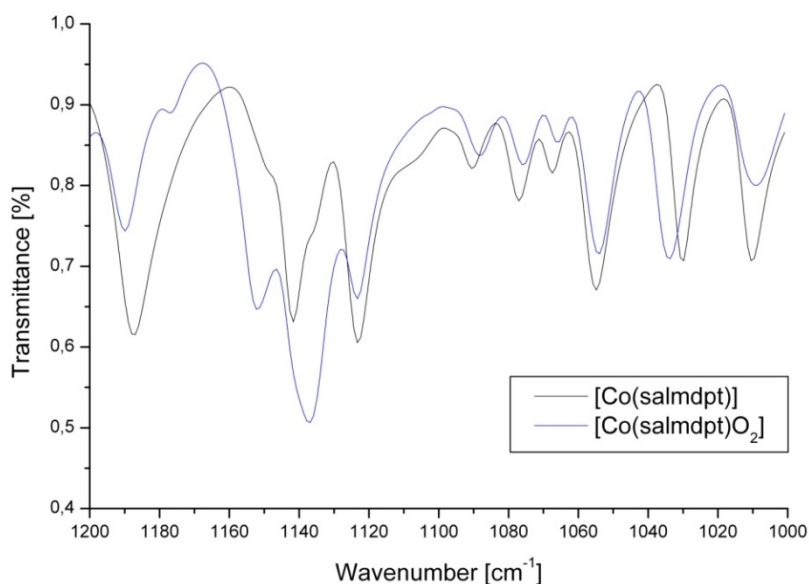


Figure 2-13: Selected Area for the Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)O₂]

2.5 Cobalt(II) Complexes with Derivatives of SaldptH₂ and a SalmdptH₂ as Ligands

As described in the introduction, the cobalt(II) complex with saldptH₂ as ligand forms a dinuclear peroxido complex.^[43] With the knowledge that sterical hindrance can suppress the formation of dinuclear species bulky groups were introduced into this ligand. Using a *tert*-butyl derivative it was aimed to stabilize the cobalt superoxido complex that must form here as an intermediate as well. However when [Co(3,5-Di-*tert*-butyl-saldpt)] (Figure 2-14) was oxidized in acetonitrile again only the dinuclear peroxido complex could be isolated.

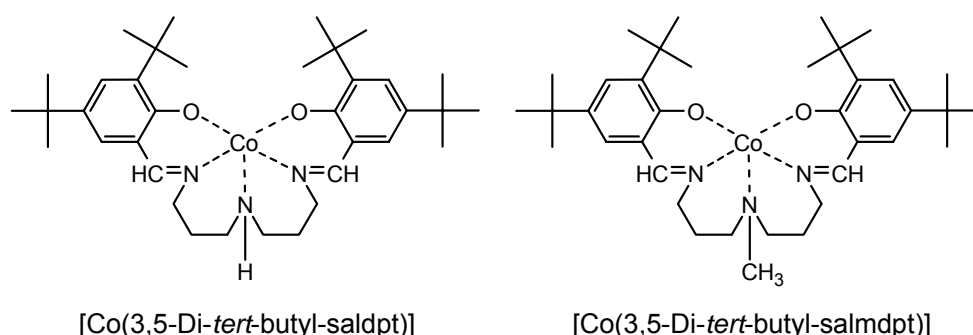
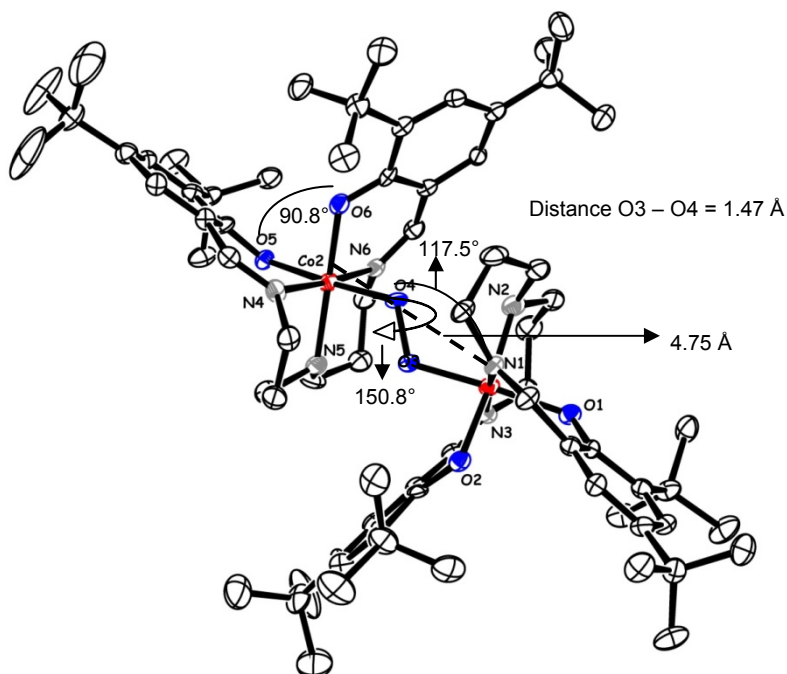


Figure 2-14: ChemDraw Plot of [Co(3,5-Di-*tert*-butyl-salmdpt)] and [Co(3,5-Di-*tert*-butyl-saldpt)]

2.5.1 Results of the X-ray Crystallographic Analysis of [Co(3,5-Di-*tert*-butyl-saldpt)O₂] from Acetonitrile

[Co(3,5-Di-*tert*-butyl-saldpt)O₂], depicted in Figure 2-15, is a dimeric structure in which the two cobalt atoms are bridged by an O-O-group. The bond length between the two oxygen atoms averages 1.47 Å, and the angle of torsion Co(1)-O(3)-O(4)-Co(2) averages 150.8° (Figure 2-15). This is a typical feature of peroxido groups.^[42-43] The octahedral environment of the cobalt atom includes three oxygen and three nitrogen atoms. Both oxygen atoms of the salicylaldehyde groups are in *cis* position, whereas the imine nitrogen atoms are in *trans* position (Figure 2-15).^[43] The equatorial plane is formed by the three nitrogen atoms and one oxygen atom of the salicylaldehyde moiety. For Co(1) these are N(1), N(2), N(3) and O(2). For Co(2) these are N(4), N(5), N(6) and O(6). The cobalt atoms are located almost exactly in the middle of the equatorial plane. The axial positions are occupied by the



Thus the structure is similar to the one depicted in Figure 1-6. Some discrepancies could be detected when comparing the cell parameters of both structures. The unit cell dimensions are not the same, as well as the crystal system and space group. Cell parameters of both complexes are shown in Table 2-12. Most likely these crystals contained electron density in the unit cell, which could not be assigned during the structure determination and refinement.

Table 2-10: Crystal Data and Structure Refinement for [Co(3,5-Di-*tert*-butyl-saldpt)O₂] from Acetonitrile

Habitus	needle	
Color	red-brown	
Crystal size	0.12 x 0.12 x 0.80 mm	
Temperature	193(2) K	
Diffractometer type	STOE IPDS	
Wavelength	0.71073 Å	
Empirical formula	C ₇₆ H ₁₁₆ Co ₂ N ₈ O _{6.75}	
Formula weight	1371.63 g/mol	
Crystal system, space group	triclinic, $P\bar{1}$ (Nr. 2)	
Unit cell dimensions	a = 14.011(3) Å	$\alpha = 72.59(3)^\circ$
	b = 15.413(3) Å	$\beta = 72.23(3)^\circ$
	c = 19.888(4) Å	$\gamma = 76.85(3)^\circ$
Volume	3858.4(13) Å ³	
Z, calculated density	2, 1.181 Mg/m ³	
Absorption coefficient	0.485 mm ⁻¹	
F(000)	1476	
Theta range for data collection	2.31 to 27.07	
Limiting indices	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25	
Reflections collected / unique	31491 / 15635 [R (int) = 0.1166]	
Completeness to theta = 27.07	92.1 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	15635 / 0 / 890	
Goodness-of-fit on F ²	0.976	
Final R indices [I > 2σ(I)]	R1 = 0.1027, wR2 = 0.2518	
R indices (all data)	R1 = 0.2117, wR2 = 0.2874	
Largest diff. peak and hole	0.842 and -0.655 eÅ ⁻³	

Table 2-11: Selected Bond Lengths [Å] and Angles [°] for [Co(3,5-Di-*tert*-butyl-saldpt)O₂] from Acetonitrile

Co(1)-N1	1.918(7)	Co(1)-O1	1.926(6)
Co(1)-N2	1.984(8)	Co(1)-O2	1.896(6)
Co(1)-N3	1.932(7)	Co(1)-O3	1.897(6)
Co(2)-N4	1.921(7)	Co(1)-O4	1.890(6)
Co(2)-N5	1.991(8)	Co(1)-O5	1.909(5)
Co(2)-N6	1.938(7)	Co(1)-O6	1.891(6)
O(3)-O(4)	1.471(7)		
N1-Co(1)-N2	89.5(3)	O2-Co(1)-N3	90.1(3)
N1-Co(1)-N3	174.6(3)	O3-Co(1)-N1	91.8(3)
N3-Co(1)-N2	95.1(3)	O3-Co(1)-N2	90.1(3)
O1-Co(1)-N1	90.1(3)	O3-Co(1)-N3	90.9(3)
O1-Co(1)-N2	92.5(3)	O1-Co(1)-O2	91.8(2)
O1-Co(1)-N3	87.0(3)	O1-Co(1)-O3	176.8(3)
O2-Co(1)-N1	85.5(3)	O2-Co(1)-O3	85.7(2)
O2-Co(1)-N2	173.4(3)	O4-O3-Co(1)	117.5(4)
N4-Co(2)-N5	87.6(3)	O5-Co(2)-N6	87.5(3)
N4-Co(2)-N6	175.3(3)	O6-Co(2)-N4	86.8(3)
N6-Co(2)-N5	95.4(3)	O6-Co(2)-N5	173.3(3)
O4-Co(2)-N4	93.6(3)	O6-Co(2)-N6	90.3(3)
O4-Co(2)-N5	90.3(3)	O4-Co(2)-O5	176.1(3)
O4-Co(2)-N6	89.9(3)	O4-Co(2)-O6	86.4(2)
O5-Co(2)-N4	88.9(3)	O5-Co(2)-O6	90.8(2)
O5-Co(2)-N5	92.9(3)	O3-O4-Co(2)	117.1(4)

Table 2-12: Cell Parameters of [Co(saldpt)O₂] and [Co(3,5-Di-*tert*-butyl-saldpt)O₂]

	[Co(saldpt)O ₂]	[Co(3,5-Di- <i>tert</i> -butyl-saldpt)O ₂]
Crystal system, space group	Monoclinic, C2/c (Nr.15)	Triclinic, P $\bar{1}$ (Nr. 2)
Unit cell dimensions	a = 10.236(7) Å / α = 90° b = 24.210(20) Å / β = 104.06(6)° c = 18.020(10) Å / γ = 90°	a = 14.011(3) Å / α = 72.59(3)° b = 15.413(3) Å / β = 72.23(3)° c = 19.888(4) Å / γ = 76.85(3)°
Volume	4331.819 Å ³	3858.4(13) Å ³

2.5.2 Results of the X-ray Crystallographic Analysis of [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone

Obviously, as described in Chapter 2.5.1, introducing *tert*-butyl groups in saldpH₂ was not sufficient to stabilize a cobalt superoxido complex because it still was able to form the dimer. Therefore again the methyl derivative, salmdpH₂, was used and the according cobalt(II) complex was synthesized (Figure 2-14). However, in contrast to our expectations no oxidation of the complex was observed in acetone and only the starting material, [Co(3,5-Di-*tert*-butyl-salmdpt)], could be crystallized. Two different types of crystals suitable for X-ray analysis from acetone were obtained.

Structure 1

[Co(3,5-Di-*tert*-butyl-salmdpt)], depicted in Figure 2-16, showed a distorted trigonal bipyramidal arrangement. The central cobalt(II) atom of the complex is five-fold coordinated and located almost in the middle of the equatorial plane. The atoms O(1), O(1a) and N(1) span the equatorial plane, and the atoms N(2) and N(2a) fill the axial positions. The bond angles are 141.19° for O(1)-Co(1)-O(1a), and 109.40° for O(1)-Co(1)-N(1) and O(1a)-Co(1)-N(1). In comparison to the structures of [Co(salmdpt)] described in Chapters 2.1.1, 2.1.2 and 2.2, the equatorial angle O(1)-Co(1)-O(1a) is wider than in the other structures. This is probably an effect of the *tert*-butyl-groups in 3rd position to the imine function of the salicylaldehyde moieties. Crystallographic data are presented in Table 2-13 and Table 2-14.

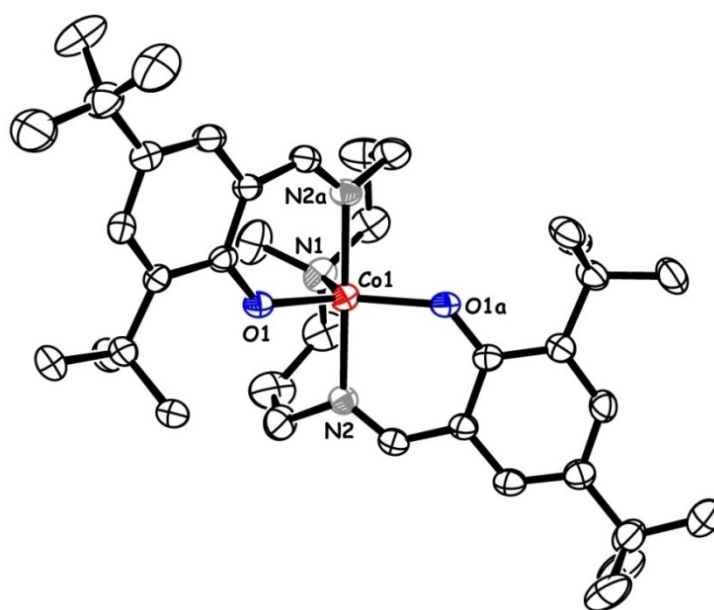


Figure 2-16: Ortep Plot of [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone (Structure 1)

Table 2-13: Crystal Data and Structure Refinement for [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone (Structure 1)

Habitus	needle
Color	brown
Crystal size	0.48 x 0.08 x 0.08 mm
Temperature	193(2) K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₃₇ H ₅₇ CoN ₃ O ₂
Formula weight	634.79 g/mol
Crystal system, space group	orthorhombic, Ccca (Nr. 68)
Unit cell dimensions	a = 20.778(4) Å α = 90.0° b = 27.141(5) Å β = 90.0° c = 13.768(3) Å γ = 90.0°
Volume	7764(3) Å ³
Z, calculated density	8, 1.086 Mg/m ³
Absorption coefficient	0.473 mm ⁻¹
F(000)	2744
Theta range for data collection	2.87 to 28.13
Limiting indices	-27 ≤ h ≤ 27, -35 ≤ k ≤ 35, -16 ≤ l ≤ 16
Reflections collected / unique	33408 / 4455 [R (int) = 0.1413]
Completeness to theta = 28.13	93.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4455 / 0 / 256
Goodness-of-fit on F ²	0.888
Final R indices [I > 2σ(I)]	R1 = 0.0531, wR2 = 0.1428
R indices (all data)	R1 = 0.1189, wR2 = 0.1621
Largest diff. peak and hole	0.845 and -0.324 eÅ ⁻³

[Co(3,5-Di-*tert*-butyl-salmdpt)] shows an orthorhombic crystal symmetry with a symmetry center. The space group of the complex is Ccca and the unit cell dimensions are bigger than in the structures of [Co(salmdpt)]. In the structure depicted in Figure 2-16, there is one long axis with 27.141 Å. The axis of approximately 20.8 Å could be also obtained in the structure of [Co(salmdpt)].

Most likely these crystals contained a solvent molecule in the unit cell, but this could not be assigned during the structure determination and refinement. Also, the *tert*-butyl group in 5th position to the imine function of the salicylaldehyde moieties is disordered. Maybe, these are reasons for the difference of the crystal symmetry, space group and unit cell parameters compared with the second set of crystals described below.

Table 2-14: Selected Bond Lengths [Å] and Angles [°] for [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone (Structure 1)

Co(1)-N1	2.138(5)	Co(1)-O1	1.967(2)
Co(1)-N2	2.062(3)	Co(1)-O1a	1.967(2)
Co(1)-N2a	2.062(3)		
N1-Co(1)-N2	89.52(10)	O1-Co(1)-N2	92.28(11)
N1-Co(1)-N2a	89.52(10)	O1a-Co(1)-N2	88.04(10)
N2-Co(1)-N2a	179.0(2)	O1-Co(1)-N2a	88.04(10)
O1-Co(1)-N1	109.40(8)	O1a-Co(1)-N2a	92.28(11)
O1a-Co(1)-N1	109.40(8)	O1-Co(1)-O1a	141.19(17)

Structure 2

[Co(3,5-Di-*tert*-butyl-salmdpt)], depicted in Figure 2-17, showed also a distorted trigonal bipyramidal arrangement as described for Structure 1. The cobalt(II) atom of the complex is five-fold coordinated and located almost in the middle of the equatorial plane spanned by the atoms O(1), O(2) and N(2). The atoms N(1) and N(3) fill the axial positions. The bond angles are 136.69° for O(1)-Co(1)-O(2), 111.63° for O(1)-Co(1)-N(2) and 111.6° for O(2)-Co(1)-N(2). In comparison to Structure 1, the equatorial angle O(1)-Co(1)-O(2) is smaller than in the other structure. In consequence of this the equatorial angle is located in the range of the structures of [Co(salmdpt)]. Crystallographic data are presented in Table 2-10 and Table 2-16.

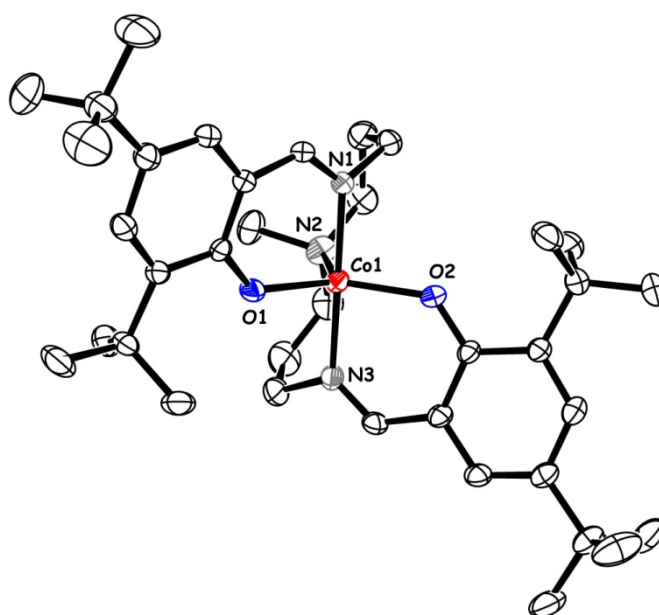
**Figure 2-17: Ortep Plot of [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone (Structure 2)**

Table 2-15: Crystal Data and Structure Refinement for [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone (Structure 2)

Habitus	plate
Color	red-brown
Crystal size	0.56 x 0.56 x 0.16 mm
Temperature	193(2) K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₃₇ H ₅₇ CoN ₃ O ₂
Formula weight	634.79 g/mol
Crystal system, space group	monoclinic, P2 ₁ /c (Nr. 14)
Unit cell dimensions	a = 15.215(3) Å α = 90.0° b = 19.983(4) Å β = 102.50(3)° c = 12.273(3) Å γ = 90.0°
Volume	3643.1(13) Å ³
Z, calculated density	4, 1.157 Mg/m ³
Absorption coefficient	0.504 mm ⁻¹
F(000)	1327
Theta range for data collection	2.21 to 28.10
Limiting indices	-18 ≤ h ≤ 18, -26 ≤ k ≤ 26, -16 ≤ l ≤ 16
Reflections collected / unique	32948 / 8399 [R (int) = 0.0921]
Completeness to theta = 28.10	94.6 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8399 / 0 / 430
Goodness-of-fit on F ²	0.838
Final R indices [I > 2σ(I)]	R1 = 0.0429, wR2 = 0.0890
R indices (all data)	R1 = 0.0882, wR2 = 0.1008
Largest diff. peak and hole	0.504 and -0.681 eÅ ⁻³

Here, [Co(3,5-Di-*tert*-butyl-salmdpt)] shows a monoclinic crystal symmetry without a symmetry center. The space group of the complex is P2₁/c and the unit cell dimensions are smaller than in the structure of [Co(3,5-Di-*tert*-butyl-salmdpt)].

Table 2-16: Selected Bond Lengths [Å] and Angles [°] for [Co(3,5-Di-*tert*-butyl-salmdpt)] from Acetone (Structure 2)

Co(1)-N1	2.0424(19)	Co(1)-O1	1.9565(17)
Co(1)-N2	2.0581(19)	Co(1)-O2	1.9604(19)
Co(1)-N3	2.149(2)		
N1-Co(1)-N2	89.96(8)	O1-Co(1)-N2	111.63(9)
N1-Co(1)-N3	179.38(8)	O2-Co(1)-N2	111.66(9)
N2-Co(1)-N3	89.51(8)	O1-Co(1)-N3	91.35(7)
O1-Co(1)-N1	88.53(7)	O2-Co(1)-N3	87.81(7)
O2-Co(1)-N1	92.70(7)	O1-Co(1)-O2	136.69(7)

2.6 Experimental Section

2.6.1 Materials and Techniques

Commercially available materials were used without further purification. Solvents for oxygen-sensitive materials were obtained from Acros and were additionally distilled under argon before usage. Oxygen-sensitive compounds and materials were handled in a glove box (M. Braun, Germany, O₂ < 0.1 ppm). [Co(saldpt)], [Co(salmdpt)] and [Co(3,5-Di-*tert*-butyl-saldpt)] were synthesized according to published procedures.^[37, 91]

2.6.2 Physical Measurements

Single crystal X-ray diffraction studies were performed with a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and an IP detector system were used. The frames were integrated with the STOE software package. No absorption corrections were applied.

Otherwise, the single crystal X-ray diffraction studies were performed with a Siemens SMART CCD 1000 diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å) equipped with a graphite monochromator and a CCD detector. The collected reflections were corrected for absorption effects (SADABS, Siemens Area Detector Absorption Correction, Siemens, Forschungszentrum Karlsruhe ITC-CPV)

All structures were solved by direct methods and refined by using full-matrix least-squares in the SHELX software package.^[92-93] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned geometrically.

^1H NMR spectra were recorded with a Bruker Aspect 2000/3000 400 MHz, a Bruker Avance II 400 MHz WB (AV 400) or a Bruker Avance II 200 MHz „Microbay“ (AV200). ATR-IR spectra were gained using a Bruker Optics ISF48 spectrometer with an ATR unit (“golden gate”, diamond, one reflexion).

2.6.3 Syntheses

[Co(salmdpt)] from Acetonitrile

For the synthesis of the cobalt(II) complexes, the ligands had to be synthesized. This was carried out by condensation reactions of the corresponding amine and salicylaldehyde. The ligand bis[3-(salicylidenimino)-propyl]methylaniline (salmdptH₂) was prepared according to the literature by a condensation reaction of *N*-methyl-*N,N'*-bis-(3-aminopropyl)-amine and salicylaldehyde.

