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Stabilization of a copper peroxido complex with a new binucleating ligand§

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The ligand L^1 (N1,N3-di[2-di(2-pyridylmethyl)aminoethyl]N1,N3-dimethyl-1,3-propandiamine) bridges two tripodal units of the amine ligand Me₂uns-penp (N1,N1-dimethyl-N2,N2-di(2-pyridylmethyl)-1,2-ethandiamine) with a propyl group. The ligand L^1 , the dinuclear copper(I) complex $[Cu_2(L^1)](BPh_4)_2$ and the dinuclear copper(II) complexes $[Cu_2Cl_2(L^1)](ClO_4)_2$, and $Cu_2Cl_2(L^1)Cl_2$ have been synthesized and structurally characterized. The copper(I) complex reacts reversibly with dioxygen at low temperatures and forms a peroxido complex that is thermally more stable than the related peroxido complex formed from two mononuclear copper(I) complexes of the ligand Me₂uns-penp.

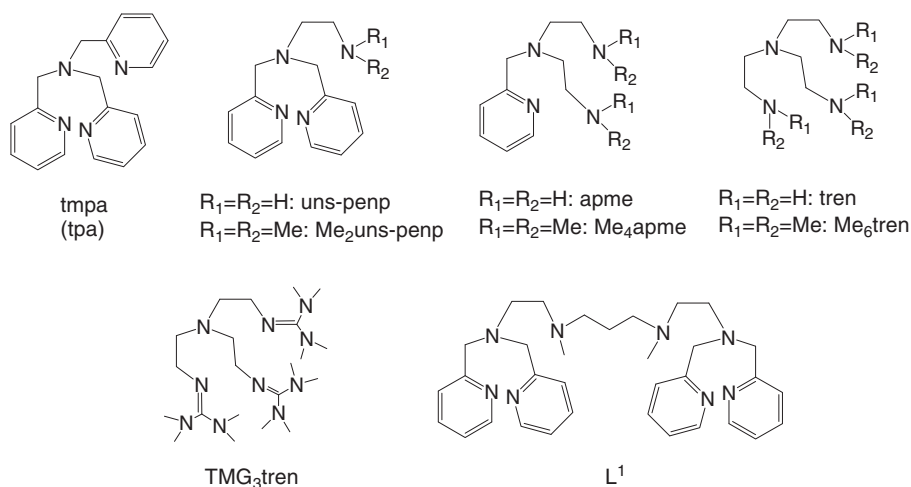
Keywords: Copper; X-ray crystallography; Peroxido complexes; Low-temperature stopped-flow studies; Tripodal tetradentate ligand

1. Introduction

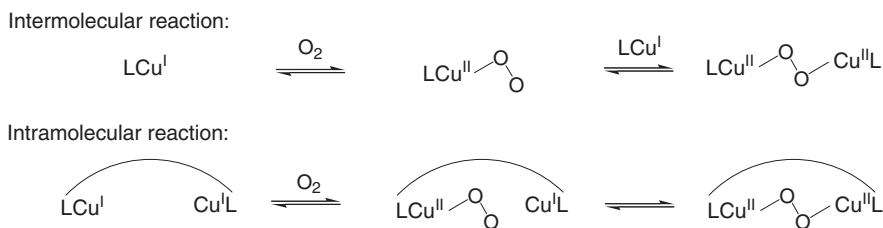
Copper(I) complexes with tetradentate tripodal ligands [1] have been used successfully in the past to model the reactivity of redox active copper enzymes toward dioxygen [2–5]. Based on the original work by Karlin and co-workers [6–12] who used tris[(2-pyridyl)-methyl]amine (tmpa, also abbreviated as tpa in iron coordination chemistry; scheme 1) to crystallographically characterize a binuclear copper peroxido complex for the first time, we applied the parental amine tris(amino-ethyl)amine (tren, scheme 1) and its derivatives as ligands in our study. One of the advantages of tren is the facile modification of this ligand. This allowed us to synthesize and fully characterize the first model complex for the end-on binding of dioxygen in the monooxygenase peptidylglycine alpha-hydroxylating monooxygenase (PHM) using the tren derivative TMG₃tren (scheme 1) [13–15]. Modeling the active site of redox active copper enzymes is not only interesting in regard to better understanding of the biochemical reaction mechanisms, but also for the possible application of such low-molecular weight

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§Dedicated to Prof Rudi van Eldik on the occasion of his 65th birthday.



