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Reactivity towards dioxygen of a copper(I) complex of tris(2-benzylaminoethyl)amine

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Abstract

The reaction of dioxygen with the copper(I) Bz_3 tren complex (Bz_3 tren = tris(2-benzylaminoethyl)amine) complex has been investigated using low temperature stopped-flow techniques. The formation of a superoxo as well as a peroxo complex as intermediates was detected spectroscopically. The copper(II) complexes [Cu(Bz_3 tren)H_2O](ClO₄)₂ and [Cu(Bz_3 tren)Cl]Cl were synthesized and structurally characterized. Both complexes react with dioxygen in solution and formation of benzaldehyde was observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper complexes; Tripodal ligands; Dioxygen activation; Peroxo/superoxo complexes

1. Introduction

Copper ions are found in the active sites of a large number of metalloproteins involved in important biological electron transfer reactions, as well as in redox processing of molecular oxygen [1-6]. Many low molecular weight model complexes for copper proteins have been synthesized and their reactions with dioxygen have been investigated [2-12]. These model compounds not only provide better understanding of the biological molecules but furthermore, they assist in the development of new homogeneous catalysts for selective oxidations under mild conditions [2,6,10,13]. A key step in these redox reactions is the activation of dioxygen upon binding at the active site prior to the reaction with a substrate. It was discovered that a whole variety of copper dioxygen adducts form when simple copper(I) complexes are reacted with dioxygen [10,11]. The course of these reactions depends on temperature, ligand and solvent. Therefore, it is of great interest to

elucidate the factors that govern the (reversible) binding and activation of dioxygen with copper(I) complexes.

The first example of a structurally characterized copper peroxo complex was obtained by Karlin and coworkers from the reaction of $[Cu(tmpa)(CH_3CN)]PF_6$ (tmpa = tris[(2-pyridyl)methyl]amine, Fig. 1) with O₂ at low temperatures [14,15]. A detailed kinetic investigation of the reversible reaction of $[Cu(tmpa)(CH_3CN)]^+$ (1) with O₂ was performed in propionitrile which allowed the spectroscopic observation of a superoxo complex prior to formation of the peroxo complex [16]. Furthermore, the influence of sterical hindrance as well as different donor atoms on the formation of the



Fig. 1. Tripodal ligands tmpa, tren, Me₆tren, Bz₃tren and L.

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peroxo complexes was studied [16-18,10,19]. More recently we have investigated the effect of chelate ring size on the properties of these complexes [20].

To further elucidate the factors that influence the reactions of dioxygen with Cu(I) complexes we have started to use tripodal ligands derived from the parent compound tris(2-aminoethyl)amine (tren, Fig. 1), an amine produced in industrial quantities [10,21]. Tren is a versatile tetradentate ligand, known to form trigonal bipyramidal complexes with copper(II) ions in the solid state as well as in solution (similar to copper(II) tmpa complexes). One of the axial positions is occupied by the tertiary amine nitrogen, the other by water or some other monodentate ligand [10,22-25]. Unfortunately, in contrast to [Cu(tmpa)(CH₃CN)]PF₆ the copper(I) tren complex does not form a stable dioxygen adduct on O_2 exposure [10,21]. In contrast, the fully methylated form of tren, Me₆tren (tris(2-dimethylaminoethyl)amine, Fig. 1) supports formation of a copper superoxo and peroxo complex in a similar manner to tmpa [21].

Therefore, we became interested in how monoalkylation of tren could influence the reactivity of its copper(I) complexes towards dioxygen. Herein we describe the properties and reactions of copper complexes of Bz_3 tren (tris(2-benzylaminoethyl)amine, Fig. 1).

