Syntheses, Structures and Properties of Copper(I) and Copper(II) Complexes of the Ligand *N*,*N*′-Bis[2′-(dimethylamino)ethyl]-*N*,*N*′-dimethylethane-1,2-diamine (Me_6trien)

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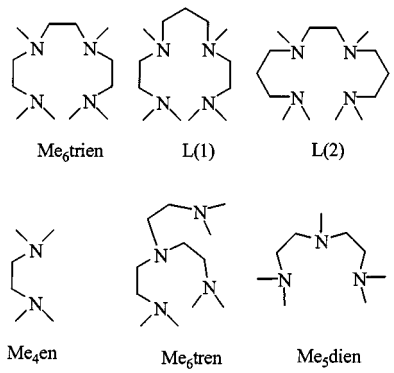
Copper(I) and copper(II) complexes of the ligand *N*,*N*′-bis[2′-(dimethylamino)ethyl]-*N*,*N*′-dimethylethane-1,2-diamine (Me_6trien) were synthesized and structurally characterized. In the solid state the complex cation $[Cu(Me_6trien)]^+$ (**1**) adopts a distorted tetrahedral configuration. Crystallography, EPR measurements, and UV/Vis spectroscopy indicate that the analogous copper(II) complex $[Cu(Me_6trien)Cl]^+$ has a square pyramidal geometry in the solid state as well as in solution. The reaction of **1** with dioxygen was investigated in different solvents. No copper dioxygen intermediates could be detected spectrophotometrically during these reactions.

Introduction

The dioxygen carrier protein hemocyanin (Hc) as well as many other metalloenzymes involved in important biological oxygen transfer reactions contain copper ions in their active sites.[1,2] A fundamental step in metalloenzyme redox reactions is the activation of dioxygen, upon binding at the active site, prior to the reaction with a substrate. Many low molecular weight model complexes for copper proteins have been synthesized and their reactions with dioxygen have been investigated.[1–23] A better understanding of these reactions will assist in the development of new homogeneous catalysts for selective oxidations under mild conditions.[24,25]

In contrast to enzymes, which react in aqueous solutions (although the copper ions are located in a relatively hydrophobic environment) at ambient conditions, the reactions of model complexes with dioxygen usually have to be investigated in organic solvents at low temperatures.[7,10,11,26] Therefore, in order to better model the reactivity of the biological systems, one should ideally study the oxidations of copper(I) complexes by dioxygen in water. This endeavor has been hampered because copper(I) complexes have a great tendency to disproportionate in aqueous solution. However, it is well-known that tertiary amine ligands can stabilize copper(I) in water; for example the copper(I) complex of the macrocyclic ligand 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclo-tetradecane is stable towards oxidation in aqueous solution.[27] Tertiary amines in general have proven to be useful in stabilizing metal complexes in low oxidation states,[28,29] and the thermodynamic properties of a series of Cu^I and Cu^{II} complexes with the tertiary amines Me_6trien, L(1) and L(2) as ligands (Scheme 1) were investigated earlier.[27,29–34] If dioxygen is excluded, dilute solutions of the copper(I) complexes of these amines can easily be synthesized in water by a comproportionation reaction. As an example, the formation of the copper(I) complex of Me_6trien is shown in Equation 1.[31,35]



Scheme 1. Me_6trien = *N*,*N*′-bis[2′-(dimethylamino)ethyl]-*N*,*N*′-dimethylethane-1,2-diamine, L(1) = *N*,*N*′-bis(2′-(dimethylamino)-ethyl)-*N*,*N*′-dimethyl-propane-1,3-diamine, L(2) = *N*,*N*′-bis(2′-(dimethylamino)propyl)-*N*,*N*′-dimethylethane-1,2-diamine, Me_4en = tetramethylethylenediamine, Me_6tren = tris(2-dimethylamino-ethyl)amine), Me_5dien = 1,1,4,7,7-penta methyldiethylethylenetriamine

$$[Cu(II)Me_6trien]^{2+} \xrightarrow{Me_6trien,\ Cu(0)} 2\,[Cu(I)Me_6trien]^{+} \quad (1)$$

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These solutions are stable under inert conditions, but are oxidized immediately to the analogous Cu^{II} complexes by dioxygen.[31,35] As part of our ongoing investigation of the reactions of copper(I) complexes with dioxygen[26,36–42] we therefore investigated these oxidations with the copper(I) complexes of the tertiary amines Me_6trien, L(1) and L(2) in more detail.

Results and Discussion

Synthesis and Crystal Structure of [Cu(Me_6trien)][$CuCl_2$] (1-[$CuCl_2$])

The comproportionation reaction shown in Equation 1 did not allow the synthesis of highly concentrated aqueous solutions of copper(I) complexes. Nevertheless, white crystals were obtained from the reaction of Me_6trien with CuCl in methanol. The molecular structure of the cation of this new complex is shown in Figure 1.

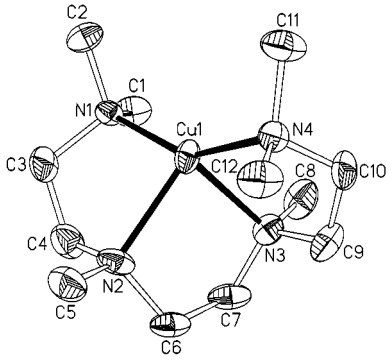

Figure 1. An ORTEP view of **1**; the thermal ellipsoids are at the 30% probability level and the hydrogen atoms are omitted for clarity

Although we had expected to obtain [CuMe_6trien]Cl (**1**-Cl) when mixing the ligand and CuCl in a stoichiometric ratio, it is obvious that the presence of the strong coordinating chloride prevents the reaction with the ligand from completing. Instead, **1**-[$CuCl_2$] is formed. In addition to the complex cation **1**, the asymmetric structural unit contains two halves of dichlorocopper(I) anions. Each of these holds a crystallographically imposed center of symmetry at the copper ion with one independent chloride. The anions are linear with Cu–Cl distances of 2.107(4) and 2.086(2) Å. These are very similar to the values that have been reported in the literature for $[CuCl_2]^-$ complexes.[43–46]

The tertiary amine tetramethylethylenediamine (Me_4en) can be regarded as one half of Me_6trien; the syntheses and structural characterizations of copper(I) complexes with Me_4en in a ratio of 1:2 were reported earlier.[28,45] The complex [Cu(Me_4en)$_2$][$CuCl_2$][45] (**2**-[$CuCl_2$]) is isostructural with **1**-[$CuCl_2$], and both complex cations adopt a distorted tetrahedral configuration. Nevertheless, close inspection of the Cu–N distances in **1** and **2** reveals significant differences. While for **2** the Cu–N bonds are consistent within the 3σ criterion [distances from 2.13(1) to 2.16(1) Å],[45] the two terminal Cu–N bonds in **1** are shorter [2.009(5) and 2.015(5) Å] than the other two Cu–N bonds [2.202(6) and 2.218(6) Å]. This clearly shows that Me_6trien in **1** is under more steric strain than Me_4en in **2**.

