

Synthesis and Reactivity of Iron(II) Complexes with a New Tripodal Imine Ligand

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Abstract: A new tripodal imine ligand tris(2-(propan-2-ylideneamino)ethyl)amine (imine₃tren) was prepared in order to stabilize high valent iron-oxido complexes. Iron complexes were synthesized in template reactions from iron(II) salts, tris(2-aminoethyl)amine (tren) and acetone. Due to the reversibility of the imine formation, complexes with different ligands were obtained depending on the reaction conditions.

Keywords: Iron • Tripodal Ligand • Oxygen Activation • Oxidation • Template Reaction

Three complexes, [Fe(imine₃tren)(OAc)₂] (**1**), [Fe(imine₃tren)(OAc)]OTf (**2**) and [(imine₃tren)₂Fe₂(F)₂](SbF₆)₂ (**3**), could be synthesized and structurally characterized. However, reactions with hydrogen peroxide, iodosobenzene or ozone did not lead to any kind of “oxygen adduct” complex that could be spectroscopically observed.

1. Introduction

Interaction of dioxygen with iron compounds leading to different iron “oxygen complexes” plays an important role in the active sites of a large number of iron proteins/enzymes.^[1] Non-heme iron enzymes especially have been investigated in great detail to learn how to model their functionality in order to accomplish the selective oxidation of organic substrates with dioxygen (air) as the sole oxidant.^[2] In that respect, iron complexes with tripodal ligands such as tris[(2-pyridyl)-methyl]amine (abbreviated either as tmpa or tpa, Figure 1a) and derivatives have been quite useful in the past to gain better understanding on the reactivity of iron enzymes towards dioxygen.^[1b,3] Furthermore, tris(2-amino-ethyl)amine (tren, Figure 1b), the aliphatic relative of tmpa is an excellent building block for a series of ligands. For example with the tripodal ligand tris[(*N'*-*tert*-butylureaylato)-*N*-ethyl]aminato ([H₃I]³⁻, Figure 1c) it was possible to stabilize monomeric M–O and M–OH iron(III) complexes by H-bonding.^[4]

Using the guanidine derivative of tren (TMG₃tren, Figure 1d) made it possible to obtain one of the few examples of an iron(IV) oxido complex in the high spin state (S=2).^[5] In contrast to the trigonal bipyramidal geometry adopted by the [Fe(TMG₃tren)O](OTf)₂ complex, the S=1 iron(IV) oxido complexes reported previously mainly have an octahedral geometry.^[6] High valent iron(IV) oxido complexes play an important role as catalysts for oxidations of quite inert substrates.^[6a,7]

Surprisingly, so far tris(2-(propan-2-ylideneamino)ethyl)amine (imine₃tren, Figure 1e) has not been used as a ligand, most likely because of the difficulties in obtaining this compound in its pure form. Due to the fact that its position is somewhat based in-between the amine, guanidine and amide-based ligands, it was considered that it could have properties

capable of supporting the stabilization of high valent iron complexes. Therefore, it seemed like a valid approach to prepare iron(II) complexes with this ligand and to study their reactivity towards oxidants such as dioxygen, peroxide iodosobenzene and ozone.

2. Results and Discussion

2.1 Synthesis and Crystallographic Characterization of Iron Complexes

Up to now, all our attempts to synthesize the ligand imine₃tren in pure form have not been successful. Additionally, efforts to prepare the corresponding nickel or iron complexes in a

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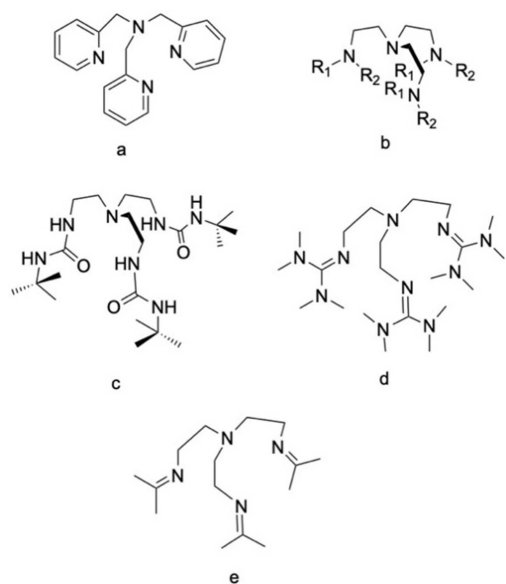