Scheme 1. Ligands discussed in the text.

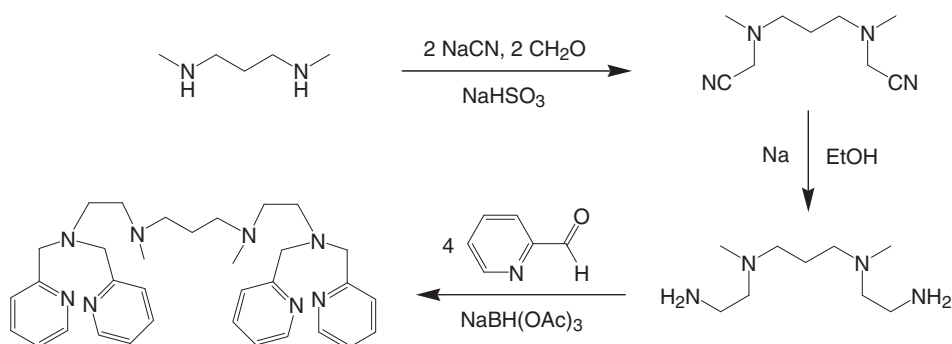


Scheme 2. Intermolecular vs. intramolecular reaction of copper(I) complexes with dioxygen.

complexes in selective oxidation of organic substrates [16]. This functional modeling would allow stoichiometric or catalytic oxidation reactions using dioxygen as an oxidant. Recent results in this field achieved by us, as well as by Karlin and co-workers, prove the successful approach we have adopted. A series of dinuclear copper peroxido complexes with tetradentate ligands such as tmpa or Me₆tren could be used to oxidize toluene to benzaldehyde [7, 17].

Due to the fact that pure aliphatic amines as ligands for copper(I) ions can cause facile disproportionation reactions [2, 9], we also investigated ligands in which the pyridyl-arms were systematically replaced by amine arms. Thus, leading from tmpa to uns-penp, apme and finally to tren (scheme 1) [7, 8]. During the kinetic analysis of the reactivity of dioxygen toward the copper(I) complexes with these ligands, we had indications that the copper peroxido complex with Me₂uns-penp seemed to be surprisingly stable [8].

It is well known that such complexes form in a two-step reaction according to scheme 2 (intermolecular reaction) [8, 11, 12]. In the first-step the end-on superoxido complex (described above) is formed; however, quite often this species cannot be detected. In a second step, the binuclear peroxido complex is formed in a reaction



Scheme 3. Ligand synthesis.

between the superoxido and the copper(I) complex. The formed peroxido complexes are usually only stable at low temperatures and readily decompose at room temperature. However, we recently found a way to successfully stabilize some of these complexes [7].

In the past, different groups have shown that stabilization of binuclear copper peroxido complexes can be achieved when a preorganized complex system is used. Here, binucleating ligands were used that allow intramolecular formation of the peroxido complexes, thus avoiding the necessity of two complexes having to undergo an intermolecular reaction (intramolecular reaction in scheme 2) [18–21].