2. Experimental

2.1. Materials and methods

Reagents and solvents used were of commercially available reagent grade quality. Bz₃tren was either synthesized according to a published procedure [26] or obtained from Aldrich. [Cu(CH₃CN)₄)]⁺ salts were synthesized and characterized according to literature methods [27]. Copper(I) Bz₃tren complexes for the time resolved UV-Vis spectra were prepared in situ by mixing stoichiometric amounts of $[Cu(CH_3CN)_4]^+$ and Bz₃tren in propionitrile or acetone under inert conditions. Preparation and handling of air-sensitive compounds was carried out in a glove box filled with argon (Braun, Garching, Germany; water and dioxygen less than 1 ppm). UV-Vis spectra were measured on a Hewlett Packard 8452 A spectrophotometer. Cyclic voltammetry was performed with an EG&G Potentiostat (Model 263) at 25 °C with a scan rate of 100 $mV s^{-1}$.

Time resolved spectra of the reactions of dioxygen with copper(I) complexes were recorded on a modified Hi Tech SF-3 L low temperature stopped-flow unit (Salisbury, UK) equipped with a J&M TIDAS 16-500 diode array spectrophotometer (J&M, Aalen, Germany). Data fitting was performed using the integrated J&M software Kinspec or the program Specfit (Spectrum Software Associates, Chapel Hill, NC, USA). Dioxygen saturated solutions for the measurements were obtained by passing dioxygen through the solvent for 20 min as described earlier [16,28,29].

Caution! Perchlorate salts are potentially explosive and should be handled with great care.

2.1.1. $[Cu(Bz_3tren)(H_2O)](ClO_4)]_2$

To a solution of 209 mg (0.5 mmol) Bz₃tren in 5 ml of methanol was added under inert conditions a solution of 185 mg (0.5 mmol) Cu(ClO₄)₂ × 6H₂O in 5 ml of methanol. Blue crystals suitable for X-ray characterization were obtained by diffusion of diethyl ether into this solution (yield: 140 mg, 40%). *Anal.* Calc. for C₂₇H₃₈N₄CuCl₂O₉: C, 46.52; H, 5.49; N, 8.04. Found: C, 46.80; H, 5.97; N, 8.05%.

2.1.2. [Cu(Bz₃tren)(Cl)]Cl

To a solution of 220 mg (0.53 mmol) Bz₃tren in 5 ml of methanol was added under inert conditions a solution of 90 mg (0.53 mmol) CuCl₂ × 2H₂O in 5 ml of methanol. Green crystals suitable for X-ray characterization were obtained by diffusion of diethyl ether into this solution (yield: 175 mg, 60%). *Anal.* Calc. for C₂₇H₃₆N₄CuCl₂: C, 58.85; H, 6.58; N, 10.17. Found: C, 58.98; H, 7.16; N, 10.04%.

2.2. X-ray data collection and structure refinement

Crystal data and experimental conditions are listed in Table 1. The molecular structures are illustrated in Figs. 3 and 4. Selected bond lengths and angles with standard deviations in parentheses are presented in Table 2. Intensity data were collected with graphite monochromated Mo K α , radiation ($\lambda = 0.71073$ Å).

X-ray diffraction data for $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$ were collected on a Nonius CAD4 MACH3. The intensities were corrected for Lorentz and polarization effects (but not for absorption). The structure was solved by direct methods [30] and refined by full-matrix least squares methods on F^2 [31]. Hydrogen atoms of $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$ were calculated for idealized geometries and allowed to ride on their preceeding atoms, their isotropic displacement parameters were tied to those of the adjacent atoms by a factor of 1.5.

X-ray diffraction data for [Cu(Bz₃tren)(Cl)]Cl were collected on a Siemens SMART 5000 CCD-diffractometer. The exposure time was 10 s per frame collected with the ω -scan technique ($\Delta \omega = 0.3^{\circ}$). The collected reflections were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 [32–34]. [Cu(Bz₃tren)-(Cl)]Cl crystallises in the orthorhombic chiral space group $P_{2_1,2_1,2}$ as a racemic twin. The high residual electron density in the final Fourier difference map was found to be located very close to the Cu(II) ion.

