Reversible Binding of Dioxygen by a Copper(I) Complex with Tris(2-dimethylaminoethyl)amine (Me_6tren) as a Ligand

Michael Becker, Frank W. Heinemann, and Siegfried Schindler*[a]

Abstract: The copper(I) complex $[Cu(Me_6tren)]ClO_4$ (Me_6tren = tris(2-dimethylaminoethyl)amine) and the copper(II) complex $[Cu(Me_6tren)Cl]ClO_4$ have been synthesized and structurally characterized. The copper(I) complex reacts reversibly with dioxygen at low temperatures to form a quite persistent superoxo complex at −90 °C in propionitrile. At higher temperatures a peroxo complex is formed which is much more stable in acetone than in propionitrile. A peroxo intermediate is not observed when the copper(I) complex of the non-methylated amine tren is treated with dioxygen.

Keywords: bioinorganic chemistry · copper · dioxygen complexes · peroxo complexes · tripodal ligands

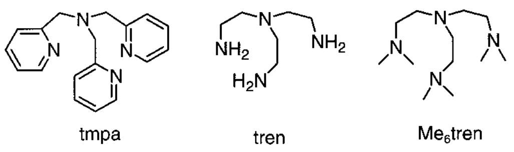
Introduction

Copper ions are found in the active sites of a large number of metalloproteins involved in important biological electron transfer reactions.[1, 2] Interest in preparing functioning model complexes for such copper proteins is twofold: first, the models provide better understanding of the biological molecules, and second, they assist in the development of new homogeneous catalysts for selective oxidations under mild conditions.[2–6]

A fundamental step in metalloenzyme redox reactions is activation upon binding of dioxygen at the active site prior to reaction with a substrate. Therefore, it is important to gain a better understanding of the reaction of dioxygen with copper(I) complexes.

The first example of a structurally characterized copper peroxo complex was obtained by Karlin and co-workers by reaction of $[Cu(tmpa)(CH_3CN)]PF_6$ (tmpa = tris[(2-pyridyl)-methyl]amine) with O_2 at low temperatures.[7, 8] A detailed kinetic investigation of the reversible reaction of $[Cu(tmpa)(CH_3CN)]^+$ (**1**) with O_2 was performed in propionitrile, which, for the first time, allowed the spectroscopic observation of a superoxo complex before formation of the peroxo complex.[9] The influence of steric hindrance as well as the effect of different donor atoms on the formation of the peroxo complexes was also studied.[9–12] Since then, various reactions of copper(I) complexes with dioxygen have been investigated and several new copper peroxo complexes with different dioxygen binding modes have been structurally characterized.[13–18] Many of the complexes formed by reaction of copper(I) with dioxygen are only stable at low temperatures. However, more recently, copper peroxo complexes have been reported which are quite stable at room temperature.[19–21] Furthermore, an unusual example of a stable copper peroxo complex was described by Krebs and co-workers; in this case four copper ions share one dioxygen ligand.[17]

In our own studies, which investigate the factors influencing the reactions of dioxygen with Cu^I complexes,[22–25] we have started to use tripodal ligands derived from the parent compound tris(2-aminoethyl)amine (tren) (Scheme 1). We recently reported that the copper(I) complex $[Cu(Me_6tren)]^+$ (**2**) (Me_6tren = tris(2-dimethylaminoethyl)amine) reacts reversibly with O_2 at low temperatures.[26] Here we describe this reaction in more detail.



$[Cu(tmpa)(CH_3CN)]^+$ = **1**, $[Cu(Me_6tren)]^+$ = **2**, $[(tmpa)Cu(O_2)Cu(tmpa)]^{2+}$ = **3**,

$[Cu(Me_6tren)O_2]^+$ = **4**, $[(Me_6tren)Cu(O_2)Cu(Me_6tren)]^{2+}$ = **5**, $[Cu(tmpa)O_2]^+$ = **6**,

$[Cu(Me_6tren)Cl]^+$ = **7**,

Scheme 1. Structures of the ligands found in complexes **1**–**7**.