Figure 1. Tripodal ligands a) tmpa, b) tren ($R_1=R_2=H$), c) protonated $[H_3.1]^{3-}$, d) TMC_3tren and e) $imine_3tren$.

template reaction under different conditions only led to the isolation of nickel or iron tren complexes.^[8] A dinuclear oxido-bridged iron(III) tren complex (**5**) could be structurally characterized. As there are many examples of related complexes reported in the literature, we did not investigate this compound any further. Crystallographic details of **5** are described in the Supporting Information. In previous work we showed that iron(II) ions can be very useful to support related template reactions when $[Fe(py)_4(SCN)_2]$ is reacted with acetone together with the ligands *uns-penp* or *apme*,^[9] but it was not possible to obtain the iron(II) $imine_3tren$ complex that way.

Recently, we observed the formation of a new tridentate macrocyclic ligand (Figure 2a) with a pendant donor arm when iron(II) chloride is reacted together with tren in acetone.^[8] These reactions (using an iron(II) salt, tren and acetone) are quite problematic in general, due to the reversibility of the imine formation reactions which lead to different reaction products. These reactions also strongly depend on several specific reaction conditions, e.g. solvent, metal cation and anion.

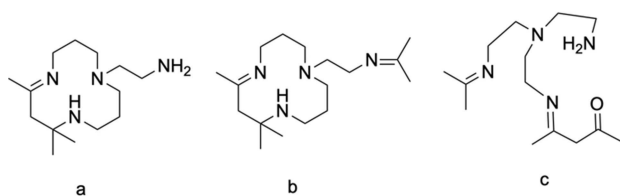


Figure 2. Different ligands obtained from the template reaction of iron(II) salts with tren and acetone.

Using iron(II) acetate finally allowed us to synthesize and crystallize the iron(II) $imine_3tren$ acetate complex $[Fe(imine_3tren)(OAc)_2]$ (**1**). The molecular structure of this complex is presented in Figure 3 (Crystallographic data are reported in Tables 1 and 2). Cyclic voltammetry measurements only showed irreversible redox reactions (see SI).

As can be seen in Figure 3, one arm of the $imine_3tren$ ligand is not coordinated to the metal center. Instead, coordination to an acetate anion is observed. One of the acetate ions could be replaced either by triflate (**2**) or tetraphenylborate (**3**) as anions leading to full coordination of the ligand. The molecular structure of the cation of $[Fe(imine_3tren)(OAc)]OTf$ (**2**) is presented in Figure 4 (Crystallographic data are reported in Tables 1 and 3). Crystallographic data of complex **3** are reported in the Supporting Information.

Fe–N bond lengths are only slightly different comparing **1** with **2**, caused by the coordination of either one or two acetate ions. Bond lengths are also quite similar to those observed for the related complex $[Fe(TMG_3tren)OTf](OTf)$.^[5]

The problems with reversible imine bond formation became obvious when the template reaction was performed using different amounts of the base NEt_3 (the presence of NEt_3 seemed to improve the template reactions). Either **1** formed, or again, a macrocyclic iron complex (**6**) formed (see SI).

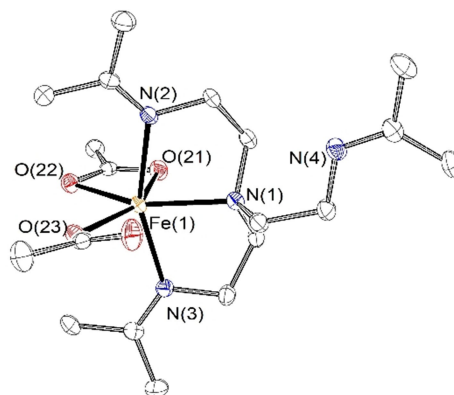


Figure 3. Molecular structure of **1**.