It is interesting to compare the molecular structure of **1** to the cation of the copper(I) complex [Cu(Me_6tren)]ClO_4 [**3**-ClO_4, Me_6tren = tris(2-dimethylaminoethyl)amine].[26] Me_6tren is an isomer of Me_6trien. In contrast to the distorted tetrahedral configuration of **1**, the geometry of **3** is best described as trigonal pyramidal (trigonal bipyramidal if the weakly coordinated perchlorate ion in the axial position is included); the copper ion is surrounded by the four amine nitrogen atoms with distances of 2.122(7) Å for the equatorial Cu–N and 2.200(14) Å for the axial Cu–N bonds.

Furthermore, bond lengths and angles in **1** are comparable to those of the complex cation of [Cu(Me_5dien)(CH_3CN)]ClO_4 (Me_5dien = 1,1,4,7,7-pentamethyldiethylethylenetriamine).[47] This compound [bond lengths for Cu–N = 2.04, 2.19, and 2.18 Å, and bond angles for N(1)–Cu–N(2) = 87.2(4) and N(2)–Cu–N(3) = 84.6(4)°] is even more distorted than **1**; its geometry was described as irregular. Me_5dien can be regarded as Me_6trien missing one arm, with the missing arm in the copper(I) complex being substituted by an acetonitrile molecule.

While it is possible to prepare dilute aqueous solutions of **1** by a comproportionation reaction (Equation 1), neither **2**, **3**, or [Cu(Me_5dien)]$^+$ could be obtained under the same conditions. However, we could prepare solutions of **3** in acetonitrile by a comproportionation reaction if Me_6tren was reacted with $CuCl_2 \times 2\ H_2O$ and copper powder under inert conditions. This reaction did not occur if Me_6trien or Me_4en were used as ligands under these conditions.

Reaction of 1 with Dioxygen

Thus far, the reactions of dioxygen with model compounds for copper proteins have been investigated mainly in organic solvents because of the disproportionation of Cu^I to Cu^0 and Cu^{II} in aqueous solutions.[1–4,24,48] For the same reason, knowledge on the kinetics of the oxidation of Cu^I complexes in water is rather limited; usually acetonitrile is chosen as a cosolvent.[39,49–55] Using the tertiary amines Me_6trien, L(1) and L(2) we tried to overcome these difficulties in order to study the formation of copper dioxygen adducts in aqueous solution, which would be similar to the oxidation of deoxy-Hc.

We successfully prepared dilute aqueous solutions of copper(I) complexes according to Equation 1. The kinetic behavior of all three amine complexes was similar; a representative example for the time resolved spectra of the reaction of dioxygen with **1** is shown in Figure 2

During the reaction, only the buildup of the product [Cu(Me_6trien)]$^{2+}$ (**4**) could be observed spectrophotometrically. No intermediate – neither a copper superoxo nor a peroxo complex – was detected. A change in pH from 7.0 to 10.0 did not alter the reaction rates significantly. Also, the rates did not depend on the concentration of dioxygen or the ionic strength. But they increased when the pressure was raised. However, these observations must be treated with caution since a detailed kinetic analysis was not possible. Computational fitting of the absorbance vs. time traces demonstrated that several reaction steps were in-

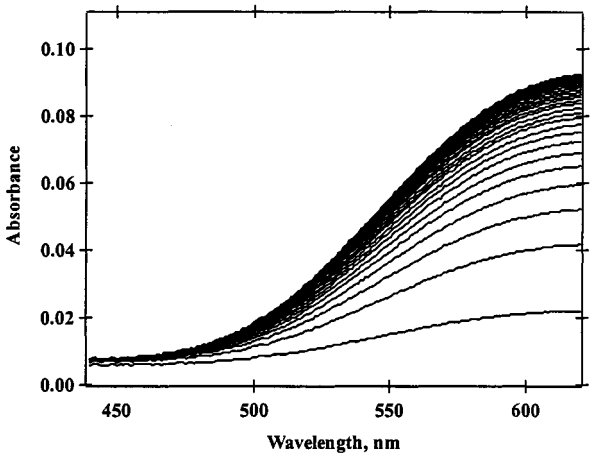

Figure 2. Reaction of **1** with dioxygen at 25 °C in water; the complex was prepared by the comproportionation reaction shown in Equation 1 ([**1**] = 0.5 mM, $[O_2]$ = 0.6225 mM, Δt = 20 s and pH = 8.0)

volved which presumably included higher order terms. To resolve these kinetic traces the spectra of intermediates and broader concentration windows for both reactants would be required.

This behavior was not unexpected because earlier investigations, mainly by Zuberbühler et al., showed that the kinetics of the reactions of copper(I) complexes with dioxygen in water are generally very complicated.[49–53,56–59] Most of these studies were performed in the presence of acetonitrile using the initial-rate treatment for the data analysis. Similar to our measurements, no copper peroxo intermediates were detected spectrophotometrically; often hydrogen peroxide was observed as a product.

To test whether hydrogen peroxide gave rise to additional reaction paths during the oxidation of **1** with dioxygen we investigated the reaction of H_2O_2 with **1** [as well as the copper(I) complexes of L(1) and L(2)]. The oxidation proceeded smoothly, but again complex kinetic behavior was observed and acceptable fitting of the data was not possible.

