Copper Peroxido Complexes

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Characterization of a Macrocyclic end-on Peroxido Copper Complex[**]

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Dedicated to Prof. Dr. Horst Elias on the occasion of his 80th birthday

Metal superoxido, peroxido, or oxido complexes are important starting materials/intermediates in selective oxidation reactions of organic substrates in industry and in nature (mainly catalyzed by enzymes with iron or copper ions in the active site). Therefore, there is high interest in better understanding of formation and reactivity of such complexes. Here ligand selection/design plays an important role; in this regard, macrocyclic ligands proved to be quite useful. The most prominent example is an iron oxido complex with tetramethylcyclam (Me_4cyclam) as ligand.[1] A recent review by Nam and co-workers summarized new exciting results on superoxido and peroxido complexes using Me_4cyclam and derivatives for a large number of metal ions.[2] However, copper complexes are absent in this review. This is surprising in that Valentine and co-workers already reported in 1979 the formation of a copper superoxido complex using a derivative of cyclam, tet b (*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), as a ligand.[3] They prepared this quite stable compound by reacting the according Cu^{II} complex with KO_2 in DMSO together with [18]crown-6. However, they only could investigate the complex in solution and did not succeed in isolating and fully characterizing this compound in the solid state.

Owing to our interest in the formation and reactivity of copper superoxido and peroxido complexes,[4] we repeated the reported reaction of $[Cu(tet\,b)]^{2+}$ with KO_2, and our UV/Vis studies confirmed the original findings. However, so far we also did not succeed in isolating crystals of the complex this way either, and decided to use an alternative approach: the reaction of the corresponding tet b copper(I) complex with dioxygen. This turned out to be quite difficult owing to the extreme tendency of this type of macrocyclic copper(I) complex to disproportionate (often this is a catalytic reaction).[5] Therefore, it was not surprising that when using tet b as well as its isomer tet a (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), almost-black-colored solutions were obtained when copper(I) salts were mixed with these macrocyclic ligands. We assume that the color of the solution derives from a mixture of a colloidal suspension of elemental copper and copper(II). However, we also recognized that these solutions still reacted with dioxygen. Diluted solutions turned first to a dark green color and then to a purple color, clearly demonstrating that not all of the copper(I) complex had undergone decomposition. It was even possible in some cases to obtain a NMR spectrum of these solutions, indicating that they contained mainly copper(I) ions (see the Supporting Information). Further support for the formation of a copper(I) complex with tet b as a ligand came from previous work on the electrochemistry of such compounds.[6] It was reported that a slightly purple colored solution of $[Cu(tet\,b)]^{+}$ in acetonitrile was obtained after electrochemical reduction of the according copper(II) complex at $-20\,°C$ (here again disproportionation was observed at higher temperatures). However, the authors did not attempt to isolate this sensitive complex as a solid. Using cyclovoltammetry, we could confirm these results as well as the reported electrochemical studies by Valentine and co-workers (see the Supporting Information).[3] Finally, after many attempts over several years with these complexes using different solvents and anions, we succeeded in separating colorless crystals from one reaction batch (by picking crystals that grew in a mixture of solids in the intensely purple-colored solution) that were suitable for X-ray analysis. The molecular structure of the cation of $[Cu(tet\,b)]OTf\cdot CH_3CN$ is shown in Figure 1 (crystallographic data are reported in the Supporting Information).

According to the Cambridge Crystallographic Data Centre, this is the first time that such a complex could be structurally characterized. This is not surprising because of the problems with disproportionation described above. The coordination geometry around the copper(I) ion can be best described as a highly distorted tetrahedron.

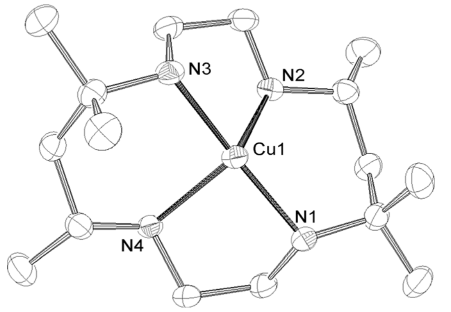

Figure 1. Molecular structure of $[Cu\ (tet\,b)]^{+}$ (ellispoids set at 50% probability; the anion, H-atoms, and solvent molecules are omitted for clarity). Selected bond lengths [Å]: Cu1–N1 2.184(1), Cu1–N2 2.001(1), Cu1–N3 2.179(1), Cu1–N4 2.007(1).

