

Investigations of metal complexes with the tripodal tetradentate ligand tris(2-(propan-2-ylideneamino)ethyl)amine (imine₃tren)

Lars Schneider,^[a] Jonathan Becker,^[a] and Siegfried Schindler^{*[a]}

Dedicated to Prof. Kaim, 70th birthday.

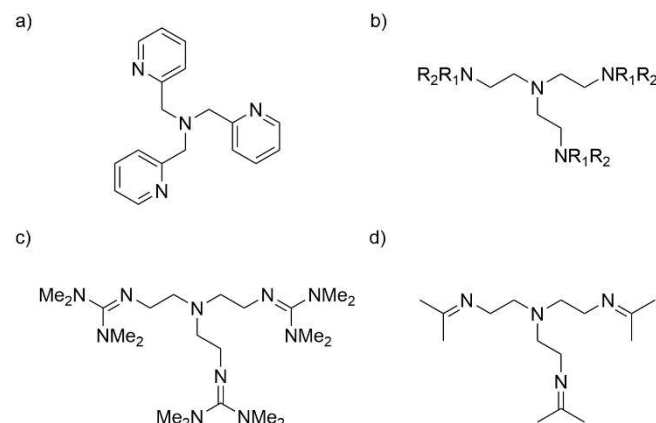
The imine ligand tris(2-(propan-2-ylideneamino)-ethyl)amine (imine₃tren) had been prepared and characterized. The complexes [Na(imine₃tren)(C₃H₆O)]BPh₄, [Cu(imine₃tren)]BPh₄, [Zn(imine₃tren)(CH₂Cl₂)₂](BPh₄)₂ and [Ni(imine₃tren)Br]BPh₄ were synthesized and structurally characterized. In contrast to

copper(I) complexes with related tripodal ligands [Cu(imine₃tren)]BPh₄ reacted quite slowly with dioxygen in solution and no “dioxygen adduct” complex could be spectroscopically detected. Cyclic voltammetry of this complex only showed an irreversible oxidation to a copper(II) species.

Introduction

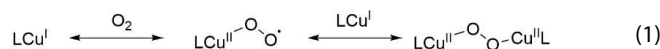
Copper dioxygen complexes play an essential role in biological systems.^[1,2] In enzymes such as e.g. peptidylglycine- α -hydroxylating monooxygenase (PHM), they are responsible for selective oxygenation of organic substrates.^[1,3,4] The catalytic species in PHM consists of an end-on superoxido copper complex and in general “dioxygen adduct” copper complexes are formed in the active sites of the enzymes.^[3,5,6] Oxygenation reactions are not only important in biology but furthermore, in industrial applications (e.g. oxygenation of toluene). Therefore, to obtain a better understanding of copper “dioxygen adduct” complexes, model compounds have been developed that resemble the active site of the enzymes.^[7] In the past, tripodal ligands have proven to be suitable systems for these investigations.^[5,8,9]

Jacobsen *et al.* described the first crystallographic characterized copper “dioxygen adduct” complex, an end-on peroxido copper system that had been studied in great detail based on the ligand tris(2-pyridylmethyl)amine (tmpa, Scheme 1).^[10] Similar reactivities have been observed with tren (tris(2-aminoethyl)amine, Scheme 1) based ligands, e.g. tris(2-dimethylaminoethyl)amine (Me₆tren, Scheme 1, R₁ = R₂ = CH₃).^[11,12] Copper(I) complexes with this ligand system react with dioxygen



Scheme 1. Tripodal ligands tmpa (a), tren, R₁ = R₂ = H (b), TMG₃tren (c) and imine₃tren (d).

according to equation 1. While the dinuclear peroxido complexes are quite persistent at low temperatures the mononuclear superoxido complexes normally can be observed only briefly spectroscopically in stopped-flow measurements.^[9,11,13]



Still it was possible for the first time to obtain a resonance Raman spectrum of the end-on superoxido complex [Cu(Me₆trenO₂)]⁺ (characteristic peak at 1122 cm⁻¹ for the vibration frequency of ¹⁶O–¹⁶O).^[11] In contrast, a guanidine derivative of tren (tris(tetramethylguanidino)tren = TMG₃tren, Scheme 1) allowed (due to the electronic and steric features of this ligand) to finally isolate and structurally characterize the first example of such a species.^[14] The reaction with dioxygen is reversible and [Cu(TM₃tren)]⁺ can be regarded as a model compound for the active center in PHM, however it lacks its catalytic properties.^[15]