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Results and Discussion

It is well known that copper(II) tren complexes show trigonal-bipyramidal geometry in the solid state and in solution.[27, 28] One axial position is occupied by the tertiary amine nitrogen, while the other is occupied by water or another monodentate ligand.[27, 29–31] The geometry is important for ligand substitution reactions because copper(II) complexes with a tetragonally distorted geometry react very fast (close to the diffusion limit), while copper(II) complexes with trigonal-bipyramidal geometry react much more slowly.[32–34] Copper(II) complexes of the related tripodal ligand tmpa also possess a trigonal-bipyramidal geometry.[35]

The interesting reaction of **1** with dioxygen gave rise to the question of whether the aliphatic ligand tren would also support the formation of copper dioxygen adducts. To answer this question we prepared [Cu(tren)]PF_6, a complex that has not yet been described. It turned out that we could not isolate this complex as a pure solid because it undergoes disproportionation to a copper(II) salt and copper metal at higher concentrations. Nevertheless, it was possible to obtain dilute solutions of [Cu(tren)]PF_6 by mixing stoichiometric amounts of $[Cu(CH_3CN)_4]PF_6$ and tren in propionitrile or acetone under inert conditions. Reaction of dioxygen with these solutions, under the same conditions used to study the formation of the copper tmpa peroxo complex,[9] did not permit observation of a copper tren peroxo complex. This behavior was not completely unexpected because we found that the formation of the peroxo complex $[(tmpa)Cu(O_2)Cu(tmpa)]^{2+}$ (**3**) was dramatically disfavored when the reaction of **1** with dioxygen was performed in methanol. Obviously, copper peroxo complexes with tripodal ligands made from tren or its derivatives are destabilized by the presence of protons from either the solvent or the ligand.

To avoid these problems we decided to use the fully methylated tren ligand that can be easily synthesized.[36] When a solution of Me_6tren and $[Cu(CH_3CN)_4]PF_6$ salt in propionitrile was allowed to react with O_2 in a Schlenk tube at −80 °C, a color change from colorless to deep blue occurred. Such an intensive color change is typical for the formation of a copper peroxo complex. The solution became colorless again when dioxygen was replaced by nitrogen (with slight warming), indicating the reversible reaction of O_2 with **2**. The cycle could be repeated several times before the solution turned green and no further reaction with O_2 was observed.

Me_6tren and tmpa are related tripodal ligands but differ in their donor atoms. In complex **1** the three pyridine nitrogen atoms of tmpa stabilize the Cu^I ion in contrast to complex **2**, where Me_6tren can provide only aliphatic nitrogen donor atoms that are not very suitable for stabilization of the Cu^I ion. As a consequence, isolation of a pure solid sample of **2** was quite difficult compared with the facile synthesis of **1**. Solutions containing Me_6tren and Cu^I salts were extremely sensitive towards traces of dioxygen or moisture (as was [Cu(tren)]PF_6 described above) and oxidation or disproportionation of the complex often occurred.

We were able to prepare a small amount of solid **2**-BF_4 but the crystals were not suitable for X-ray characterization. Finally, we were able to isolate white needles of **2** as a perchlorate salt that could be characterized structurally. An ORTEP plot of the molecular structure of **2**-ClO_4 is shown in Figure 1.

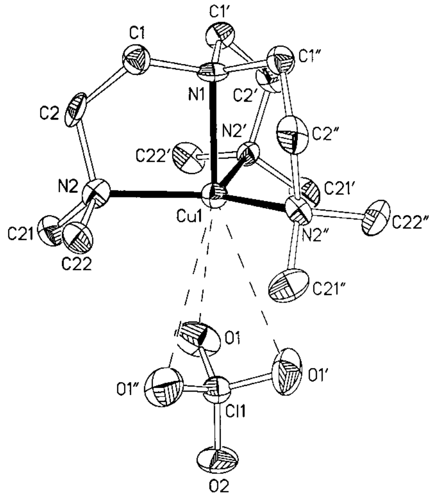

Figure 1. An ORTEP view of **2**-ClO_4 The thermal ellipsoids are at the 50 % probability level and the hydrogen atoms are omitted for clarity.

The geometry is best described as trigonal pyramidal; the copper ion is surrounded by the four amine nitrogen atoms with bond lengths of 2.122(7) Å for the equatorial Cu–N and 2.200(14) Å for the axial Cu–N bonds. Furthermore, weak interaction with the perchlorate anion cannot be neglected, since the anion can be regarded as being in the axial position of a trigonal-bipyramidal arrangement; the distance between the copper ion and three of the four oxygen atoms is 3.53(1) Å. The Cl–O bond lengths in the perchlorate ion are normal and range from 1.419(8) to 1.436(11) Å. The copper ion lies only slightly (0.191(8) Å) below the plane of the three equatorial nitrogens, towards the perchlorate ion.