3.14 g (21.64 mmol) *N*-methyl-*N,N'*-bis-(3-aminopropyl)-amine and 5.29 g (43.29 mmol) salicylaldehyde were dissolved in 48 mL ethanol. The mixture was heated for 15 min. A solution of 1.8 g (45 mmol) NaOH and 10 mL H₂O was added. Afterwards, a hot solution of 6 g (24 mmol) cobalt acetate tetrahydrate in 20 mL H₂O was added drop wise. The mixture was refluxed for 30 min. The reaction mixture was cooled over night, filtered off, washed two times with 20 mL of ethanol and dried *in vacuo*. A brown powder was obtained.

For purification, the precipitate was extracted in a soxhlet-apparatus. Acetonitrile was used as solvent. After cooling the solution, brown, square crystals were obtained.

[Co(salmdpt)] from Butyronitrile

0.5 g (1.21 mmol) [Co(salmdpt)] was heated under reflux in a small amount of butyronitrile while dioxygen was flushed through the solution for 10 min. After this, the solution was filtered while hot. The resulting brown solution was allowed to cool very slowly from 80°C to room temperature in a Dewar flask filled with hot water. The brown solution was then stored in a fridge to yield crystals. After a few hours, dark brown crystals suitable for structural characterization formed.

[Co(salmdpt)] from Benzonitrile

0.268 g (0.65 mmol) [Co(salmdpt)] was heated under reflux in a small amount of benzonitrile. This reaction was carried out under influence of air. The solution was

then heated to reflux for another 30 min. and filtered while hot. The resulting solution was allowed to cool over night in a Dewar flask filled with hot water. Subsequent to this, the solution was stored in a fridge. However, no crystals formed even after a few days. Therefore, the solution was flushed with dioxygen for 15 min. and stored in the fridge again. Colorless crystals suitable for X-ray analysis could be obtained. ^1H NMR (200 MHz, CDCl_3) of Benzamide: [ppm] = 7.9 – 7.4 (m, 5 H, ArH); 7,26 (s, CDCl_3); 6 (br, 2H, NH_2). IR Spectrum (ATR-technique) of Benzamide: 3355.53 cm^{-1} N-H-Valency; 3152.08 cm^{-1} C-H (Ar-H); 1621.84 cm^{-1} C=O-Valency; 1398.14 cm^{-1} C=C-Valency (Aryl); 767.53 cm^{-1} C-H-Valency (Ar-H).

[Co(salmdpt)] from Dichloromethane

1.0 g (2.4 mmol) [Co(salmdpt)] was dissolved in dichloromethane (25 mL) while dioxygen was flushed through the solution for 10 min. A brown solution was obtained after the reaction mixture was filtered. The filtrate was then stored in a fridge. After two days, brown crystals suitable for structural characterization formed.

[Co(salmdpt)] from Toluene

0.5 g (1.2 mmol) [Co(salmdpt)] was dissolved in 25 mL toluene. The solution was stirred for 10 min. and afterwards filtered. The saturated solution was flushed with dioxygen for 10 min. The flask was stored under 800 mbar dioxygen over pressure at room temperature to form crystals. After a few more days brown, prismatic crystals suitable for structural X-ray characterization were obtained.

[Co(salmdpt)O₂] from Benzene

0.5 g (1.2 mmol) [Co(salmdpt)] was dissolved in 20 mL benzene. The solution was stirred for 10 min. at room temperature. The excess of the complex was afterwards filtered off and the saturated solution was flushed with dioxygen for 10 min. The flask was stored under 800 mbar dioxygen over pressure at room temperature to form crystals. Even after a few days no crystals were formed. The solution was stored in a fridge. We repeated this experiment a couple of times, but as a product we always obtained a black powder.

[Co(3,5-Di-tert-butyl-saldpt)O₂] from Acetonitrile

155.1 mg (10 mmol) [Co(3,5-Di-tert-butyl-saldpt)] was dissolved in 25 mL acetonitrile. The solution was stored at room temperature and under influence of air. After a few days, brown crystals suitable for structural characterization formed.

[Co(3,5-Di-tert-butyl-salmdpt)] from Acetone (Structure 1)

A solution of the complex 0.3 g (5×10^{-4} mol) in 5 mL acetone was prepared in a glove box. The solution was filtered and stored at room temperature outside of the glove box to form crystals. After the solvent was evaporated, crystals suitable for X-ray crystallographic analysis could be obtained.

[Co(3,5-Di-tert-butyl-salmdpt)] from Acetone (Structure 2)

A solution of the complex 0.3 g (5×10^{-4} mol) in 5 mL acetone was prepared in a glove box. Afterwards the solution was filtered, flushed with dioxygen for 5 minutes and stored at room temperature outside of the glove box to form crystals. After the solvent was evaporated, crystals suitable for X-ray crystallographic analysis could be obtained.

3 Synthesis and Properties of a Cobalt Cyanido Complex

3.1 Transformation of Nitrile to Cyanide and Aldehyde Using a Cobalt(II) Complex and Dioxygen

This work has been published previously in *Angewandte Chemie*

Jörg Müller, Christian Würtele, Olaf Walter and Siegfried Schindler

Angew. Chem. **2007**, 119, 7922 (*Angew. Chem. Int. Ed.* **2007**, 46, 7775)

Activation of carbon-carbon bonds under mild conditions is of great interest in organometallic chemistry and some transition metal complexes proved to be active in C–C bond cleavage.^[94] However, C(α)-CN bond cleavage in nitriles using transition-metal complexes has been studied in detail (a few examples are given in the references), and usually the corresponding cyanide complexes and alkanes or alkenes were observed as products.^[94-99] Furthermore, such a reaction was observed using a cobalt dinitrogen complex.^[99]

In that regard, the recent report by Lu et al. of the transformation of a nitrile into the corresponding alcohol and cyanide using a relative simple dinuclear copper(II) cryptate complex was quite interesting.^[100] However, this result has been questioned by Nelson and co-workers, who could not reproduce the findings during their detailed investigations.^[101] According to our own studies on related copper systems,^[102] we believe that the reported formation of cyanide might occur, provided that the exact reaction conditions are met (although we disagree with the postulated reaction mechanism). Most recently, additional support for these findings was provided by Karlin and co-workers, who demonstrated that during oxidation with O₂ a dinuclear copper(I) complex with a phenol derivative of our previously reported ligand 1,3-bis[bis(2-pyridylmethyl)-amino]benzene (1,3-tpbd)^[103-104] caused hydroxylation of the nitrile substrate to cyanide and aldehyde.^[105-108] Furthermore, heterolytic cleavage of the C–C bond of acetonitrile with simple monomeric copper(II) complexes has been described by Mascharak and co-workers.^[109] We think that this C(α)-CN is a more general reaction that can occur with different transition-metal complexes and we report herein such a reaction using a well-known cobalt complex.

The cobalt(II) complex of the dianion of bis[3-(salicylideneimino)propyl]methylamine (salmdptH₂), [Co(salmdpt)] (**1**), has been reported and is commercially available.^[37, 91] Reaction of **1** with dioxygen in benzene forms an end-on superoxido complex [Co(salmdpt)O₂] (**2**), which has been structurally characterized previously (1:1 cocrystallization with unreacted **1**).^[48-49] Wanting to better understand the formation and reactivity of 1:1 dioxygen–metal adduct complexes,^[110-111] we successfully repeated this oxidation reaction. Cini and Orioli claimed that the reaction can only occur in benzene,^[48-49] but recent work with a silyl derivative of salmdptH₂ showed that such products can be obtained in nitrile solvents as well.^[53] Therefore, we hoped that we might obtain a better yield of **2** using acetonitrile as solvent for the reaction with dioxygen. Reaction of **1** with air or dioxygen under reflux in acetonitrile for 10 min. resulted in the unexpected formation of the cyanide Co(III) complex [Co(salmdpt)CN] (**3**) in approximately 50% yield. The molecular structure of **3** is shown in Figure 3-1.

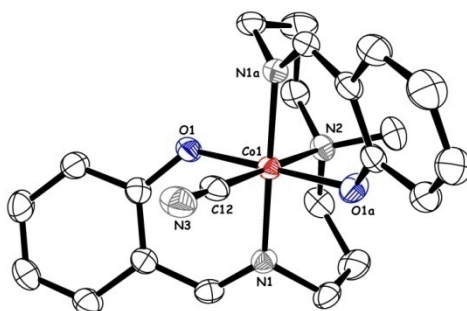
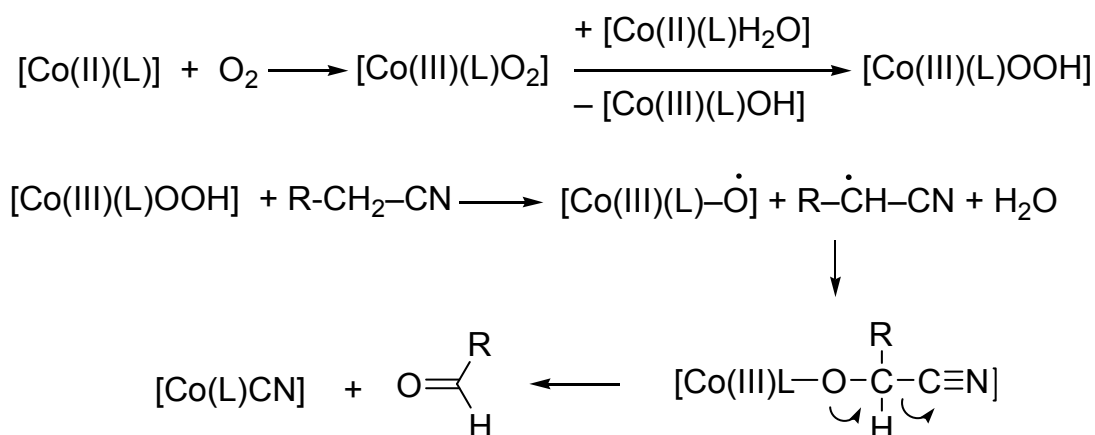


Figure 3-1: Molecular Structure of [Co(salmdpt)CN] (3**); Thermal Ellipsoids are set at 50% Probability; Hydrogen Atoms and Acetonitrile Solvent Molecules present in the Crystal Lattice are not shown). Selected Bond Lengths [Å] and Angles [°]: C12–N3 1.150(4), C12–Co1 1.890(3); N3–C12–Co1 180.0.**

Crystallographic data of **3** are similar to other known Co–CN complexes described in the literature (only a few examples are given in the references).^[112-114]

For this reaction, we propose the mechanism shown in Scheme 3-1, which is supported by several different findings. As discussed above, the existence of the end-on superoxido cobalt complex has been confirmed by X-ray crystallography.^[48-49]



Scheme 3-1: Postulated Reaction Mechanism (L=Salmdpt)

Furthermore, a detailed kinetic study on the formation of **2** in acetone has been reported by Busch and co-workers.^[115] So far, we do not have proof of the occurrence of a hydroperoxido complex $[\text{Co(III)(salmdpt)OOH}]$ (**4**) as an intermediate, but such compounds are known, and the first full characterization of such a species with a macrocyclic ligand has been reported by Guzei and Bakac.^[116]

Furthermore, Karlin and co-workers observed a dinuclear copper hydroperoxido complex (characterized by UV/Vis and Resonance Raman spectroscopy).^[105-108] The presence of dioxygen and water is necessary, because under inert conditions **1** could be recrystallized from acetonitrile solution. However, when a solution of **1** in toluene was heated in the presence of water and air, the cobalt hydroxido complex $[\text{Co(III)(salmdpt)OH}]$ (**5**; shown in Scheme 3-1) was formed, again in line with the proposed mechanism (unfortunately, we were not yet able to isolate **5** from the reaction in acetonitrile). The molecular structure of **5** is shown in Figure 3-2. A similar reaction pathway has been proposed for the oxidation of a related cobalt Schiff base complex in methanol.^[117]

To date we have support neither for the interaction between **4** and the nitrile molecule nor for the O-O cleavage and can only suggest the mechanism in Scheme 3-1 as a possible pathway. In general, the reaction could be performed in acetonitrile, propionitrile and butyronitrile. While it was not possible to unambiguously detect formaldehyde or acetaldehyde under our reaction conditions, we could clearly detect **3**, and we observed the formation of propionaldehyde in ^1H NMR spectra and by GC-MS analysis if butyronitrile was used as a solvent. Karlin and co-workers detected

benzaldehyde by GC-MS analysis in their experiments using a mixture of benzylnitrile and CH_2Cl_2 .^[105]

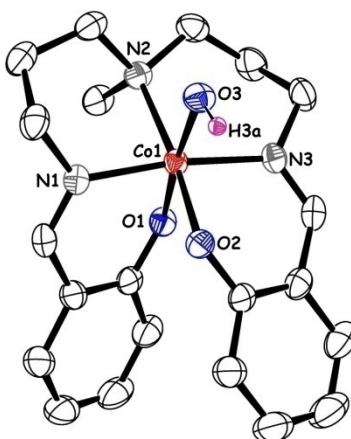


Figure 3-2: Molecular Structure of [Co(salmdpt)OH] (5); Thermal Ellipsoids are set at 50% Propability; Hydrogen atoms except H of OH and Water and Methanol Molecules present in the Crystal Lattice are not shown). Selected Bond Lengths [Å] and Angles [°]: O1-Co1 1.901(2), O2-Co1 1.903(2), O3-Co1 1.897(2), N1-Co1 1.933(2), N2-Co1 1.965(2), N3-Co1 2.065(2); O3-Co1-O1 175.01(8)

In the future, complexes of the type discussed herein might be useful in organic synthesis if these reactions can be further optimized. Specifically, such a reaction could be performed in a solvent such as toluene (using an excess of the cobalt complex) with a nitrile compound as a substrate to obtain the corresponding aldehyde shortened by one carbon atom.

3.1.1 Experimental Section

$\text{H}_2\text{Salmdpt}$ and **1** were prepared according to the literature.^[37, 91]

3: Complex **1** (1.0 g, 2.437 mmol) was heated at reflux in acetonitrile (approximately 25 mL) while O_2 was passed through the solution for 10 min. Subsequently, the solution was filtered while hot. The resulting brown solution was allowed to cool very slowly from 80°C to room temperature in a Dewar flask filled with hot water. After two days, dark brown crystals suitable for structural characterization formed.

5: Similar to the preparation of **3**, complex **1** (1.0 g, 2.437 mmol) was heated at reflux in toluene (25 mL) for one hour after bubbling dioxygen through the hot solution for

10 min. A brown solution was obtained after the reaction mixture was filtered while hot. The filtrate was allowed to cool very slowly from 80°C to room temperature in a Dewar flask filled with hot water. After two days, dark brown crystals suitable for structural characterization formed.

CCDC-642243 (**3**) and 642244 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3.2 Selected Parts of Supporting Information and Unpublished Results for Chapter 3.1

3.2.1 Results of the ^1H NMR Analysis of Propionaldehyde

After the reaction of butyronitrile in toluene with the complex and dioxygen, a ^1H NMR spectrum of the product collected in a cryo trap was prepared. The spectrum is shown in Figure 3-3.

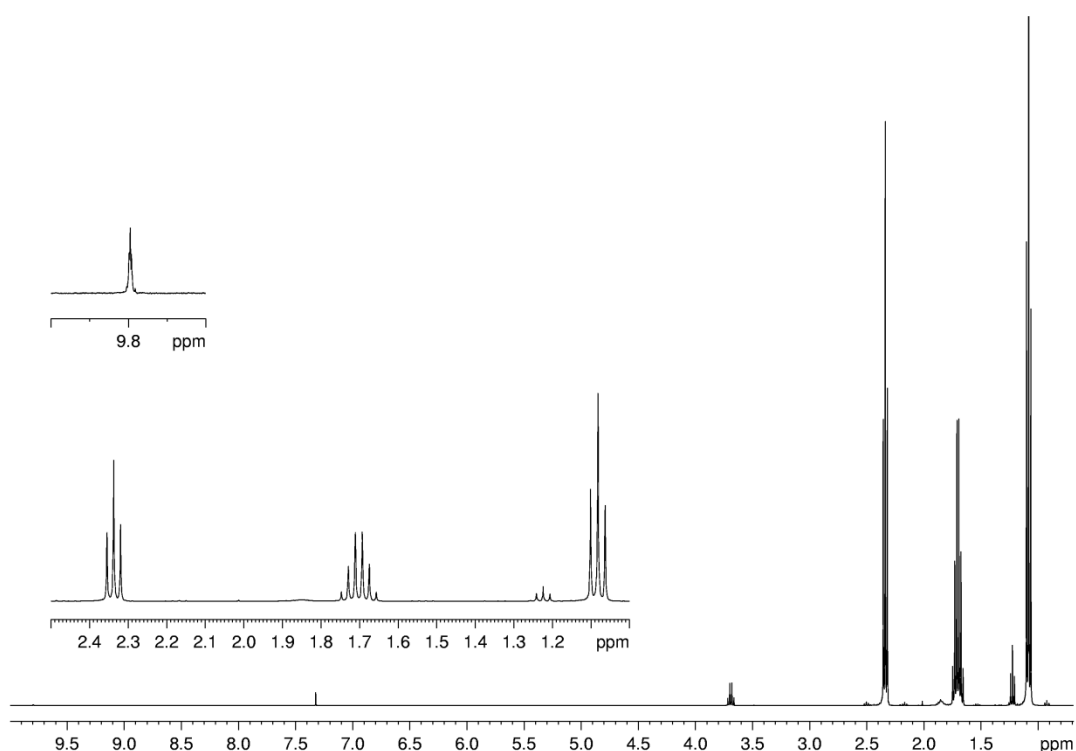


Figure 3-3: ^1H NMR (400 MHz, CDCl_3) of Propionaldehyde: [ppm] = 9.8 (t, 1 H, -COH); 7.3 (s, CDCl_3); 2.34 (t, 2H, -CH₂-); 1.09 (t, 3H, -CH₃) (all other signals are solvent or educt)

3.2.2 Results of the GC-MS Analysis of Butyronitrile and Propionaldehyde

To confirm the findings from the ^1H NMR results, GC-MS measurements of the reaction mixtures before and after the reaction were prepared. The results are depicted in Figure 3-4.

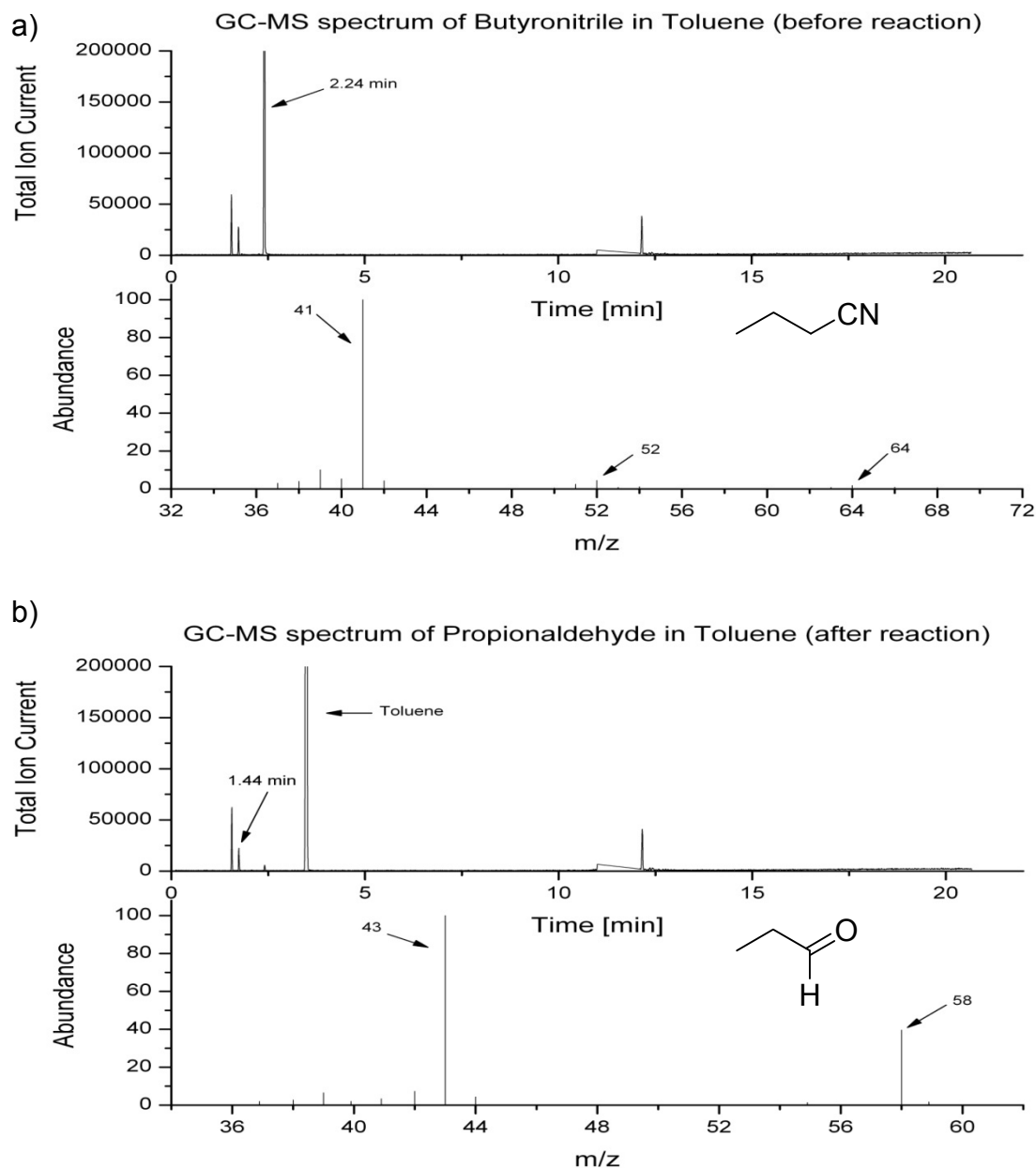


Figure 3-4: a) GC-MS Spectrum of the Reaction Mixture Before Reaction. b) GC-MS Spectrum of the Reaction Mixture After Reaction.

Spectrum a) shows the butyronitrile before the reaction with dioxygen and [Co(salmdtp)] in toluene. Toluene is faded out in this spectrum. Spectrum b) shows the propionaldehyde the after reaction. In this spectrum the toluene is still present.

3.2.3 Results of the X-ray Crystallographic Analysis of [Co(salmdpt)CN] from Acetonitrile

This complex was obtained during the recrystallization of the Co^{II} complex in acetonitrile. While recrystallizing, the solution was flushed with dioxygen for 10 min. After this the filtered solution was cooled very slowly to room temperature in a Dewar flask filled with hot water. The crystal structure obtained is depicted in Figure 3-1. Crystallographic data is presented in Table 3-1 and Table 3-2.

In this cyanido complex, the cobalt atom is six-fold coordinated. The complex shows a slightly distorted octahedral arrangement. The cobalt atom is situated almost exactly in the middle of the equatorial plane, spanned by the atoms O(1), O(2), N(2) and C(22). The axial positions are occupied by the two nitrogen atoms N(1) and N(3). The Co-N bond length varies between 1.9236 Å and 2.080 Å, the Co-O bond length average 1.9862 Å and 1.9863 Å, respectively. The Co-C bond length averages 1.890 Å. The bond angles of the equatorial plane are in the range 90° to 180°, respectively.