Table 1 Crystal data and structure refinement for $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$ and $[Cu(Bz_3tren)Cl]Cl$

Complex	[Cu(Bz ₃ tren)(H ₂ O)](ClO ₄) ₂	[Cu(Bz ₃ tren)Cl]Cl
Empirical formula	C ₂₇ H ₃₈ Cl ₂ CuN ₄ O ₉	C ₂₇ H ₃₆ Cl ₂ CuN ₄
Formula weight	695.04	548.01
Temperature (K)	293(2)	200(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\overline{1}$	$P_{21,21,2}$ (No. 19)
Unit cell dimensions		-1,-1,- , ,
a (Å)	9.982(5)	9.65530(10)
b (Å)	15.114(5)	15.39400(10)
c (Å)	11.569(5)	18.3699(2)
α (°)	91.711(5)	90
β (°)	115.399(5)	90
γ (°)	94.341(5)	90
$V(Å^3)$	1568.4(12)	2730.39(4)
Ζ	2	4
$D_{\text{calc}} (\text{mg m}^{-3})$	1.438	1.333
Absorption coefficient (mm ⁻¹)	0.919	1.018
<i>F</i> (000)	706	1144
Crystal size (mm)	$0.36 \times 0.29 \times 0.14$	$0.2 \times 0.2 \times 0.4$
2θ Range (°)	2.53-24.96	1.73–28.34
Index ranges	$-11 \le h \le 11, -17 \le k \le 17, -13 \le l \le 13$	$-12 \le h \le 12, -20 \le k \le 20, -24 \le l \le 24$
Reflections collected/unique	11 020	28 376
Independent reflections	5510 $[R_{int} = 0.0449]$	6672 $[R_{int} = 0.1210]$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5510/240/388	6672/0/313
Goodness-of-fit on F^2	1.040	0.998
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0543, \ wR_2 = 0.1371$	$R_1 = 0.0760, \ wR_2 = 0.1714$
R indices (all data)	$R_1 = 0.0957, \ wR_2 = 0.1594$	$R_1 = 0.1243, \ wR_2 = 0.1935$
Largest difference peak and hole (e $Å^{-3}$)	0.851 and -0.766	2.702 and -0.819
		Completeness to $\theta = 28.3/99.2\%$
		Absolute structure parameter 0.48(2)

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3. Results and discussion

Small changes in the ligand environment can have a dramatic effect on the reaction behavior of copper(I) complexes towards dioxygen and make it necessary to study systematically varied systems [10,20]. In that regard the ligand tmpa and its derivatives (as well as many other ligands described in the literature) have the disadvantage that chemical modification of these compounds can be difficult and/or time consuming. In contrast modifying the amine tren is quite facile and a whole family of new tripodal ligands can be obtained.

For example, tren readily reacts with aldehydes to form Schiff base derivatives that can be used as new ligands for metal ions (this approach has been especially useful for the synthesis of dinuclear macrocyclic complexes and cryptands) [35–40]. Imine nitrogen donor atoms are well suited to stabilize the 'soft' copper(I) ion but so far only a few mononuclear copper(I) complexes with such ligands have been structurally characterized [41–44].

At the beginning of our investigations we synthesized the now commercially available amine Bz₃tren by reacting benzaldehyde with tren followed by reduction with sodium borohydride [26]. This prompted us, as well as

Table 2								
Selected	bond	lengths	(Å)	and	bond	angles	(°)	for
[Cu(Bz ₃ tre	n)(H ₂ O	$(ClO_4)_2$ a	und [C	u(Bz ₃ tr	en)Cl]Cl			