The structure is exceptional because of the weak interaction of the perchlorate anion with the copper(I) cation. Especially after crystallizing **2**-ClO_4 from acetonitrile, we had expected to find an additional acetonitrile molecule coordinated to the copper ion in the axial position (instead of perchlorate) as had been found for **1** and a structurally characterized derivative of **1**.[8] Comparison of these complexes with **2**-ClO_4 reveals that bond lengths and angles are quite different. In the derivative of **1** the copper ion lies 0.568 Å above the plane of the three equatorial nitrogens, towards the acetonitrile molecule; the axial nitrogen atom is only weakly coordinated (Cu–N = 2.439(8) Å).[8a] Because in **2**-ClO_4 the axial nitrogen atom is coordinated more strongly to the copper ion it may not need an additional acetonitrile in its coordination sphere. Therefore, it only interacts weakly with the perchlorate ion in the solid state. Compound **2**-ClO_4 resembles the complex $[Cu(Me_5dien)(CH_3CN)]ClO_4$ (Me_5dien = 1,1,4,7,7-pentamethyldiethylethylenetriamine) more closely (the bond lengths and angles are similar) if Me_5dien is regarded as Me_6tren missing one arm.[37] But even in this case an acetonitrile molecule is coordinated and interaction with the perchlorate ion was not observed. The Cambridge Structural Data Base does not show any other example of such a weak interaction between a Cu^I ion and three oxygen atoms as in **2**-ClO_4.[38]

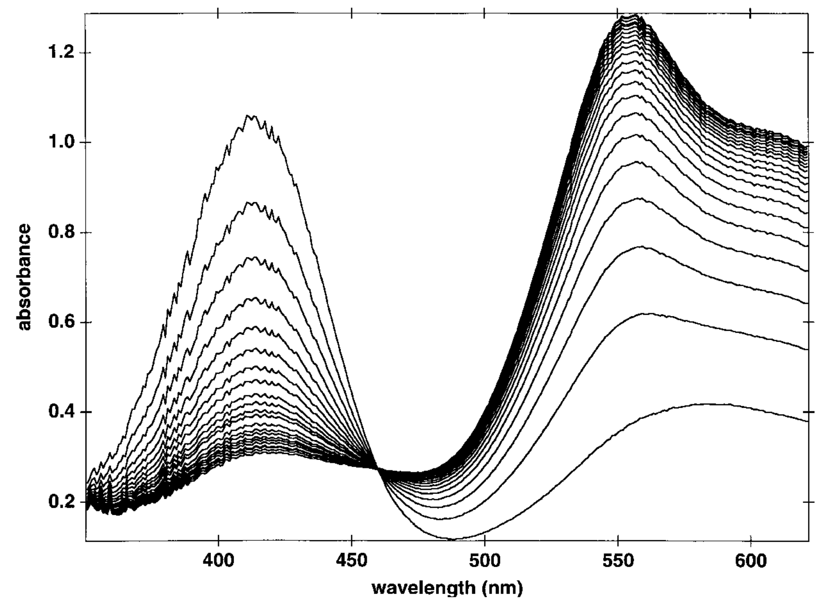

Figure 2. Reaction of **2** with dioxygen at $-60\,^{\circ}C$ in dry propionitrile ([complex] = 0.27 mM, $[O_2] = 4.4$ mM, $\Delta t = 0.1$ s).