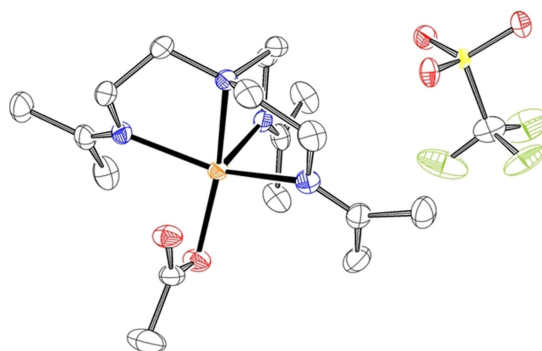


Figure 4. Molecular structure of **2**.

Table 1. Crystallographic data of 1, 2 and 4.

	1	2	4
Empirical formula	C ₁₉ H ₃₆ FeN ₄ O ₄	C ₁₈ H ₃₃ F ₃ FeN ₄ O ₅ S	C ₁₅ H ₃₀ F ₇ FeN ₄ Sb
M _r	440.37	530.39	577.03
Crystal size [mm]	0.300 × 0.257 × 0.130	0.597 × 0.234 × 0.196	0.250 × 0.250 × 0.150
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P $\bar{1}$	C2/c	P2 ₁ /n
a [Å]	8.9937(5)	26.5956(7)	11.814(2)
b [Å]	11.1032(6)	12.0482(3)	14.283(3)
c [Å]	11.7756(6)	c = 16.8118(4)	13.510(3)
α [°]	93.565(2)	90	90
β [°]	102.532(2)°	114.5970(10)°	111.47(3)
γ [°]	106.449(2)	90	90
V [Å ³]	1091.26(10)	4898.2(2)	2121.5(8)
Z	2	8	4
F(000)	472	2224	1152
ρ _{calcd.} [Mg m ⁻³]	1.340	1.438	1.807
μ [mm ⁻¹]	0.722	0.759	2.025
Total reflections	52779	57199	39698
Unique reflections	4628	6596	4895
R(int)	0.0922	0.0593	0.0409
Scan range θ _{max} [°]	2.436 to 26.731	2.490 to 29.130	2.338 to 27.602
Completeness to θ _{max} [%]	99.9	99.9	99.8
Index ranges	−11 < h < 11, −14 < k < 13, −14 < l < 14	−36 < h < 36, −16 < k < 16, −23 < l < 23	−14 < h < 15, −18 < k < 18, −17 < l < 17
Data/restraints/parameters	4628/0/261	6596/90/363	4895/874/324
R1, ^{[a],[b]} wR2 [I > 2σ(I)] ^[c]	0.0398, 0.0828	0.0388, 0.0899	0.0248, 0.0586
R1, ^{[a],[b]} wR2 [all data] ^{[c],[d]}	0.0630, 0.0918	0.0539, 0.0961	0.0318, 0.0618
Goodness/of-fit on F ²	1.050	1.040	1.042
Mx./min. el. dens. [e*Å ⁻³]	0.415, −0.358	0.507, −0.391	0.395, −0.851

Table 2. Selected interatomic distances/Å and angles/° for complex 1.

Fe(1)–N(1)	2.242	N(1)–Fe(1)–N(2)	78.48
Fe(1)–N(2)	2.198	N(1)–Fe(1)–N(3)	79.22
Fe(1)–N(3)	2.192	N(1)–Fe(1)–O(21)	85.18
Fe(1)–O(21)	2.227	N(1)–Fe(1)–O(22)	143.18
Fe(1)–O(22)	2.297	N(1)–Fe(1)–O(23)	126.95
Fe(1)–O(23)	2.009	N(2)–Fe(1)–N(3)	157.67
		N(2)–Fe(1)–O(21)	89.83
		N(2)–Fe(1)–O(22)	98.00
		N(2)–Fe(1)–O(23)	97.66
		N(3)–Fe(1)–O(21)	87.19
		N(3)–Fe(1)–O(22)	99.14
		N(3)–Fe(1)–O(23)	96.60
		O(21)–Fe(1)–O(22)	58.05
		O(21)–Fe(1)–O(23)	147.82
		O(22)–Fe(1)–O(23)	89.86

Table 3. Selected interatomic distances/Å and angles/° for complex 2.