[a] L. Schneider, Dr. J. Becker, Prof. Dr. S. Schindler
Institute of Inorganic and Analytic Chemistry
Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 17
35392 Gießen (Germany)
E-mail: Siegfried.schindler@ac.jlug.de
Homepage: <https://www.uni-giessen.de/fbz/fb08/Inst/iaac/schindler>

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/zaac.202100048>

© 2021 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Introducing sterically more demanding alkyl groups into the tren ligand e.g. isoprop₃tren (Scheme 1, R₁ = H, R₂ = isopropyl), also suppresses the formation of dinuclear peroxido complexes according to eq. 1. However, the mononuclear superoxido complexes observed are not stable over time and could not be isolated as solids.^[16,17] Obviously alkyl groups in tren alone seem not capable to stabilize the copper superoxido complexes enough for thorough investigations while guanidine groups stabilize it too much to afford catalytic oxygenation reactions. Therefore, it seemed likely that the imine ligand tris(2-(propan-2-ylideneamino)ethyl)amine (imine₃tren, Scheme 1), in a way an intermediate ligand type between isoprop₃tren and TMG₃tren, might be a suitable candidate for optimization of the stability as well as the reactivity of the corresponding copper superoxido complex. Here we now report the synthesis, characterization and reactivity of the copper complex [Cu(imine₃tren)]⁺ together with a series of other metal complexes with this ligand.

Results and Discussion

Despite the fact that it was quite easy to obtain the ligand isoprop₃tren by an in situ reduction of imine₃tren (Scheme 1),^[16] it turned out to be extremely difficult to synthesize the imine itself in pure form. Previously, imine₃tren was synthesized in a template reaction with different iron salts, however, we did not succeed to obtain the free ligand that way.^[18] While it was possible to prepare and structurally characterize some iron(II) complexes such as [Fe(imine₃tren)(OAc)₂], different attempts to optimize the reaction with regard to higher yields failed and side reactions turned out to be a big problem. However, these iron complexes did not show any reactivity towards dioxygen. Furthermore, experiments to exchange the central ion or to remove it had failed. An additional problem were the limited yields and side reactions that led to the formation of iron complexes with a macrocyclic ligand (formed during the template reaction).^[18,19] During our efforts to obtain pure iron complexes in better yields with this ligand and different iron salts, we synthesized a sodium complex instead. Later on we obtained suitable crystals of [Na(imine₃tren)]BPh₄ (**1**) for XRD characterization and the molecular structure of the cation of this complex is presented in Figure 1 (crystallographic data are reported in the Supporting Information) which is coordinated in a distorted trigonal bipyramidal geometry.

Finally, after a large number of experiments it turned out that the ligand can be synthesized using pyrrolidine as an assisting reagent. According to Scheme 2 it was used to activate the ketone acetone and thus promoted the imine formation.^[20] The purification was performed by Kugelrohr distillation under an argon atmosphere. Still, it turned out that the product contained a small amount of impurities that could not be removed. However, the product was pure enough to finally allow the preparation of the copper(I) complex by reacting it with [Cu(MeCN)₄]PF₆ followed by an anion exchange with sodium tetraphenylborate. The complex [Cu(imine₃tren)]BPh₄ (**2**) was obtained as a light yellow crystalline product that could be structurally characterized.

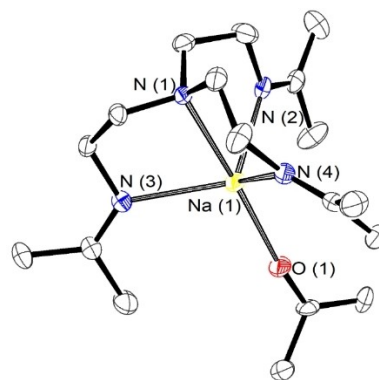
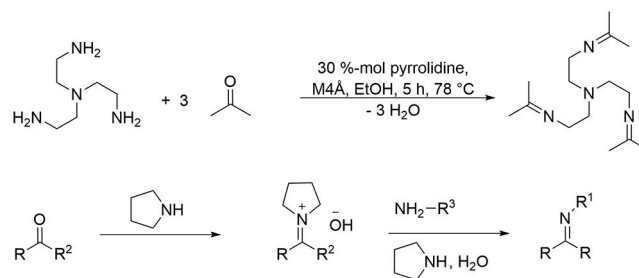


Figure 1. The molecular structure of **1** (the anion and H atoms are omitted for clarity), an acetone molecule is coordinated as an additional ligand.