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Samples of [Cu(tetb)]$^+$ are extremely sensitive towards oxidation. The reaction of [Cu(tetb)]$^+$ with dioxygen in acetone was followed using low-temperature stopped-flow techniques.[7] Even at low temperatures, a green colored species immediately formed and our detection is not fast enough to spectroscopically observe a buildup of this species. Absorbance maxima at 395 nm and 669 nm are consistent with the previous findings of Valentine and co-workers for their postulated superoxido complex [Cu(tetb)O$_2$]ClO$_4$ (the colorless copper(I) complex does not absorb in that region).[3] Time-resolved spectra of the slow beginnings of a consecutive reaction are shown in Figure 2. The rate constant k_{obs} at -88 °C for the decomposition of the superoxido complex with a value of 7×10^{-4} s^{-1} is much smaller (several orders of magnitude) than for the according reaction of [Cu(Me$_6$tren)O$_2$]$^+$ under the same conditions.

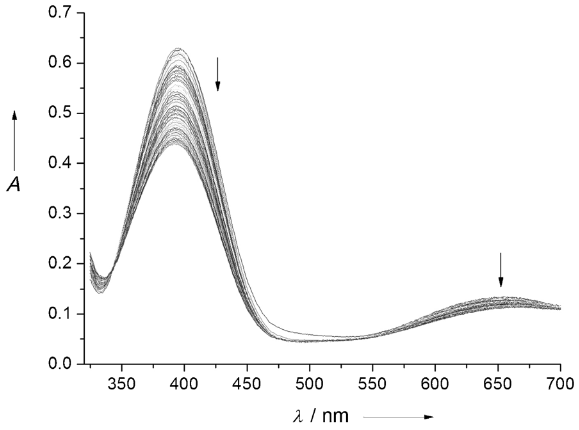
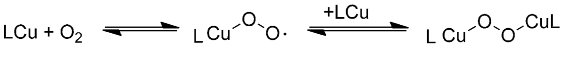


Figure 2. Time resolved UV/Vis spectra of the reaction of O$_2$ with [Cu(tetb)]OTf in acetone at -88 °C ($\Delta t = 15$ s, overall time $= 900$ s).

It is interesting to note that the superoxido complexes obtained from superoxide and the according copper(II) complexes were much more persistent compared with [Cu(tetb)O$_2$]$^+$ prepared from [Cu(tetb)]$^+$ and O$_2$. The most likely reason for this is an excess of superoxide anions (from the added KO$_2$) in solution that push the equilibrium to the superoxido complex. We had a similar finding in related iron chemistry: in that case an iron peroxido complex was much more persistent when prepared from H$_2$O$_2$ in contrast to its formation from Fe^{II} with O$_2$.[8]

Most surprisingly however was the fact that warming the solution did lead to the formation of a purple colored compound. This is in stark contrast to the reaction of superoxide with [Cu(tetb)]$^{2+}$. Decomposition here led to a brown colored solution. A brown solid was separated; however it could not be characterized as yet. From earlier work by us and others, we could assign the purple colored species to a dinuclear end-on peroxido copper complex that forms according to the following equation (charges are omitted):[4,7,9]



$$\mathrm{LCu} + \mathrm{O_2} \rightleftharpoons \mathrm{LCu{-}O{-}O}^{\bullet} \xrightleftharpoons{+\mathrm{LCu}} \mathrm{LCu{-}O{-}O{-}CuL} \quad (1)$$

This reaction behavior is well known for copper complexes with tripodal ligands such as tmpa (tris[(2-pyridyl)methyl]amine) and Me$_6$tren (tris[2-(dimethylamino)ethyl]amine).[4b,e,7a,9]

Valentine and co-workers did not report the observation of a purple-colored compound, and the formation of a dinuclear peroxido complex was completely unexpected owing to the persistence/stability of the copper superoxido complex. Most surprising however is the fact that the formed dinuclear peroxido complex is quite persistent as well, and solutions of this complex persist for several minutes at room temperature. While several dinuclear copper peroxido complexes are now known that are quite stable in solution, all of these compounds are stabilized by using a preorganized ligand.[10] In all of these systems, specially designed dinuclear copper(I) complexes were reacted with dioxygen that support formation of quite stable peroxido complexes. This is completely different for [(tetb)CuO$_2$Cu(tetb)](OTf)$_2$ where two mononuclear complexes have to react. In contrast, the analogous dinuclear peroxido complexes formed from mononuclear copper complexes with tripodal ligands are much less stable. Kinetic studies are in progress; however, they are extremely complicated owing to a large number of different equilibria in solution, which are strongly dependent on solvent, anions, and temperature.