Bond lengths for $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$							
Cu-O(9)	1.964(4)	Cu–N(2)	2.095(4)				
Cu-N(1)	2.005(4)	Cu–N(3)	2.171(4)				
Cu-N(4)	2.087(4)						
Bond lengths for [Cu(Bz ₃ tren)Cl]Cl							
Cu-Cl(1)	2.276(2)	Cu–N(2)	2.137(5)				
Cu-N(1)	2.042(4)	Cu–N(3)	2.139(4)				
Cu–N(4)	2.085(5)						
Bond angles for $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$							
O(9) - Cu - N(1)	1/9.0(2)	N(4)– Cu – $N(2)$	132.1(2)				
O(9)– Cu – $N(4)$	94.4(2)	O(9)-Cu-N(3)	94.3(2)				
N(1)– Cu – $N(4)$	85.2(2)	N(1)-Cu-N(3)	85.0(2)				
O(9)-Cu-N(2)	95.4(2)	N(4)-Cu-N(3)	112.1(2)				
N(1)-Cu-N(2)	85.5(2)	N(2)-Cu-N(3)	113.6(2)				
Bond angles for [Cu(Bz ₃ tren)Cl]Cl							
N(1)-Cu(1)-N(2)	83.86(19)	N(3)-Cu(1)-N(4)	115.7(2)				
N(1)-Cu(1)-N(3)	84.6(2)	N(1)-Cu(1)-Cl(1)	178.05(15)				
N(2)–Cu(1)–N(3)	127.7(2)	N(2)-Cu(1)-Cl(1)	94.28(15)				
N(1)-Cu(1)-N(4)	84.32(18)	N(3)-Cu(1)-Cl(1)	96.15(14)				
N(2)-Cu(1)-N(4)	113.5(2)	N(4)-Cu(1)-Cl(1)	96.97(13)				



Fig. 2. Time resolved spectra. Reaction of $[Cu(Bz_3tren)(CH_3CN)]PF_6$ with dioxygen at -80 °C in dry acetone ([complex] = 0.2 mM, $[O_2] = 0.92$ mM, $\Delta t = 39$ s).

others, to investigate copper(I) complexes of the initially formed imine ligand (L, Fig. 1) [41,44,45]. The synthesis of this complex is facile and it was structurally characterized by X-ray crystallography [41,44]. However, when this complex was reacted with dioxygen in a variety of solvents at different temperatures dioxygen intermediates were not detected [44,45]. This finding is well in line with our earlier results on the reaction of dioxygen with different copper imine complexes. All our kinetic investigations suggest the formation of a copper peroxo (or superoxo) complex, but we were unable to spectroscopically detect these compounds [46,47]. Most likely, the dioxygen intermediate immediately reacts further to yield a decomposition product (steady state conditions). So far, we are unable to explain why this especially seems to be the case for copper(I) imine complexes.

In contrast to the trivial synthesis of copper(I) complexes with the imine ligand L, our efforts to isolate copper(I) complexes using Bz₃tren proved unsuccessful. In all the experiments (performed in a glove box) disproportionation of the copper(I) complexes to copper metal and copper(II) was observed at higher concentrations as described earlier for other copper(I) amine complexes [10,21]. It was not possible to synthesize a copper(I) complex of Bz₃tren as a solid. However, it can be easily prepared in situ by mixing equimolar amounts of the ligand with the appropriate copper(I) salts in propionitrile or acetone under inert conditions (concentrations upto 1 mM were possible but solutions needed to be freshly prepared because disproportionation occurred over longer time intervals). These solutions were reacted with dioxygen at low temperatures in a stopped-flow unit equipped with a diode array detector. A typical example of time resolved spectra for this reaction at -80 °C in acetone is shown in Fig. 2. These spectra provide evidence for the formation of $[(Bz_3tren)CuO_2]^+$ and $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ because the spectral features are very similar to known UV-Vis spectra of copper superoxo and peroxo complexes [16,21]. We assigned the absorbance maxima of the superoxo $[(Bz_3tren)CuO_2]^+$ ($\lambda_{max} = 406$ nm) and peroxo [(Bz₃tren)CuO₂Cu(Bz₃tren)]²⁺ ($\lambda_{max} = 506$ nm) complexes accordingly. Therefore, in Fig. 2 the formation of $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ can be observed by the increase of the absorbance maximum at 506 nm. Under these conditions the total reaction time of 1000 s is not long enough for the complete formation of the peroxo complex to be observed. The increase of the absorbance of $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ is accompanied by a decrease of the absorbance attributable to the superoxo complex. From these results we conclude that the reaction pathway follows Eqs. (1)-(3) as described previously for [(tmpa)Cu(CH₃CN)]⁺ and $[Cu(Me_6 tren)(CH_3 CN)]^+$. Clear differences in the rate of formation and the stability of the dioxygen adducts of the three complexes were observed and therefore, a detailed kinetic study on the reactions of [Cu(Me₆tren)- (CH_3CN)]⁺ and $[Cu(Bz_3tren)(CH_3CN)]$ ⁺ with dioxygen is in progress to gain more insight into these differences.