Scheme 2. Top: Synthesis of the ligand imine₃tren with pyrrolidine as a catalyst; bottom: Activation of a substrate by pyrrolidine in general.^[20]

The molecular structure of the cation of **2** is presented in Figure 2 (crystallographic data are reported in Tables 1 and 2). Furthermore, it was possible to synthesize and structurally characterize [Cu(imine₃tren)]OTf (see Supporting Information). In **2**, the copper(I) ion is coordinated in a distorted trigonal pyramidal geometry by four N-Donor atoms. No additional acetonitrile molecule is coordinated as an additional ligand that has been observed for some copper(I) complexes with tripodal ligands. Bond lengths and angles (Table 1) are averaged over

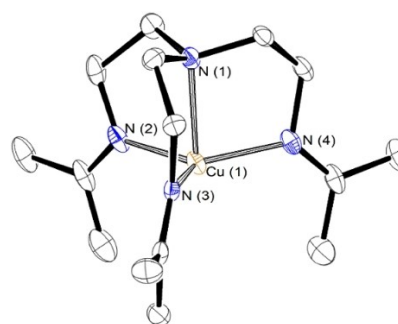


Figure 2. The molecular structure of the cation of **2** (only one of the two complexes in the asymmetric unit is presented).

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

Cu(1)–N(1)	2.153	N(1)–Cu(1)–N(2)	85.36
Cu(1)–N(2)	2.006	N(1)–Cu(1)–N(3)	85.26
Cu(1)–N(3)	2.018	N(1)–Cu(1)–N(4)	85.26
Cu(1)–N(4)	1.998	N(3)–Cu(1)–N(2)	123.95
		N(4)–Cu(1)–N(2)	118.5
		N(4)–Cu(1)–N(3)	115.81

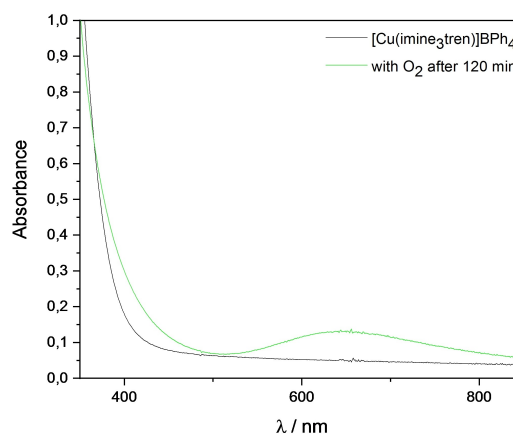
two independent copper(I) complexes in the asymmetric unit. In comparison to the related copper complexes with the tripodal ligands TMG₃tren and isoprop₃tren (Table 3), the Cu–N bond lengths in **2** are shorter.

Unfortunately, and in contrast to the complexes [Cu(TMG₃tren)]SbF₆ and [Cu(isoprop₃tren)]BPh₄, **2** showed only sluggish reactivity towards dioxygen. Intensive investigations with this complex only led to a simple slow oxidation to a copper(II) complex according to the UV/vis spectrum presented in Figure 3.