When small amounts of H_2O_2 were added to an aqueous solution of the copper(II) complexes, changes in the UV/Vis spectrum were not detected. When larger amounts were added (> tenfold excess) bubbles of dioxygen resulting from decomposition of H_2O_2 were observed.

A comparison between the oxidation of **1** and of deoxy-Hc shows clear differences in the reaction behavior. Deoxy-Hc reacts much faster than **1** (ca. 10000 times) with dioxygen (this rate is not dependent on pressure).[60,61] Furthermore, in contrast to the oxidation of **1**, the reaction of the protein is reversible. A major reason for these differences is the fact that the active site of deoxy-Hc is a preorganized dinuclear copper(I) site while **1** is mononuclear. In accordance with this, it has been shown earlier that a preorganized dinuclear copper(I) complex reacted extremely fast with dioxygen in organic solvents.[62] Presently, we are designing new dinuclear copper(I) complexes with tertiary amines in order to develop a system that will react similarly to the protein.

Recently, we found that **3** reacts reversibly with dioxygen in propionitrile or acetone at low temperatures, forming copper superoxo and peroxo complexes.[26][40] This reaction cannot be investigated in aqueous solution because disproportionation of **3** occurs. An investigation in methanol demonstrated that the peroxo complex is not stable in the presence of protons.[26]

The assumption that **1**, an isomer of **3**, would form dioxygen adducts in organic solvents as well, could not be confirmed. The only effect observed when **1** was reacted with dioxygen in methanol, acetone, or propionitrile was a decrease of the overall reaction rate compared to the studies in aqueous solutions. Lowering the temperature to –90 °C also slowed down the oxidation rate. No dioxygen intermediates could be observed spectrophotometrically under these conditions.

For comparison we also investigated the reaction of dioxygen with **2** (prepared in situ from $[Cu(CH_3CN)_4]PF_6$ and Me_4en) in propionitrile or acetone. The kinetic measurements did not provide evidence for the reversible formation of a peroxo intermediate and again an acceptable fitting of the data was not possible. However, it is known (also from kinetic studies) that peroxo and oxo-bridged dinuclear copper species are formed when copper(I) complexes of Me_4en, Et_4en and similar ligands (in a stoichiometric ratio of 1:1) are reacted with dioxygen in organic solvents.[63–70] Recently, a bis μ-oxo-copper complex and a trinuclear cluster with two μ_3-oxide ligands were obtained (and structurally characterized) from the reaction of copper(I) complexes of peralkylated-1,2-cyclohexanediamines with dioxygen.[18,71]

Synthesis and Crystal Structure of $[Cu(Me_6trien)Cl]ClO_4$ (4-Cl–ClO_4)

Copper(II) complexes of Me_6trien were easily prepared. The molecular structure was solved for **4**-Cl–ClO_4; its cation, with a square pyramidal geometry, is shown in Figure 3.

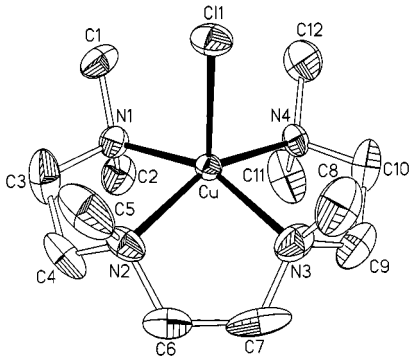

Figure 3. An ORTEP view of the cation of **4**-Cl–ClO_4; the thermal ellipsoids are at the 30% probability level and the hydrogen atoms are omitted for clarity

Structural characterization of copper complexes with Me_6trien or the related amines L(1) and L(2) (Scheme 1) was not available until recently, when the structure of the Cu^{II} complex $[CuL(1)](ClO_4)_2$ [L(1) = *N*,*N*′-bis[2′-(dimethylamino)ethyl]-*N*,*N*′-dimethylpropane-1,3-diamine]

Table 1. Selected bond lengths and bond angles with standard deviations in parentheses for **1**-[$CuCl_2$], **4**-Cl–ClO_4 and **5** × 2 H_2O

Bond lengths (Å) for **1**-[$CuCl_2$]			
Cu(1)–N(1)	2.009(5)	Cu(1)–N(4)	2.015(5)
Cu(1)–N(2)	2.202(6)	Cu(1)–N(3)	2.218(6)
Cu(2)–Cl(1)	2.107(4)	Cu(2)–Cl(1)[a]	2.107(4)
Cu(3)–Cl(2)[b]	2.086(2)	Cu(3)–Cl(2)	2.086(2)
Bond angles (°) for **1**-[$CuCl_2$]			
N(1)–Cu(1)–N(4)	146.8(2)	N(1)–Cu(1)–N(2)	87.3(2)
N(4)–Cu(1)–N(2)	119.3(2)	N(1)–Cu(1)–N(3)	117.7(2)
N(4)–Cu(1)–N(3)	86.4(2)	N(2)–Cu(1)–N(3)	84.5(3)
Cl(1)[a]–Cu(2)–Cl(1)	180.0	Cl(2)[b]–Cu(3)–Cl(2)	180.0
Bond lengths (Å) for **4**-Cl–ClO_4			
Cu–N(2)	2.072(5)	Cu–N(1)	2.158(4)
Cu–N(3)	2.082(5)	Cu–Cl(1)	2.420(2)
Cu–N(4)	2.125(5)		
Bond angles (°) for **4**–Cl–ClO_4			
N(2)–Cu–N(3)	82.4(2)	N(4)–Cu–N(1)	100.0(2)
N(2)–Cu–N(4)	156.0(2)	N(2)–Cu–Cl(1)	103.5(2)
N(3)–Cu–N(4)	85.4(2)	N(3)–Cu–Cl(1)	102.7(2)
N(2)–Cu–N(1)	83.6(2)	N(4)–Cu–Cl(1)	99.2(1)
N(3)–Cu–N(1)	155.9(2)	N(1)–Cu–Cl(1)	99.6(1)
Bond lengths (Å) for **5** × 2 H_2O			
Cu(1)–O(1)	1.911(4)		
Cu(1)–O(1)[c]	1.915(4)		
Cu(1)–N(1)	2.027(4)		
Cu(1)–N(2)	2.040(4)		
Cu(1)–Cu(1)[c]	2.976(1)		
Bond angles (°) for **5** × 2 H_2O			
O(1)–Cu(1)–O(1)[c]	77.9(2)	O(1)[c]–Cu(1)–N(2)	170.7(2)
O(1)–Cu(1)–N(1)	172.7(2)	N(1)–Cu(1)–N(2)	86.7(2)
O(1)[c]–Cu(1)–N(1)	97.4(2)	O(1)–Cu(1)–Cu(1)[c]	39.0(1)
O(1)–Cu(1)–N(2)	97.2(2)	O(1)[c]–Cu(1)–Cu(1)[c]	38.9(1)
N(1)–Cu(1)–Cu(1)[c]	136.0(1)	N(2)–Cu(1)–Cu(1)[c]	135.7(1)