In regard to these findings it seemed obvious to connect two uns-penp ligand units to a new binuclear ligand and to investigate the reactivity of its copper(I) complex toward dioxygen. As protons in amines can lead to the formation of hydrogen peroxide and therefore excluding the possibility to observe the copper dioxygen adduct intermediate complexes, we usually use the methylated forms of the amines (Me₆tren, Me₄apme, Me₂uns-penp, and scheme 1) [2, 9]. Thus, we synthesized the new ligand L¹ (scheme 1) that can be regarded as a connected Me₂uns-penp system. Herein we describe the copper complexes with this ligand and the reactivity of the copper(I) L¹ complex toward dioxygen in comparison to the copper(I) complex of Me₂uns-penp.

2. Experimental

2.1. General

Preparation and handling of air-sensitive compounds was carried out in a glove box filled with argon (MBraun, Garching, Germany; water, and dioxygen <0.1 ppm). Synthesis and characterization of the copper complex [Cu(CH₃CN)]ClO₄ and the ligand Me₂uns-penp are described elsewhere [7, 22, 23]. Caution: Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

2.2. Syntheses

L¹ was prepared in a three-step reaction (scheme 3) according to published procedures with slight modifications [22, 24].

2.2.1. [NCCH₂N(Me)CH₂]₂CH₂. Sodium metabisulfite (4.75 g, 0.05 mol) was dissolved in water (10 mL) and 37% aqueous formaldehyde (3.5 mL) was added. The solution was boiled for 10 min, then cooled to room temperature, and *N,N'*-dimethyl-1,3-diaminopropane (2.35 g, 0.023 mol) was added under vigorous stirring. After 4 h, a solution of sodium cyanide (2.55 g, 0.052 mol) in water (5 mL) was added. The mixture was left to stir overnight and further extracted with diethyl ether (3 × 20 mL). The combined extracts were dried with anhydrous sodium sulfate, filtered and the solvent removed with a rotary evaporator to leave a yellow oil. Yield: 83.2% (3.45 g, 0.019 mol); ¹H-NMR (400 MHz, CDCl₃/TMS, δ/ppm): 1.62 (q, 2H-CH₂-CH₂-CH₂-); 2.36 (s, 6H-CH₃); 2.51 (t, 4H-N-CH₂-CH₂-); 3.53 (s, 4H-N-CH₂-CN); ¹³C-NMR (100 MHz, CDCl₃/TMS, δ/ppm): 25.32 (-CH₂-CH₂-CH₂-); 41.92(-CH₃); 45.37 (-N-CH₂-C≡N); 53.30 (-N-CH₂-CH₂-); 114.61 (-C≡N).

2.2.2. [H₂NCH₂CH₂N(Me)CH₂]₂CH₂. A slurry of [NCCH₂N(Me)CH₂]₂CH₂ (3.4 g, 0.019 mol) in ethanol (38 mL) was stirred under argon while adding small pieces of sodium metal (3.0 g, 0.13 mol) over a period of 1.5 h. The mixture was heated to 75°C for 4 h, and after cooling to room temperature, water (40 mL) was added. The product was extracted with dichloromethane (3 × 30 mL). The combined extracts were dried with anhydrous sodium sulfate, filtered and the solvent removed with a rotary evaporator to leave a pale yellow oil. The product was further distilled in vacuum to give a colorless oil. Yield: 26.3% (0.94 g, 0.005 mol); ¹H-NMR (400 MHz, CDCl₃/TMS, δ/ppm): 1.64 (q, 2H-CH₂-CH₂-CH₂-); 2.21 (s, 6H-CH₃); 2.37 (t, 4H-N-CH₂-CH₂-); 2.41 (t, 4H-N-CH₂-CH₂-NH₂); 2.76 (t, 4H-N-CH₂-CH₂-NH₂); ¹³C-NMR (100 MHz, CDCl₃/TMS, δ/ppm): 25.14 (-CH₂-CH₂-CH₂-); 39.55(-CH₃); 42.13 (CH₂-CH₂-NH₂); 55.85 (-N-CH₂-CH₂-); 60.57 (-N-CH₂-CH₂-NH₂).