Stopped-flow measurements at different temperatures (and under different conditions) did not provide spectroscopic evidence for the formation of the expected *end-on* superoxido copper complex. Neither did other oxidants such as hydrogen peroxide led to any kind of a “dioxygen adduct” complex. This was furthermore supported by cyclic voltammetry: no reversible

Table 3. Selected interatomic distances/Å of [Cu(TMG₃tren)]SbF₆ (a), [Cu(isoprop₃tren)]BPh₄ (b), [Cu(imine₃tren)]BPh₄ (c) for comparison.^[16,21]

	a	b	c
Cu(1)–N(1)	2.175	2.209	2.153
Cu(1)–N(2)	2.048	2.089	2.006
Cu(1)–N(3)	2.048	2.058	2.018
Cu(1)–N(4)	2.048	2.087	1.998

**Figure 3.** UV/Vis spectra of **2** ([complex] = 1 mmol/L) before and after the reaction with dioxygen in methanol at room temperature.**Table 2.** Crystallographic data and structure refinement for **2**, **3** and **4**.

	2	3	4
CCDC No	2051597	2051598	2051599
Empirical formula	C ₃₉ H ₅₀ BCuN ₄	C ₆₅ H ₇₄ B ₂ Cl ₄ N ₄ Zn	C ₃₉ H ₅₀ BBrN ₄ Ni
M _t	649.18	1140.07	724.26
Crystal size [mm]	0.284 × 0.107 × 0.008	0.210 × 0.152 × 0.138	0.137 × 0.104 × 0.022
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space Group	P2 ₁ /c	P2 ₁ /n	P2 ₁ /n
a [Å]	15.9849(8)	20.0415(10)	16.760(5)
b [Å]	14.7006(8)	11.9321(6)	13.546(3)
c [Å]	29.4309(15)	25.2090(12)	16.843(4)
α [°]	90°	90°	90°
β [°]	90.4444(14)°	104.101(2)°	109.596(10)°
γ [°]	90°	90°	90°
V [Å ³]	6915.7(6)	5846.8(5)	3602.2(16)
Z	8	4	4
F(000)	2768	2400	1520
ρ _{calc} [Mg m ^{−3}]	1.247	1.295	1.335
μ [mm ^{−1}]	0.665	0.647	1.681
Reflections collected	105479	69940	73231
Independent reflections	13123	10321	6587
R[int]	0.0992	0.0819	0.0947
Scan range θ _{max} [°]	2.330 to 25.681	1.489 to 25.026	1.977 to 25.350
Completeness to θ _{max} [°]	99.9	100.0	100.0
Index ranges	−19 ≤ h ≤ 19 −17 ≤ k ≤ 17 −39 ≤ l ≤ 35	−23 ≤ h ≤ 23 −14 ≤ k ≤ 14 −30 ≤ l ≤ 30	−20 ≤ h ≤ 20 −16 ≤ k ≤ 16 −20 ≤ l ≤ 20
Data/restraints/parameters	13123/0/823	10321/4915/1538	6587/2325/807
R1, wR2 [I > 2σ(I)]	0.0463, 0.0821	0.0641, 0.1553	0.0383, 0.0799
R1, wR2 [all data]	0.0839, 0.0924	0.1151, 0.1841	0.0696, 0.0921
Goodness-of-fit on F ²	1.023	1.011	1.047
Max./min. el. Dens [e Å ^{−3}]	0.306, −0.515	0.590, −0.526	0.450, −0.442

oxidation of copper(II) to copper(III) could be observed. See Supporting Information for details on these measurements.

In a way this was not completely unexpected due to the fact that copper(II) complexes with tripodal ligands with imine groups proved to be unstable even as a regular copper(II) complex. For example, imine ligands obtained from tren and benzaldehyde decomposed over time in the presence of air and moisture when coordinated to copper(II) ions.^[22] Furthermore, no dioxygen adduct complex was detected when the copper(I) complex with this imine ligand was reacted with dioxygen in contrast to the reaction with Bz₃tren or Bz₃Me₃tren as a ligand that allowed observation of the dinuclear end-on peroxido as well as the mononuclear end-on superoxido copper complex as reactive intermediates.^[17,22,23]

With nearly pure imine₃tren at hand it furthermore was possible to obtain the corresponding zinc complex by reacting ZnCl₂ with imine₃tren followed by an anion exchange with sodium tetraphenylborate. The molecular structure of the cation

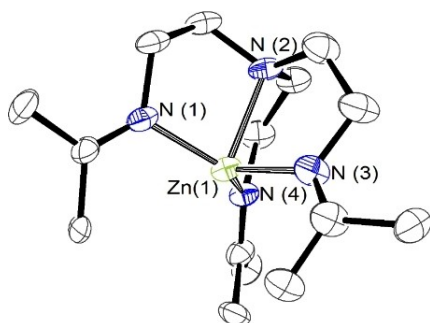


Figure 4. The molecular structure of **3** (anion, solvent molecules and hydrogen atoms are omitted for clarity).