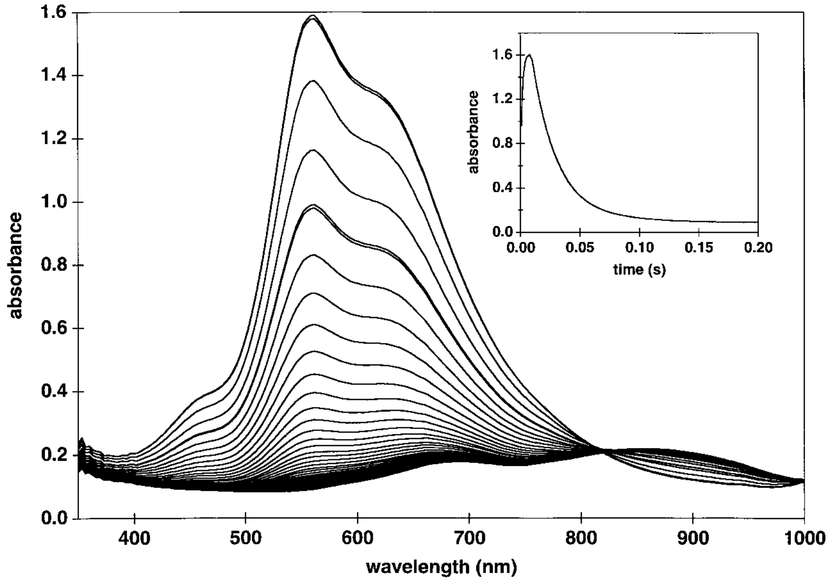

Figure 3. Reaction of **2** with dioxygen at $20\,^{\circ}C$ in dry acetone ([complex] = 0.5 mM, $[O_2] = 0.92$ mM, $\Delta t = 4$ ms). The insert shows the absorbance vs. time trace at 555 nm.

When **2** was treated with O_2 at low temperature in a stopped-flow instrument the spectral changes for the formation of dioxygen adducts were observed. An example of the time-resolved spectra at $-60\,^{\circ}C$ is shown in Figure 2.

The spectral features are similar to UV/Vis spectra of known copper superoxo and peroxo complexes.[9, 11] Therefore, we assigned the absorbance maxima to the superoxo complex $[Cu(Me_6tren)O_2]^+$ (**4**) ($\lambda_{max} = 412$ nm, $\varepsilon \approx 4000\,cm^{-1}M^{-1}$) and peroxo $[(Me_6tren)Cu(O_2)Cu(Me_6tren)]^{2+}$ (**5**) ($\lambda_{max} = 560$ nm, $\varepsilon \approx 10\,000\,cm^{-1}M^{-1}$) complexes accordingly. Complex **4** has nearly identical spectral features to $[Cu(tmpa)O_2]^+$ (**6**) ($\lambda_{max} = 410$ nm, $\varepsilon = 4000\,cm^{-1}M^{-1}$). But the absorbance maximum of **5** is shifted by 35 nm towards lower energy compared with that of **3** ($\lambda_{max} = 525$ nm, $\varepsilon = 15\,000\,cm^{-1}M^{-1}$). Complex **5** was characterized further by its resonance Raman spectrum in propionitrile. The intense peak for the oxygen–oxygen stretching frequency ν(O–O) was observed at 880 cm^{-1} compared with 826 cm^{-1} for **3**.[39]

At $-90\,^{\circ}C$ the formation of **4** alone can be observed. The reaction was studied under pseudo-first-order conditions ($[O_2] \gg [\mathbf{2}]$) and the absorbance-time trace at 410 nm was fitted to an exponential function. A plot of the observed rate constant k_{obs} vs. $[O_2]$ showed a linear dependence with an intercept that indicated a reversible reaction. The kinetic findings demonstrate that at low temperature complex **2** reacted with dioxygen in a stoichiometric ratio of 1:1 to form **4**. This compound is much more persistent than **6** under the same conditions. Complex **6** immediately underwent further reaction to give the peroxo complex, while **4** only reacted slowly to yield **5**. The formation of **4** became much faster at higher temperatures. Therefore, only its decomposition could be observed with simultaneous production of the peroxo complex **5** (see Figure 2). Above $-20\,^{\circ}C$ the formation of **5** was too fast to be observed spectroscopically under these conditions.