Table 3-1: Crystal Data and Structure Refinement for [Co(salmdpt)CN] from Acetonitrile

Habitus	needle
Color	red-brown
Crystal size	0.30 x 0.35 x 0.20 mm
Temperature	200(2) K
Diffractometer type	SIEMENS SMART 5000 CCD
Wavelength	0.71073 Å
Empirical formula	C ₁₃ H _{15.5} Co _{0.5} N ₃ O
Formula weight	259.25 g/mol
Crystal system, space group	monoclinic, C2/c (Nr. 15)
Unit cell dimensions	a = 18.8869(16) Å α = 90° b = 11.8944(10) Å β = 110,2640(10)° c = 12.1188(10) Å γ = 90°
Volume	2554.0(4) Å ³
Z, calculated density	8, 1.348 Mg/m ³
Absorption coefficient	0.707 mm ⁻¹
F(000)	1088
Theta range for data collection	2.06 to 28.32
Limiting indices	-25 ≤ h ≤ 24, -15 ≤ k ≤ 15, -16 ≤ l ≤ 15
Reflections collected / unique	15037 / 3137 [R (int) = 0,0459]
Completeness to theta = 28.32	49.3 % [due to c-cell type]
Absorption correction	Multi-scan (SADABS)
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3137 / 0 / 181
Goodness-of-fit on F ²	1.052
Final R indices [I > 2σ(I)]	R1 = 0.0351, wR2 = 0.0828
R indices (all data)	R1 = 0.0537, wR2 = 0.0882
Largest diff. peak and hole	0.341 and -0.273 eÅ ⁻³

Table 3-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)CN] from Acetonitrile

Co(1)-N1	1.9236(14)	Co(1)-O2	1.9863(12)
Co(1)-N2	2.080(2)	Co(1)-C22	1.890(3)
Co(1)-N3	1.9236(14)	N(2)-C21	1.505(4)
Co(1)-O1	1.9862(12)		
N1-Co(1)-N2	89.44(5)	O2-Co(1)-N3	90.47(6)
N1-Co(1)-N3	178.89(9)	O1-Co(1)-O2	178.54(8)
N2-Co(1)-N3	89.44(5)	C22-Co(1)-N1	90.56(5)
O1-Co(1)-N1	90.47(6)	C22-Co(1)-N2	180.0
O1-Co(1)-N2	90.73(4)	C22-Co(1)-N3	90.56(5)
O1-Co(1)-N3	89.55(6)	C22-Co(1)-O1	89.27(4)
O2-Co(1)-N1	89.55(6)	C22-Co(1)-O2	89.27(4)
O2-Co(1)-N2	90.73(4)		

3.2.4 Results of the X-ray Crystallographic Analysis of [Co(salmdpt)OH] from Toluene

This complex was obtained during the recrystallization of the Co^{II} complex in toluene. During the recrystallization, the solution was flushed with dioxygen for 10 min. After this, the filtered solution was cooled very slowly to room temperature in a Dewar flask filled with hot water.

The crystal structure of the complex is shown in Figure 3-2. Crystallographic data is presented in Table 3-3 and Table 3-4. The cobalt(III) ion in this complex is coordinated six-fold. The crystal arrangement is strongly distorted octahedral. The equatorial plane is also distorted and is spanned by the atoms O(1), O(2), O(3) and N(2). The cobalt atom is located almost in the middle of the equatorial plane. The dioxygen atoms O(1) and O(3) stand in a slight cis-position to each other, as well as the atoms O(2) and N(2), however in an opposite direction. This is the reason for the molecule's distortion.

Table 3-3: Crystal Data and Structure Refinement for [Co(salmdpt)OH] from Toluene

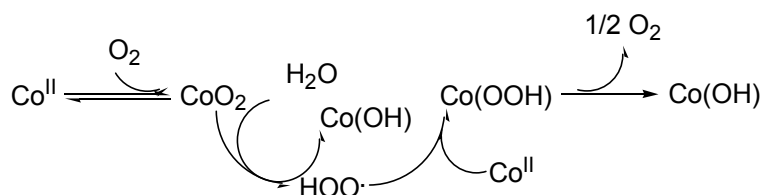
Habitus	needle
Color	darkbrown
Crystal size	0.4 x 0.3 x 0.3 mm
Temperature	200(2) K
Diffractometer type	SIEMENS
	SMART 5000 CCD
Wavelength	0.71073 Å
Empirical formula	C ₂₂ H ₃₈ CoN ₃ O ₈
Formula weight	531.48 g/mol
Crystal system, space group	monoclinic, P2/c (Nr. 13)
Unit cell dimensions	a = 19.2903(16) Å α = 90° b = 9.9745(8) Å β = 100.5320(10)° c = 13.8585(11) Å γ = 90°
Volume	2621.6(4) Å ³
Z, Calculated density	4, 1.347 Mg/m ³
Absorption coefficient	0.703 mm ⁻¹
F(000)	1128
Theta range for data collection	2.04 to 28.31
Limiting indices	-25 ≤ h ≤ 25, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18
Reflections collected / unique	31314 / 6368 [R (int) = 0,0667]
Completeness to theta = 28.31	92.3 %
Absorption correction	Multi-scan (SADABS)
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6368 / 0 / 370
Goodness-of-fit on F ²	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1185
R indices (all data)	R1 = 0.0640, wR2 = 0.1281
Largest diff. peak and hole	0.888 and -0.636 eÅ ⁻³

In contrast to the hitherto described structures, the two salicylaldehyde groups are not 10 Å away from each other. The distance between the two salicylaldehyde groups is about 4.5 Å, in which the aromatic rings are angled to each other. In the structure described above, this could not be detected. Accumulation of the [Co(salmdpt)OH] complex occurred in all probability with the aid of water in the solvent.

Table 3-4: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)OH] from Toluene

Co(1)-N1	1.9033(2)	Co(1)-O1	1.9010(17)
Co(1)-N2	2.065(2)	Co(1)-O2	1.9033(17)
Co(1)-N3	1.965(2)	Co(1)-O3	1.8966(17)
N1-Co(1)-N2	87.38(9)	O2-Co(1)-N3	90.03(8)
N1-Co(1)-N3	172.67(9)	O3-Co(1)-N1	93.90(8)
N2-Co(1)-N3	98.47(9)	O3-Co(1)-N2	88.20(8)
O1-Co(1)-N1	90.82(8)	O3-Co(1)-N3	90.71(8)
O1-Co(1)-N2	93.64(8)	O1-Co(1)-O2	91.51(8)
O1-Co(1)-N3	84.43(8)	O1-Co(1)-O3	175.01(8)
O2-Co(1)-N1	84.50(8)	O2-Co(1)-O3	87.34(8)
O2-Co(1)-N2	170.45(8)	O3-Co(1)-N1	93.90(8)

Reason for this is the accumulation of the Co^{II} complex in dried toluene described in Chapter 2.3. So far, no definite explanation for the accumulation of the [Co(salmdpt)OH] complex could be given. However, two explanations for this could be possible. Either the complex was formed by water solvent, analog to the lines of the mechanism, described in the literature, for the accumulation of Co^{II} Schiff base complexes in alcohol.^[117] The postulated mechanism is depicted in Scheme 3-2.



Scheme 3-2: Schematic Depiction of the Possible Oxidation of $[\text{Co}^{\text{II}}(\text{salmdpt})]$ in Toluene

Another explanation for the formation of the [Co(salmdpt)OH] complex is the oxidative decomposition of the solvent itself. Here, the toluene is oxidized by the Co^{II} superoxido complex under formation of benzoic acid, or its precursors like benzyl alcohol or benzaldehyde, and the hydroxido complex. At present we have no evidence for this as we have problems to detect the possibly formed benzoic acid. This is due to the bad solubility of benzoic acid in toluene. If water is in the solvent, the benzoic acid dissolves in the water and not in toluene. These results could be obtained by experiments with benzoic acid and toluene as blank samples. As water is needed to get the hydroxido complex, the benzoic acid or its precursors in the toluene solvent could not be obtained. This problem should be solved by additional experiments in the near future.

3.3 Experimental Section

3.3.1 Materials and Techniques

Commercially available materials were used without further purification. Solvents for oxygen-sensitive materials were obtained from Acros and were additionally distilled under argon before usage. Oxygen-sensitive compounds and materials were handled in a glove box (M. Braun, Germany, O₂ < 0.1 ppm). [Co(saldpt)], [Co(salmdpt)] and [Co(3,5-Di-*tert*-butyl-saldpt)] were synthesized according to published procedures.^[37, 91]

3.3.2 Physical Measurements

The single crystal X-ray diffraction studies were performed with a Siemens SMART CCD 1000 diffractometer with Mo-K α radiation (λ = 0.71073 Å) equipped with a graphite monochromator and a CCD detector. The collected reflections were corrected for absorption effects (SADABS, Siemens Area Detector Absorption Correction, Siemens, Forschungszentrum Karlsruhe ITC-CPV)

All structures were solved by direct methods and refined by using full-matrix least-squares in the SHELX software package.^[92-93] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned geometrically.

¹H NMR spectra were recorded with a Bruker Aspect 2000/3000 400 MHz, a Bruker Avance II 400 MHz WB (AV 400) or a Bruker Avance II 200 MHz „Microbay“ (AV200).

ATR-IR spectra were gained using a Bruker Optics ISF48 spectrometer with an ATR unit (“golden gate”, diamond, one reflexion).

GC-MS spectra were obtained using a HP-GC-MS 5973.

4 End-on Cobalt Superoxido Complexes in Organic Synthesis

4.1 Introduction

One of the particular challenges in medicinal chemistry is the differentiation of cells. In immune-mediated diseases for example, cells produced naturally in the body need to be differentiated from those that are not produced in the body (bacteria or antigens). In cancer therapy or cancer diagnostics it is necessary to differentiate salutary cells from malignant cells. Cell surface epitopes offer a possibility for the differentiation between cells. An epitope (antigen determinants) is a small area of an antigen on the cell surface. In nature antigen determinants are proteins, which are individual for each species.^[118]

One approach for cancer diagnostics is based on the fact that on surface of tumor cells specific membrane proteins are available on higher density.^[119] Such tumor markers could be used as receptors for modular ligands, which are additionally linked to contrast agents. This enables the selective identification and the piloting of tumor cells (Figure 4-1).

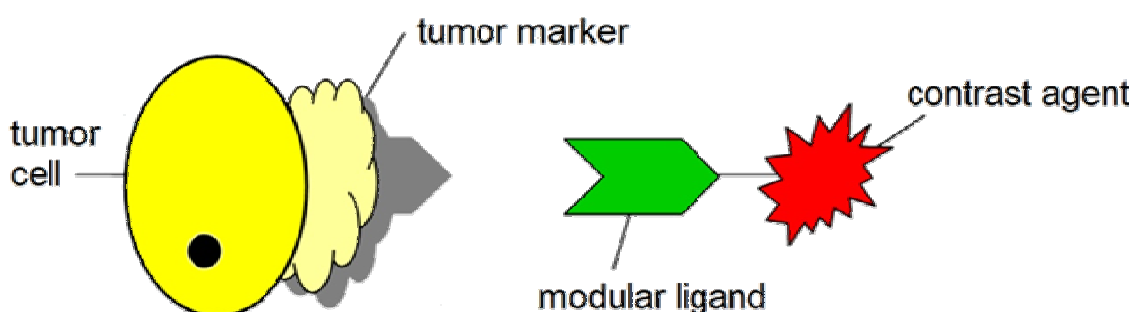


Figure 4-1: Receptor-Ligand-Model

In nature, most cell recognition processes and thereby resulting signal transfers underlie multivalent interactions. For example an antibody could bind to alien cells by multivalent interactions and thus, evoke their death. Therefore, synthetic multivalent ligands offer a promising approach to differentiate the cell surface of for example bacteria, tumor cells or antigens.^[118]

The research group of Prof. Maison (JLU Gießen) is interested in the synthesis of such multivalent ligands. Therefore, monovalent ligands have to be linked by a skeletal structure or matrix. Several matrices could be used for the linkage of the ligands. One of these matrices is adamantane. Adamantane

(tricyclo[3.3.1.1^{3,7}]decane) is a cycloalkane and the simplest diamondoid. Its formal structure consists of four cyclohexane molecules attached in a chair conformation. In nature, traces of adamantane can be found in some rock crystals or in petroleum, where it was discovered first in 1933.^[120] Its name derives from the Greek *adamantinos*, due to its diamond-like structure. Adamantane is the most stable isomer of C₁₀H₁₆. As an unfunctionalized hydrocarbon, adamantane itself is not very useful in contrast to its derivatives that are applied.

By using adamantane as a matrix for multivalent ligands, it can be selectively substituted four times on its bridge-head atoms. Therefore, it can be utilized as matrix for monovalent, bivalent, trivalent and tetravalent ligands (Figure 4-2). Some adamantane derivatives are known in healthcare. They are used against neurodegenerative diseases and viral infections.^[118]

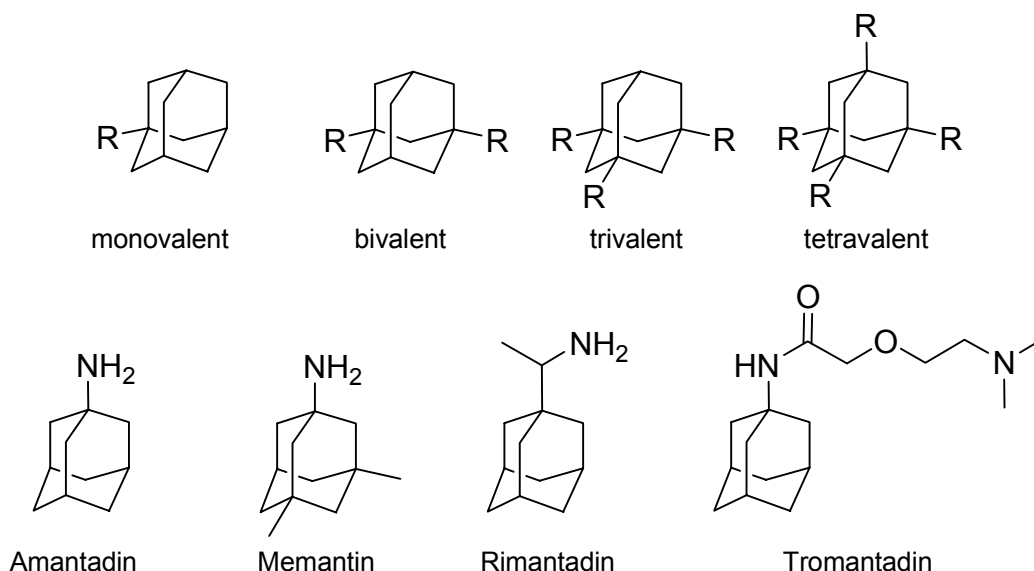


Figure 4-2: Substitution Archetypes of Adamantane and Synthesized Biologically Active Derivatives^[121-124]

Maison and co-workers prefer tetrasymmetric substituted adamantane carboxylic acids for their research. One synthetic route for such carboxylic acids of adamantane is based on cyanoethyladamantanes which are transferred by acidic hydrolysis to the according carboxylic acids.^[118, 125]

Due to the reactions observed during the oxidation of [Co(salmdpt)] described in Chapter 3, it was likely that these transformations of a nitrile group to an aldehyde group might be useful for the synthesis of adamantane derivatives as well. Therefore,

in co-operation with the group of Prof. Maison the following reaction was performed (Figure 4-3).

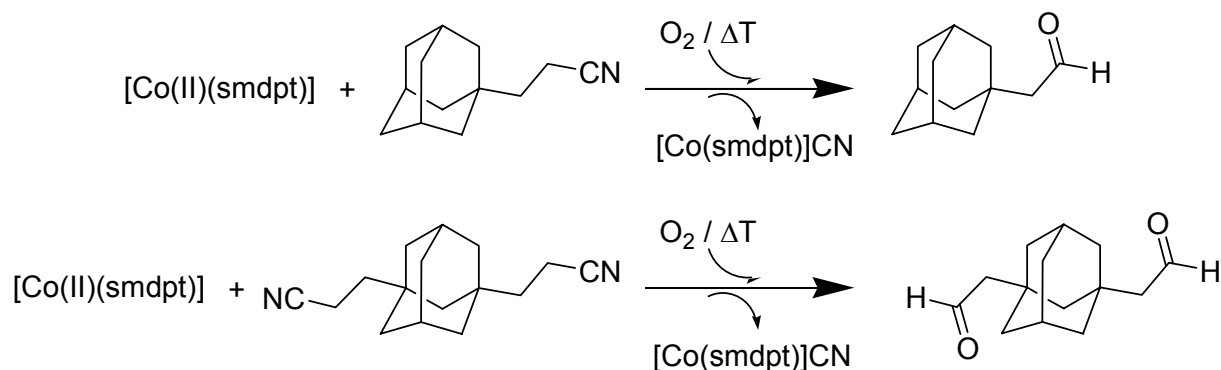


Figure 4-3: Expected Reactions of Adamantane Derivatives and the Complex [Co(salmdpt)]

4.2 Results

4.2.1 Reaction of Butyronitrile with [Co(salmdpt)] in Toluene

Before beginning with the experiments with 3-adamantane-1-yl-propionitrile (Ada-CN) some experiments with the complex in toluene were carried out. As described in Chapter 3, it should be tested if such a reaction could be performed in a solvent such as toluene (using an excess of the cobalt complex) with a nitrile compound as a substrate to obtain the corresponding aldehyde shortened by one carbon atom. Thus, a reaction with butyronitrile was performed to obtain the corresponding propionaldehyde (Figure 4-4).

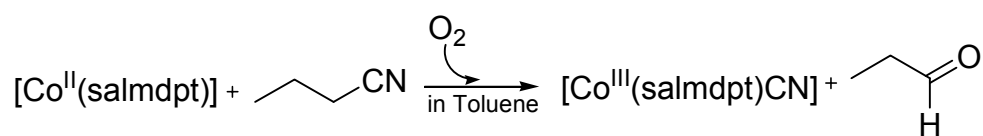


Figure 4-4: Reaction of [Co(salmdpt)] and Butyronitrile with Dioxygen in Toluene

A mixture of butyronitrile and [Co(salmdpt)] in toluene was heated under reflux. During the reaction dioxygen was flushed through the reaction mixture. The reaction gases were guided through a cryo trap to collect volatile components. This procedure was necessary, because of the lower boiling point of the product propionaldehyde. Due to the low boiling point of propionaldehyde it was carried away when dioxygen was flushed through the solution. The sample obtained in the cryo trap was analyzed

by ^1H NMR spectroscopy. These results showed that similar to the results reported in Chapter 3.2.1, propionaldehyde was formed. Furthermore, GC-MS spectrometric measurements confirmed this result.

4.2.2 Experiments with Hydrogen Peroxide as Oxidant

In addition to the experiments described in Chapter 4.2.1 hydrogen peroxide was tested as an oxidant instead of dioxygen. Therefore, the reaction of butyronitrile with $[\text{Co}(\text{salmcpt})]$ in toluene was carried out with hydrogen peroxide as oxidant (Figure 4-5).

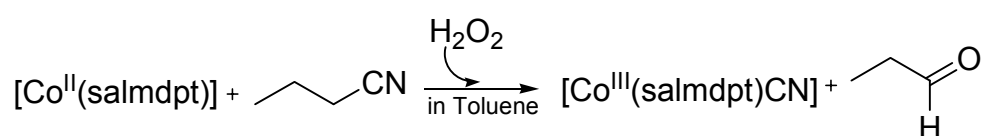


Figure 4-5: Reaction of $[\text{Co}(\text{salmcpt})]$ and Butyronitrile with Hydrogenperoxide in Toluene

During these experiments crystals of the complex $[\text{Co}(\text{salmcpt})\text{CN}]$ were obtained. Thus, it seemed that this was also a possible pathway to achieve the cyanido complex of $[\text{Co}(\text{salmcpt})]$ and the corresponding aldehyde. However, yields were low and reaction conditions need to be improved in the future.

4.2.3 Reactions of 3-Adamantane-1-yl-propionitrile with $[\text{Co}(\text{salmcpt})]$ in Toluene

In regard to the results obtained for the reaction of $[\text{Co}(\text{salmcpt})]$ with dioxygen or hydrogen peroxide together with a nitrile in toluene described above, the reactions of the adamantane derivatives shown in Figure 4-3 were investigated.

In the beginning of the experiments Ada-CN was used as educt. Therefore, a stoichiometric ratio of the cobalt(II) complex and Ada-CN (2:1) for the experiments was used. The reactants were dissolved in toluene and the reaction mixture was heated under reflux, constantly flushing dioxygen through the solution.

Parallel to the experiments with dioxygen, experiments with hydrogen peroxide instead of dioxygen were carried out. Therefore, a solution of the cobalt(II) complex and Ada-CN in a stoichiometric ratio like the experiments with dioxygen was

prepared. To this solution hydrogen peroxide was added. Indeed, these solutions were not heated under reflux but reacted at room temperature.

In these reactions no crystals suitable for X-ray crystallographic analysis could be obtained. Therefore, the expected reaction product adamantane-1-yl-acetaldehyde should be detected by ^1H NMR spectroscopic and GC-MS spectrometric measurement. However, problems arose when trying to detect the expected adamantane aldehyde with ^1H NMR spectroscopy. During these investigations it became clear that the original sample Ada-CN supplied by the Maison group was impure. Therefore, 3-[3-(2-cyano-ethyl)-adamantane-1-yl]-propionitrile (Ada-CN₂) was used for further experiments instead.

4.2.4 Reactions of 3-[3-(2-Cyano-ethyl)-adamantane-1-yl]-propionitrile with [Co(salmdpt)] in Toluene

The reaction of Ada-CN₂ with [Co(salmdpt)] and hydrogen peroxide was carried out in the same way as described for the reaction of Ada-CN. Here, crystals of the [Co(salmdpt)CN] complex, suitable for X-ray crystallographic analysis could be obtained in one experiment. The quality of the resulting data was not good enough for a complete structure determination and refinement, but the structure of the cyanide complex could be obtained. Therefore, it is most likely that aldehyde formation took place as well. However, so far no clean analytical data could prove that the aldehyde has formed. One of the problems is that it is difficult to distinguish the NMR of the product from the NMR signals of the educt. Furthermore, so far there are no analytical data reported for the adamantane aldehyde in the literature.

4.3 Experimental Section

4.3.1 Materials and Techniques

Commercially available materials were used without further purification. Solvents for oxygen-sensitive materials were obtained from Acros and were additionally distilled under argon before usage. Oxygen-sensitive compounds and materials were handled in a glove box (M. Braun, Germany, O₂ < 0.1 ppm). [Co(saldpt)], [Co(salmdpt)] and [Co(3,5-Di-*tert*-butyl-saldpt)] were synthesized according to published procedures.^[37, 91]

4.3.2 Physical Measurements

Single crystal X-ray diffraction studies were performed with a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K α radiation (λ = 0.71073 Å), a graphite monochromator, and an IP detector system were used. The frames were integrated with the STOE software package. No absorption corrections were applied.

All structures were solved by direct methods and refined by using full-matrix least-squares in the SHELX software package.^[92-93] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned geometrically.

¹H NMR spectra were recorded with a Bruker Aspect 2000/3000 400 MHz, a Bruker Avance II 400 MHz WB (AV 400) or a Bruker Avance II 200 MHz „Microbay“ (AV200).

ATR-IR spectra were gained using a Bruker Optics ISF48 spectrometer with an ATR unit (“golden gate”, diamond, one reflexion).

GC-MS spectra were obtained using a HP-GC-MS 597.