2.2.3. Preparation of L¹. To a solution of [H₂NCH₂CH₂N(Me)CH₂]₂CH₂ (0.9 g, 0.0048 mol) and 2-pyridinecarboxaldehyde (2.14 g, 0.02 mol) in 1,2-dichloroethane (40 mL), NaBH(OAc)₃ (5.3 g, 0.025 mol) was added and the cloudy solution was stirred at room temperature for 3 h. The reaction was quenched by addition of an aqueous solution of NaOH (20 mL, 2 mol L⁻¹). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 100 mL). The organic fractions were combined and washed with a saturated aqueous solution of NaCl (100 mL). The organic fractions were dried with anhydrous sodium sulfate, filtered and the solvent removed with a rotary evaporator to leave a golden-colored oil. Yield: 88.9% (2.35 g, 0.0043 mol); ¹H-NMR (400 MHz, CDCl₃/TMS, δ/ppm): 1.54 (q, 2H-CH₂-CH₂-CH₂-); 2.13 (s, 6H-CH₃); 2.26 (t, 4H-N-CH₂-CH₂-); 2.53 (t, 4H-N-CH₂-CH₂-); 2.69 (t, 4H-N-CH₂-CH₂-); 3.85 (s, 8H-N-CH₂-Pyr); 7.12 (dt, 4H Pyr); 7.53 (d, 4H Pyr); 7.63 (dt, 4H Pyr); 8.51 (dd, 4H Pyr); ¹³C-NMR (100 MHz, CDCl₃/TMS, δ/ppm): 24.89 (-CH₂-CH₂-CH₂-); 42.31(-CH₃); 52.04 (-N-CH₂-CH₂-); 55.59 (-N-CH₂-CH₂-); 55.83 (-N-CH₂-CH₂-); 60.77 (-N-CH₂-Pyr); 121.77 (Pyr); 122.88 (Pyr); 135.21 (Pyr); 148.88 (Pyr); 159.81 (Pyr); IR (Film, $\tilde{\nu}$ /cm⁻¹): 3063/3009 ν (C-H Pyr); 2958 ν (C-H CH₂/CH₃); 2805 ν (C-N amine); 1590/1569 ν (C=C Pyr); 1473/1433 ν (C=N Pyr); 1147/1124/1047/994 ν (C-N amine); 761 δ (C-N Pyr); SF-MS (*m/z*): 552 [C₃₃H₄₄N₈]⁺.

2.2.4. [Cu(Me₂uns-penp)]BPh₄. [Cu(CH₃CN)]ClO₄ (0.28 g, 0.85 mmol) was dissolved in a methanol-acetone mixture (5 mL : 1 mL) containing Me₂uns-penp (0.25 g, 0.93 mmol), to which a methanol solution (5 mL) of NaBPh₄ (0.55 g, 1.6 mmol) was added. The complex [Cu(Me₂uns-penp)]BPh₄ precipitated as a yellow solid. The solid was filtered and dried in vacuum for 2 h, yielding 89% (0.49 g, 0.76 mmol) of the product.

2.2.5. [Cu₂(L¹)](BPh₄)₂. [Cu(CH₃CN)]ClO₄ (0.28 g, 0.85 mmol) was dissolved in a methanol-acetone mixture (5 mL : 1 mL) containing L¹ (0.25 g, 0.45 mmol), to which a methanol solution (5 mL) of NaBPh₄ (0.55 g, 1.6 mmol) was added. The complex [Cu₂(L¹)](BPh₄)₂ was precipitated as a yellow solid. The solid was filtered and dried in vacuum for 2 h, yielding 59% (0.33 g, 0.25 mmol) of the product. X-ray quality crystals of this compound were obtained by ether diffusion into an acetone solution.