[a] $-x, -y, -z$. – [b] $1-x, -y, -z$. – [c] $-x+1, -y+1, -z+1$.

was reported.[72] L(1) differs from Me_6trien by an additional –CH_2– group. The bond lengths for Cu–N in **4**-Cl–ClO_4 (Table 1) are similar to those generally found for other tertiary amine copper(II) complexes, and differ only slightly from those for [CuL(1)]$(ClO_4)_2$.[72] The main difference between the two structures is that [CuL(1)]$(ClO_4)_2$ has a tetragonally elongated *trans*-CuN_4O_2 coordination sphere with Cu–O distances of 2.562(7) Å while **4**-Cl–ClO_4 is clearly square pyramidal with a Cu–Cl bond length of 2.420(2) Å. No interaction between copper and the perchlorate anion was observed. A direct structural comparison of [CuL(1)]-$(ClO_4)_2$ with **4**-$(ClO_4)_2$ was not possible since the obtained crystals of the latter were not suitable for X-ray crystallography. The Cu–N bond lengths in **4**-Cl–ClO_4 are slightly longer than those in the analogous copper complex [Cu(trien)(SCN)](SCN), with the nonmethylated amine [Cu–N bond length from 2.008(7)–2.030(5) Å].[73] Similarly, the Cu–N bond lengths of [CuL(1)]$(ClO_4)_2$ are longer than in the analogous nonmethylated complex [Cu(2,3,2-tet)]-(ClO_4), (Cu–N bond length from 2.016(6)–2.032(6) Å).[74]

The molecular structure of [Cu(Me_5dien)(H_2O)($OCMe_2$)] was described as distorted square pyramidal [bond lengths Cu–N = 2.036, 2.034, and 2.022 Å, and bond angles for N(1)–Cu–N(3) = 158.8(3) and O(1)–Cu–N(2) = 172.1(4)°] with the acetone molecule in the axial position [bond length Cu–O = 2.222(6) Å].[47] All Cu–ligand bond lengths in this complex are shorter than in **4**-Cl–ClO_4.

The bond lengths for the two isomeric complexes **4**-Cl–ClO_4 and **3**-Cl–ClO_4 [Cu–N_{axial} = 2.040(6) and Cu–$N_{equatorial}$ = 2.186(2) Å] are similar with the exception of the Cu–Cl bond length, which is shorter in **3**-Cl–ClO_4 [2.234(2) Å].[26] Bond angles are different for the two complexes. Complex **4**-Cl–ClO_4 has square pyramidal geometry, while the molecular structure of **3**-Cl–ClO_4 must be described as trigonal bipyramidal.

The different solid state geometries of the two complexes, **4**-Cl–ClO_4 and **3**-Cl–ClO_4, are retained in solution. An absorbance maximum for **4**-Cl–ClO_4 in water at 643 nm (ε = 248 $cm^{-1}M^{-1}$) is typical for a tetragonal distorted copper(II) complex; this coordination is further confirmed by the EPR spectrum [*g* values: *g*(x) = 2.042, *g*(y) = 2.066, *g*(z) = 2.229; nuclear hyperfine coupling constants: *A*(x) = 20 G, *A*(y) = 18 G, *A*(z) = 168 G]. The same behavior was observed for **4**-$(ClO_4)_2$ [λ_{max} = 643 nm (ε = 248 $cm^{-1}M^{-1}$); *g* values: *g*(x) = 2.039, *g*(y) = 2.064, *g*(z) = 2.241; nuclear hyperfine coupling constants: *A*(x) = 19 G, *A*(y) = 26 G, *A*(z) = 169 G]. These data are in accord with the results of our earlier measurements with solutions of **4**-SO_4.[29] Furthermore, they are comparable to those reported for [CuL(1)]$(ClO_4)_2$ as discussed above.[72] In contrast, **3**-Cl–ClO_4 represents a

typical trigonal bipyramidal complex with an absorbance maximum at 876 nm (ε = 447 $cm^{-1}M^{-1}$). The trigonal bipyramidal geometry was confirmed by EPR measurements [*g* values: *g*(x) = 2.170, *g*(y) = 2.187, *g*(z) = 2.010; nuclear hyperfine coupling constants: *A*(x) = 88 G, *A*(y) = 96 G, *A*(z) = 81 G]; the spectral parameters are consistent with those measured in the solid state.[75]

Synthesis and Crystal Structure of $[Cu_2(Me_4en)_2(OH)_2](ClO_4)_2 \times 2\ H_2O$ (**5** × 2 H_2O)

Crystalline salts of $[Cu(Me_4en)_2Cl]ClO_4$ could not be synthesized. This was expected since it was previously suggested that the Cu^{II} ion is too small to form a 1:2 complex with Me_4en.[76] When we reacted Me_4en with a mixture of $CuCl_2$ and $Cu(ClO_4)_2$ in the same way as **4**-Cl–ClO_4 was synthesized, we obtained $[Cu_2(Me_4en)_2(OH)_2](ClO_4)_2$ (**5**) instead. The molecular structure of **5** is shown in Figure 4 (bond lengths and angles are given in Table 1).