4.3.3 Syntheses

Reaction of 3-Adamantan-1-yl-propionitrile with [Co(salmdpt)] (1a)

0.23 g (1.22 mmol) 3-adamantane-1-yl-propionitrile and 1.00 g (2.44 mmol) [Co(salmdpt)] were dissolved in 20 mL toluene. To this solution 10 drops of water were added. Afterwards, the reaction mixture was heated under reflux for four hours. During this time, it was flushed with O₂. The cobalt complex was afterwards separated by SiO₂ in a chromatography column. Toluene was used as eluent. After that, the solvent was evaporated. The resulting product was reviewed by ¹H NMR spectroscopy. The spectrum showed an aldehyde band at ~10 ppm, but also a lot of aromatic bands and educt bands. The product/educt occurred in a 5:1 ratio. Probably the reviewed product still contained a small amount of the cobalt complex.

Reaction of 3-Adamantan-1-yl-propionitrile with [Co(salmdpt)] (1b)

2.18 g (5.31 mmol) [Co(salmdpt)] and 0.5 g (2,6 mmol) 3-adamantane-1-yl-propionitrile were dissolved in 50 mL toluene. 0.5 mL water was added to this solution. The reaction mixture was then heated under reflux for 48 hours. During this time the mixture was flushed several times with O₂. The cobalt complex was then

separated by SiO₂ in a chromatography column. As eluent, toluene was used. After that, the solvent was evaporated. The resulting product was reviewed by ¹H NMR spectroscopy.

Reaction of 3-Adamantan-1-yl-propionitrile with [Co(salmdpt)] (1c)

0.2 g (0.5 mmol) [Co(salmdpt)] was dissolved in 5 mL toluene. To this solution 0.47 mg (0.25 mmol) 3-adamantane-1-yl-propionitrile and 0.061 g hydrogen peroxide (34%) were added.

In another approach, 0.025 g triethylamine was additionally added to the solution.

In this experiment, crystals suitable for X-ray diffraction analysis could be obtained. However, the quality of the resulting data was not good enough for a complete structure determination and refinement, but we could observe the structure of the cyanide complex.

Reaction of 3-[3-(2-Cyano-ethyl)-adamantane-1-yl]-propionitrile with [Co(salmdpt)] (2)

0.2 g (0.5 mmol) [Co(salmdpt)] was dissolved in 5 mL toluene. To this solution, 0.59 mg (0.25 mmol) 3-[3-(2-Cyano-ethyl)-adamantane-1-yl]-propionitrile and 0.061 g hydrogen peroxide (34%) were added.

In another approach, 0.025 g triethylamine was additionally added to the solution.

5 Cobalt Nitrogen Oxide Complexes

As described in the introduction NO metal complexes are interesting in comparison with dioxygen adduct compounds and are furthermore of potential interest in medical applications. Thus, it became clear to additionally probe the reaction of [Co(salmdpt)] with NO. The latter was prepared according to a published procedure.^[126-127] It was quite important to purify NO by flushing it through a 2 M sodium hydroxide solution. In contrast to the reaction with dioxygen, the reaction with nitrogen oxide led to crystals of [Co(salmdpt)NO] suitable for X-ray analysis.

5.1 Crystal Structure of [Co(salmdpt)NO] from Dichloromethane

The structure depicted in Figure 5-1 shows a distorted octahedral coordination of the cobalt(III) atom. The cobalt(III) atom is also six-fold coordinated and located almost in the middle of the equatorial plane, which is spanned by the atoms O(1), O(2), N(1) and N(3). N(2) and N(4) fill the axial positions. The space group of the structure described here is *Pbca* with an orthorhombic crystal system. Crystallographic data are presented in Table 5-1 and Table 5-2.

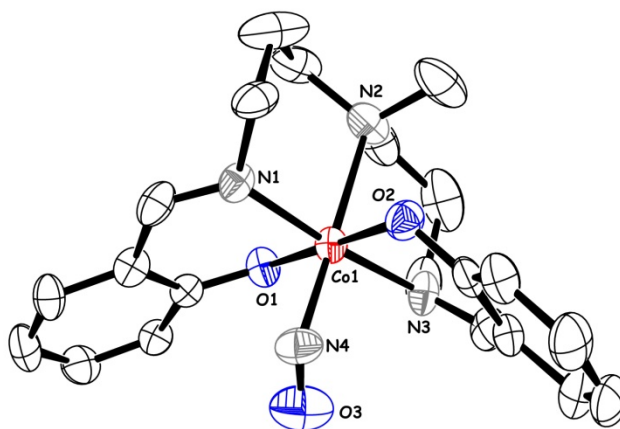


Figure 5-1: Ortep Plot of [Co(salmdpt)NO] from Dichloromethane

Table 5-1: Crystal Data and Structure Refinement for [Co(salmdpt)NO] from Dichloromethane

Habitus	block shaped
Color	red-brown
Crystal size	0.16 x 0.12 x 0.08 mm
Temperature	193 K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₂₁ H ₂₅ CoN ₄ O ₃
Formula weight	440.38 g/mol
Crystal system, space group	orthorhombic, Pbca (Nr. 61)
Unit cell dimensions	a = 14.892(3) Å α = 90° b = 13.088(3) Å β = 90° c = 21.805(4) Å γ = 90°
Volume	4050.2(14) Å ³
Z, calculated density	8, 1.444 Mg/m ³
Absorption coefficient	0.878 mm ⁻¹
F(000)	1840
Theta range for data collection	2.31 to 25.99
Limiting indices	-17 ≤ h ≤ 17, -12 ≤ k ≤ 16, -23 ≤ l ≤ 26
Reflections collected / unique	15643 / 3906 [R (int) = 0.1386]
Completeness to theta = 25.99	98.3 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3906 / 0 / 364
Goodness-of-fit on F ²	0.807
Final R indices [I > 2σ(I)]	R1 = 0.0482, wR2 = 0.0941
R indices (all data)	R1 = 0.1274, wR2 = 0.1146
Largest diff. peak and hole	0.462 and -0.342 eÅ ⁻³

The bond length of the nitrogen monoxide is 1.118(6) Å and the angle Co(1)-N(4)-O(3) is 122.6(5)°. Therefore, the angle is in the range of ~120°, which accounts for a nitrosyl group. The bond lengths of Co(1)-N(1), Co(1)-N(2), Co(1)-N(3), and Co(1)-N(4) are in the range 1.8 Å to 2.3 Å.

Table 5-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)NO] from Dichloromethane

Co(1)-N1	1.932(4)	Co(1)-O1	1.912(3)
Co(1)-N2	2.277(5)	Co(1)-O2	1.926(3)
Co(1)-N3	1.928(4)	N4-O3	1.118(6)
Co(1)-N4	1.832(5)		
N1-Co(1)-N2	86.79(19)	O1-Co(1)-N3	90.49(18)
N1-Co(1)-N3	174.0(2)	O1-Co(1)-N4	92.0(2)
N1-Co(1)-N4	91.4(2)	O2-Co(1)-N1	89.81(17)
N2-Co(1)-N3	87.19(19)	O2-Co(1)-N2	90.66(17)
N2-Co(1)-N4	177.5(2)	O2-Co(1)-N3	90.48(17)
N3-Co(1)-N4	94.6(2)	O2-Co(1)-N4	87.6(2)
O1-Co(1)-N1	89.26(16)	O1-Co(1)-O2	178.99(15)
O1-Co(1)-N2	89.67(17)	Co(1)-N4-O3	122.6(5)

In comparison with the crystal structure of the complex [Co(salen)NO] (Chapter 1.7.2) some differences are noted.^[73] The structure of [Co(salmdpt)NO] contains only one molecule of the complex versus two separate molecules in the structure of [Co(salen)NO]. The unit cell dimensions, the crystal system and the space group are completely different (Table 5-3). Quite good agreements in bond lengths and bonding angles of the NO bonds of the two structures are notably. In the structure of [Co(salen)NO] the average NO bond length is 1.155(11) Å and the average bond angle of Co-N-O is 127.0(4)°. In the structure of [Co(salmdpt)NO] the NO bond length is 1.118(6) Å and the Co(1)-N(4)-O(3) bond angle is 122.6(5)°. The average Co-NO distance in [Co(salen)NO] amounts to 1.807(5) Å, in [Co(salmdpt)NO] the Co(1)-N(4)O(3) distance amounts to 1.832(5) Å. This distances and angles of the two structures are nearly identical and typical for nitrosyl compounds. The other distances to the remaining ligands of the cobalt atom in [Co(salmdpt)NO] are comparable with the ranges of other structures of [Co(salmdpt)] and its derivatives.

In comparison with [Co(salmdpt)O₂] the NO bond length and the Co(1)-N(4)-O(3) bond angle are similar to the O-O bond length and the Co-O-O bond angle (Table 5-3).^[48-49]

Table 5-3: Comparison of the Cell Parameters, some Selected Bond Lengths and Angles of [Co(salen)NO]^[73] [Co(salmdpt)NO] and [Co(salmdpt)O₂]^[48-49]

	[Co(salen)NO]	[Co(salmdpt)NO]	[Co(salmdpt)O ₂]
Crystal system, space group	monoclinic, P2 ₁ /c	orthorhombic, Pbca	triclinic, P $\bar{1}$
Unit cell dimensions	a = 14.417(7) Å α = 90° b = 11.982(7) Å β = 100.39(4)° c = 17.481(9) Å γ = 90°	a = 14.892(3) Å α = 90° b = 13.088(3) Å β = 90° c = 21.805(4) Å γ = 90°	a = 17.045(4) Å α = 90.23(3)° b = 12.697(3) Å β = 90.06(3)° c = 11.668(3) Å γ = 100.43(3)°
Volume	2970.2 Å ³	4050.2(14) Å ³	2476.2(8) Å ³
bond length ^{a)}	N-O = 1.155(11) Å	N-O = 1.118(6) Å	O-O = 1.05(5) Å
bond angle ^{a,b)}	Co-N-O = 127.0(4)°	Co-N-O 122.6(5)°	Co-O-O = 135.35(4)°
M-X distance ^{a)}	Co-NO = 1.807(5) Å	Co-NO = 1.832(5) Å	Co-O ₂ = 1.89(2) Å
a) The data from [Co(salen)NO] Is the average of the two molecules b) The data of [Co(salmdpt)O ₂] Is the average of both angles of Co-O(3)-O(4) and Co-O(3)-O(4')			

5.1.1 IR Spectra of [Co(salmdpt)NO] from Dichloromethane

Infrared spectra of the cobalt(II) precursor complex [Co(salmdpt)] and the obtained Co^{III} nitrosyl complex [Co(salmdpt)NO] have been prepared. The spectrum of [Co(salmdpt)NO] is depicted in Figure 5-2. Figure 5-3 shows the comparison of the nitrosyl complex with the Co^{II} complex [Co(salmdpt)]. In this comparison it can be seen, that some bands have decreased in contrast to the cobalt(II) precursor complex. At 1705 cm⁻¹, a new very pronounced band can be observed. Probably this is the band of the NO stretching vibration. Compared with other cobalt-NO examples, the ν(NO) vibrations are located almost in the range of 1750-1650 cm⁻¹.^[90] Another two bands can be observed at 632.5 cm⁻¹ and 578.5 cm⁻¹. These are probably the stretching vibrations of the M-N bond and the deformation vibrations of the M-NO bond. Comparisons with other cobalt examples support these assumptions.^[90]

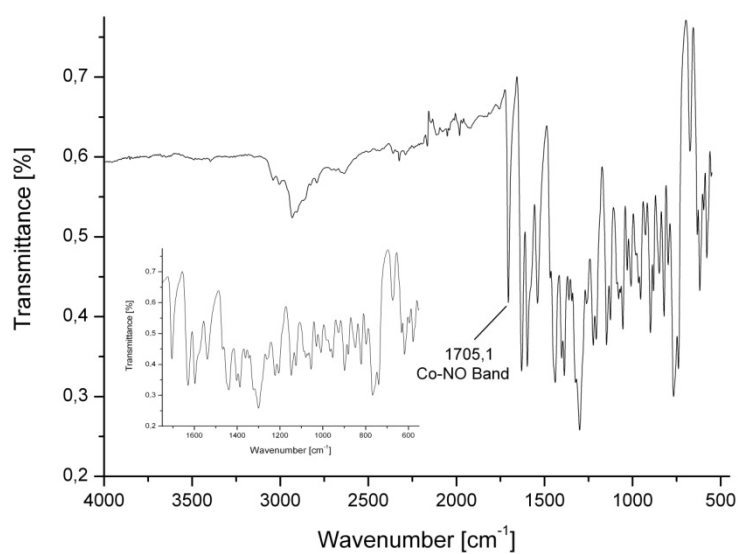


Figure 5-2: IR Spectrum of [Co(salmdpt)NO] from Dichloromethane

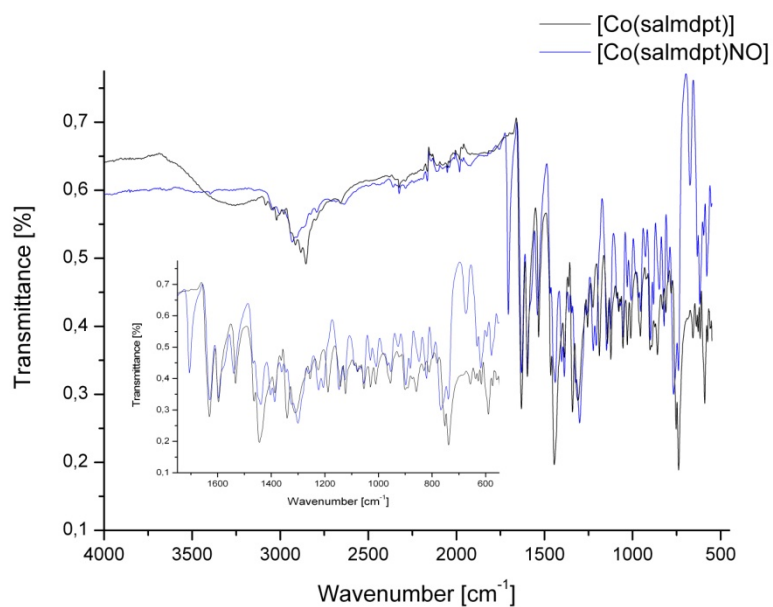


Figure 5-3: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)NO] from Dichloromethane

5.2 Experimental Section

5.2.1 Materials and Techniques

Commercially available materials were used without further purification. Solvents for oxygen-sensitive materials were obtained from Acros and were additionally distilled under argon before usage. Oxygen-sensitive compounds and materials were handled in a glove box (M. Braun, Germany, O₂ < 0.1 ppm). [Co(saldpt)], [Co(salmdpt)] and [Co(3,5-Di-*tert*-butyl-saldpt)] were synthesized according to published procedures.^[37, 91]

5.2.2 Physical Measurements

Single crystal X-ray diffraction studies were performed with a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo-K_α radiation (λ = 0.71073 Å), a graphite monochromator, and an IP detector system were used. The frames were integrated with the STOE software package. No absorption corrections were applied.

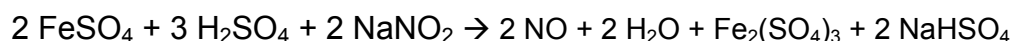
All structures were solved by direct methods and refined by using full-matrix least-squares in the SHELX software package.^[92-93] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned geometrically.

ATR-IR spectra were gained using a Bruker Optics ISF48 spectrometer with an ATR unit ("golden gate", diamond, one reflexion).

5.2.3 Syntheses

Generation of Unpurified Nitrogen Monoxide

In our experiments nitrogen monoxide was synthesized according to the following equation.^[126-127]



Nitrogen monoxide was generated by the reaction of a degassed solution of iron(II)sulfate heptahydrate and sulfuric acid with sodium nitrite in an argon atmosphere. The nitric oxide was then transferred to the complex solutions with an

argon flow. The structure described in Chapter 6.1 showed that the generated nitric oxide contained a massive amount of nitrogen dioxide.

Generation of Purified Nitrogen Monoxide

For further purification, the generated gas was purged through a degassed 2 M sodium hydroxide solution to trap the impurities. Nitrogen monoxide was generated by the procedure described above. The gas was then purified by purging it through a 2 M sodium hydroxide solution. The obtained nitric oxide was then transferred to the complex solutions with an argon flow.

[Co(salmdpt)NO] from Dichloromethane

5 mg (0.0121 mmol) [Co(salmdpt)] was dissolved in 2 mL acetonitrile. Purified nitrogen monoxide was then flushed through the solution for 3 min. The solution was stored in a fridge and ether was condensed into the solution. After a few weeks, small red brown crystals suitable for structural characterization were formed.

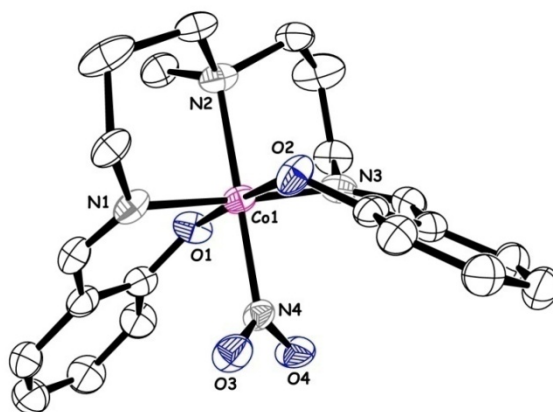
6 Attempts to Isolate and Characterize a Cobalt Oxido Complex

In the introduction it was described that different cobalt “oxygen complexes” can form. Some characterized examples of such compounds are shown in Figure 1-11. However, so far a mononuclear cobalt(IV) oxido complex could not be characterized. Such high-valent species are quite interesting and their importance have been described for a fully-characterized iron(IV) oxido species.^[128-129] In Chapter 3, a cobalt oxido complex has been postulated as an intermediate complex as well, however without any solid experimental proof. Synthetic procedures vary from reactions with hydrogen peroxide to oxidations with iodoso benzene. An interesting possibility is the photochemical decomposition of an oxygen-bonded nitro or nitrate complex or an ozonido complex.^[130-132]

6.1 Crystal Structure of [Co(salmdpt)NO₂] from Acetonitrile

During the efforts to synthesize [Co(salmdpt)NO] described in Chapter 4 in two reactions the nitro complex [Co(salmdpt)NO₂] was obtained instead. This was either caused by impure NO gas (already partially oxidized) or by oxidation of the NO complex.

The molecular structure depicted in Figure 6-1 shows a distorted octahedral arrangement and the presence of a nitro group in the coordination sphere of the cobalt(III) atom. As a consequence of the trans influence of the NO₂ moiety, the bond length Co(1)-N(2) of 2.068(2) Å is longer than Co(1)-N(1) 1.930(2)Å and Co(1)-N(3) 1.922(3)Å. The bond length of Co(1)-N(4) 1.929(2)Å lies within the range of bond length found in related cobalt(III) nitro complexes.^[130] Crystallographic data are presented in Table 6-1 and Table 6-2.

Figure 6-1: Ortep Plot of $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from AcetonitrileTable 6-1: Crystal Data and Structure Refinement for $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Acetonitrile

Habitus	block shaped
Color	red-brown
Crystal size	0.48 x 0.24 x 0.16 mm
Temperature	193 K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	$\text{C}_{23}\text{H}_{28}\text{CoN}_5\text{O}_4$
Formula weight	497.43 g/mol
Crystal system, space group	monoclinic, C2/c (Nr. 15)
Unit cell dimensions	$a = 25.363(5) \text{ Å}$ $b = 10.627(2) \text{ Å}$ $c = 17.089(3) \text{ Å}$
	$\alpha = 90^\circ$ $\beta = 99.04(3)^\circ$ $\gamma = 90^\circ$
Volume	$4548.7(16) \text{ Å}^3$
Z, calculated density	8, 1.453 Mg/m^3
Absorption coefficient	0.795 mm^{-1}
F(000)	2080
Theta range for data collection	3.19 to 28.07
Limiting indices	$-31 \leq h \leq 31, -14 \leq k \leq 14, -22 \leq l \leq 22$
Reflections collected / unique	19637 / 5256 [$R(\text{int}) = 0.0673$]
Completeness to theta = 28.07	95.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5256 / 0 / 330
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0495, wR2 = 0.1342$
R indices (all data)	$R1 = 0.0642, wR2 = 0.1450$
Largest diff. peak and hole	0.730 and -0.793 eÅ^{-3}

The structure shows a six-fold coordination of the cobalt(III) ion. The cobalt atom is located almost in the middle of the equatorial plane, spanned by the atoms N(1), N(3), O(1) and O(2). The atoms N(2) and N(4) fill the axial positions.

Table 6-2: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)NO₂] from Acetonitrile

Co(1)-N1	1.930(2)	Co(1)-O1	1.8883(18)
Co(1)-N2	2.068(2)	Co(1)-O2	1.8936(17)
Co(1)-N3	1.922(3)	N4-O3	1.234(3)
Co(1)-N4	1.929(2)	N4-O4	1.228(3)
N1-Co(1)-N2	89.06(10)	O1-Co(1)-N4	88.39(9)
N1-Co(1)-N3	177.54(9)	O2-Co(1)-N1	90.94(9)
N1-Co(1)-N4	90.40(9)	O2-Co(1)-N2	91.41(8)
N2-Co(1)-N3	88.62(10)	O2-Co(1)-N3	89.93(9)
N2-Co(1)-N4	179.34(10)	O2-Co(1)-N4	88.23(8)
N3-Co(1)-N4	91.92(10)	O1-Co(1)-O2	176.49(8)
O1-Co(1)-N1	90.02(9)	Co(1)-N4-O3	120.46(17)
O1-Co(1)-N2	91.98(8)	Co(1)-N4-O4	119.80(17)
O1-Co(1)-N3	89.24(9)	O3-N4-O4	119.7(2)

The crystal structure of [Co(salmdpt)NO₂] is very similar to the complex described previously by Anderson et al.^[130] The molecular structure of this complex is shown in Figure 6-2.

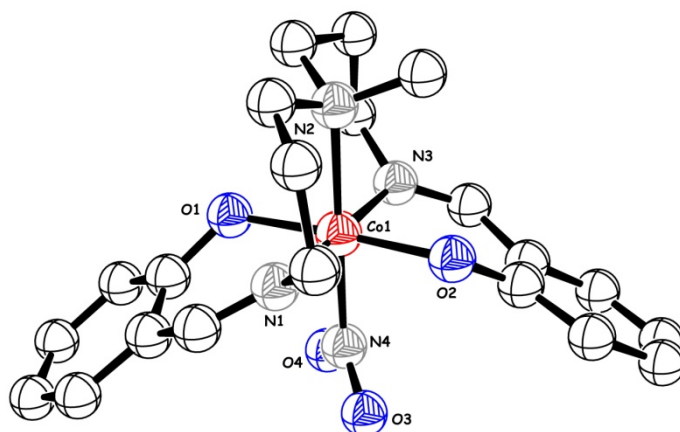


Figure 6-2: Ortep Plot of Nitro-(*N,N'*-4-Azaheptane-1,7-diylbis-(salicylaldehyde-iminato)cobalt(III) [Co(salmdpt)NO₂]^[130]

The cobalt atom lies almost exactly in the equatorial plane spanned by the atoms N(1), N(2), N(3), and N(4). O(1) and O(2) fill the axial positions. [Co(salmdpt)NO₂]

crystallizes in monoclinic space group $P12_1/n1$. The unit cell parameters are $a = 12.818(4) \text{ \AA}$, $b = 11.763(3) \text{ \AA}$, $c = 17.830(3) \text{ \AA}$, $\beta = 103.59(2)^\circ$, and $V = 2613.1 \text{ \AA}^3$.^[130]

As a consequence of the influence of the NO_2 ligand, the bond $\text{Co}(1)\text{-N}(2)$ length amounts to $2.078(6) \text{ \AA}$ and is thus slightly longer than the $\text{Co}(1)\text{-N}(1)$ and $\text{Co}(1)\text{-N}(3)$ bond lengths, which are $1.936(6) \text{ \AA}$ and 1.913 \AA . The $\text{Co}(1)\text{-N}(4)$ bond length amounts to $1.932(6) \text{ \AA}$ and lies within the range of $1.908(3) \text{ \AA}$ to $1.954(2) \text{ \AA}$ found in related cobalt(III)- NO_2 complexes. The NO_2 group is symmetrically tilted as can be seen in the angles $\text{Co}(1)\text{-N}(4)\text{-O}(3) 119.2(5)^\circ$ and $\text{Co}(1)\text{-N}(4)\text{-O}(4) 120.9(5)^\circ$.^[130]

The unit cell parameters for the determined complex are different from the one described above. For the structure described in this work, the space group is $C2/c$ and for the structure published by Anderson et al. the space group is $P12_1/n1$.