2.2.6. [Cu₂Cl₂(L¹)](ClO₄)₂·H₂O. To a solution of L¹ (0.1 g, 0.18 mmol) in methanol (1 mL) a solution of CuCl₂·2H₂O (0.031 g, 0.18 mol) and Cu(ClO₄)₂·6H₂O (0.066 g, 0.018 mol) in water (1 mL) was added. The resulting solution was allowed to stand for a few days to give blue crystals.

2.2.7. [Cu₂Cl₂(L¹)]Cl₂·9H₂O. CuCl₂·2H₂O (0.062 g, 0.36 mmol) and L¹ (0.1 g, 0.18 mmol) were dissolved in a small amount of water (1 mL). The dark-green complex solution was stirred for 5 min, filtered and purified by column chromatography (Sephadex-SP C25 40–120μ) with a sodium chloride solution (0.3 mol L⁻¹). X-ray quality crystals of [Cu₂Cl₂(L¹)]Cl₂·9H₂O were obtained by slow evaporation of the aqueous complex solution.

2.3. Physical measurements

2.3.1. NMR-spectroscopy. ¹H-NMR spectra were recorded on a Bruker AM400WB spectrometer at 298 K in 5 mm NMR tubes. The chemical shifts (δ) were obtained in deuterated solutions using TMS as an internal reference.

2.3.2. MS experiments. Measurements with the ligand were performed using a Finnigan MAT 95 double focusing sector field mass spectrometer.

2.3.3. Low-temperature stopped-flow studies. Time-resolved UV-Vis spectra of the reaction of these tripodal copper(I) complexes with dioxygen were performed using a Hi-Tech Scientific stopped-flow unit (SF-61SX2) with a 2 mm path length cell, equipped with a diode array spectrometer. Details on our low-temperature stopped-flow measurements have been described previously [8, 11].

2.3.4. Crystal structure analyses. The X-ray crystallographic data for [Cu₂Cl₂(L¹)](ClO₄)₂·H₂O were collected on a STOE IPDS diffractometer equipped with a low-temperature system (Karlsruher Glastechnisches Werk). No absorption

corrections were applied. X-ray data for $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ and $[\text{Cu}_2\text{Cl}_2(\text{L}^1)]\text{Cl}_2 \cdot 9\text{H}_2\text{O}$ were collected on a Nonius KappaCCD diffractometer. An empirical absorption correction was applied. For all measurements, Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) and a graphite monochromator were used. Single crystals were coated with polyfluoroether oil and mounted onto a glass fiber. The structures were solved by direct methods and refined by full-matrix least squares using the SHELX-program package [25]. All non-hydrogen atoms were refined anisotropically, all C–H hydrogens were positioned geometrically and the O–H hydrogens of solvent water were found and isotropically refined.

3. Results and discussion

3.1. Synthesis and characterization

The ligand Me₂uns-penp and its copper(I)/(II) complexes have been described previously [8, 22]. The copper(I) complex of Me₂uns-penp was prepared for this study with tetraphenylborate as an anion and was used only for our comparative studies on the formation of binuclear copper peroxido complexes. A more detailed mechanistic analysis on the reaction of dioxygen with $[\text{Cu}(\text{Me}_2\text{uns-penp})]\text{PF}_6$ has been reported in our previous study on this system [8].

According to scheme 3, the new ligand N1,N3-di[2-di(2-pyridylmethyl)aminoethyl]N1,N3-dimethyl-1,3-propandiamine (L^1) could be prepared in acceptable yields similar to slightly modified already published procedures for related compounds [8, 22, 24]. As discussed in section 1, L^1 is a pre-organized ligand, based on the tripodal ligand Me₂uns-penp [8]. Preliminary theoretical calculations and previous results based on the tmpa system made us think that the propyl group in L^1 should be an ideal spacer in regard to flexibility and distance, and thus should support intramolecular formation of a quite stable binuclear copper peroxido complex.