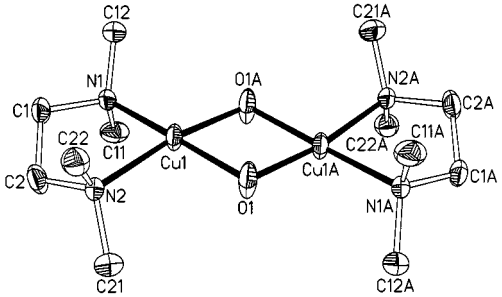

Figure 4. An ORTEP view of the cation of **5** × 2 H_2O; the thermal ellipsoids are at the 30% probability level and the hydrogen atoms are omitted for clarity

A crystal structure of **5** was described earlier by Pavkovik and co-workers.[77] It is not identical with the structure we report here because the latter holds two additional water molecules. This leads to significant differences in the dimensions and the volume of the unit cell. Furthermore, bond lengths and angles in the coordinated Me_4en of the complex described by Pavkovik (bond length C–C 1.377 Å and bond angles of 116.2° and 115.9° around the carbon atoms) do not correspond to the expected C–C bond lengths in this ligand. The authors do not discuss this, but possibly it is due to a disorder in the CH_2–CH_2 group. In contrast to these findings, we obtained a bond length of 1.493(3) Å for the two carbon atoms and bond angles of 109.2(5)° and 109.6(5)°, which are typical for a C–C bond in Me_4en.[78]

Conclusion

The study has shown that copper(I) complexes with related polymethylated aliphatic amines react very differently with dioxygen. Even though it was possible to oxidize **1** [or the copper(I) complexes of L(1) and L(2)] or **2** with dioxygen in different solvents, no dioxygen complexes could be observed as intermediates during these reactions. In contrast, it was shown earlier that the reaction of **3** with dioxygen at low temperatures in nitrile solvents allowed the observation of copper-superoxo and -peroxo complexes as intermediates.[26]

The reason for the different behavior towards dioxygen can be explained by the different geometries of the copper(I)/copper(II) complexes of these ligands. While **3** has a trigonal bipyramidal geometry; in solution a nitrile molecule replaces the weakly coordinated perchlorate,[26] **1** and **2** are best described as pseudo-tetrahedral. The coordination geometry of **3** already closely resembles that of the copper(II) complex, the peroxo product.[26] This is not the case for **1** and **2**. When the pseudo-tetrahedral **1** is oxidized it is turned into the distorted square pyramidal **4**. Evidence for the retention of the coordination geometry in solution is provided by UV/Vis and EPR spectroscopy. Thus, **1** has to undergo a geometrical rearrangement during the reaction with dioxygen; it may even be necessary for one arm of the four dentate ligand to open up before the copper(I) complex can react with dioxygen. Furthermore, the dioxygen ligand in a tetragonal elongated copper complex is kinetically more labile to substitution than in a trigonal bipyramidal geometry. This may be an important reason for the difference in behavior.[79]

It was also found that the nature of the ligand affects the stability of the copper(I) or copper(II) complexes. It was also responsible for the different behavior concerning comproportionation. Furthermore, the study clearly demonstrates that the reactions of copper(I) complexes with dioxygen vary with the solvent used.

The present findings fit well with recent reports on different copper(I) complexes that showed the influence of the ligand and the solvent on the formation of copper complexes with different peroxide binding modes; hereby an equilibrium of a peroxo complex with a bis μ-oxo copper species was discovered.[4,5,7,19–23] While it is still not possible to exactly predict the pathway for the reaction of a copper(I) complex with dioxygen, the findings presented here allow a better understanding of these reactions.

Experimental Section

General Remarks: Reagents and solvents used were of commercially-available reagent-grade quality. Distilled water was used for the preparation of aqueous solutions. The ligand Me_6trien was either synthesized as the free amine,[80] as a hydrochloride salt similar to a published procedure[81] or purchased from Aldrich. $[Cu(CH_3CN)_4]^+$ salts were synthesized and characterized according to literature methods.[82,83] CuCl was either synthesized according to a published procedure[84] or purchased from Aldrich. It was purified in a glove box under an inert atmosphere by washing the light green crystals with methanol until the solid was uniformly white. 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). Air sensitive aqueous solutions were handled by Schlenk techniques or in a glove bag. UV/Vis spectra were measured on a CARY 5G UV/Vis-NIR spectrophotometer. Electron spin resonance measurements at X-band frequency were obtained using a Bruker EMX-113 spectrometer. Samples in methanol/DMF (3:1 mixtures) were measured at 100 K. Time resolved spectra of the reactions of dioxygen with copper(I)

Table 2. The crystal data and structure refinement for **1**-[$CuCl_2$], **4**-Cl–ClO_4 and **5** × 2 H_2O

Complex	**1**-[$CuCl_2$]	**4**-Cl–ClO_4	**5** × 2 H_2O
Empirical formula	$C_{12}H_{30}Cl_2Cu_2N_4$	$C_{12}H_{30}Cl_2CuN_4O_4$	$C_{12}H_{38}Cl_2Cu_2N_4O_{12}$
Formula weight	428.38	428.84	628.44
Temperature (K)	200	293	200
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_1/c$
a (Å)	14.461(4)	13.075(5)	7.855(1)
b (Å)	14.916(4)	79.721(5)	15.124(2)
c (Å)	8.977(2)	14.861(5)	11.320(2)
β (°)	97.34(2)	90.0	106.77(1)
Volume (Å^3)	1920(1)	1889(1)	1287(1)
Z	4	4	2
Density calcd. (Mg/m^3)	1.482	1.508	1.621
Absorpt. coeffic. (mm^{-1})	2.489	1.461	1.918
F(000)	888	900	652
Crystal size (mm)	0.80 × 0.40 × 0.40	0.53 × 0.45 × 0.34	0.60 × 0.40 × 0.30
Diffractometer used	Siemens P4	Nonius CAD4 MACH3	Siemens P4
scan technique	ω scan	ω-2θ scan	ω scan
θ range for data collect. (°)	2.5 to 27.1	2.5 to 24.05	2.31 to 27.00
Index ranges	$-18 < h < 18$, $-19 < k < 0$, $-11 < l < 3$	$-14 < h < 14$, $-11 < k < 11$, $0 < l < 10$	$-10 < h < 1$, $-1 < k < 19$, $-14 < l < 14$
Reflections collected	5465	14208	3679
Independent refl., R_{int}	4214, 0.0255	2693, 0.1243	2803, 0.0565
Obs. reflect. [$F_o \geq 4\sigma(F)$]	2411	2406	1923
Data/restraints/parameters	4214/0/184	2693/23/ 214	2803/0/230
Goodness of fit on F^2	1.064	1.009	1.057
R_1[a] [$F_o > 4\sigma(F)$]	0.0789	0.0461	0.0560
wR_2[a] (all data)	0.2429	0.1306	0.1467
abs. structure parameter[88]	–	0.03(3)	–
q,r[a]	0.138, 0	0.100, 0	0.0664, 0.8047
Largest diff. peak and hole	3.426, –1.231	0.457, –0.262	0.830, –0.530