Nitriles are excellent ligands for copper(I) and compete strongly with dioxygen [Eq. (1) and (2)]. Therefore nitriles

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

$$[Cu(L)O_2]^+ + [Cu(L)RCN]^+ \rightleftharpoons [Cu_2(L)_2O_2]_2^+ + RCN \qquad (2)$$

are not ideal solvents for these reactions. This is also true for dichloromethane because it reacts with **1**.[8] Methanol on the other hand destabilizes the peroxo complex (as discussed above), but we could still observe the transient formation of the peroxo intermediate at low temperatures. In the end, acetone proved to be the solvent of choice and, compared with propionitrile, the peroxo complex **3** was highly stabilized in this solvent.[20]

When complex **2** is allowed to react with dioxygen in acetone at $-90\,^{\circ}C$ the formation of **4** was much faster than in

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propionitrile. For this reason only a minor part of the reaction could be observed. Additionally, a larger amount of **4** was formed. These findings clearly demonstrate that in solution—in contrast to the solid state—a nitrile molecule is coordinated to **2** [Eq. (1) and (2)]. Even more dramatically, the change of solvent affected the stability of **5**. Unlike in propionitrile, it was possible to observe the formation of **5** in acetone at room temperature. The spectral changes during the reaction of **2** with dioxygen in acetone at 20 °C are shown in Figure 3 (the absorbance time trace for the formation and decomposition of the peroxo species is shown as an insert).

So far, efforts to isolate crystals of the peroxo complex **5** at low temperatures for structural characterization have been unsuccessful. Comparison with the spectral data for **3** suggests that it is most likely a *trans*-μ-1,2-peroxo complex. In contrast, a copper(II) complex, [Cu(Me$_6$tren)Cl]ClO$_4$ (**7**-ClO$_4$), was easily obtained. An ORTEP plot of the crystal structure of its cation is shown in Figure 4.

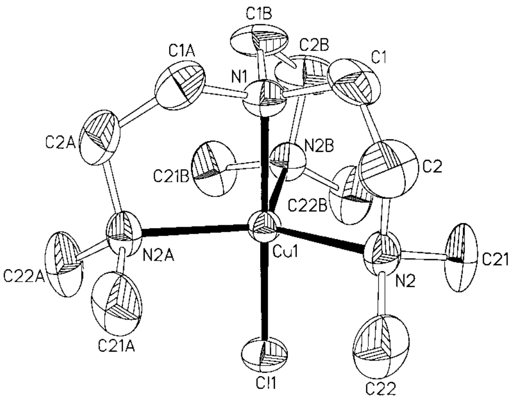

Figure 4. An ORTEP view of **7**. The thermal ellipsoids are at the 50% probability level and the hydrogen atoms are omitted for clarity.

Complex **7** has a nearly ideal trigonal-bipyramidal geometry with the chloride ion in an axial position and the copper ion positioned slightly below the plane (0.208(3) Å) of the three equatorial nitrogens, towards the chloride ion. Bond lengths and angles are similar to those of other Cu^{II} complexes derived from Me$_6$tren.[40–43] Furthermore, the structure of **7** compares well with that of complex **2**, as both are characterized by a crystallographically imposed threefold axis (C_3 symmetry). While the bond lengths for the equatorial Cu–N bonds in **2** and **7** are comparable, the axial Cu–N bond is much shorter in **7** (2.040(6) Å). This is different for the copper tmpa analogue, [Cu(tmpa)Cl]ClO$_4$, in which the C–N bond lengths are all very similar (2.050 – 2.072 Å).[35] The angles N$_{\text{axial}}$-Cu-N$_{\text{equatorial}}$ (84.55(7)°) are slightly larger in **7** than in [Cu(tmpa)Cl]ClO$_4$ (80.8 – 81.5°), while the angles in the plane are very similar. The Cu–Cl bond lengths are identical in the two complexes.

Comparison of the two complexes is quite useful because [Cu(tmpa)Cl]ClO$_4$ is structurally very much similar to the peroxo complex **3**.[8, 35] Therefore, we suggest that the complexes **5** and **7** should also have a similar structure. The UV/Vis spectra of **7** in solution (water, $\lambda = 876$ nm, $\varepsilon = 248$ cm^{-1}M^{-1}) are typical for trigonal-bipyramidal Cu^{II} complexes and confirm that this geometry is retained in solution.[30]

Taken together the findings show that the oxidation of **2**, as with complex **1**, is not accompanied by the dramatic geometry change normally observed for copper(I) oxidation reactions. This is most likely the reason for the facile formation of tripodal copper dioxygen adducts of **2**. Furthermore, as discussed above, once the trigonal-bipyramidal copper peroxo complex is formed it should be more stable towards ligand substitution reactions, than an analogous square-pyramidal copper peroxo complex.