When we reacted copper(I) salts with L^1 in solution, we expected to isolate the binuclear complex $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ with the two copper(I) ions coordinated to each tripodal ligand unit and an additional acetonitrile molecule as a co-ligand. While in solution this expectation is not unlikely (see below), in the solid state a surprising result was obtained. Crystals of $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ suitable for X-ray analysis were obtained by ether diffusion into an acetone solution of the yellow precipitate that was formed during synthesis. The molecular structure of this complex is shown in figure 1 and a summary of the crystallographic data and refinement parameters are presented in table 1. Selected bond lengths and angles are listed in table 2.

In contrast to our expectations, the copper(I) atoms are not located in the separated tripodal units. Instead, one of the copper(I) atoms is coordinated in a distorted tetrahedral geometry by one aliphatic and two pyridine N-donors of one tripodal unit, as well as by a pyridine N-donor of the second tripodal unit. The other copper(I) is in a distorted tetrahedral environment and coordinated by one pyridine and three aliphatic N-donors, two from the same and one of the other tripodal unit. The crystal structure includes two non-coordinated tetraphenylborate anions. Instead of bridging the two units here the propyldiamine is coordinated directly to one copper(I). That we obtained such a species was not completely unexpected, because such ligand rearrangements were

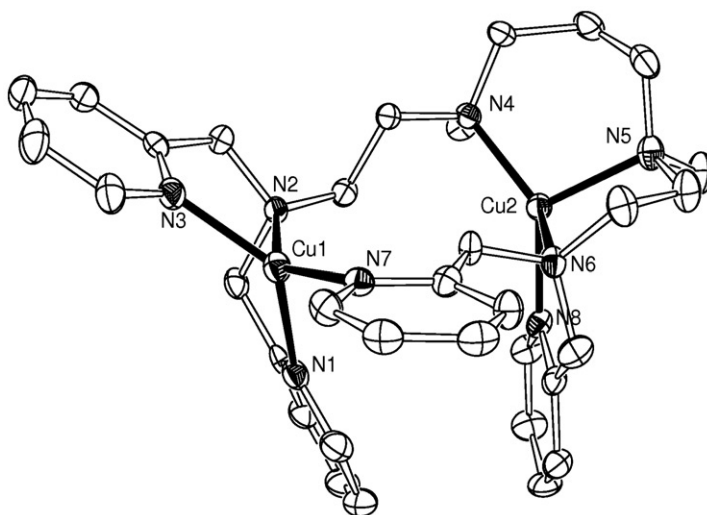


Figure 1. Molecular structure of the cation of $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$. ORTEP plot with thermal ellipsoids set at 50% probability (hydrogens and tetraphenylborate are not shown).

Table 1. Crystal data for the Cu(I) and Cu(II) complexes of L^1 .