However, most important is the difference in the syntheses of these two compounds. The nitro complex described by Anderson et al. was prepared using a nitrite salt in contrast to the synthesis described herein, where NO or NO_2 was used.

Probably the formation of this complex either results from impure NO gas (already partially oxidized) or from a subsequent oxidation of the NO complex.

6.1.1 IR Spectra of $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Acetonitrile

Additionally, infrared spectroscopy was performed with the crystals obtained from acetonitrile. The resulting spectrum is shown in Figure 6-3, and the comparison with the cobalt(II) complex $[\text{Co}(\text{salmdpt})]$ is depicted in Figure 6-4. In the spectrum of the nitro complex bands in the typical range of $1470\text{-}1370 \text{ cm}^{-1}$ and $1340\text{-}1320 \text{ cm}^{-1}$ for coordinated nitro groups could be observed.^[90] Some of these bands are still in the spectrum of the Co^{II} complex, but in contrast to the $\text{Co}^{\text{III}}\text{-NO}_2$ complex they are more pronounced. One small band at 1705 cm^{-1} is new in the spectrum of the $[\text{Co}(\text{salmdpt})\text{NO}_2]$ complex. Maybe this band derives from stretching vibrations of N=O because in the spectrum of the $[\text{Co}(\text{salmdpt})\text{NO}]$ complex (Figure 5-2 and Figure 5-3) this band could also be seen. In this case the bond is much more pronounced. Nitro groups also show a small double bond character of the N=O bond like nitrosyl groups.

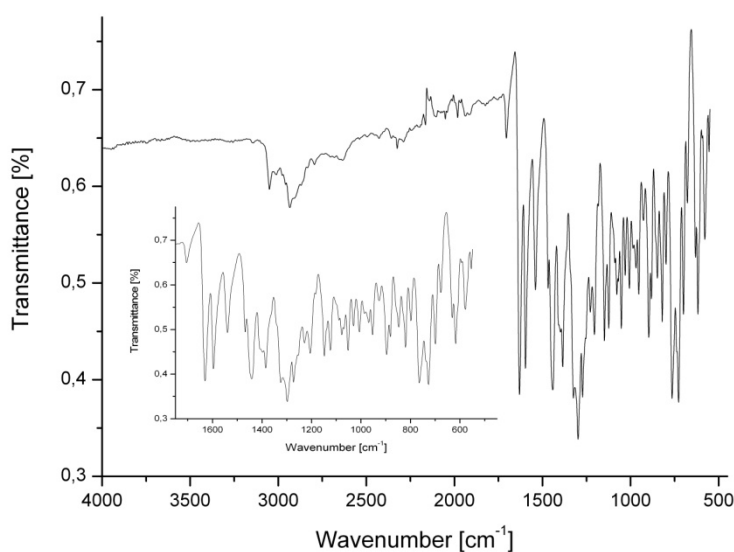


Figure 6-3: IR Spectrum of $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Acetonitrile

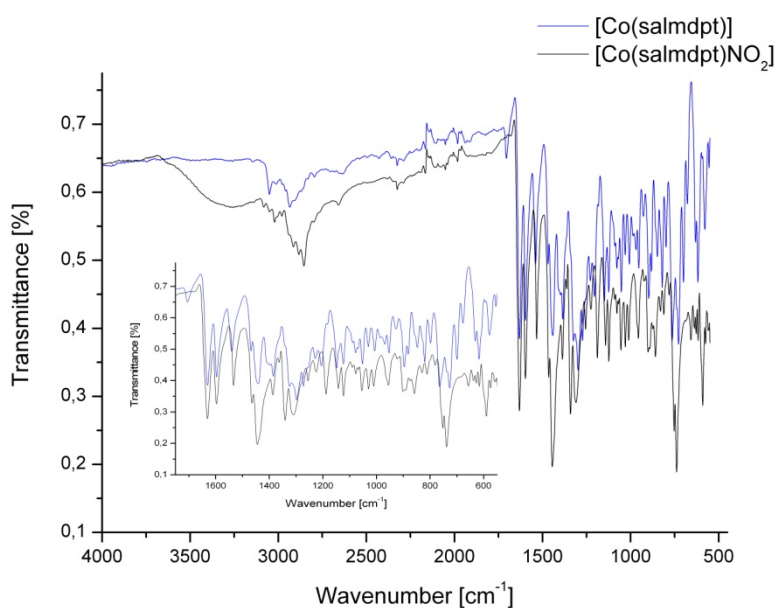


Figure 6-4: Comparison of the IR Spectra of $[\text{Co}(\text{salmdpt})]$ and $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Acetonitrile

6.2 Crystal Structure of $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Methanol

In another effort to prepare the nitrogen monoxide complex of $[\text{Co}(\text{salmdpt})]$, methanol was used as a solvent. However, crystals of the NO_2 complex suitable for X-ray crystallographic analysis could be obtained.^[133] The crystal structure is also similar to the ones described above.

The molecular structure depicted in Figure 6-5 shows a six-fold coordination of the cobalt atom and a distorted octahedral arrangement. The cobalt atom is almost located exactly in the middle of the equatorial plane, which is spanned by the atoms O(1), O(2), N(2) and N(3), whereas the atoms N(2) and N(4) fill the axial positions. Unlike the structures described in Chapter 6.1, the structure described here shows the space group $P2_1/c$ (compared to $C2/c$ of the one from acetonitrile). The unit cell dimensions are also different to the one in acetonitrile. Crystallographic data are presented in Table 6-3 and Table 6-4.

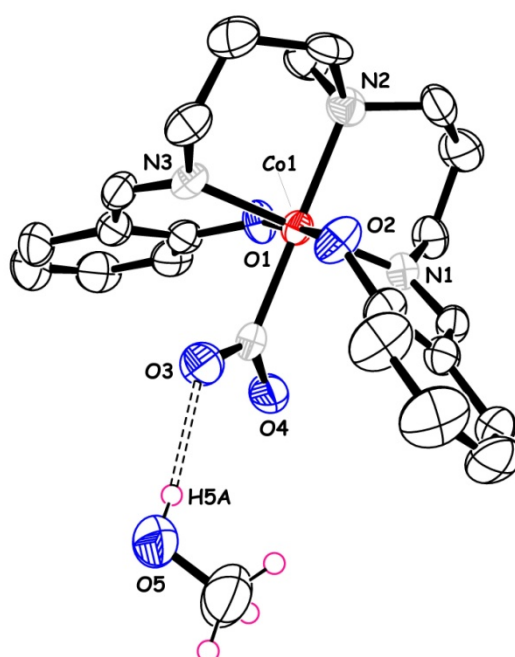


Figure 6-5: Ortep Plot of $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Methanol

The formation of this complex is also probably caused by impure NO gas (already partially oxidized) or by subsequent oxidation of the NO complex.

Table 6-3: Crystal Data and Structure Refinement for [Co(salmdpt)NO₂] from Methanol

Habitus	needle
Color	red
Crystal size	0.56 x 0.16 x 0.04 mm
Temperature	193 K
Diffractometer type	STOE IPDS
Wavelength	0.71073 Å
Empirical formula	C ₂₂ H ₂₉ CoN ₄ O ₅
Formula weight	488.42 g/mol
Crystal system, space group	monoclinic, P2 ₁ /c (Nr. 14)
Unit cell dimensions	a = 10.197(2) Å α = 90° b = 8.4990(17) Å β = 100.08(3)° c = 26.372(5) Å γ = 90°
Volume	2250.2(8) Å ³
Z, calculated density	4, 1.442 Mg/m ³
Absorption coefficient	0.804 mm ⁻¹
F(000)	1024
Theta range for data collection	2.77 to 28.11
Limiting indices	-15 ≤ h ≤ 15, -20 ≤ k ≤ 21, -17 ≤ l ≤ 17
Reflections collected / unique	22443 / 6124 [R (int) = 0,0892]
Completeness to theta = 28.11	93.4 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5141 / 0 / 338
Goodness-of-fit on F ²	0.866
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1054
R indices (all data)	R1 = 0.0815, wR2 = 0.1206
Largest diff. peak and hole	0.785 and -0.969 eÅ ⁻³

The structure shows the presence of a nitro group in the environment of the cobalt(III) atom that is located almost exactly in the middle of the equatorial plane. The bond lengths and bond angles of the structure are quite similar to the structure of Anderson et al. and to the one described in Chapter 6.1.^[130] The synthesis of this complex is similar to the one described in Chapter 6.1.

Table 6-4: Selected Bond Lengths [Å] and Angles [°] for [Co(salmdpt)NO₂] from Methanol

Co(1)-N1	1,920(2)	Co(1)-O2	1,881(2)
Co(1)-N2	2.046(3)	N4-O3	1.242(3)
Co(1)-N3	1.914(2)	N4-O4	1.232(4)
Co(1)-N4	1.912(3)	O3-H5A	2.0368
Co(1)-O1	1,881(2)		
N1-Co(1)-N2	89.21(11)	O2-Co(1)-N1	90.00(10)
N1-Co(1)-N3	178.85(11)	O2-Co(1)-N2	91.01(11)
N1-Co(1)-N4	91.14(11)	O2-Co(1)-N3	90.38(10)
N2-Co(1)-N3	89.70(12)	O2-Co(1)-N4	87.94(12)
N2-Co(1)-N4	178.90(12)	O1-Co(1)-O2	177.45(12)
N3-Co(1)-N4	89.96(11)	Co(1)-N4-O3	120.2(2)
O1-Co(1)-N1	89.11(10)	Co(1)-N4-O4	121.2(2)
O1-Co(1)-N2	91.37(11)	O3-N4-O4	118.6(3)
O1-Co(1)-N3	90.55(10)	N4-O3-H5A	117.7
O1-Co(1)-N4	89.68(12)		

The structure from methanol contains, unlike the structure from Anderson et al. and the one from acetonitrile, an additional hydrogen bond between the hydrogen atom of the hydroxide group of the methanol molecule and the oxygen atom O(3) of the nitro group of the [Co(salmdpt)NO₂] complex. The bond length of 2.0368 Å (O(3)-H(5A)) and the bond angle of 117.7 ° (N(4)-O(3)-H(5A)) coincide with the data for moderate to weak hydrogen bonds, which are based on weak electrostatic interactions (Table 6-5).^[134-135]

Table 6-5: Strong, Moderate, and Weak Hydrogen Bonds following the Classification of Jeffrey^[134-135]

	Strong	Moderate	Weak
Interaction Type	strongly covalent	mostly electrostatic	electrostat. / dispers.
Bond Lengths [Å] H·····A	1.2 – 1.5	1.5 – 2.2	2.2 – 3.2
Bond Angles [°]	170 – 180	130 – 180	90 – 150
relat. IR shift $\Delta\nu_{\text{XH}}$ [cm ⁻¹]	25%	10 – 25%	< 10
Bond Energy [kcal mol ⁻¹]	15 – 40	4 – 15	< 4

6.2.1 IR Spectra of [Co(salmdpt)NO₂] from Methanol

An IR spectrum of the [Co(salmdpt)NO₂] complex and its Co^{II} precursor complex was prepared. In difference to the spectra in Chapter 6.1.1 it was prepared as a KBr disk. The spectrum of the nitro complex obtained in methanol is shown in Figure 6-6. The spectrum shows bands in the ranges of 1470-1370 cm⁻¹ and 1340-1320 cm⁻¹ which are characteristic for nitro groups in transition metal complexes.^[90] In Figure 6-7, a comparison of the spectra of [Co(salmdpt)] and [Co(salmdpt)NO₂] in methanol is shown. These bands could also be observed in the spectrum of the [Co(salmdpt)] complex, but not as pronounced as in the spectrum of the [Co(salmdpt)NO₂] complex. A new band could be observed at 1700 cm⁻¹. We have the same explanation for this band as for the [Co(salmdpt)NO₂] complex obtained in acetonitrile (Chapter 6.1.1). Maybe this band derives from stretching vibrations of N=O because in the spectrum of the [Co(salmdpt)NO] complex (Figure 5-2 and Figure 5-3) this band could also be obtained. In this case the bond is much more pronounced. Nitro groups also show a small double bond character of the N=O bond like nitrosyl groups.

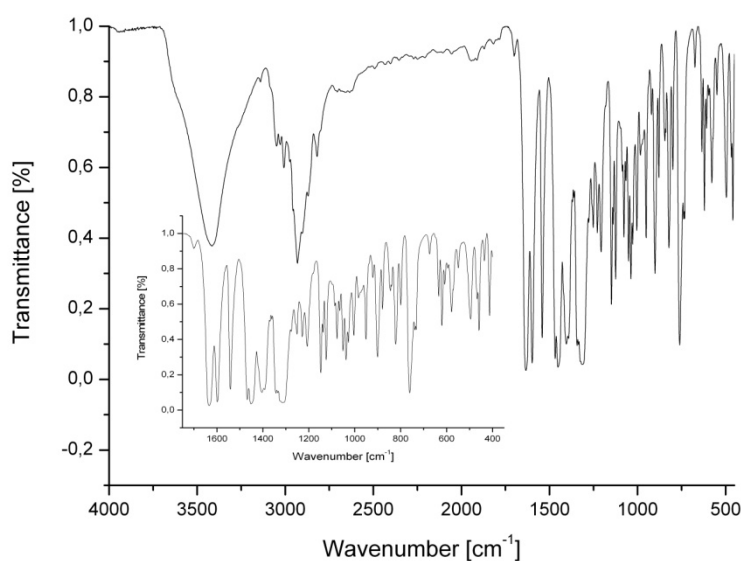


Figure 6-6: IR Spectrum of $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Methanol

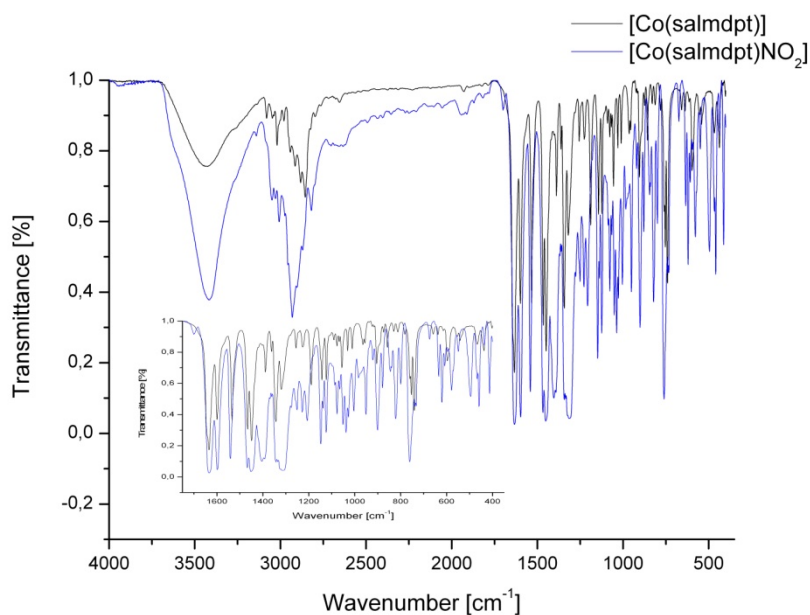


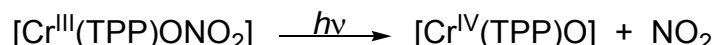
Figure 6-7: Comparison of the IR Spectra of $[\text{Co}(\text{salmdpt})]$ and $[\text{Co}(\text{salmdpt})\text{NO}_2]$ from Methanol

6.3 Nitrate Complexes of $[\text{Co}(\text{salmdpt})]$

As described above the nitrite ion is coordinated through the nitrogen atom to the cobalt ion. Therefore, in this case it is not possible to eliminate NO from the complex to obtain the according cobalt oxido complex. In contrast, using nitrate as an anionic

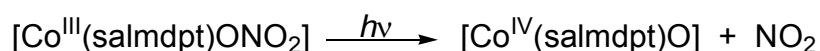
ligand photochemical elimination of NO₂ should offer the possibility to obtain the cobalt oxido complex.

That this is principally possible has been demonstrated by Radford et al. who described the photochemical cleavage of a nitrate ion coordinated to a Cr^{III} porphyrin.^[131] [Cr(TPP)ONO₂] (TPP²⁻ = *meso*-tertaphenylporphyrinato dianion) leads to a β-cleavage of the Cr^{III}-O-NO₂ bond and results in the formation of NO₂ and the according [Cr^{IV}(TPP)O] complex.

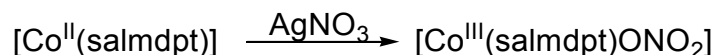


The formation of such oxido compounds is well known in other photoactive systems that release NO₂ and also form a high-valent metal oxido species e.g. with metal atoms as manganese, iron, copper and chromium.^[136-139]

Taking this into consideration, it was desired to use this reaction to form an oxido compound of the complex [Co(salmdpt)] according to the following equation:



Therefore, nitrate complexes of [Co(salmdpt)] were prepared according to the method described by Radford et al.^[131] IR spectra of the product were measured to verify if the [Co(salmdpt)ONO₂] complex was formed.



The IR spectrum of the Co^{II} complex is shown in Figure 6-8 and the one of the expected Co^{III}-O-NO₂ complex in Figure 6-9.

An infrared spectrum of the resulting product from the synthesis of [Co(salmdpt)NO₃] was prepared. In comparison to the [Co(salmdpt)] complex, in the spectrum of the nitrate complex new bands at 730 cm⁻¹, at 750 cm⁻¹, at 1268 cm⁻¹, and at 1305 cm⁻¹ could be detected. More pronounced bands at 1449 cm⁻¹, at 1466 cm⁻¹, at 1599 cm⁻¹, and at 1634 cm⁻¹ could be observed. It might be possible that these bands are from the three stretching vibrations of the coordinated nitrate ion. 1599 cm⁻¹ and 1634 cm⁻¹ for the NO double bond, 1449 cm⁻¹, 1466 cm⁻¹, 1305 cm⁻¹, and 1268 cm⁻¹ for the two stretching vibrations of NO₂. The bands at 730 cm⁻¹ and 750 cm⁻¹ probably account for the stretching vibrations of the M-O bond. Therefore, it is possible that the formation of the [Co(salmdpt)NO₃] complex was successful. The spectrum of the

nitrate complex is shown in Figure 6-9 and the comparison with the cobalt(II) precursor complex is depicted in Figure 6-10.

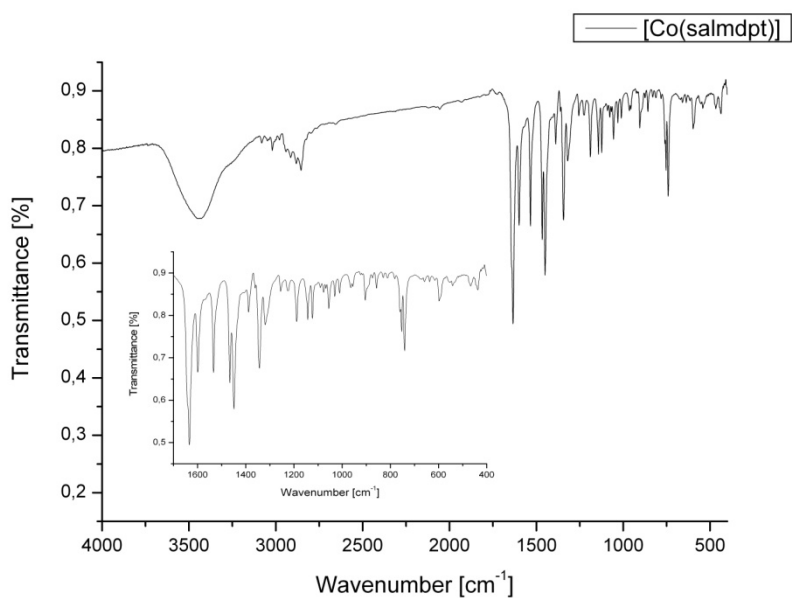


Figure 6-8: IR Spectrum of the Cobalt(II) Complex [Co(salmdpt)]

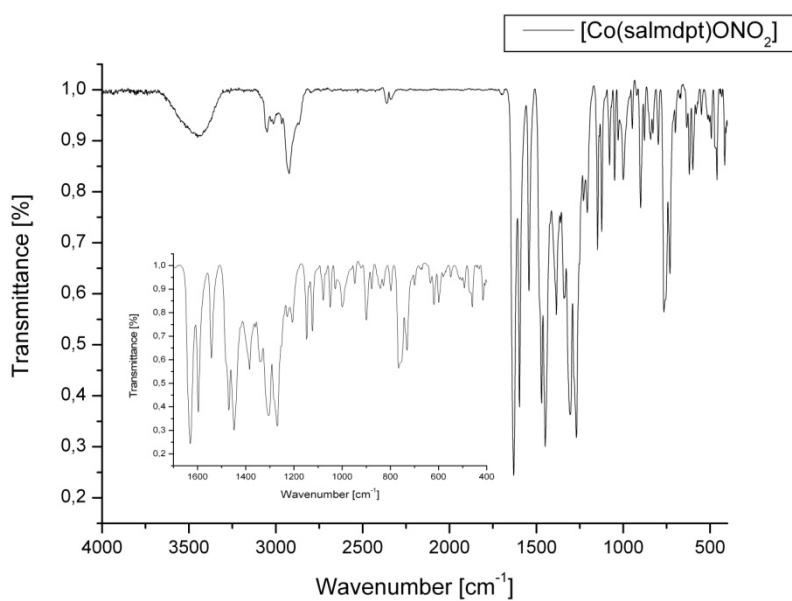


Figure 6-9: IR Spectrum of the Cobalt(III) Complex [Co(salmdpt)ONO₂]

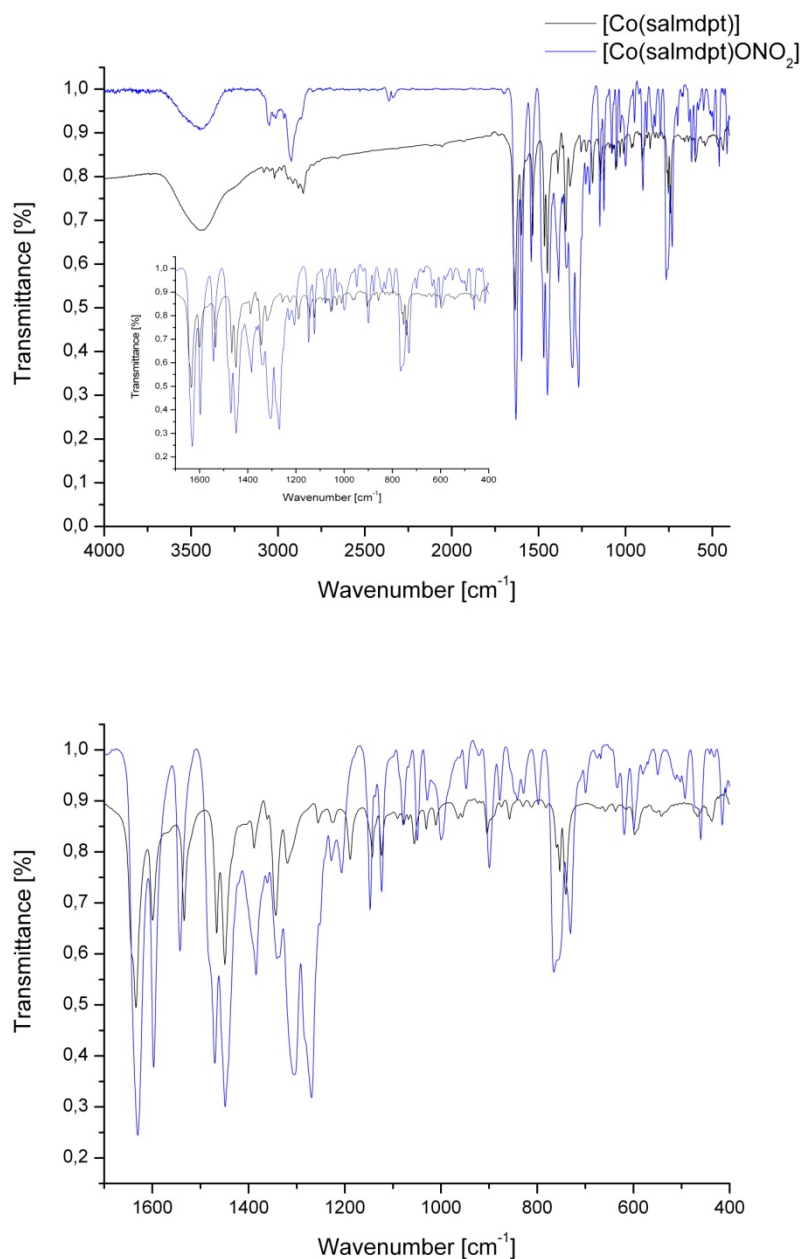


Figure 6-10: Comparison of the IR Spectra of [Co(salmdpt)] and [Co(salmdpt)ONO₂]

Until now, it seems that the formation of the nitrate complex could be observed, but it was not possible to obtain any crystals for structural characterization and for photochemical experiments.