The formation of [(tetb)CuO$_2$Cu(tetb)](OTf)$_2$ could be confirmed by IR spectroscopy in solution and in the solid state. The (O-O) band was observed at 815 cm^{-1} in acetone and 818 cm^{-1} in solid KBr. Furthermore, Raman spectra of a solid sample of [(tetb)CuO$_2$Cu(tetb)](OTf)$_2$ had two bands at 811 cm^{-1} and 828 cm^{-1}. This is consistent with previous results.[4b,c,7a,9c] Measurements of ^{18}O labeled-samples were performed; however, unfortunately the band is hidden under much more intense bands of the complex itself and/or solvent and thus could not yet be detected.

Final confirmation of the formation of the dinuclear peroxido complex was achieved when the purple compound could be crystallized at low temperatures. The molecular structure of the cation of [(tetb)CuO$_2$Cu(tetb)](OTf)$_2$·5-(CH$_3$)$_2$CO is shown in Figure 3 (crystallographic data are reported in the Supporting Information). This is only the fourth example of a structurally characterized copper end-on peroxido complex. However, even more important is the fact that for the first time a copper dioxygen adduct complex could be structurally characterized using a macrocyclic ligand, tetb, a derivative of cyclam. All of the three known other end-on copper peroxido complexes are related to each other in their coordination to a tripodal ligand.

The molecular structure of [(tetb)CuO$_2$Cu(tetb)](OTf)$_2$ is quite interesting because in the solid state, the peroxido ligand is coordinated in an equatorial position of a square-pyramidal environment. In the beginning of our studies we did expect axial coordination owing to the fact that the copper(II) complex of tetb, [Cu (tetb)H$_2$O]$^{2+}$ (red isomer), is square-pyramidal and coordinates the water molecule in the axial position.[11] Thus we assumed that this might be the reason that neither superoxido or peroxido copper complexes with macrocyclic ligands have yet been structurally characterized. Jahn–Teller distortion would cause the axial dioxy-

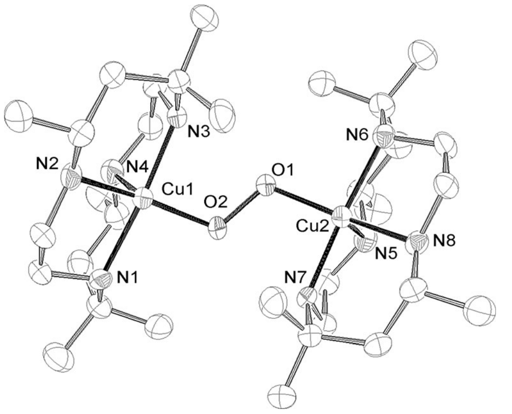


Figure 3. Molecular structure of the cation of $[(\text{tetb})\text{CuO}_2\text{Cu}(\text{tetb})]$-$(\text{OTf})_2$ (ellipsoids set at 50% probability; the solvent molecules and anions are omitted for clarity). Selected bond lengths [Å]: Cu1–N1 2.108(3), Cu1–N2 2.073(4), Cu1–N3 2.026(3), Cu1–N4 2.249(4), Cu1–O2 1.924(3), O1–O2 1.495(4).

gen-like ligand to be very labile. However, as discussed below, the situation for tetb turned out to be quite different.

It is interesting to note that the molecular structures of $[(\text{tetb})\text{CuO}_2\text{Cu}(\text{tetb})](\text{OTf})_2$ and [Cu(tetb)]OTf are rather similar. During the oxidation and coordination of the peroxido ligand, the copper cation only undergoes slight changes in its coordination environment. In [Cu(tetb)]OTf the bond angles between N2-Cu1-N4 (109.7°) and N1-Cu1-N3 (169.8°) are similar to the ones in $[(\text{tetb})\text{CuO}_2\text{Cu}(\text{tetb})]$-$(\text{OTf})_2$ (N2-Cu1-N4 103.42°; N3-Cu1-N1 175.33°). Coordination of the peroxido ligand slightly pulls the copper ion out. While this describes correctly only the solid state situation it still provides a good explanation for the fast reaction of [Cu(tetb)]OTf with O_2. No large geometrical reordering is necessary for binding dioxygen.

In $[(\text{tetb})\text{CuO}_2\text{Cu}(\text{tetb})]^{2+}$ the copper ions are found in a distorted square-pyramidal coordination environment ($\tau = 0.3$) in contrast to $[(\text{Me}_6\text{tren})\text{CuO}_2\text{Cu}(\text{Me}_6\text{tren})]^{2+}$ where a trigonal-bipyramidal coordination geometry ($\tau = 0.9$) is observed.[4b] The τ values were calculated according to Addison et al.[12] In $[(\text{Me}_6\text{tren})\text{CuO}_2\text{Cu}(\text{Me}_6\text{tren})]^{2+}$ dioxygen is coordinated in an axial position while being equatorial in the tetb analogue. Still Cu–O bond lengths in both complexes are similar (Table 1).