$$[(Bz_3tren)Cu(RCN)]^+ + O_2$$

$$\rightleftharpoons [(Bz_3tren)Cu(O_2)]^+ + RCN \qquad (1)$$

$$[(Bz_3tren)Cu(RCN)]^+ + [(Bz_3tren)Cu(O_2)]^+$$

$$\Rightarrow [(Bz_3tren)Cu(O_2)Cu(Bz_3tren)]^{2+} + RCN \qquad (2)$$

 $[(Bz_3tren)Cu(O_2)Cu(Bz_3tren)]^{2+} \rightarrow \text{irreversible decay}$ (3)

 $[(Bz_3tren)CuO_2]^+$ and $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ could only be observed spectroscopically at low temperatures. Increasing the temperature showed faster reaction rates and at higher temperature only the decomposition of the peroxo complex could be observed. Similar to the reactions of dioxygen with $[(tmpa)Cu(CH_3CN)]^+$ and $[Cu(Me_6tren)(CH_3CN)]^+$ it was found that acetone had a 'stabilizing' effect on $[(Bz_3tren)CuO_2]^+$ and $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$ indicating that nitrile is coordinated to the copper(I) Bz_3tren complex [21,48].

Efforts to isolate crystals of $[(Bz_3tren)CuO_2Cu-(Bz_3tren)]^{2+}$ at low temperatures for structural characterization were unsuccessful. In comparison to the spectral data for $[(tmpa)CuO_2Cu(tmpa)]^{2+}$ it is most likely a *trans-µ*-1,2-peroxo complex [14,15]. It was observed earlier that $[(tmpa)CuO_2Cu(tmpa)]^{2+}$ is structurally very similar to other copper(II) tmpa complexes e.g. $[Cu(tmpa)Cl]ClO_4$ [15,49]. Therefore, synthesis and characterization of simple copper(II) complexes with Bz_3tren as ligand can also provide valuable information on $[(Bz_3tren)CuO_2Cu(Bz_3tren)]^{2+}$. According to the Cambridge Structural Data Base no metal complexes with Bz_3tren as ligand have been characterized so far.



Fig. 3. ORTEP drawing of the cation of [Cu(Bz₃tren)(H₂O)](ClO₄)₂.



Fig. 4. ORTEP drawing of the cation of [Cu(Bz₃tren)Cl]Cl.

Only a zinc complex with a substituted Bz_3 tren ligand and chloride as an additional ligand was reported that is similar to [Cu(Bz_3 tren)Cl]Cl described below [50]. Furthermore, some mononuclear copper(II) complexes with cryptands as ligands include Bz_3 tren in its coordination sphere [51,52].