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

complexes were recorded on a modified Hi Tech SF-3 L low temperature stopped-flow unit (Salisbury, UK) equipped with a JM TIDAS 16–500 diode array spectrophotometer (JM, Aalen, Germany). Data fitting was performed using the integrated JM software Kinspec or the program Specfit (Spectrum Software Associates, Chapel Hill, USA). Dioxygen saturated solutions for the kinetic measurements were obtained by passing dioxygen through the solvent for 20 minutes described earlier.[7,10,11,26] Concentration of dioxygen was varied by mixing dioxygen saturated solutions with argon saturated solutions in syringes.

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

[Cu(Me$_6$trien)][CuCl$_2$] (1-[CuCl$_2$]): In a glove box, a solution of Me_6trien (1 g, 4.34 mmol) in 10 mL of methanol was added, with stirring, to a suspension of CuCl (0.42 g, 4.34 mmol) in 10 mL of methanol. The solution turned slightly green and a small amount of red copper metal deposited. After filtration, diethyl ether was added to precipitate the complex. The white solid was filtered off and washed with diethyl ether. Drying in vacuum yielded 0.4 g (43%). – $Cu_2C_{12}H_{30}N_4Cl_2$: calcd. C 33.64, H 7.07, N 13.07; found C 33.89, H 7.14, N 13.13. Colorless crystals of **1**-[$CuCl_2$] were obtained from vapor diffusion of diethyl ether into a methanol solution of CuCl and Me_6trien.

[Cu(Me$_6$trien)Cl]ClO4 (4-Cl–ClO$_4$): To a solution of Me_6trien (1.152 g, 5 mmol) in 15 mL of methanol was added a solution of $CuCl_2 \times 2\ H_2O$ (0.42 g, 2.5 mmol) and $Cu(ClO_4)_2 \times 6\ H_2O$ (0.92 g, 2.5 mmol) in 20 mL of water. The solution was stirred for 15 minutes and filtered. After several days turquoise crystals formed suitable for X-ray analysis. Yield 1.4 g (65%). – $CuC_{12}H_{30}N_4Cl_2O_4$: calcd. C 33.61, H 7.05, N 13.06; found C 33.57, H 7.38, N 12.99.

[Cu(Me$_6$trien])(ClO$_4$)$_2$ [4-(ClO$_4$)$_2$]: To a solution of Me_6trien (0.576 g, 2.5 mmol) in 15 mL of methanol was added a solution of $Cu(ClO_4)_2 \times 6\ H_2O$ (0.92 g, 2.5 mmol) in 20 mL of water. Crystals immediately formed and more water was added, while heating the solution on a water bath, until most of the solid material was dissolved. After filtering the solution, deep blue crystals formed on standing for one day. Yield 0.65 g (50%). – $CuC_{12}H_{30}N_4Cl_2O_4 \times 1\ CH_3OH$: calcd. C 29.75, H 6.53, N 10.67; found C 29.67, H 6.52, N 10.93.

[Cu$_2$(Me$_4$en)$_2$(OH)$_2$](ClO$_4$)$_2$ (5): To a solution of Me_4en (1.16 g, 10 mmol) in 25 mL of methanol was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.92 g, 2.5 mmol) and $CuCl_2 \times 2\ H_2O$ (0.42 g, 2.5 mmol) in 25 mL of water. The solution was stirred for 10 min and filtered. Soon afterwards crystals began to form which were suitable for X-ray analysis. Yield 0.55 g (35%). – $Cu_2C_{12}H_{38}N_4Cl_2O_{12}$: calcd. C 22.93, H 6.09, N 8.92; found C 23.03, H 5.73, N 8.83.

X-ray Crystallographic Study: Crystal data and experimental conditions for **1**-[$CuCl_2$], **4**-Cl–ClO_4 and **5** × 2 H_2O are listed in Table 2. The molecular structures are illustrated in Figures 1, 3, and 4. Selected bond lengths and bond angles with standard deviations in parentheses are presented in Table 1. Intensity data were collected with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected reflections were corrected for Lorentz and polarization effects (but not for absorption). The structures were solved by direct methods [85,86] and refined by full matrix least squares methods on F^2.[85,87] Hydrogen atoms of **4**-Cl–ClO_4 were calculated for idealized geometries and allowed to ride on their preceding atoms, their isotropic displacement parameters were tied to those of the adjacent atoms by a factor of 1.5. For **1**-[$CuCl_2$] and **5** × 2