Table 4. Selected interatomic distances/Å and angles/° for complex **3**.

Zn(1)–N(1)	1.965(16)	N(1)–Zn(1)–N(2)	86.8(6)
Zn(1)–N(2)	2.141(13)	N(1)–Zn(1)–N(3)	125.1(9)
Zn(1)–N(3)	1.953(14)	N(1)–Zn(1)–N(4)	116.2(10)
Zn(1)–N(4)	2.042(15)	N(2)–Zn(1)–N(3)	85.8(5)
		N(2)–Zn(1)–N(4)	83.1(6)
		N(3)–Zn(1)–N(4)	116.7(9)

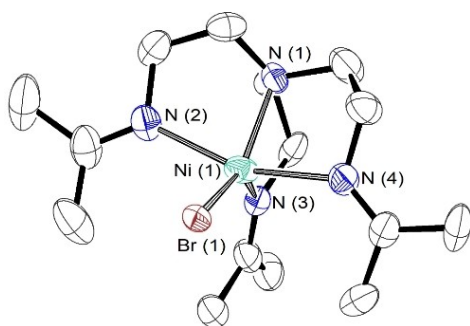


Figure 5. The molecular structure of **4** (not coordinated anion and hydrogen atoms are omitted for clarity).

of **3** is depicted in Figure 4 (crystallographic data are reported in Table 2 and 4). A comparison of the molecular structure between the zinc and the copper complex shows similarities in terms of bond angles and lengths and the same coordination geometry (distorted trigonal pyramidal) of both complexes. Cyclic voltammetry of **3** that contains redox inactive Zn(II) was performed in the presence of ferrocene to obtain an idea about the redox behaviour of the ligand system (see Supporting Information). An irreversible oxidation of the ligand in this complex was observed at 1.32 V vs. ferrocene.

In addition, a nickel(II) complex could be prepared with nickel(II)bromide and imine₃tren followed by an anion exchange with sodium tetraphenylborate. The molecular structure of [(imine₃tren)NiBr]BPh₄, **4** (Figure 5) shows a distorted trigonal bipyramidal geometry and the bond angles and lengths are reported in Table 5.

Prior to the successful preparation described herein by applying the free ligand all our attempts to isolate a nickel complex with this ligand had ended with the crystallization of nickel tren complexes instead.^[18,19] Furthermore, we did not succeed to crystallize nickel(II) imine₃tren complexes with other anions. The molecular structure of **4** is similar to the corresponding iron complex [Fe(imine₃tren)(OAc)]OTf reported previously.^[18] There is nothing unusual about the UV-vis spectrum of **4** and the cyclic voltammogram is complex as expected (Supporting Information).

Conclusions

Finally, after many attempts (over years) it was possible to obtain the ligand imine₃tren in nearly pure form that allowed us to synthesize and structurally characterize zinc, nickel and two copper(I) complexes with this ligand. While the zinc and the nickel complex as redox inactive complexes have been prepared to investigate the coordination behavior with this ligand additionally to iron complexes reported previously,^[18] the copper(I) complexes were synthesized to investigate their reactivity towards dioxygen. With a ligand that can be classified in between the pure aliphatic tren alkyl ligands and the guanidine derivatives we had hoped to obtain a copper complex that would form a quite stable but still reactive *end-on* superoxido complex. Unfortunately, this was not the case and in contrast to our expectations no “dioxygen adduct” copper

Table 5. Selected interatomic distances/Å and angles/° for complex **4**.