The copper(II) complexes, $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$ and [Cu(Bz₃tren)Cl]Cl were obtained from a reaction mixture of the ligand with the appropriate copper(II) salts. ORTEP plots of the crystal structures of their cations are shown in Figs. 3 and 4. The geometry of both complexes is best described as trigonal bipyramidal and the bond lengths and angles are similar to those found in [Cu(Me₆tren)Cl]ClO₄ and [Cu(Me₆tren)-(H₂O)](ClO₄)₂ [21,53]. The main difference between $[Cu(Bz_3tren)(H_2O)](ClO_4)_2$ and $[Cu(Bz_3tren)Cl]Cl$ is the bond distance of the Cu-axial ligand. As expected the Cu–O bond length of 1.964(4) Å is much shorter than the Cu–Cl bond length of 2.276(2) Å and is very similar to the Cu-O bond length of 1.973(4) Å in [Cu(Me₆tren)(H₂O)](ClO₄)₂ [53]. The Cu–O bond length of 1.852(5) Å in $[(tmpa)CuO_2Cu(tmpa)]^{2+}$ is slightly shorter than in [Cu(Bz₃tren)(H₂O)](ClO₄)₂ [14] The Cu-Cl bond distances of the three complexes $[Cu(Bz_3tren)Cl]Cl, [Cu(Me_6tren)Cl]ClO_4 and [Cu (tmpa)Cl]ClO_4$ are very similar [21,49].

The trigonal bipyramidal geometry of $[Cu(Bz_3tren)-(H_2O)](ClO_4)_2$ is retained in solution as was confirmed by the UV–Vis spectrum in methanol ($\lambda_{max} = 857$ nm, $\varepsilon = 292$ M⁻¹ cm⁻¹) typical for trigonal bipyramidal copper(II) complexes [54,55]. [Cu(Bz_3tren)(H_2O)]-(ClO_4)_2 and [Cu(Bz_3tren)Cl]Cl as well as Cu(II) Me₆tren complexes show irreversible cyclic voltammograms in contrast to [Cu(tmpa)(H_2O)](ClO_4)_2 supporting the finding that the Cu(I) complexes have a high tendency towards disproportionation.

Surprisingly it turned out to be problematic to obtain pure copper(II) complexes of Bz_3 tren if the synthesis was not performed under inert conditions. If air had access to the reaction vessels the solutions started to become cloudy after a few hours and the characteristic odor of benzaldehyde could be detected. Most likely this process can be divided into two separate parts. In the first part the imine bonds are formed while in the second part hydrolysis of the imine occurs releasing benzaldehyde. Oxidations of amine complexes to imine complexes are well known and an excellent discussion on these reactions is described in the literature [56]. From these findings most likely the reaction sequence (shown only for one amine arm) presented in Scheme 1 occurs.

The first step is deprotonation of the NH groups caused by the coordination of the Cu(II) ion that lowers the pK_a of the NH groups in Bz₃tren. Formal electron transfer leads to a Cu(I) complex with radical ligand. Cu(I) can be oxidized by air, now leading to a



Scheme 1.

Cu(II) complex with a radical ligand. Further reduction of Cu(II) to Cu(I) and loss of a proton leads to a Cu(I) imine complex. As described above the Cu(I) imine complex will be again oxidized by air to the according Cu(II) complex. But this complex is unstable towards hydrolysis (similar to some related copper complexes; [56] e.g. the copper complex of the ligand derived from tren and pyridine-2-aldehyde [57]) and the copper amine complex and benzaldehyde is formed. This reaction scheme can be completely suppressed if the complexes are synthesized and kept under inert conditions.

4. Conclusions

An exciting finding of this work is that complete alkylation of tren is unnecessary to obtain amine ligands that support formation of copper peroxo complexes; monoalkylation of each amine arm is enough to stabilize such intermediates. As discussed above this allows facile modification of tren to obtain a series of new amine ligands for a study of systematically varied systems.

Furthermore, it is interesting to note that the introduction of the three benzyl groups did not provide any sterical hindrance to suppress formation of $[(Bz_3tren)-CuO_2Cu(Bz_3tren)]^{2+}$. The benzyl groups are oriented in a propeller like fashion, away from the copper(II) ion.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 161783 for compound [Cu(Bz₃tren)(H₂O)](ClO₄)₂ and CCDC No. 161192 for compound [Cu(Bz₃tren)Cl]Cl. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033;

e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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