H_2O the positions of all hydrogen atoms were localized in a difference Fourier synthesis. The positions and a common isotropic displacement parameter were kept fixed during the refinement of **1**-[$CuCl_2$]. The high residual electron density of **1**-[$CuCl_2$] (3.426 e A^{-3}) is located near the copper atom (0.877 Å), and can be attributed to absorption effects. For **5** × 2 H_2O the positional parameters were refined with a fixed common isotropic displacement parameter. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-107373 (**1**-[$CuCl_2$]), –130856 (**4**-Cl–ClO_4), –130857 (**5** × 2 H_2O). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: int. code + 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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[1] N. Kitajima, *Adv. Inorg. Chem.* **1992**, *39*, 1–77.
[2] K. D. Karlin, Z. Tyeklár, *Bioinorganic Chemistry of Copper*; Chapman Hall, New York, **1993**.
[3] T. N. Sorrell, *Tetrahedron* **1989**, *45*, 3–68.
[4] N. Kitajima, Y. Moro-oka, *Chem. Rev.* **1994**, *94*, 737–757.
[5] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, L. J. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1994**, *116*, 9785–9786.
[6] S. Mahapatra, J. A. Halfen, E. C. Wilkinson, G. F. Pan, C. J. Cramer, L. Que, W. B. Tolman, *J. Am. Chem. Soc.* **1995**, *117*, 8865–8866.
[7] J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, L. Que, A. D. Zuberbühler, W. B. Tolman, *Science* **1996**, *271*, 1397–1400.
[8] L. Casella, M. Gullotti, G. Pallanza, L. Rigoni, *J. Am. Chem. Soc.* **1988**, *110*, 4221–4227.
[9] L. Casella, M. Gullotti, R. Radaelli, P. Di Gennaro, *J. Chem. Soc., Chem. Commun.* **1991**, 1611–1612.
[10] K. D. Karlin, M. S. Nasir, B. I. Cohen, R. W. Cruse, S. Kaderli, A. D. Zuberbühler, *J. Am. Chem. Soc.* **1994**, *116*, 1324–1336.
[11] K. D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus, A. Zuberbühler, D., *J. Am. Chem. Soc.* **1993**, *115*, 9506–9514.
[12] T. N. Sorrell, D. L. Jameson, *Inorg. Chem.* **1982**, *21*, 1014–1019.
[13] R. Menif, A. E. Martell, P. J. Squattrito, A. Clearfield, *Inorg. Chem.* **1990**, *29*, 4723–4729.
[14] O. J. Gelling, F. van Bolhuis, A. Meetsma, B. L. Feringa, *J. Chem. Soc., Chem. Commun.* **1988**, 552–554.
[15] W. B. Tolman, *Acc. Chem. Res.* **1997**, *30*, 227–237.
[16] D. Ghosh, T. K. Lal, S. Ghosh, R. Mukherjee, *Chem. Comm.* **1996**, 13–14.
[17] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 1277–1291.
[18] A. P. Cole, D. E. Root, P. Mukherjee, E. I. Solomon, T. D. P. Stack, *Science* **1996**, *273*, 1848–1850.
[19] J. Reim, B. Krebs, *Angew. Chem.* **1994**, *106*, 2040–2041, *Angew. Chem. Int. Ed. Engl.* 1969–1971.
[20] T. N. Sorrell, W. E. Allen, P. S. White, *Inorg. Chem.* **1995**, *34*, 952–960.
[21] J. E. Bol, W. L. Driessen, A. Y. N. Ho, B. Maase, L. Que, J. Reedijk, *Angew. Chem.* **1997**, *109*, 1022–1025, Angew. Chem. Int. Ed. Engl. 998–1000.
[22] H. Börzel, P. Comba, C. Katsichis, W. Kiefer, A. Lienke, V. Nagel, H. Pritzkow, *Chem. Eur. J.* **1999**, *5*, 1716–1721.
[23] K. D. Karlin, D.-H. Lee, S. Kaderli, A. D. Zuberbühler, *Chem. Comm.* **1997**, 475–476.
[24] J. Reedijk (Ed.), *Bioinorganic Catalysis*, 2nd ed., Marcel Dekker, New York, **1999**.
[25] R. A. Sheldon, *J. Mol. Catal., A: Chemical*, special ed., **1997**, vol. 117.
[26] M. Becker, F. W. Heinemann, S. Schindler, *Chem. Europ. J.* **1999**, *5*, 3124–3129.
[27] N. Jubran, H. Cohen, Y. Koresh, D. Meyerstein, *J. Chem. Soc., Chem. Commun.* **1984**, 1683–1684.
[28] M. Pasquali, C. Floriani, G. Venturi, A. G. Manfredotti, A. Chiesi-Villa, *J. Am. Chem. Soc.* **1982**, *104*, 4092–4099.
[29] G. Golub, H. Cohen, P. Paoletti, A. Bencini, L. Messori, I. Bertini, D. Meyerstein, *J. Am. Chem. Soc.* **1995**, *117*, 8353–8361.
[30] E. Kimura, T. Koike, M. Kodama, D. Meyerstein, *Inorg. Chem.* **1989**, *28*, 2998–3001.
[31] G. Golub, H. Cohen, D. Meyerstein, *J. Chem. Soc., Chem. Comm.* **1992**, 397–398.
[32] G. Golub, I. Zilbermann, H. Cohen, D. Meyerstein, *Supramolecular Chem.* **1996**, *6*, 275.
[33] G. Golub, A. Lashaz, H. Cohen, P. Paoletti, A. Bencini, B. Valtancoli, D. Meyerstein, *Inorg. Chim. Acta* **1997**, *255*, 111–115.
[34] D. Meyerstein, *Coord. Chem. Rev.* **1999**, *186*, 141–147.
[35] G. Golub, H. Cohen, P. Paoletti, A. Bencini, D. Meyerstein, *J. Chem. Soc., Dalton Trans.* **1996**, 2055–2060.
[36] S. Schindler, D. J. Szalda, C. Creutz, *Inorg. Chem.* **1992**, *31*, 2255–2264.
[37] M. Becker, S. Schindler, R. van Eldik, *Inorg. Chem.* **1994**, *33*, 5370–5371.
[38] S. Ryan, H. Adams, D. E. Fenton, M. Becker, S. Schindler, *Inorg. Chem.* **1998**, *37*, 2134–2140.
[39] S. Goldstein, G. Czapski, R. van Eldik, H. Cohen, D. Meyerstein, *J. Phys. Chem.* **1991**, *95*, 1282–1285.
[40] S. Schindler, C. D. Hubbard, R. van Eldik, *Chem. Soc. Rev.* **1998**, *27*, 387–393.
[41] M. Becker, S. Schindler, K. D. Karlin, T. A. Kaden, S. Kaderli, T. Palanché, A. D. Zuberbühler, *Inorg. Chem.* **1999**, 1989–1995.
[42] N. Navon, H. Cohen, R. van Eldik, D. Meyerstein, *J. Chem. Soc., Dalton Trans.* **1998**, 3663–3666.
[43] S. Andersson, S. Jagner, *Acta Chem. Scand.* **1986**, *A40*, 52–57.
[44] M. Asplund, S. Jagner, M. Nilson, *Acta Chem. Scand.* **1983**, *A37*, 57–62.
[45] L. Engelhardt, M., R. Papsergio, I., A. White, H., *Aust. J. Chem.* **1984**, *37*, 2207–2213.
[46] B. W. Skelton, A. F. Waters, A. White, H., *Aust. J. Chem.* **1991**, *44*, 1207–1215.
[47] M. J. Scott, R. H. Holm, *J. Am. Chem. Soc.* **1994**, *116*, 11357–11367.
[48] E. Spodine, J. Manzur, *Coord. Chem. Rev.* **1992**, *119*, 171–198.
[49] A. D. Zuberbühler in *Metal Ions in Biological Systems* (Ed.: H. Sigel), Marcel Dekker, New York, **1976**, vol. 5, p. 133–189.
[50] H. Gampp, A. Zuberbühler in *Metal Ions in Biological Systems* (Ed.: H. Sigel), Marcel Dekker, New York, **1981**, vol. 12, p. 133–189.
[51] M. Güntensperger, A. Zuberbühler, *Helv. Chim. Acta* **1977**, *60*, 2584–2593.
[52] L. Mi, A. D. Zuberbühler, *Helv. Chim. Acta* **1991**, *75*, 1679–1688.
[53] L. Mi, A. D. Zuberbühler, *Helv. Chim. Acta* **1992**, *75*, 1547–1556.
[54] M. Masarwa, H. Cohen, D. Meyerstein, D. L. Hickman, A. Bakac, J. H. Espenson, *J. Am. Chem. Soc.* **1988**, *110*, 4293–4297.
[55] S. Goldstein, G. Czapski, *Inorg. Chem.* **1985**, *24*, 1087–1092.
[56] K. D. Karlin, J. Zubieta (Eds.), *Copper Coordination Chemistry*, Adenine, New York, **1983**, p. 237–258.
[57] H. Gampp, A. Zuberbühler, *J. Mol. Catal.* **1980**, *7*, 81–88.
[58] H. Gampp, A. D. Zuberbühler, *Chimia* **1978**, *32*, 54–56.
[59] G. Rainoni, A. Zuberbühler, *Chimia* **1974**, *28*, 67–70.
[60] C. R. Andrew, K. P. McKillop, A. G. Sykes, *Biochim. Biophys. Acta* **1993**, *1162*, 105–114.
[61] H. D. Projahn, S. Schindler, R. van Eldik, D. G. Fortier, C. R. Andrew, A. G. Sykes, *Inorg. Chem.* **1995**, *34*, 5935–5941.
[62] R. W. Cruse, S. Kaderli, K. D. Karlin, A. D. Zuberbuehler, *J. Am. Chem. Soc.* **1988**, *110*, 6882–6883.