Fe(1)–N(1)	2.19	N(1)–Fe(1)–N(2)	78.33
Fe(1)–N(2)	2.20	N(1)–Fe(1)–N(3)	80.64
Fe(1)–N(3)	2.17	N(2)–Fe(1)–N(3)	95.98
Fe(1)–N(4)	2.20	N(1)–Fe(1)–O(22)	165.58
Fe(1)–O(22)	2.11	N(2)–Fe(1)–O(22)	97.38
Fe(1)–O(21)	2.29	N(3)–Fe(1)–O(22)	113.63

However, this time the free “amine arm” of the macrocycle had also reacted with another acetone molecule (Figure 2b).

Changing reaction conditions (e. g. different amounts of NEt₃ added) often led to mixtures of products. Crystallization of an iron(II) complex with a partially reacted tren ligand (Figure 2c) clearly demonstrated some of the reactions occurring during the course of the imine formation, either leading to imine₃tren or to the macrocyclic ligand. The molecular structures of two iron complexes with this ligand and different anions (**7**, **8**) are reported in the Supporting Information. Efforts to obtain the ligand or corresponding complexes using hexafluoroacetone instead of acetone were not successful either. Only iron tren complexes were obtained, co-crystallized with an iron hexafluoroacetone complex in which the hexafluoroacetone had reacted with water (**9**, see SI).

It was furthermore possible to obtain an iron(II) complex with fully coordinated imine₃tren using the iron(II) salt [Fe(CH₃CN)₆](SbF₆)₂. Its molecular structure is shown in Figure 5 (crystallographic data are reported in Tables 1 and 4). Unfortunately, only a few crystals were obtained after several months that merely allowed structural characterization. Due to the lack of material, no further characterizations or investigations were possible.

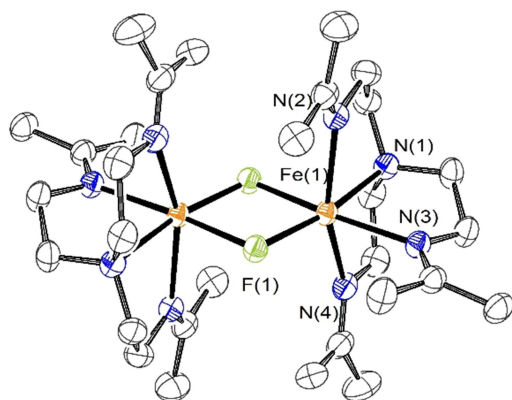


Figure 5. Molecular structure of the cation of **4**.

Table 4. Selected interatomic distances/Å and angles/° for complex **4**.

Fe(1)–N(1)	2.146	N(1)–Fe(1)–N(2)	77.78
Fe(1)–N(2)	2.222	N(1)–Fe(1)–N(3)	81.08
Fe(1)–N(3)	2.171	N(1)–Fe(1)–N(4)	77.61
Fe(1)–N(4)	2.232	N(1)–Fe(1)–F(1)	166.54
Fe(1)–F(1)	1.923	N(1)–Fe(1)–F(1) _i	88.32
Fe(1)–F(1) _i	2.153	N(2)–Fe(1)–N(3)	92.42
		N(2)–Fe(1)–N(4)	155.37
		N(2)–Fe(1)–F(1)	101.96
		N(2)–Fe(1)–F(1) _i	89.98
		N(3)–Fe(1)–N(4)	82.82
		N(3)–Fe(1)–F(1)	112.33
		N(3)–Fe(1)–F(1) _i	168.37
		N(4)–Fe(1)–F(1)	102.19
		N(4)–Fe(1)–F(1) _i	90.28
		Fe(1)–F(1)–F(1) _i	78.21

As can be seen in Figure 5, a fluoride abstraction from the anion must have occurred which is then coordinated in the dinuclear complex $[(\text{Fe}(\text{imine}_3\text{tren}))_2(\text{F})_2](\text{SbF}_6)_2$ (**4**). Furthermore, crystallographic characterization with a different anion was accomplished (**10**, see SI). However, fluoride abstraction is not unusual and has been observed previously.^[10]

All of our efforts to obtain other iron(II) complexes without a coordinating anion have unfortunately been unsuccessful so far.