	$[\text{Cu}_2(\text{L}^1)](\text{B}(\text{C}_6\text{H}_5)_4)_2$	$[\text{Cu}_2\text{Cl}_2(\text{L}^1)](\text{Cl})_2 \cdot 9\text{H}_2\text{O}$	$[\text{Cu}_2\text{Cl}_2(\text{L}^1)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
Empirical formula	$\text{C}_{81}\text{H}_{84}\text{B}_2\text{Cu}_2\text{N}_8$	$\text{C}_{33}\text{H}_{62}\text{Cl}_4\text{Cu}_2\text{N}_8\text{O}_9$	$\text{C}_{33}\text{H}_{46}\text{Cl}_4\text{Cu}_2\text{N}_8\text{O}_9$
Formula weight	1318.26	983.79	967.66
Temperature (K)	100(2)	100(2)	193(2)
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$Fdd2$	$P\bar{1}$
Unit cell dimensions (\AA , $^\circ$)			
<i>a</i>	13.345(2)	60.291(7)	11.316(2)
<i>b</i>	13.759(2)	14.566(2)	12.734(3)
<i>c</i>	18.580(1)	20.562(3)	15.717(3)
α	93.537(7)	90	113.43(3)
β	91.088(6)	90	100.38(3)
γ	96.549(9)	90	95.66(3)
Volume (\AA^3), <i>Z</i>	3381.7(7), 2	18058(4), 16	2007.5(7), 2
Calculated density (Mg m^{-3})	1.295	1.447	1.601
Absorption coefficient, μ (mm^{-1})	0.681	1.235	1.388
<i>F</i> (000)	1388	8224	996
Crystal size (mm^3)	$0.25 \times 0.15 \times 0.10$	$0.35 \times 0.23 \times 0.05$	$0.6 \times 0.32 \times 0.16$
θ range for data collection ($^\circ$)	3.30–26.37	3.30–26.37	2.69–28.15
Limiting indices	$-16 \leq h \leq 16$; $-17 \leq k \leq 17$; $-23 \leq l \leq 23$	$-74 \leq h \leq 75$; $-18 \leq k \leq 18$; $-25 \leq l \leq 25$	$-14 \leq h \leq 14$; $-16 \leq k \leq 16$; $-20 \leq l \leq 20$
Reflections collected	64816	40396	18082
Independent reflections	13803 [$R(\text{int}) = 0.1408$]	9056 [$R(\text{int}) = 0.0387$]	8869 [$R(\text{int}) = 0.0460$]
Absorption correction	Semi-empirical	Semi-empirical	None
Data/restraints/parameters	13803/0/840	9056/19/586	8869/16/546
Goodness-of-fit on F^2	1.041	1.356	0.948
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0568$, $wR_2 = 0.1248$	$R_1 = 0.0496$, $wR_2 = 0.1202$	$R_1 = 0.0418$, $wR_2 = 0.1188$
Largest difference peak and hole (e \AA^{-3})	0.456 and -0.532	1.021 and -0.565	0.654 and -0.853

Table 2. Selected bond distances (Å) and angles (°) for the Cu(I) and Cu(II) complexes of L¹.