Ni(1)–N(1)	2.025(6)	N(1)–Ni(1)–N(2)	80.9(3)
Ni(1)–N(2)	2.147(7)	N(1)–Ni(1)–N(3)	87.6(3)
Ni(1)–N(3)	1.984(6)	N(1)–Ni(1)–N(4)	82.2(3)
Ni(1)–N(4)	2.102(6)	N(1)–Ni(1)–Br(1)	134.6(2)
Ni(1)–Br(1)	2.418(3)	N(2)–Ni(1)–N(3)	96.1(4)
		N(2)–Ni(1)–N(4)	158.1(4)
		N(2)–Ni(1)–Br(1)	91.3(4)
		N(3)–Ni(1)–N(4)	97.3(3)
		N(3)–Ni(1)–Br(1)	137.8(2)
		N(4)–Ni(1)–Br(1)	90.4(2)

complex was observed with different oxidants. This might be a consequence of the instability in general of tren imine ligands in combination with copper(II) ions as observed by us and others previously.^[22] However, even these negative results are important in obtaining a better understanding for optimizing these copper complex systems in general towards their ability to perform selective oxygenation reactions. We have observed several times that within these complexes only slight ligand modifications can have a dramatic effect on their reactivity and therefore needed to be tested.

Experimental Section

Material and Methods

The used reagents and solvents have the degree of purity p.a and were bought from AcrosOrganics, Alfa Aesar, Merck and Sigma Aldrich or were synthesized as described below. The solvents were distilled over a drying agent under an argon atmosphere and stored in the glove box. Experiments were performed under inert conditions. ¹H-NMR and ¹³C-NMR spectra were obtained using an Avance II 400 MHz WB (Bruker BioSpin GmbH). The measurements were performed at room temperature and the program MestReNova 14.1.2 was used for data analysis. The UV-Vis measurements were carried out at room temperature with an Agilent 8543-spectrometer. Time resolved stopped-flow measurements at low temperatures were performed on a SF-61SX2 and a CSF-61DX2 instrument (Hi-Tech, Salisbury, UK, now TgK Scientific, Bradford-on-Avon, UK). The quartz cell had a diameter of 1 cm and the spectral range is between 300 and 700 nm. For GC-MS measurements a MS 5977B with a 7820A GC-system by Agilent Technologies was used. The IR measurements were performed with a FT/IR-4100 instrument (JASCO Deutschland GmbH, Pfungstadt, DE). Details of X-Ray crystal structure determination are reported in the Supporting Information. Electrochemical data were recorded with an e-corder 410 by edaq (eDAQ, Colorado Springs, US) and the program eChem. For cyclic voltammetry a glassy carbon electrode as working electrode, a platinum/titanium electrode (counter electrode) and an Ag/AgCl reference electrode were used. The solvent was acetone or acetonitrile and NBu₄PF₆ or NBu₄BF₄ as conducting salt (0.1 M) was applied. The complex concentrations were adjusted to 1 × 10⁻³ M and ferrocene was used as an internal standard (E⁰ = 0.49 V was measured under these conditions).

Synthesis of imine₃tren: Tris(2-aminoethyl)amine (1.5 mL, 10 mmol) and molecular sieve 4 Å (5.0 g) was added to ethanol (10 mL) under inert conditions. Pyrrolidine (0.25 mL, 3.0 μmol) and acetone (2.3 mL, 30 mmol) were added dropwise and the solution was heated to reflux for 5 h. The yellow coloured suspension was filtered and the solvent and the pyrrolidine was removed under reduced pressure. After purification, the product could be obtained as a yellow coloured oily liquid with a yield of 40%. ¹H-NMR (δ/ppm): 3.33 (m), 2.83 (m), 1.96 (m), 1.80 (m); ¹³C-NMR: 167.75, 55.44, 49.70, 29.07, 18.44; GC-MS: 25.353 min.

Synthesis of [Na(imine₃tren)(acetone)]BPh₄ (1): A solution of imine₃tren (79.9 mg, 0.300 mmol), NaBPh₄ (103 mg, 0.300 mmol) and acetone (1 mL) was stirred overnight. The next day, the solution was filtered and added dropwise to diethyl ether (18 mL). After 1 day at -40 °C colourless crystals could be obtained, which were suitable for X-Ray analysis. Yield: 83.1 mg (42%) Anal. Calc. for C₄₂H₅₆BN₄NaO: C 75.66 %, H 8.47 %, N 8.40 % found: C 75.58 %, H 8.64 %, N 8.51 %. IR data are reported in the SI.