[63] J. S. Thompson, *J. Am. Chem. Soc.* **1984**, *106*, 8308–8309.
[64] G. Davies, M. A. El-Sayed, *Inorg. Chem.* **1983**, *22*, 1257–1266.
[65] G. Davies, M. A. El Sayed, *Comments Inorg. Chem.* **1985**, *4*, 151–162.
[66] G. Davies, M. A. El-Sayed, M. Henary, *Inorg. Chem.* **1987**, *26*, 3266–3273.
[67] M. A. El-Sayed, El-Toukhy, G. Davies, *Inorg. Chem.* **1985**, *24*, 3387–3390.
[68] M. A. El-Sayed, A. A. Abu-Raqabah, G. Davies, A. El-Toukhy, *Inorg. Chem.* **1989**, *28*, 1909–1914.
[69] M. A. El-Sayed, G. Davies, T. Kasem, S., *Inorg. Chem.* **1990**, *29*, 4730–4735.
[70] J. L. DuBois, P. Mukherjee, A. M. Collier, J. M. Mayer, E. I. Solomon, B. Hedman, T. D. P. Stack, K. O. Hodgson, *J. Am. Chem. Soc.* **1997**, *119*, 8578–8579.
[71] V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lal, E. I. Solomon, T. D. P. Stack, *J. Am. Chem. Soc.* **1997**, *119*, 11996–11997.
[72] P. V. Bernhardt, *J. Am. Chem. Soc.* **1997**, *119*, 771–774.
[73] G. Marongiu, E. C. Lingafelter, P. Paoletti, *Inorg. Chem.* **1969**, *8*, 2763–2767.
[74] T. G. Fawcett, S. M. Rudich, B. H. Toby, R. A. Lalancette, J. A. Potenza, H. J. Schugar, *Inorg. Chem.* **1980**, *19*, 940–945.
[75] M. Q. Ehsan, Y. Ohba, S. Yamauchi, M. Iwaizumi, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2201–2209.
[76] D. W. Meek, S. A. Ehrhardt, *Inorg. Chem.* **1965**, *4*, 584–587.
[77] C. Arcus, K. P. Fivizzani, S. F. Pavkovic, *J. Inorg. Nucl. Chem.* **1977**, *39*, 285–287.
[78] E. D. Estes, W. E. Estes, W. E. Hatfield, D. J. Hodgson, *Inorg. Chem.* **1975**, *14*, 106–109.
[79] D. H. Powell, A. E. Merbach, I. Fábián, S. Schindler, R. van Eldik, *Inorg. Chem.* **1994**, *33*, 4468–4473.
[80] R. Barbucci, G. Paoletti, G. Ponticelli, *J. Chem. Soc. A* **1971**, 1637–1640.
[81] R. N. Icke, B. B. Wisegarver, G. A. Alles, H. R. Snyder, *Org. Synth. Coll. Vol.* **1941**, *3*, 723.
[82] M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41–44.
[83] G. J. Kubas, B. Monzyk, A. L. Crumbliss, *Inorg. Synth.* **1979**, *19*, 90–92.
[84] R. N. Keller, H. D. Wzcoff, *Inorg. Synth.* **1946**, *2*, 1–4.
[85] *SHELXTL 5.03 for Siemens Crystallographic Research Systems*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, **1995**.
[86] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1992**, *22*, 389–393.
[87] G. M. Sheldrick, *SHELXL-92*, Univ. of Göttingen, **1992**.
[88] H. D. Flack, *Acta Crystallogr.* **1983**, *A39*, 876.

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