Usually chlorido or aqua copper(II) complexes are structurally similar to the analogous superoxido or peroxido complexes.[4b,e] While this is confirmed for the series of Me_6tren complexes it does not fit for the copper complexes with tetb as a ligand (Table 1). Here bond lengths between copper(II) and the ligands chloride or water are much longer compared with the Cu–O bond length in the peroxido complex. The complexes $[\text{Cu}(\text{tetb})\text{Cl}]^+$ and $[\text{Cu}(\text{tetb})\text{H}_2\text{O}]^{2+}$ have been described in the literature previously, and they adopt a trigonal-bipyramidal and/or square-pyramidal geometry with water or chloride in an equatorial or axial position.[11,13]

Table 1: Selected bond lengths of the chlorido, aqua, and peroxido copper complexes with the ligands tetb and Me_6tren.[4b,e,10,13]

Ligand	Cu–Cl		CuO_2Cu	Cu–OH_2
tetb	2.387(1)	Cu–O	1.924(3)	2.434(4)
		O–O	1.495(4)	
Me_6tren	2.208(1)	Cu–O	1.907(2)	1.98
		O–O	1.368	

Despite the fact that the molecular structures of $[(\text{Me}_6\text{tren})\text{CuO}_2\text{Cu}(\text{Me}_6\text{tren})]^{2+}$ and $[(\text{tetb})\text{CuO}_2\text{Cu}(\text{tetb})]^{2+}$ in the solid state are different, the situation might be different in solution. The UV/Vis spectra of the two complexes in solution are slightly different, indicating that the geometries are retained in solution; however, we do not yet have final evidence for this (UV/Vis spectra of the solids are broad; see the Supporting Information). Still it is most likely that the equatorial coordinated peroxido ligand is responsible for the increased stability of $[(\text{tetb})\text{CuO}_2\text{Cu}(\text{tetb})]^{2+}$ in solution. This has been discussed previously by us for the uns-penp system[7b] and in great detail by Comba and co-workers for copper bispidine complexes.[10c,14]

In conclusion, we have finally been successful in preparing and structurally characterizing the missing dioxygen adduct complex in the series of transition-metal complexes with macrocyclic ligands derived from cyclam. Owing to the extremely high stability of the copper superoxido complex $[\text{Cu}(\text{tetb})\text{O}_2]^+$ at room temperature, we are furthermore optimistic to structurally characterize this compound in the future. Unfortunately, to date we only obtained green crystals that were not suitable for structural characterization. Finally it is interesting to note that Valentine and co-workers did excellent work already more than thirty years ago in regard to copper "dioxygen adduct" complexes and correctly assigned the formation of a copper superoxido complex. Surprisingly, despite large efforts in that research area no other group has followed up on these results. The system itself is very interesting in regard to the facile formation of a copper superoxido as well as a dinuclear copper peroxido complex from mononuclear copper complex units. The equilibrium of the two species is complicated; however, it allows to study both complexes at the same time.

Experimental Section

Tetb was synthesized according to a procedure described previously.[15] [Cu(tetb)]OTf was prepared under inert conditions in a glove box. A solution of $[\text{Cu}(\text{CH}_3\text{CN})_4]$OTf (188.4 mg, 0.5 mmol) dissolved in a small amount of acetonitrile was added very slowly to a solution of tetb (142.2 mg, 0.5 mmol) in acetonitrile under vigorous stirring. The colorless solution changed to an intensive purple color and a small amount of colloidal copper metal precipitated. The solution was allowed to stand for several weeks at −30 °C under an inert atmosphere. A small amount of purple colored powder precipitated (caused by disproportionation) together with colorless triangular crystals of [Cu(tetb)]OTf that were suitable for crystal structure determination.[16]

$[\text{Cu}_2(\text{tetb})_2\text{O}_2](\text{OTf})_2$: A saturated solution of isolated [Cu(tetb)]OTf crystals in acetone was cooled. At −90 °C, dry dioxygen gas was bubbled through the solution for a few seconds. The solution immediately turned to a dark green color. Storing the solution overnight in a fridge at −80 °C caused the formation of dark purple crystals that could be structurally characterized.[16]

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[16] CCDC 891988 ([Cu(tetb)]OTf) and CCDC 891989 ([Cu_2(tetb)$_2O_2$](OTf)$_2$) 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.