2.2 Reactivity of the Iron(II) Complexes **1** and **3** towards Dioxygen Peroxides and Ozone

Our hopes, to stabilize high valent iron complexes with the $\text{imine}_3\text{tren}$ ligand, were not fulfilled. Only a sluggish reaction of **1** or **3** with dioxygen was observed. Also, in contrast to related work no peroxido, hydroperoxido or oxido complexes were spectroscopically detected when **1** was reacted with either hydrogen peroxide, iodosobenzene or ozone (see SI). Most likely, the ligand decomposed under these conditions.

3. Summary

So far it has not been possible to obtain the new tripodal imine ligand $\text{imine}_3\text{tren}$ (Figure 1) in pure form. However, it was possible to obtain the corresponding iron(II) complexes $[\text{Fe}(\text{imine}_3\text{tren})(\text{OAc})_2]$ (**1**), $[\text{Fe}(\text{imine}_3\text{tren})(\text{OAc})]\text{OTf}$ (**2**) and $[(\text{imine}_3\text{tren})_2\text{Fe}_2(\text{F})_2](\text{SbF}_6)_2$ (**3**), in template reactions with iron(II) salts and to structurally characterize them. Fluoride abstraction of the anion caused the formation of a dinuclear fluorido-bridged complex. Complex **1** or **2** did not show any formation of a spectroscopically detectable “oxygen adduct” iron complex when oxidized with different oxidants.

4. Experimental

4.1 General

All chemicals used were of p.a. quality and were purchased from either Acros Organics or Sigma Aldrich. Dry solvents purchased for air sensitive synthesis were redistilled under argon. The preparation and handling of air sensitive compounds were performed in a glovebox or under standard Schlenk-techniques. Electrospray-ionization MS (ESI-MS) measurements were performed on a Bruker microTOF mass spectrometer. Elemental analysis was performed by a Thermo Scientific FlashEA 1112.

4.2 Crystallographic Characterization

Details of X-ray crystal structure determination are described in the Supporting Information.

4.3 Synthesis of **1**

$\text{Fe}(\text{OAc})_2$ (174 mg, 1.00 mmol) was added to acetone (1 mL). Afterwards, a solution of tren (147 mg, 1.01 mmol) in acetone (1 mL) was added dropwise. The yellow suspension was stirred for 3 h at room temperature. After filtration, a greenish solution was obtained. The solution was stored at -40°C and after 1–2 months crystals could be separated from the solution. They were washed with diethyl ether three times and dried. Yield: 94 mg (21 %). Anal. Calc. for $\text{FeC}_{19}\text{H}_{36}\text{N}_4\text{O}_4$: C, 51.8; H, 8.2; N, 12.7. Found: C, 50.5; H, 8.2; N, 12.8. ESI-MS (m/z): calculated for the ligand ($\text{C}_{15}\text{H}_{30}\text{N}_4 + \text{H}^+$) 267.255; found, 227.256 ($\text{Imine}_3\text{tren} + \text{H}^+$) calculated for the complex ($\text{C}_{17}\text{H}_{33}\text{FeN}_4\text{O}_2^+$) 381.195; found, 381.198 ($[\text{Fe}(\text{Imine}_3\text{tren})\text{OAc}]^+$). IR data are reported in the SI. Obtained crystals were suitable for structural characterization.

4.4 Synthesis of 2

A solution of tren (73 mg, 0.50 mmol) in 1 mL acetone was added dropwise to a solution of NEt_3 (30 mg, 0.30 mmol) together with $\text{Fe}(\text{OAc})_2$ (87 mg, 0.50 mmol) in 1 mL of acetone. After stirring for 3 h, AgOTf (128 mg, 0.50 mmol) was added. It was stirred for 5 min and stored at -40°C for 30 min. The grey suspension was filtered, added to diethyl ether and kept at -40°C . Light yellow crystals which turned out to be suitable for X-ray analysis were obtained.

4.5 Synthesis of 4

To a suspension of $[\text{Fe}(\text{MeCN})_6](\text{SbF}_6)_2$ (154 mg, 0.02 mmol) in acetone (1 mL) a solution of tren (28 mg, 0.02 mmol) in acetone (1 mL) was added dropwise. The light orange coloured solution was stirred for 3 h at room temperature. It was then filtered and diethyl ether was added. Slow evaporation at -40°C was allowed. After storage for 8 months, a few orange coloured crystals formed that turned out to be suitable for crystallographic characterization.

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