Synthesis of [Cu(imine₃tren)]BPh₄ (2): A solution of imine₃tren (133 mg, 0.500 mmol) in acetone (1 mL) was added dropwise to a suspension of [Cu(MeCN)₄]PF₆ (186 mg, 0.500 mmol) in acetone (1 mL). After stirring for 2 h, the suspension was filtered and solid NaBPh₄ (171 mg, 0.500 mmol) was added. The next day the solution was filtered and added dropwise to diethyl ether (18 mL). After one day at -40 °C, yellow crystals could be obtained, which were washed with diethyl ether and dried. The crystals were suitable for X-Ray analysis. Yield: 73%. Anal. Calc. for C₃₉H₅₀BCuN₄: C 72.15 %, H 7.76 %, N 8.63 % found: C 72.12 %, H 7.78 %, N 8.16 %. IR data are reported in the SI.

Synthesis of [Zn(imine₃tren)](CH₂Cl₂)₂(BPh₄)₂: A solution of imine₃tren (60.0 mg, 0.225 mmol) in acetone (1 mL) was added dropwise to a suspension of ZnCl₂ (30.7 mg, 0.225 mmol) in acetone (1 mL). After stirring for 2 h, solid NaBPh₄ (154 mg, 0.450 mmol) was added and it was stirred for overnight at room temperature. The next day, the solution was filtered and added dropwise to diethyl ether (18 mL). After 1 day at -40 °C, a light yellow coloured solid could be obtained. The solvent was removed and the solid was washed with diethyl ether. Then it was dried and dissolved in CH₂Cl₂. The solvent was slowly evaporated in a vial with a cannula inside the glove box and after a few days light yellow crystals could be obtained, which were suitable for X-Ray analysis. Yield: < 1 %. However, the small batch of the non crystalline product turned out to contain impurities and no correct elemental analysis could be obtained. The IR data are reported in the SI.

Synthesis of [Ni(imine₃tren)(Br)]BPh₄: A solution of imine₃tren (79.9 mg, 0.300 mmol) in acetone (2 mL) was added dropwise to a suspension of NiBr₂ (65.5 mg, 0.300 mmol) in acetone (1 mL). After stirring for 2 h, solid NaBPh₄ (205 mg, 0.600 mmol) was added and it was stirred for overnight at 65 °C. On the next day, the solution was filtered and the solvent was slowly removed. After a few days, a few dark green crystals (which were suitable for X-Ray analysis) together with a powder in an overall yield of 15.9 % could be obtained. The powder contained additionally a small amount of Ni(BPh₄)₂ and dichloromethane from washing the sample. Anal. Calc. for (C₃₉H₅₀BBBrN₄Ni)(C₄₈H₄₀B₂Ni)_{1/6}(CH₂Cl₂)_{1/6}: C 66.29 %, H 6.72 %, N 6.56 % found: C 66.10 %, H 7.05 %, N 6.86%. The IR data are reported in the SI.

Acknowledgments

We gratefully acknowledge the Deutsche Forschungsgemeinschaft (DFG) for financial support (SCHI 377/18-1). Furthermore, we would like to thank Aizuddin Sultan from the University College Dublin, Ireland for some of the experiments he did within this work during the summer school at the JLU he attended in 2019. Open access funding enabled and organized by Projekt DEAL.

Keywords: Copper · nickel · zinc · complexes · dioxygen activation · tripodal ligand

- [1] E. I. Solomon, D. E. Heppner, E. M. Johnston, J. W. Ginsbach, J. Cirera, M. Qayyum, M. T. Kieber-Emmons, C. H. Kjaergaard, R. G. Hadt, L. Tian, *Chem. Rev.* **2014**, *114*, 7, 3659–3853.
- [2] D. A. Quist, D. E. Diaz, J. J. Liu, K. D. Karlin, *J. Biol. Inorg. Chem.* **2017**, *22*, 2–3, 253–288.