Conclusions

We have shown that a copper(I) complex with the aliphatic tripodal amine Me$_6$tren as a ligand reacts reversibly with dioxygen at low temperatures. During this oxidation a much more stable superoxo complex is formed than during a similar reaction of the copper(I) tmpa complex. The peroxo complex is highly stabilized if the reaction takes place in acetone instead of nitrile solvents. The overall findings show that copper compounds with ligands derived from derivatives of tren are well suited for the activation of dioxygen. Therefore, we have started to investigate a whole series of copper(I) complexes with modified tren ligands.

Experimental Section

Materials and methods: Reagents and solvents used were of commercially available reagent-grade quality. Me$_6$tren, [Cu(CH$_3$CN)$_4$]$^+$ salts and **1** were synthesized and characterized according to literature methods.[8, 36, 44] Preparation and handling of air-sensitive compounds were 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. Resonance Raman spectra (excitation frequency of 5145 Å) were measured in propionitrile at −70 °C in a low-temperature, four-window cell. Time-resolved UV/Vis spectra of the reactions of dioxygen with copper(I) complexes were recorded with a modified Hi-Tech SF-3L low-temperature stopped-flow unit equipped with a J&M TIDAS 16-500 diode array spectrophotometer (J&M, Aalen, Germany). Data fitting was carried out in the integrated J&M software Kinspec or the program Specfit (Spectrum Software Associates, Chapel Hill, NC, USA).

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

[Cu(Me$_6$tren)]ClO$_4$ (2-ClO$_4$): [Cu(CH$_3$CN)$_4$]ClO$_4$ (0.33 g, 1 mmol) was added with stirring to a solution of Me$_6$tren (0.23 g, 1 mmol) in a small amount of acetonitrile in a glove-box. Colorless crystals suitable for X-ray characterization were obtained by diffusion of diethyl ether into this solution. Yield: 39 mg (10%); CuC$_{12}$H$_{30}$N$_4$ClO$_4$: calcd C 36.64, H 7.69, N 14.24; found C 36.38, H 8.21, N 13.95.

[Cu(Me$_6$tren)]BF$_4$ (2-BF$_4$): [Cu(Me$_6$tren)]BF$_4$ was synthesized in the same way as [Cu(Me$_6$tren)]ClO$_4$ from [Cu(CH$_3$CN)$_4$]BF$_4$. Yield: 30%; CuC$_{12}$H$_{30}$N$_4$BF$_4$: calcd C 37.86, H 7.94, N 14.71; found C 37.54, H 8.18, N 14.50.

[Cu(Me$_6$tren)Cl]ClO$_4$ (7-ClO$_4$): A solution of Cu(ClO$_4$)$_2 \cdot 6$H$_2$O (0.46 g, 1.25 mmol) and CuCl$_2 \cdot 2$H$_2$O (0.21 g, 1.25 mmol) in water (20 mL) was added to a solution of Me$_6$tren (0.576 g, 2.5 mmol) in methanol (10 mL). The solution was stirred for a few minutes and then filtered. Turquoise crystals suitable for X-ray analysis were formed soon afterwards. Yield: 0.75 g (70%); CuC$_{12}$H$_{30}$N$_4$Cl$_2$O$_4$: calcd C 33.61, H 7.05, N 13.06; found C 33.61, H 7.27, N 13.00.

Table 1. The crystal data and structure refinement for **2**-ClO_4 and **7**-ClO_4.