6.4 Ozonolysis

Parallel to the investigations on the nitrate complexes it was tried to synthesize an ozonide complex of [Co(salmdpt)]. In iron chemistry, Grapperhaus et al. reported previously that an iron(IV) oxido complex could be generated by ozonolysis of an iron(III)-cyclam-acetato complex.^[128] The formation of this oxido species occurred during the reaction of ozone with an iron cyclam complex in an acetone/water mixture at -80°C. The generation of the iron oxido species could be detected by UV/Vis- and Mössbauer analysis and the following mechanism (Figure 6-11) for the formation of this species was proposed.

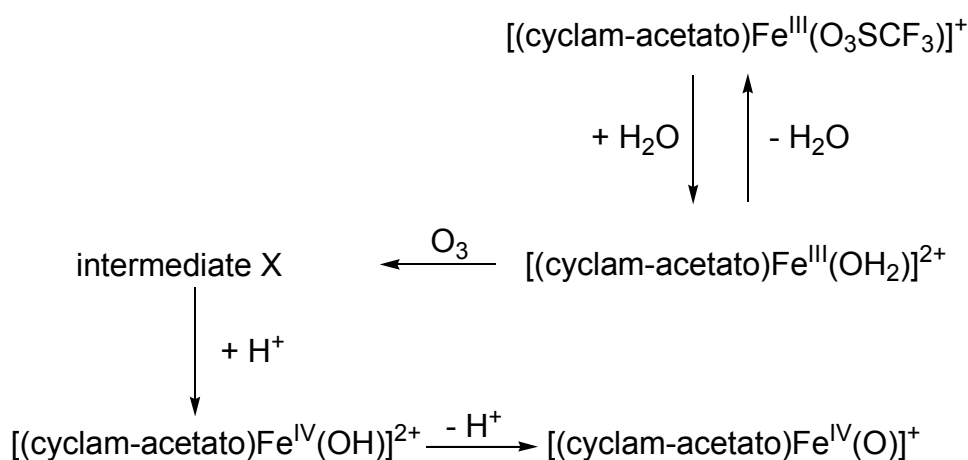


Figure 6-11: Generation of an Iron(IV) Oxido Species by Oxidation with O₃

6.4.1 Reactions of [Co(salmdpt)] with Ozone

With this background it seemed promising to use a similar approach for the synthesis of the desired cobalt oxido complex. Therefore, a solution of [Co(salmdpt)] in acetone was cooled to -80°C and ozone (using different amounts/concentrations) was flushed through it. The color of the solution turned from red to brown (or red-brown). The complex solution was then stored at -80°C in a freezer to form crystals. The experiment was carried out in other solvents too. The reaction was prepared in acetonitrile, dichloromethane, toluene, THF, methanol, and ethanol. We also used different temperatures like -40°C and room temperature. However, until now, it was not possible to obtain crystals. With low temperature stopped flow experiments it was possible to detect the formation of a cobalt(III) complex at -96°C as an intermediate (Figure 6-12).

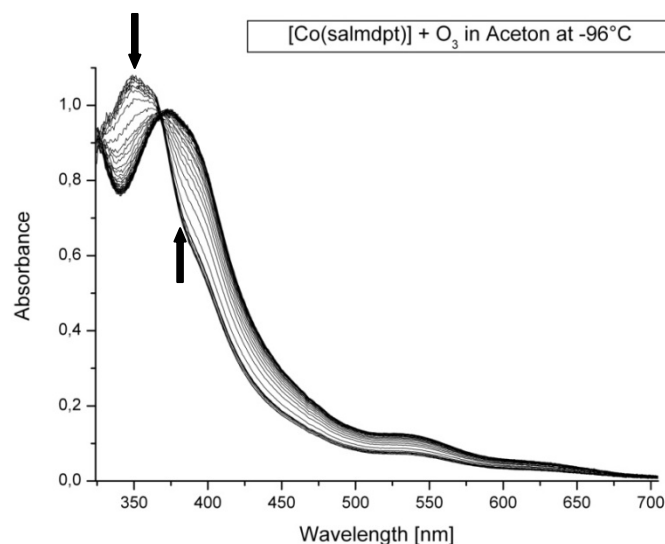


Figure 6-12: UV/Vis Spectrum of the Reaction of [Co(salmdpt)] with Ozone at -96°C

A build-up of an absorbance maximum at 378 nm and a decrease of absorbance at 348 nm could be observed. At -40°C, the dissolution of the built product could be observed (Figure 6-13). So far, it is not known for sure what kind of product and intermediate is formed. Maybe an intermediate such as a dioxygen, an ozonido or an oxido species is formed. Additional experiments and low temperature stopped flow techniques in order to analyze the formation of a possible superoxido or ozonido adduct complex should be performed in the near future.

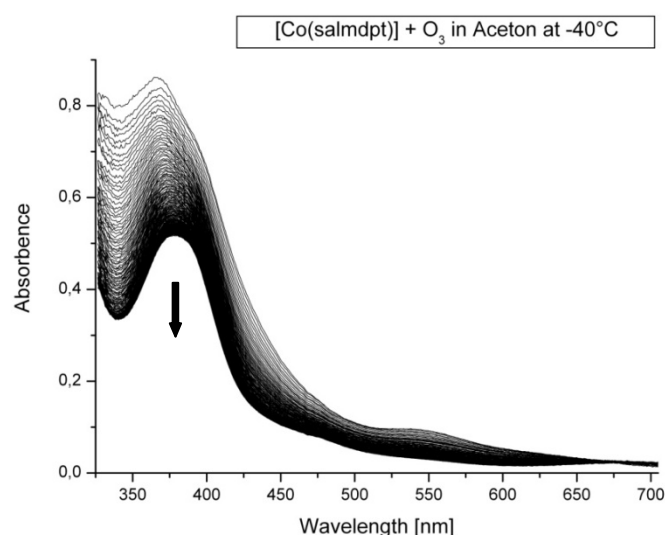


Figure 6-13: UV/Vis Spectrum of the Reaction of [Co(salmdpt)] with Ozone at -40°C

6.5 Experimental Section

6.5.1 Materials and Techniques

Commercially available materials were used without further purification. Solvents for oxygen-sensitive materials were obtained from Acros and were additionally distilled under argon before usage. Oxygen-sensitive compounds and materials were handled in a glove box (M. Braun, Germany, $O_2 < 0.1$ ppm). [Co(saldpt)], [Co(salmdpt)] and [Co(3,5-Di-*tert*-butyl-saldpt)] were synthesized according to published procedures.^[37, 91]

6.5.2 Physical Measurements

Single crystal X-ray diffraction studies were performed with a STOE IPDS-diffractometer equipped with a low temperature system (Karlsruher Glastechnisches Werk). Mo- K_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and an IP detector system were used. The frames were integrated with the STOE software package. No absorption corrections were applied.

All structures were solved by direct methods and refined by using full-matrix least-squares in the SHELX software package.^[92-93] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were positioned geometrically.

ATR-IR spectra were gained using a Bruker Optics ISF48 spectrometer with an ATR unit ("golden gate", diamond, one reflexion).

Stopped-flow experiments were performed with a commercially available Hi Tech (Salisbury, GB), SF-61DX2 instrument. Detailed descriptions on low temperature stopped flow kinetics were published previously.^[140]

The solutions of the cobalt(II) complexes were prepared in a glove box and afterwards transferred into glass syringes with attached valves. The concentration of the cobalt(II) complex solutions was usually adjusted to 2.0×10^{-4} mol/l.

An ozone saturated solution was prepared by flushing ozone for 10 minutes through acetone. Ozone was provided by an ozone generator (Ozonosan PM 80, Germany).

6.5.3 Syntheses

Generation of Nitrogen Monoxide

For the generation of nitrogen monoxide the same reaction was used as described in Chapter 5.2.3.

[Co(salmdpt)NO₂] from Acetonitrile

The preparation was carried out in two ways.

50 mg (0.12 mmol) of [Co(salmdpt)] was dissolved in acetonitrile while unpurified nitrogen monoxide was flushed through the solution. After the reaction the complex solution was stored in a fridge and ether was condensed into the solution. After a few days, red-brown crystals suitable for structural characterization were formed.

5 mg (0.0121 mmol) [Co(salmdpt)] was dissolved in 2 mL acetonitrile. Unpurified nitrogen monoxide was flushed through the solution for 3 min. The solution was stored in a fridge and ether was condensed into the solution. After a few days, red-brown crystals were obtained and suitable for structural X-ray characterization.

[Co(salmdpt)NO₂] from Methanol

95 mg (0.23 mmol) [Co(salmdpt)] was dissolved in 5 mL methanol. Afterwards, the red brown solution was flushed with purified nitrogen monoxide. A dark red solid precipitated from the solution. After a few days in a freezer at -33.5°C, also dark brown needles were obtained, suitable for structural characterization.

[Co(salmdpt)ONO₂]

The synthesis of [Co(salmdpt)ONO₂] was accomplished by stirring a biphasic mixture of saturated solution of [Co(salmdpt)] in dichloromethane and a saturated aqueous AgNO₃ solution overnight. A deep red product was obtained and filtered off. Afterwards, the organic layer was separated and the solvent was removed to give another fraction of the product. Both products were characterized by IR spectroscopy.

A saturated solution of the resulting product in acetone was stored in a fridge to form crystals. So far, we could not observe any crystals suitable for X-ray crystallographic analysis.

Ozonolysis

The preparation was carried out in many solvents. Acetone shall be used exemplarily for all other solvents.

0.103 g (0.249 mmol) [Co(salmdpt)] was dissolved in 25 mL acetone. 2 mL of this solution was transferred into a small bottle for gas chromatography. The solution was then cooled down to -40°C and flushed with ozone. The small bottle was then put into a bigger one which contained ether. This bottle was stored in a freezer at -40°C . No crystals were formed.

Another 2 mL of the parent solution was transferred into a small bottle for gas chromatography. This one was cooled to -80°C and then flushed with ozone. The solution was stored in a freezer at -80°C while ether was condensed into the solution. No crystals suitable for X-Ray characterization formed.

7 Summary

As described in Chapter 1, the cobalt(II) complex Bis[3-(salicylideneimino)-propyl]methylenecobalt(II), [Co(salmdpt)] can bind dioxygen reversibly and forms a cobalt(III) superoxido complex during this process (Figure 7-1).^[48-49]

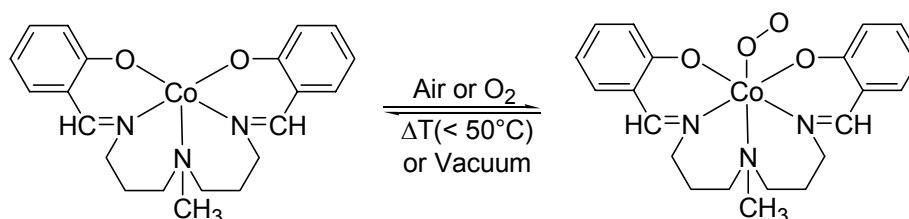


Figure 7-1: Reversible Reaction of [Co(salmdpt)] with Air or Dioxygen

One topic of the present work was the investigation of the dioxygen activation on cobalt complexes and the characterization of the dioxygen adduct complexes of the ligand saldptH₂ and its derivatives.

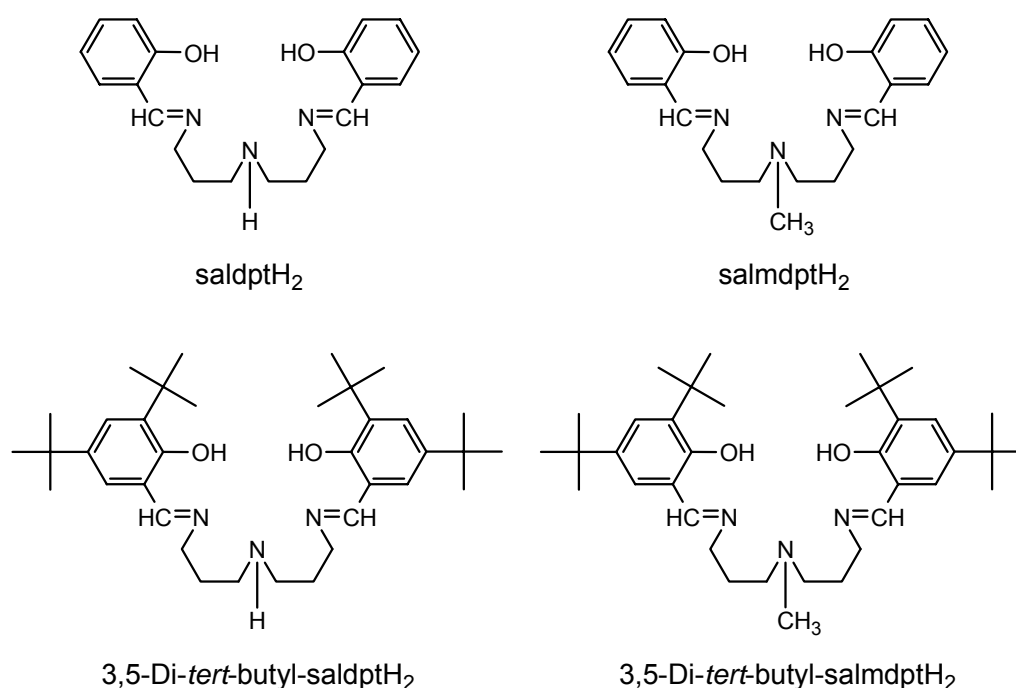


Figure 7-2: The Ligand saldptH₂ and its Derivatives Reviewed in the Present Work

To synthesize the cobalt(III) superoxido complex of [Co(salmdpt)] different solvents were used. With acetonitrile, butyronitrile and dichloromethane only the cobalt(II)

complex of the ligand salmdptH_2 was obtained. From toluene the precursor complex could be crystallized with an additional solvent molecule in its molecular structure. Variation of the reaction conditions in toluene caused formation of a cobalt(III) hydroxido complex instead of the cobalt(III) superoxido complex. When benzene was used as solvent, a black powder could be obtained. Based on infrared spectra it is most likely that here the superoxido complex was formed (however, no crystals could be obtained in contrast to the report in the literature).^[48-49] It is interesting to note that even though the crystal structure of the superoxido complex had been obtained so far no spectroscopic characterization (IR or Resonance Raman) of this complex type has been reported. During further experiments in acetonitrile crystals of a cobalt(III) cyanido complex (Chapter 3) were obtained. Performing the reaction in butyronitrile, allowed furthermore to detect propionaldehyde as a product according to the following equation:

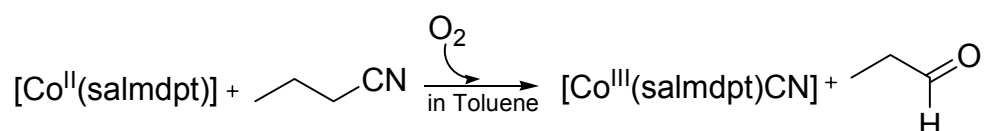


Figure 7-3: Reaction of $[\text{Co}(\text{salmdpt})]$ and Butyronitrile with Dioxygen in Toluene

In co-operation with the group of Prof. Maison it was tried to synthesize aldehydes from adamantane nitriles. The following reactions were studied under different conditions:

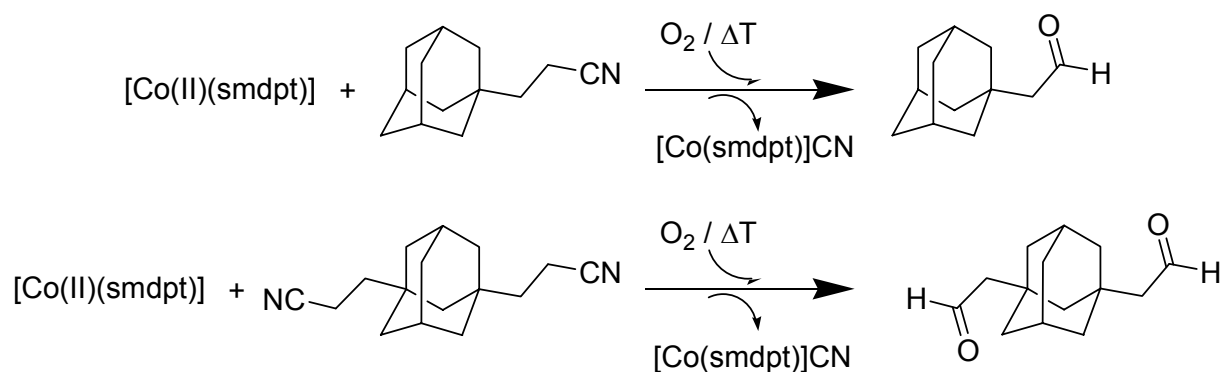
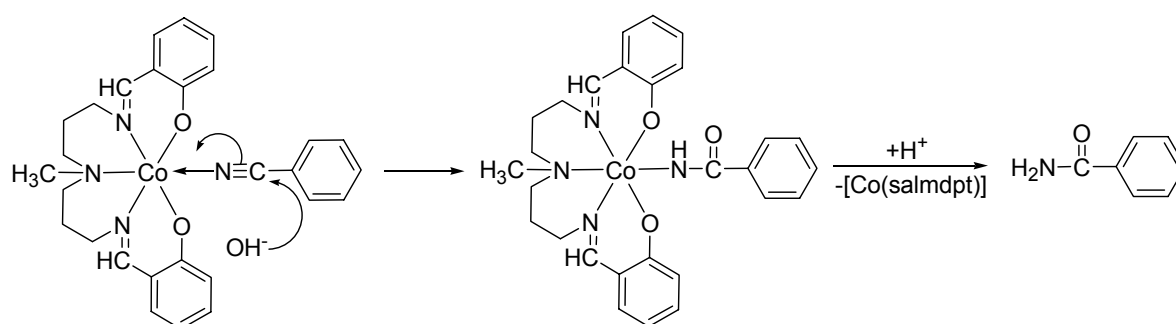


Figure 7-4: Expected Reactions of Adamantane Derivatives and the Complex $[\text{Co}(\text{salmdpt})]$

The results demonstrated that these reactions are possible. However, there is still need for improvement in regard to yields and optimization of the reaction conditions (Chapter 4.2.4).

When phenylacetonitrile was used as solvent for the reaction of [Co(salmdpt)] and dioxygen, colorless crystals of benzamide could be obtained. Here, the cobalt complex catalyzed the transformation of phenylacetonitrile into benzamide. The reaction probably proceeded according to the following mechanism (Scheme 7-1) that has been observed for other cobalt complexes as well.^[89]



Scheme 7-1: ChemDraw Plot of the Reaction of Benzonitrile to Benzamide using [Co(salmdpt)]

Due to the fact that the experiments did not allow to obtain the cobalt(III) superoxido complex the ligands saldptH₂ and salmdptH₂ were modified by adding two *tert*-butyl groups in 3rd and 5th position to the aldehyde group of each salicylaldehyde moiety. Here it was assumed that these additional steric effects might improve the formation of an end-on cobalt superoxido complex.

Reactions of the cobalt(II) complex with the ligand 3,5-Di-*tert*-butyl-saldptH₂ and dioxygen leads to a dimeric peroxido bridged complex. Keeping in mind that cobalt(II) complexes with the ligand saldptH₂ only form peroxido complexes, this result is not surprising. In contrast [Co(3,5-Di-*tert*-butyl-salmdpt)] did not react with air or dioxygen and only crystals of the starting material, the cobalt(II) complex, could be obtained (see 2.5.2).

As described in the introduction NO metal complexes are interesting in comparison with dioxygen adduct compounds. Thus it was clear to also react [Co(salmdpt)] with NO. In contrast to the reaction with dioxygen the reaction with nitrogen oxide led to crystals of [Co(salmdpt)NO] suitable for X-ray analysis. In comparison with a nitrogen

monoxide complex of cobalt salen [Co(salen)NO] and the superoxido complex of [Co(salmdpt)] the selected bond lengths and angles are similar. Both complexes [Co(salen)NO] and [Co(salmdpt)O₂] are already known in the literature.^[48-49, 73]

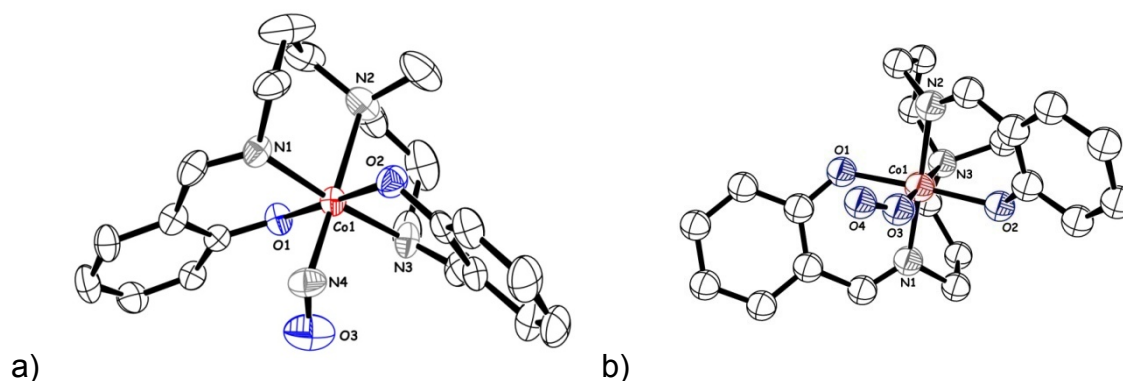


Figure 7-5: Comparison of the Ortep Plots of a) [Co(salmdpt)NO] and b) [Co(salmdpt)O₂]

The formation of a cobalt(III) cyanido complex described above most likely is based on a cobalt(IV) oxido complex as a reactive intermediate. This complex is shown in the following Figure.