- [3] S. T. Prigge, B. A. Eipper, R. E. Mains, L. M. Amzel, *Science* **2004**, *304*, 5672, 864.
- [4] P. Chen, J. Bell, B. A. Eipper, E. I. Solomon, *Biochemistry* **2004**, *43*, 19, 5735–5747.
- [5] C. E. Elwell, N. L. Gagnon, B. D. Neisen, D. Dhar, A. D. Spaeth, G. M. Yee, W. B. Tolman, *Chem. Rev.* **2017**, *117*, 3, 2059–2107.
- [6] S. Fukuzumi, Y.-M. Lee, W. Nam, *Dalton Trans.* **2019**, *48*, 26, 9469–9489.
- [7] a) S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski, *Chem. Rev.* **2013**, *113*, 8, 6234–6458; b) H. R. Lucas, L. Li, A. A. N. Sarjeant, M. A. Vance, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2009**, *131*, 9, 3230–3245; c) C. Würtele, O. Sander, V. Lutz, T. Waitz, F. Tuzcek, S. Schindler, *J. Am. Chem. Soc.* **2009**, *131*, 22, 7544–7545.
- [8] a) L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 2, 1013–1045; b) S. Schindler, *Eur. J. Inorg. Chem.* **2000**, *11*, 2311–2326.
- [9] S. Itoh, *Acc. Chem. Res.* **2015**, *48*, 7, 2066–2074.
- [10] a) R. R. Jacobson, Z. Tyeklar, A. Farooq, K. D. Karlin, S. Liu, J. Zubieta, *J. Am. Chem. Soc.* **1988**, *110*, 11, 3690–3692; b) Z. Tyeklar, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta, K. D. Karlin, *J. Am. Chem. Soc.* **1993**, *115*, 7, 2677–2689.
- [11] M. Weitzer, S. Schindler, G. Brehm, S. Schneider, E. Hörmann, B. Jung, S. Kaderli, A. D. Zuberbühler, *Inorg. Chem.* **2003**, *42*, 6, 1800–1806.
- [12] a) M. Becker, F. W. Heinemann, S. Schindler, *Chem. Eur. J.* **1999**, *5*, 11, 3124–3129; b) Y. J. Choi, K.-B. Cho, M. Kubo, T. Ogura, K. D. Karlin, J. Cho, W. Nam, *Dalton Trans.* **2011**, *40*, 10, 2234–2241.
- [13] C. X. Zhang, S. Kaderli, M. Costas, E.-I. Kim, Y.-M. Neuhold, K. D. Karlin, A. D. Zuberbühler, *Inorg. Chem.* **2003**, *42*, 6, 1807–1824.
- [14] a) C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem. Int. Ed.* **2006**, *45*, 23, 3867–3869; b) 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*, 33, 4360–4363.
- [15] D. Maiti, D.-H. Lee, K. Gaoutchenova, C. Würtele, M. C. Holthausen, A. A. Narducci Sarjeant, J. Sundermeyer, S. Schindler, K. D. Karlin, *Angew. Chem.* **2008**, *120*, 1, 88–91.
- [16] J. Will, C. Würtele, J. Becker, O. Walter, S. Schindler, *Polyhedron* **2019**, *171*, 448–454.
- [17] K. Komiyama, H. Furutachi, S. Nagatomo, A. Hashimoto, H. Hayashi, S. Fujinami, M. Suzuki, T. Kitagawa, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1, 59–72.
- [18] J. Will, L. Schneider, J. Becker, S. Becker, A. Miska, C. Gawlig, S. Schindler, *Isr. J. Chem.* **2020**, *60*, 999–1003.
- [19] K. I. Alexopoulou, L. Schneider, A. Miska, C. Würtele, S. Schindler, *Z. Anorg. Allg. Chem.* **2018**, *644*, 14, 759–762.
- [20] S. Morales, F. G. Guijarro, J. L. García Ruano, M. B. Cid, *J. Am. Chem. Soc.* **2014**, *136*, 3, 1082–1089.
- [21] Christian Würtele, *End-on “copper dioxygen adduct complexes”, Dissertation, Gießen, 2008.*
- [22] M. Schatz, M. Becker, O. Walter, G. Liehr, S. Schindler, *Inorg. Chim. Acta* **2001**, *324*, 1–2, 173–179.
- [23] D. Walther, K. Hamza, H. Görls, W. Imhof, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1135–1143.

Manuscript received: February 13, 2021

Revised manuscript received: March 23, 2021

Accepted manuscript online: March 24, 2021