Complex	[Cu(Me_6tren)]ClO_4	[Cu(Me_6tren)Cl]ClO_4
empirical formula	$C_{12}H_{30}ClCuN_4O_4$	$C_{12}H_{30}Cl_2CuN_4O_4$
formula weight	393.39	428.84
temperature [K]	200(2)	293
crystal system	hexagonal	rhombohedral
space group	$P6_3$	$R3c$
a [Å]	9.923(3)	9.988(2)
b [Å]	9.923(3)	9.988(2)
c [Å]	10.991(5)	33.535(7)
α [°]	90	90.0
β [°]	90	90.0
γ [°]	120	120.0
volume [$Å^3$]	937.2(6)	2897(1)
Z	2	6
ρ [$Mg\,m^{-3}$]	1.394	1.475
μ [mm^{-1}]	1.328	1.429
F(000)	416	1350
crystal size [mm^3]	$0.80 \times 0.25 \times 0.10$	$0.50 \times 0.30 \times 0.30$
diffractometer	Siemens P4	Nicolet R3m/V
scan technique	ω scan	ω scan
θ-range for data collection	2.3 to 27.0	2.6 to 27.0
index ranges	$-1 \le h \le 11$, $-12 \le k \le 1$, $-1 \le l \le 14$	$-1 \le h \le 12$, $-12 \le k \le 11$, $-42 \le l \le 42$
reflections collected	1939	4418
independent refl.	790	1404
R_{int}	0.0971	0.0336
observed reflections [$F \ge 4\sigma(F)$]	563	989
data/restraints/parameters	790/1/69	1404/1/100
goodness of fit on F^2	1.025	0.911
$R1$ [$F_0 \ge 4\sigma(F)$][a]	0.0612	0.0285
wR_2 (all data)[a]	0.1506	0.0695
Flack parameter x[47]	−0.08(6)	−0.01(2)
q[b]	0.0747	0.0467
r[b]	0.5287	0
largest diff. peak and hole	0.619 −1.639	0.193 −0.329

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [b] $w = 1/[\sigma^2(F_o^2) + (q \times P)^2 + rP]$, $P = ((F_o^2 + 2F_c^2)/3$.

Single-crystal X-ray structure determinations: Crystal data and experimental conditions for the two complexes are listed in Table 1. The molecular structures are illustrated in Figures 1 and 4. Selected bond lengths and angles with standard deviations in parentheses are presented in Table 2. Intensity data were collected with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The collected reflections were corrected for Lorentz and polarization effects. An empirical correction with psi-scans of 20 reflections ($7.3° \le 2\Theta \le 26.7°$, $T_{min} = 0.4820$, $T_{max} = 0.5784$) was performed for **2**-ClO_4, while absorption effects in **7**-ClO_4 were neglected. The structures were solved by direct methods and refined by full matrix least squares methods on F^2.[45] Hydrogen positions of **7**-ClO_4 were geometrically positioned and allowed to ride on their carrier atoms during the refinement; their isotropic displacement parameters were tied to those of the adjacent carbon atoms by a factor of 1.5. For **7**-ClO_4 all the hydrogen atom positions were taken from a difference Fourier synthesis and refined with a common fixed isotropic u parameter.[46]

Table 2. Selected bond lengths [Å] and bond angles [°] with standard deviations in parentheses for the complexes **2**-ClO_4 and **7**-ClO_4.

	2-ClO_4		
Cu(1)−N(2)#1	2.122(7)	Cu(1)−N(2)#2	2.122(7)
Cu(1)−N(2)	2.122(7)	Cu(1)−N(1)	2.200(14)
N(2)#1-Cu(1)-N(2)#2	119.20(7)	N(2)#2-Cu(1)-N(1)	84.8(2)
N(2)#1-Cu(1)-N(2)	119.20(7)	N(2)-Cu(1)-N(1)	84.8(2)
N(2)#2-Cu(1)-N(2)	119.20(7)	N(2)#1-Cu(1)-N(1)	84.8(2)
#1: $-y+2$, $x-y+2$,z		#2: $-x+y$, $-x+2$, z	
	7-ClO_4		
Cu(1)−N(1)	2.040(6)	Cu(1)−N(2)#2	2.186(2)
Cu(1)−N(2)	2.186(2)	Cu(1)−Cl(1)	2.234(2)
Cu(1)−N(2)#1	2.186(2)		
N(1)-Cu(1)-N(2)	84.55(7)	N(2)#1-Cu(1)-N(2)#2	119.11(2)
N(1)-Cu(1)-N(2)#1	84.55(7)	N(1)-Cu(1)-Cl(1)	180.0
N(2)-Cu(1)-N(2)#1	119.11(2)	N(2)-Cu(1)-Cl(1)	95.45(7)
N(1)-Cu(1)-N(2)#2	84.55(7)	N(2)#1-Cu(1)-Cl(1)	95.45(7)
N(2)-Cu(1)-N(2)#2	119.11(2)	N(2)#2-Cu(1)-Cl(1)	95.45(7)
#1: $-y+1$; $x-y-2$; z		#2: $-x+y+3$; $-x+1$; z	

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[46] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102297 (**2**) and CCDC-102298 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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