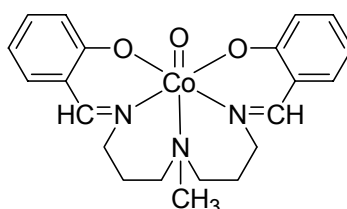


Figure 7-6: ChemDraw Plot of the Expected [Co^{IV}(salmdpt)O] Complex

While such a species already has been fully-characterized in related iron chemistry the according cobalt complex could not be obtained so far. Therefore, it was tried to use known methods to isolate this species. For different metal complexes it has been possible to obtain oxido complexes from the according nitro, nitrate or ozonido complexes. Here for example radiation leads to loss of NO, NO₂ or O₂ and thus leaving the according oxido complexes. The cobalt nitrito complex, [Co(salmdpt)NO₂], was synthesized and could be structurally characterized. Unfortunately in this complex the nitrite is coordinated through the nitrogen atom and not through the oxygen atom. Therefore this complex could not be used for this

purpose. In contrast this is not possible for the nitrate complex shown in the following Figure.

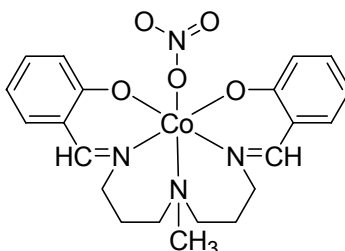


Figure 7-7: ChemDraw Plot of the Expected [Co(salmdpt)ONO₂] Complex

This complex could be synthesized; however, it was not possible to structurally characterize this compound so far.

Furthermore, it was tried to obtain the according ozonido complex. While it was not possible to synthesize this complex in pure form low temperature stopped-flow measurements indicated the formation of this complex. Time resolved UV/Vis spectra of the reaction of [Co(salmdpt)] with ozone are shown in the following Figure.

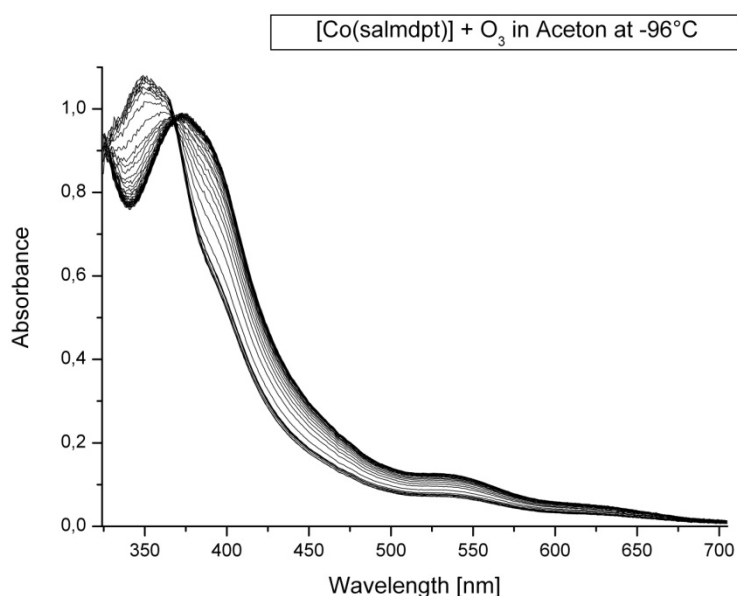


Figure 7-8: UV/Vis Spectrum of the Reaction of [Co(salmdpt)] with Ozone at -96°C

8 Zusammenfassung

Wie in Kapitel 1 beschrieben, ist der Cobalt(II) Komplex Bis[3-(salicylidanimino)-propyl]methyamincobalt(II), [Co(salmdpt)] in der Lage Sauerstoff reversibel zu binden und bildet während diesem Prozess einen Cobalt(III)-Superoxido-Komplex (Abb. 8-1).^[48-49]

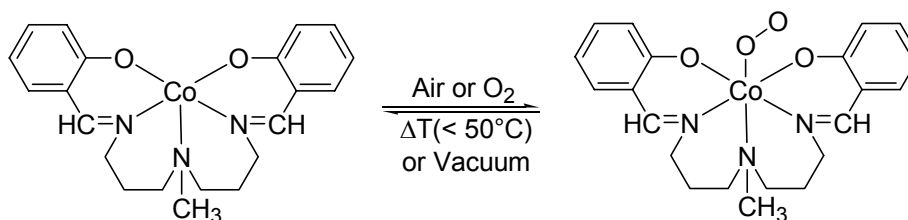


Abb. 8-1: Reversible Reaktion von [Co(salmdpt)] mit Luft oder Sauerstoff

Ein Thema dieser Arbeit war die Untersuchung der Sauerstoffaktivierung an Cobalt(II) Komplexen. Dabei sollten unter anderem die Cobalt-Sauerstoffaddukt-Komplexe des Liganden salmdptH₂ und seiner Derivate untersucht werden.

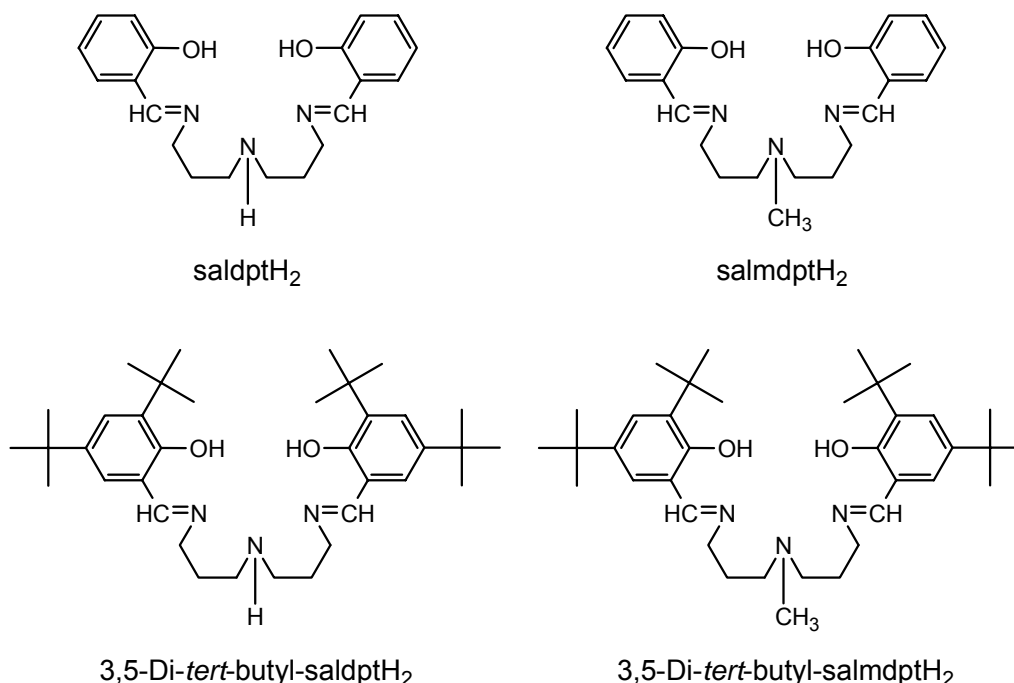


Abb. 8-2: Der in dieser Arbeit untersuchte Ligand salmdptH₂ und seine Derivate

Um die Cobalt(III) Superoxido Komplexe zu synthetisieren, wurden verschiedene Lösungsmittel verwendet. Mit Acetonitril, Butyronitril und Dichlormethan konnten nur die Cobalt(II) Komplexe des Liganden salmdptH₂ erhalten werden. Aus Toluol konnte der Precursor Komplex mit einem weiteren Lösungsmittelmolekül in der Molekülstruktur kristallisiert werden. Variation der Reaktionsbedingungen führte zur Bildung eines Cobalt(III)-Hydroxido-Komplexes an Stelle des Cobalt(III)-Superoxido-Komplexes. Wurde Benzol als Lösungsmittel verwendet, konnte ein schwarzes Pulver erhalten werden. Mit Hilfe der Infrarot-Spektroskopie konnte gezeigt werden, dass hier sehr wahrscheinlich der erwartete Superoxido-Komplex gebildet wurde (Entgegen dem Bericht in der Literatur konnten hier keine Kristalle erhalten werden).^[48-49] Interessant ist auch, dass obwohl die Kristallstruktur des Superoxido Komplexes bekannt ist, bis jetzt keine spektroskopische Charakterisierung (IR oder Resonanz Raman) dieses Komplex Typs veröffentlicht wurden. Bei weiteren Experimenten in Acetonitril konnten Kristalle eines Cobalt(III)-Cyanido-Komplexes (Kapitel 3) erhalten werden. Wurde die Reaktion in Butyronitril durchgeführt, so konnte Propionaldehyd als ein weiteres Produkt entsprechend der folgenden Gleichung identifiziert werden.

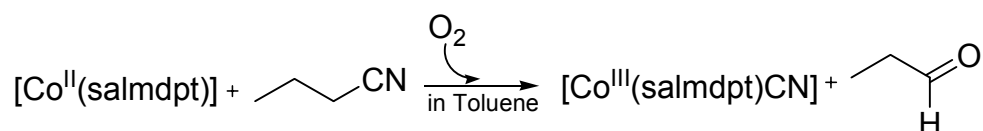


Abb. 8-3: Reaktion von [Co(salmdpt)] und Butyronitril mit Sauerstoff in Toluol

In Zusammenarbeit mit der Arbeitsgruppe von Prof. Maison sollten Aldehyde ausgehend von Adamantannitrilen synthetisiert werden. Die folgenden Reaktionen wurden unter verschiedenen Bedingungen untersucht.

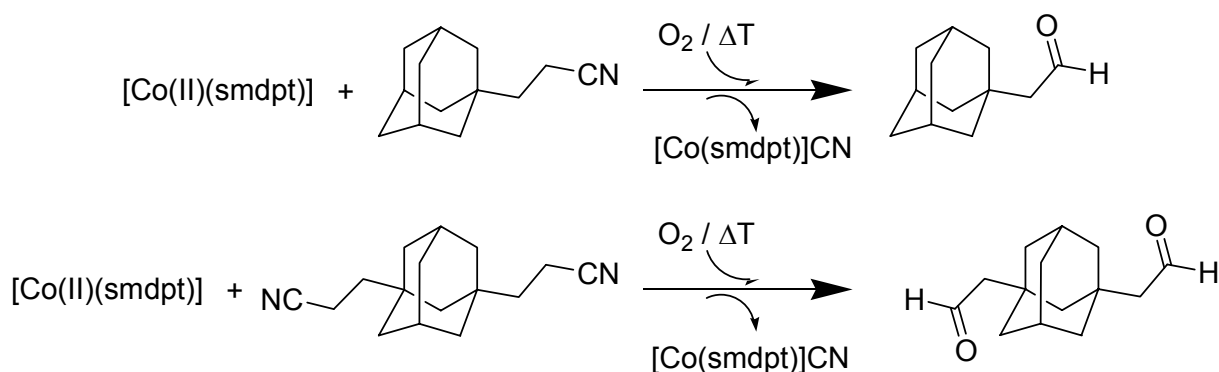
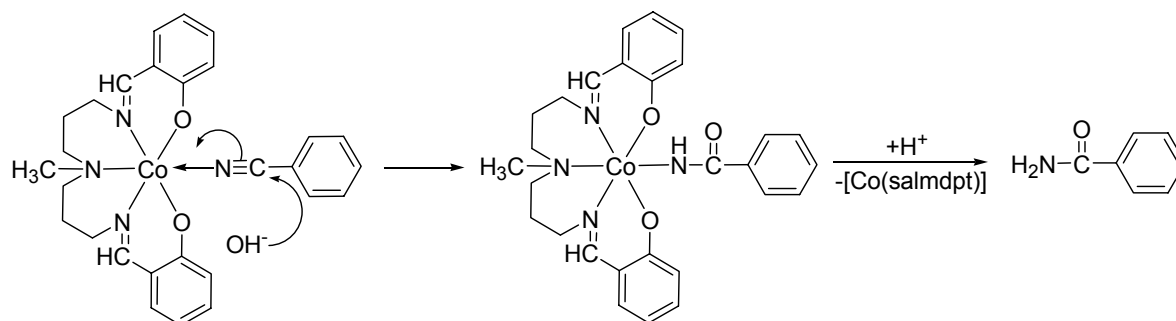


Abb. 8-4: Erwartete Reaktionen der Adamantan Derivate mit dem Komplex [Co(salmdpt)]

Die Ergebnisse dieser Untersuchungen haben gezeigt, dass solche Reaktionen möglich sind. Dennoch ist hier eine Verbesserung, im Hinblick auf Ausbeute und Optimierung der Reaktionsbedingungen nötig (Kapitel 4.2.4).

Wurde Phenylacetonitril als Lösungsmittel für die Reaktion von [Co(salmdpt)] mit Sauerstoff verwendet, so wurden farblose Benzamidkristalle erhalten. Der Cobalt-Komplex katalysiert hier die Umsetzung von Phenylacetonitril in Benzamid. Die Reaktion läuft wahrscheinlich über folgenden Mechanismus (Schema 8-1), der bereits für andere Cobalt-Komplexe beobachtet wurde, ab.^[89]



Schema 8-1: ChemDraw Zeichnung der Reaktion von Benzonitril zu Benzamid unter Verwendung des Komplexes [Co(salmdpt)]

Da mit den bisherigen Experimenten der Cobalt(III)-Superoxido-Komplex nicht erhalten werden konnte, wurden die Liganden saldptH₂ und salmdptH₂ modifiziert. Dazu wurden an der 3. und 5. Position zur Aldehydfunktion an jedem Salicyladehydrest zwei *tert*-butyl Gruppen eingebracht. Dabei wurde erwartet, dass die zusätzlich eingebrachten sterischen Effekte die Bildung eines end-on Cobalt-Superoxido-Komplexes begünstigen würden.

Reaktionen des Cobalt(II) Komplexes mit dem Liganden 3,5-Di-*tert*-butyl-salmdptH₂ und Sauerstoff führten zu einem dimeren Peroxido verbrückten Komplex. Vor dem Hintergrund, dass der Cobalt(II)-Komplex des Liganden salmdptH₂ ausschließlich Peroxido-Komplexe bildet, war diese Ergebnis nicht überraschend. Im Gegensatz dazu reagierte der Cobalt(II)-Komplex [Co(3,5-Di-*tert*-butyl-salmdpt)] nicht mit Luft oder Sauerstoff, und es konnten nur Kristalle der Ausgangsverbindung, des Cobalt(II)-Komplexes erhalten werden (siehe 2.5.2).

Wie in der Einleitung beschrieben, sind NO-Metall-Komplexe interessant für den Vergleich mit Sauerstoff-Addukt-Verbindungen. Daher war es logisch, den [Co(salmdpt)] Komplex ebenfalls mit NO reagieren zu lassen. Im Gegensatz zu den Reaktionen mit Sauerstoff konnten in diesem Fall Kristalle des entsprechenden [Co(salmdpt)NO] Komplexes erhalten werden, die mittels Röntgenstrukturanalyse untersucht wurden. Im Vergleich mit einem Stickstoffmonoxid Komplex von Cobalt-Salen [Co(salen)NO] und dem Superoxido-Komplex [Co(salmdpt)O₂] sind die ausgewählten Bindungslängen und -winkel ähnlich. Beide Komplexe [Co(salen)NO] und [Co(salmdpt)O₂] sind bereits in der Literatur bekannt.^[48-49, 73]

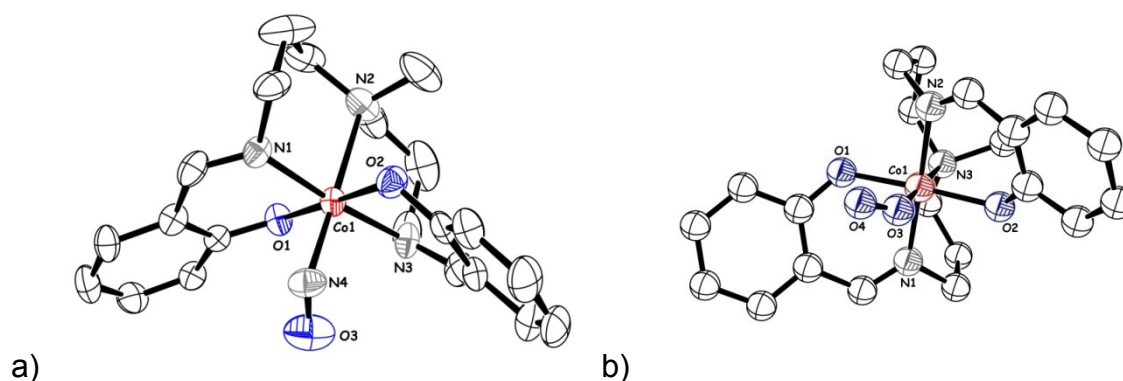


Abb. 8-5: Vergleich der Ortep Bilder von a) [Co(salmdpt)NO] und b) [Co(salmdpt)O₂]

Die oben beschriebene Bildung eines Cobalt(III)-Cyanido-Komplexes verläuft sehr wahrscheinlich über einen Cobalt(IV)-Oxido-Komplex als reaktives Zwischenprodukt. Dieser Komplex ist in der folgenden Abbildung gezeigt.

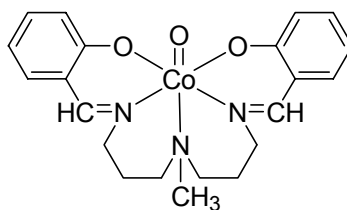


Abb. 8-6: ChemDraw Zeichnung des vermuteten $[\text{Co}^{\text{IV}}(\text{salmdpt})\text{O}]$ Komplexes

Während in der verwandten Eisenchemie eine solche Spezies bereits vollständig charakterisiert und beschrieben wurde, konnte der entsprechende Cobalt-Komplex noch nicht erhalten werden. Daher sollte versucht werden, die entsprechende Spezies mit bereits bekannten Methoden aus anderen Bereichen darzustellen. Für verschiedene Übergangsmetall-Komplexe war es möglich den Oxido-Komplex über die entsprechenden Nitro-, Nitrat- oder Ozonido-Komplexe darzustellen. Der entsprechende Oxido-Komplex kann hier z. B. durch Bestrahlung dieser Komplexe erhalten werden. Dabei wird dementsprechend NO , NO_2 oder O_2 abgespalten. Der Cobalt-Nitro-Komplex, $[\text{Co}(\text{salmdpt})\text{NO}_2]$, wurde synthetisiert und konnte strukturell charakterisiert werden. Unglücklicherweise ist die Nitro-Gruppe in diesem Komplex durch ein Stickstoffatom und nicht durch ein Sauerstoffatom an das Metallatom koordiniert. Daher kann dieser Komplex nicht für diesen Zweck verwendet werden. Im Gegensatz dazu ist dies für den in der folgenden Abbildung gezeigten Nitrat-Komplex nicht möglich.

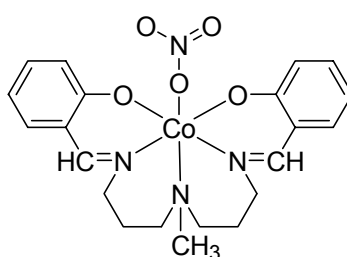


Abb. 8-7: ChemDraw Zeichnung des $[\text{Co}(\text{salmdpt})\text{ONO}_2]$ Komplexes

Die Darstellung dieses Komplexes war sehr wahrscheinlich erfolgreich, dennoch konnten bisher keine Kristalle für eine Röntgenstrukturanalyse erhalten werden.

Weiterhin sollte versucht werden, den entsprechenden Ozonido-Komplex darzustellen. Da es nicht möglich war den Komplex in reiner Form darzustellen, wurden Tieftemperatur-Stopped-Flow Experimente durchgeführt. Dabei konnte sehr

wahrscheinlich die Bildung eines Cobalt(III)-Ozonido-Komplexes beobachtet werden. Zeitaufgelöste UV/Vis-Spektren der Reaktion von $[\text{Co}(\text{salmcpt})]$ mit Ozon sind in der folgenden Abbildung gezeigt.

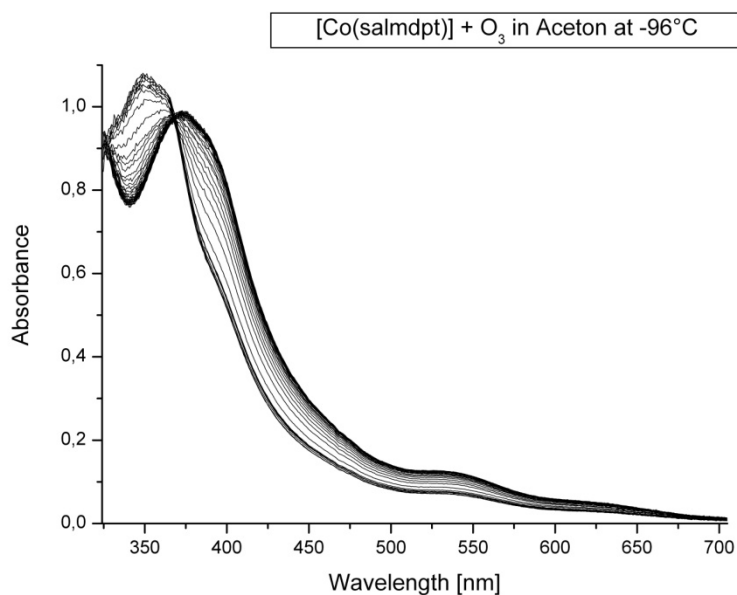
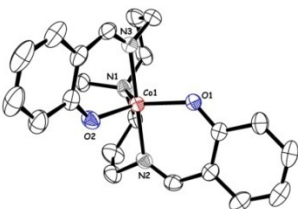
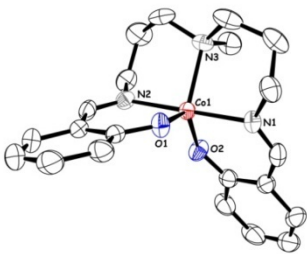
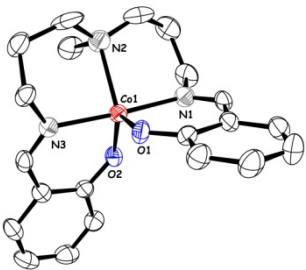
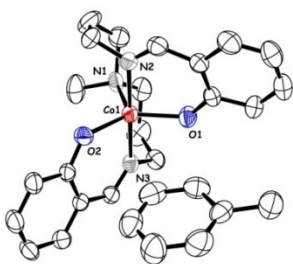
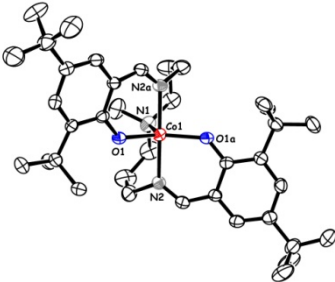
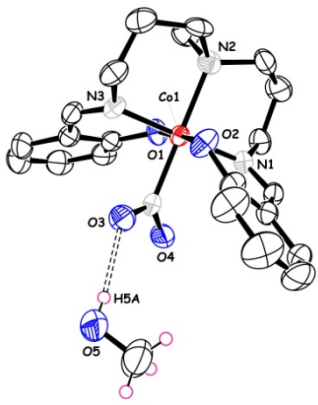
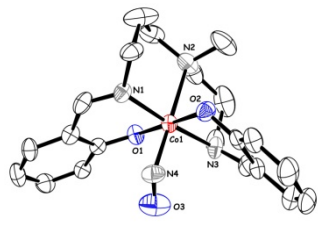


Abb. 8-8: UV/Vis-Spektren der Reaktion von $[\text{Co}(\text{salmcpt})]$ mit Ozon bei -96°C

List of Crystal Structures

Ortep Plot	Compound, Formula, Formula weight [g/mol]	Name, weight	Crystal system, space group	Cell dimension [Å] Angles [°] Volumes [Å ³]
	[Co(salmdpt)] in CH ₃ CN C ₂₁ H ₂₅ CoN ₃ O ₂ 410.37		monoclinic P2 ₁ /c	[a, b, c] = [6.7627(6), 13.7463(12), 20.8444(18)] [α, β, γ] = [90, 92.6030(10), 90] V = 1935.7(3)
	[Co(salmdpt)] in C ₃ H ₇ CN C ₂₁ H ₂₅ CoN ₃ O ₂ 410.37		monoclinic P2 ₁ /c	[a, b, c] = [6.7560(14), 13.767(3), 20.801(4)] [α, β, γ] = [90, 92.50(3), 90] V = 1932.9(7)
	[Co(salmdpt)] in CH ₂ Cl ₂ C ₂₂ H ₂₇ Cl ₂ CoN ₃ O ₂ 495.30		orthorhombic Pna2 ₁	[a, b, c] = [13.097(3), 15.280(3), 11.524(2)] [α, β, γ] = [90, 90, 90] V = 2306.2(8)
	[Co(salmdpt)] in C ₇ H ₈ C ₂₈ H ₃₃ CoN ₃ O ₂ 502.50		monoclinic P2 ₁ /c	[a, b, c] = [11.4552(15), 16.6517(15), 13.3868(18)] [α, β, γ] = [90, 94.567(16), 90] V = 2545.4(5)
	[Co(3,5-Di- <i>tert</i> -butyl- salmdpt)] in C ₃ H ₆ O C ₃₇ H ₅₇ CoN ₃ O ₂ 634.79		orthorhombic Ccca	[a, b, c] = [20.778(4), 27.141(5), 13.768(3)] [α, β, γ] = [90, 90, 90] V = 7764(3)

LIST OF CRYSTAL STRUCTURES

Ortep Plot	Compound, Formula, Formula weight [g/mol]	Name, weight	Crystal system, space group	Cell dimension [Å] Angles [°] Volumes [Å ³]
	[Co(salmdpt)NO ₂] in CH ₃ OH C ₂₂ H ₂₉ CoN ₄ O ₅ 488.42		monoclinic P2 ₁ /c	[a, b, c] = [10.197(2), 8.4990(17), 26.372(5)] [α, β, γ] = [90, 100.08(3), 90] V = 2250.2(8)
	[Co(salmdpt)NO] in CH ₂ Cl ₂ C ₂₁ H ₂₅ CoN ₄ O ₃ 440.38		orthorhombic Pbca	[a, b, c] = [14.192(3), 13.088(3), 21.805(4)] [α, β, γ] = [90, 90, 90] V = 4050.2(14)

Publication

- Transformation of Nitrile to Cyanide and Aldehyde Using a Cobalt(II) Complex and Dioxygen
Jörg Müller, Christian Würtele, Olaf Walter and Siegfried Schindler
Angew. Chem., **2007**, 119, 7922 [Angew. Chem. Int. Ed., **2007**, 46, 7775]

Presentations

Poster Presentations

- GDCh-Wissenschaftsforum Ulm (09/2007)
„Nitrile to Cyanide and Aldehyde Using a Cobalt(II) Complex and Dioxygen“
- Koordinationschemie-Treffen Universität Giessen (02/2008)
„Nitrile to Cyanide and Aldehyde Using a Cobalt(II) Complex and Dioxygen“
- 2nd EuCheMS Chemistry Congress Turin, Italien (09/2008)
„End-on Cobalt Superoxo Complexes in Organic Synthesis“
- GDCh-Wissenschaftsforum Frankfurt/Main (09/2009)
„Efforts to Characterise a Cobalt Oxo Complex“

Oral Presentations

- Koordinationschemie-Treffen Universität Erlangen (02/2009)
„Ungewöhnliche Darstellung eines Cobalt(III)-Cyanido-Komplexes“

**Der Lebenslauf wurde aus der elektronischen
Version der Arbeit entfernt.**

**The curriculum vitae was removed from the
electronic version of the paper.**

10 Bibliography

- [1] W. Kaim, B. Schwederski, *Bioanorganische Chemie*, Teubner Verlag, Stuttgart, **1991**.
- [2] S. J. Lippard, J. M. Berg, *Bioanorganische Chemie*, Spektrum Akademischer Verlag, Heidelberg - Berlin - Oxford, **1995**.
- [3] R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**.
- [4] *Oxygen Complexes and Oxygen Activation by Transition Metals*, Eds.: A. E. Martell, D. T. Sawyer, Plenum, New York, **1988**.
- [5] in *Proceedings of the Fourth International Symposium on Dioxygen Activation and Homogeneous Catalytic Oxidation*, Vol. 66 (Ed.: L. I. Simandi), Elsevier, **1991**, pp. 1.
- [6] O. M. Reinaud, G. P. A. Yap, A. L. Rheingold, K. H. Theopold, *Angew. Chem. Int. Ed.* **1995**, 34, 2051.
- [7] L. F. Trueb, *Die Chemischen Elemente - Ein Streifzug durch das Periodensystem*, S. Hirzel Verlag Stuttgart - Leipzig, **1996**.
- [8] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Vol. 101, de Gruyter, Berlin; New York, **1995**.
- [9] H. Franzen, O. von Mayer, *Ber.* **1906**, 39, 3377.
- [10] A. Werner, *Ber.* **1908**, 41, 3007.
- [11] S. Deakin, M. Scott, B. D. Steele, *Z. physik. Chem.* **1910**, 69, 123.
- [12] G. H. Whipple, F. S. Robscheit-Robbins, *Am. J. Physiol.* **1925**, 72, 408.
- [13] G. R. Minot, W. P. Murphy, *JAMA, J. Am. Med. Assoc.* **1926**, 87, 470.
- [14] E. L. Smith, *Nature* **1948**, 161, 638.
- [15] E. L. Rickes, N. G. Brink, F. R. Koniuszy, T. R. Wood, K. Folkers, *Science* **1948**, 107, 396.
- [16] E. L. Rickes, N. G. Brink, F. R. Koniuszy, T. R. Wood, K. Folkers, *Science* **1948**, 108, 134.

- [17] R. Banerjee, S. W. Ragsdale, *Annu. Rev. Biochem.* **2003**, 72, 209.
- [18] D. C. Hodgkin, A. W. Johnson, A. R. Todd, *Chem. Soc. (London)* **1955**, No. 3, 109.
- [19] D. C. Hodgkin, J. Kamper, M. Mackay, J. Pickworth, K. N. Trueblood, J. G. White, *Nature (London, U. K.)* **1956**, 178, 64.
- [20] D. C. Hodgkin, *Fortschr. Chem. org. Naturstoffe* (L. Zechmeister, editor. Springer-Verlag) **1958**, 15, 167.
- [21] E. L. Smith, *Nature (London, U. K.)* **1958**, 181, 305.
- [22] H. A. Barker, H. Weissbach, R. D. Smyth, *Proc. Natl. Acad. Sci. U. S. A.* **1958**, 44, 1093.
- [23] R. Bonnett, *Chem. Rev.* **1960**, 63, 573.
- [24] R. Banerjee, *Chem. Rev. (Washington, DC, U. S.)* **2003**, 103, 2083.
- [25] K. L. Brown, *Chem. Rev. (Washington, DC, U. S.)* **2005**, 105, 2075.
- [26] Z. Schneider, A. Stroinski, *Comprehensive B12. Chemistry: Biochemistry: Nutrition: Ecology: Medicine*, **1987**.
- [27] B. Krautler, D. Arigoni, B. T. Golding, Editors, *Vitamin B12 and B12-Proteins. (Proceedings of the 4th European Symposium held in Innsbruck, Austria, in September 1996.)*, **1998**.
- [28] D. H. Busch, P. J. Jackson, M. Kojima, P. Chmielewski, N. Matsumoto, J. C. Stevens, W. Wu, D. Nosco, N. Herron, et al., *Inorg. Chem.* **1994**, 33, 910.
- [29] R. P. Hanzlik, D. Williamson, *J. Am Chem. Soc.* **1976**, 98, 6570.
- [30] M. T. Reetz, K. Töllner, *Tetrahedron Lett.* **1995**, 36, 9461.
- [31] S. L. Jain, B. Sain, *Angew. Chem. Int. Ed.* **2003**, 42, 1265.
- [32] J. Müller, C. Würtele, O. Walter, S. Schindler, *Angew. Chem. Int. Ed.* **2007**, 46, 7775.
- [33] R. Ho, J. Liebmann, J. Valentine, (Eds.: C. Foote, J. Valentine, A. Greenberg, J. Liebmann), Chapman & Hall, **1995**, p. p. 2 ff.
- [34] P. Pfeiffer, E. Breith, E. Lubbe, T. Tsumaki, *Ann.* **1933**, 503, 84.

- [35] T. Tsumaki, *Bull. Chem. Soc. Jpn.* **1938**, 13, 252.
- [36] M. Calvin, C. H. Barkelew, *J. Am. Chem. Soc.* **1946**, 68, 2267.
- [37] R. H. Bailes, M. Calvin, *J. Am. Chem. Soc.* **1947**, 69, 1886.
- [38] W. K. Wilmarth, S. Aranoff, M. Calvin, *J. Am. Chem. Soc.* **1946**, 68, 2263.
- [39] M. Calvin, R. H. Bailes, W. K. Wilmarth, *J. Am. Chem. Soc.* **1946**, 68, 2254.
- [40] C. H. Barkelew, M. Calvin, *J. Am. Chem. Soc.* **1946**, 68, 2257.
- [41] R. D. Jones, D. A. Summerville, F. Basolo, *Chem. Rev.* **1979**, 79, 139.
- [42] S. C. Abrahams, R. L. Collin, W. N. Lipscomb, *Acta Cryst.* **1951**, 4, 15.
- [43] L. A. Lindblom, W. P. Schaefer, R. E. Marsh, *Acta Cryst, Sect B: Struct Sci.* **1971**, 27, 1461.
- [44] R. Cini, P. Orioli, *Inorg. Chim. Acta.* **1982**, 63, 243.
- [45] P. Zanello, R. Cini, A. Cinquantini, P. L. Orioli, *J. Chem. Soc., Dalton Trans.* **1983**, 2159.
- [46] R. H. Niswander, L. T. Taylor, *Inorg. Chim. Acta.* **1976**, 18, L7.
- [47] R. H. Niswander, L. T. Taylor, *J. Am. Chem. Soc.* **1977**, 99, 5935.
- [48] R. Cini, P. Orioli, *J. Chem. Soc., Chem. Commun.* **1981**, 196.
- [49] R. Cini, P. Orioli, *J. Chem. Soc., Dalton Trans.* **1983**, 2563.
- [50] G. A. Rodley, W. T. Robinson, *Nature (London)* **1972**, 235, 438.
- [51] D. E. De Vos, F. Thibault-Starzyk, P. A. Jacobs, *Angew. Chem. Int. Ed.* **1994**, 33, 431.
- [52] J. F. Krebs, A. S. Borovik, *Chem. Commun.* **1998**, 553.
- [53] F. Carré, R. J. P. Corriu, E. Lancelle-Beltran, A. Mehdi, C. Reyé, R. Guillard, J. Sýkora, A. van der Lee, *Dalton Trans.* **2003**, 3211.
- [54] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6 ed., John Wiley & Sons, inc., New York - Chichester - Weinheim - Brisbane - Singapore - Toronto, **1999**.
- [55] C. Bianchini, R. W. Zoellner, *Advances in Inorganic Chemistry*, Vol. 44, Academic Press, San Diego - London, **1997**.

- [56] U. Thewalt, R. E. Marsh, *J. Am Chem. Soc.* **1967**, 89, 6364.
- [57] G. G. Christoph, R. E. Marsh, W. P. Schaefer, *Inorg. Chem.* **1969**, 8, 291.
- [58] N. W. Terry, III, E. L. Amma, L. Vaska, *J. Amer. Chem. Soc.* **1972**, 94, 653.
- [59] L. D. Brown, K. N. Raymond, *Inorg. Chem.* **1975**, 14, 2595.
- [60] J. Halpern, B. L. Goodall, G. P. Khare, H. S. Lim, J. J. Pluth, *J. Am. Chem. Soc.* **1975**, 97, 2301.
- [61] D. B. Crump, R. F. Stepaniak, N. C. Payne, *Can. J. Chem.* **1977**, 55, 438.
- [62] R. S. Gall, J. F. Rogers, W. P. Schaefer, G. G. Christoph, *J. Am. Chem. Soc.* **1976**, 98, 5135.
- [63] R. S. Gall, W. P. Schaefer, *Inorg. Chem.* **1976**, 15, 2758.
- [64] G. B. Jameson, W. T. Robinson, G. A. Rodley, *J. Chem. Soc., Dalton Trans.* **1978**, 191.
- [65] W. P. Schaefer, B. T. Huie, M. G. Kurilla, S. E. Ealick, *Inorg. Chem.* **1980**, 19, 340.
- [66] A. E. Martell, *Acc. Chem. Res.* **1982**, 15, 155.
- [67] T. Ohishi, K. Kashiwabara, J. Fujita, S. Ohba, T. Ishii, Y. Saito, *Bull. Chem. Soc. Jpn.* **1986**, 59, 385.
- [68] J. W. Egan, Jr., B. S. Haggerty, A. L. Rheingold, S. C. Sendlinger, K. H. Theopold, *J. Am Chem. Soc.* **1990**, 112, 2445.
- [69] E. Hohenester, C. Kratky, B. Kraeutler, *J. Am. Chem. Soc.* **1991**, 113, 4523.
- [70] S. Hikichi, M. Akita, Y. Moro-oka, *Coord. Chem. Rev.* **2000**, 198, 61.
- [71] X. Hu, I. Castro-Rodriguez, K. Meyer, *J. Am. Chem. Soc.* **2004**, 126, 13464.
- [72] A. F. M. M. Rahman, W. G. Jackson, A. C. Willis, *Inorg. Chem.* **2004**, 43, 7558.
- [73] K. J. Haller, J. H. Enemark, *Acta Crystallogr., Sect. B* **1978**, B34, 102.
- [74] A. Avdeef, W. P. Schaefer, *Inorg. Chem.* **1976**, 15, 1432.
- [75] P. C. Ford, I. M. Lorkovic, *Chem. Rev. (Washington, D. C.)* **2002**, 102, 993.
- [76] R. Eisenberg, C. D. Meyer, *Acc. Chem. Res.* **1975**, 8, 26.

- [77] J. A. McCleverty, *Chem. Rev.* **1979**, 79, 53.
- [78] F. Bottomley, *React. Coord. Ligands* **1989**, 2, 115.
- [79] J. C. Fanning, *Coord. Chem. Rev.* **1991**, 110, 235.
- [80] S. Moncada, R. M. J. Palmer, E. A. Higgs, *Pharmacol. Rev.* **1991**, 43, 109.
- [81] P. L. Feldman, O. W. Griffith, D. J. Stuehr, *Chem. Eng. News* **1993**, 71, 26.
- [82] A. R. Butler, D. L. H. Williams, *Chem. Soc. Rev.* **1993**, 22, 233.
- [83] M. Feelisch, J. S. Stamler, Editors, *Methods in Nitric Oxide Research*, **1996**.
- [84] L. J. Ignarro, Editor, *Nitric oxide: Biology and Pathobiology*, **2000**.
- [85] S. Erkoç, *J. Mol. Struct. THEOCHEM* **2001**, 574, 127.
- [86] L. Andrews, A. Citra, *Chem. Rev. (Washington, D. C.)* **2002**, 102, 885.
- [87] J. Heck, Justus-Liebig-Universität Gießen (Germany) **2009**.
- [88] B. R. Penfold, J. C. B. White, *Acta Crystallogr.* **1959**, 12, 130.
- [89] E. C. Constable, *Metals and Ligand Reactivity*, VCH Verlagsgesellschaft mbH, Weinheim, **1996**.
- [90] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., John Wiley & Sons, Inc., New York; Chichester; Weinheim; Brisbane; Singapore; Toronto, **1997**.
- [91] L. Sacconi, I. Bertini, *J. Am. Chem. Soc.* **1966**, 88, 5180.
- [92] G. M. Sheldrick, in *SHELX-97*, Universität Göttingen, **1997**.
- [93] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, 64, 112.
- [94] S. Murai, Editor, *Activation of unreactive bonds and organic synthesis. [In: Top. Organomet. Chem., 1999; 3]*, **1999**.
- [95] J. J. Garcia, A. Arevalo, N. M. Brunkan, W. D. Jones, *Organometallics* **2004**, 23, 3997.
- [96] M. Tobisu, Y. Kita, N. Chatani, *J. Am. Chem. Soc.* **2006**, 128, 8152.
- [97] G. W. Parshall, *J. Am. Chem. Soc.* **1974**, 96, 2360.
- [98] Q. X. Liu, F. B. Xu, Q. S. Li, H. B. Song, Z. Z. Zhang, *Organometallics* **2004**, 23, 610.
-

- [99] F. Ozawa, K. Iri, A. Yamamoto, *Chem. Lett.* **1982**, 1707.
- [100] T. Lu, X. Zhuang, Y. Li, S. Chen, *J. Am. Chem. Soc.* **2004**, 126, 4760.
- [101] A. D. Bond, S. Derossi, F. Jensen, F. B. Larsen, C. J. McKenzie, J. Nelson, *Inorganic Chemistry* **2005**, 44, 5987.
- [102] M. Schatz, M. Becker, O. Walter, G. Liehr, S. Schindler, *Inorg. Chim. Acta* **2001**, 324, 173.
- [103] S. Schindler, D. J. Szalda, C. Creutz, *Inorg. Chem.* **1992**, 31, 2255.
- [104] S. Foxon, J.-Y. Xu, S. Turba, M. Leibold, F. Hampel, F. W. Heinemann, O. Walter, C. Wuertele, M. Holthausen, S. Schindler, *Eur. J. Inorg. Chem.* **2007**, 429.
- [105] L. Li, A. A. N. Sarjeant, M. A. Vance, L. N. Zakharov, A. L. Rheingold, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2005**, 127, 15360.
- [106] S. Thyagarajan, N. N. Murthy, A. A. N. Sarjeant, K. D. Karlin, S. E. Rokita, *J. Am. Chem. Soc.* **2006**, 128, 7003.
- [107] L. Li, N. N. Murthy, J. Telser, L. N. Zakharov, G. P. A. Yap, A. L. Rheingold, K. D. Karlin, S. E. Rokita, *Inorg. Chem.* **2006**, 45, 7144.
- [108] L. Li, A. A. Narducci Sarjeant, K. D. Karlin, *Inorg. Chem.* **2006**, 45, 7160.
- [109] D. S. Marlin, M. M. Olmstead, P. K. Mascharak, *Angew. Chem. Int. Ed.* **2001**, 40, 4752.
- [110] M. Schatz, V. Raab, S. P. Foxon, G. Brehm, S. Schneider, M. Reiher, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem. Int. Ed.* **2004**, 43, 4360.
- [111] C. Wuertele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem. Int. Ed.* **2006**, 45, 3867.
- [112] O. Rotthaus, S. LeRoy, A. Tomas, K. M. Barkigia, I. Artaud, *Eur. J. Inorg. Chem.* **2004**, 1545.
- [113] A. L. Reiff, E. M. Garcia-Frutos, J. M. Gil, O. P. Anderson, L. S. Hegedus, *Inorg. Chem.* **2005**, 44, 9162.
- [114] M. Zabel, A. L. Poznyak, V. I. Pawlowski, *J. Struct. Chem.* **2005**, 46, 556.
-

- [115] E. V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D. H. Busch, *Inorg. Chem.* **1997**, 36, 2746.
- [116] I. A. Guzei, A. Bakac, *Inorg. Chem.* **2001**, 40, 2390.
- [117] A. Nishinaga, T. Kondo, T. Matsuura, *Chem. Lett.* **1985**, 905.
- [118] N. Pannier, Doctoral thesis, Justus-Liebig-Universität (Gießen), **2008**.
- [119] B. A. Chabner, T. G. Roberts, *Nature Reviews Cancer* **2005**, 5, 65.
- [120] S. Landa, V. Machacek, J. Mzourek, *Chem. Listy Vedu Prum.* **1933**, 27, 415.
- [121] J. G. Henkel, J. T. Hane, G. Gianutsos, *J. Med. Chem.* **1982**, 25, 51.
- [122] K. Aigami, Y. Inamoto, N. Takaishi, K. Hattori, *J. Med. Chem.* **1975**, 18, 713.
- [123] A. S. Monto, S. E. Ohmit, K. Hornbuckle, C. L. Pearce, *Antimicrob. Agents and Chemother.* **1995**, 39, 2224.
- [124] A. Scherm, D. Peteri, (Merz und Co. K.-G.). Application: DE, **1971**.
- [125] W. Maison, J. V. Frangioni, N. Pannier, *Org. Lett.* **2004**, 6, 4567.
- [126] B. Mattson, J. Lannan, *Chem13 News (informal magazine of the Department of Chemistry, University of Wisconsin)* **1997**, see: [http://mattson.creighton.edu/NOx/\(index.html](http://mattson.creighton.edu/NOx/(index.html).
- [127] M. G. Suryaraman, A. Viswanathan, *J. Chem. Educ.* **1949**, 594.
- [128] C. A. Grapperhaus, B. Mienert, E. Bill, T. Weyhermueller, K. Wieghardt, *Inorg. Chem.* **2000**, 39, 5306.
- [129] J. U. Rohde, J. H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Munck, W. Nam, L. Que, *Science* **2003**, 299, 1037.
- [130] J. R. Anderson, A. Baklien, V. Djajamahadja, B. O. West, E. R. T. Tiekink, Z. *Kristallogr. - New Cryst. Struct.* **1998**, 213, 49.
- [131] R. J. Radford, M. D. Lim, R. Santana Da Silva, P. C. Ford, *J. Coord. Chem.* **2010**, 63, 2743.
- [132] B. Flemmig, P. T. Wolczanski, R. Hoffmann, *Journal of the American Chemical Society* **2005**, 127, 1278.
- [133] A. Schultheis, Justus-Liebig-Universität Gießen (Germany) **2010**.
-

- [134] G. A. Jeffrey, Editor, *An Introduction to Hydrogen Bonding*, **1997**.
- [135] T. Steiner, *Angew. Chem., Int. Ed.* **2002**, 41, 48.
- [136] K. S. Suslick, R. A. Watson, *Inorg. Chem.* **1991**, 30, 912.
- [137] D. N. Harischandra, R. Zhang, M. Newcomb, *J. Am. Chem. Soc.* **2005**, 127, 13776.
- [138] H. Kunkely, A. Vogler, *J. Am. Chem. Soc.* **1995**, 117, 540.
- [139] M. Cheng, A. Bakac, *J. Am. Chem. Soc.* **2008**, 130, 5600.
- [140] M. Weitzer, M. Schatz, F. Hampel, F. W. Heinemann, S. Schindler, *Dalton Trans.* **2002**, 686.