[Cu ₂ (L ¹)](B(C ₆ H ₅) ₄) ₂		[Cu ₂ Cl ₂ (L ¹)](Cl) ₂ · 9H ₂ O		[Cu ₂ Cl ₂ (L ¹)](ClO ₄) ₂ · H ₂ O	
Cu(1)–N(1)	2.047(3)	Cu(1)–N(1)	2.042(4)	Cu(1)–N(2)	1.990(3)
Cu(1)–N(2)	2.406(3)	Cu(1)–N(2)	2.036(4)	Cu(1)–N(3)	2.004(3)
Cu(1)–N(3)	1.995(3)	Cu(1)–N(3)	2.113(4)	Cu(1)–N(1)	2.064(3)
Cu(1)–N(7)	2.018(3)	Cu(1)–N(4)	2.102(4)	Cu(1)–N(4)	2.304(3)
Cu(2)–N(4)	2.025(3)	Cu(1)–Cl(1)	2.253(2)	Cu(2)–N(5)	2.037(3)
Cu(2)–N(5)	2.100(3)	Cu(2)–N(5)	2.189(4)	Cu(2)–N(6)	2.047(3)
Cu(2)–N(6)	2.291(3)	Cu(2)–N(6)	2.039(4)	Cu(2)–N(7)	2.127(3)
Cu(2)–N(8)	1.973(3)	Cu(2)–N(7)	2.043(4)	Cu(2)–N(8)	2.130(3)
N(1)–Cu(1)–N(2)	78.8(2)	Cu(2)–N(8)	2.091(4)	Cu(1)–Cl(1)	2.2561(10)
N(1)–Cu(1)–N(3)	125.4(2)	Cu(2)–Cl(2)	2.237(2)	Cu(2)–Cl(2)	2.2408(14)
N(1)–Cu(1)–N(7)	104.6(2)	N(1)–Cu(1)–N(2)	81.2(2)	N(2)–Cu(1)–N(3)	157.87(11)
N(2)–Cu(1)–N(3)	77.3(2)	N(1)–Cu(1)–N(3)	116.1(2)	N(2)–Cu(1)–N(1)	83.96(12)
N(2)–Cu(1)–N(7)	140.0(2)	N(1)–Cu(1)–N(4)	132.6(2)	N(3)–Cu(1)–N(1)	80.89(12)
N(3)–Cu(1)–N(7)	124.6(2)	N(1)–Cu(1)–Cl(1)	98.0(2)	N(2)–Cu(1)–Cl(1)	97.69(8)
N(4)–Cu(2)–N(5)	106.0(2)	N(2)–Cu(1)–N(3)	81.0(2)	N(3)–Cu(1)–Cl(1)	95.86(9)
N(4)–Cu(2)–N(6)	125.7(2)	N(2)–Cu(1)–N(4)	86.3(2)	N(1)–Cu(1)–Cl(1)	174.00(8)
N(4)–Cu(2)–N(8)	132.5(2)	N(2)–Cu(1)–Cl(1)	178.9(2)	N(2)–Cu(1)–N(4)	92.07(11)
N(5)–Cu(2)–N(6)	84.2(2)	N(3)–Cu(1)–N(4)	106.5(2)	N(3)–Cu(1)–N(4)	102.54(11)
N(5)–Cu(2)–N(8)	116.2(2)	N(3)–Cu(1)–Cl(1)	98.6(2)	N(1)–Cu(1)–N(4)	85.04(11)
N(6)–Cu(2)–N(8)	80.6(2)	N(4)–Cu(1)–Cl(1)	94.7(2)	Cl(1)–Cu(1)–N(4)	100.64(8)
		N(5)–Cu(2)–N(6)	85.3(2)	N(5)–Cu(2)–N(6)	81.81(11)
		N(5)–Cu(2)–N(7)	124.2(2)	N(5)–Cu(2)–N(7)	81.11(12)
		N(5)–Cu(2)–N(8)	103.3(2)	N(6)–Cu(2)–N(7)	118.36(11)
		N(5)–Cu(2)–Cl(2)	97.5(2)	N(5)–Cu(2)–N(8)	84.93(11)
		N(6)–Cu(2)–N(7)	81.5(2)	N(6)–Cu(2)–N(8)	130.72(11)
		N(6)–Cu(2)–N(8)	81.0(2)	N(7)–Cu(2)–N(8)	105.95(11)
		N(6)–Cu(2)–Cl(2)	176.3(2)	N(5)–Cu(2)–Cl(2)	178.03(8)
		N(7)–Cu(2)–N(8)	127.2(2)	N(6)–Cu(2)–Cl(2)	96.75(8)
		N(7)–Cu(2)–Cl(2)	98.6(2)	N(7)–Cu(2)–Cl(2)	98.45(9)
		N(8)–Cu(2)–Cl(2)	95.9(2)	N(8)–Cu(2)–Cl(2)	97.03(8)

observed previously by us and others for related mononuclear copper(I) complexes [26–32].

The isolation and characterization of copper peroxido complexes is often quite difficult and in many cases these complexes cannot be prepared, because they decompose even at very low temperatures. To still get an idea what such a complex looks like, simple copper(II) complexes have been prepared in the past [2, 9]. Usually, facile preparation of the copper(II) complexes using chloride as an additional coordinating ligand is already satisfying [7, 9]. Thus, L¹ reacted with a mixture of copper(II) perchlorate and copper(II) chloride. Perchlorate ions help form suitable crystals for crystallographic characterization. As expected we obtained the binuclear complex [Cu₂Cl₂(L¹)](ClO₄)₂. The molecular structure of its cation is shown in figure 2. The summary of the crystallographic data, refinement parameters and selected bond lengths and angles are given in tables 1 and 2.

In contrast to the copper(I) complex, the two copper(II) ions are located in the two separated tripodal units of the ligand, coordinated by two aliphatic, two pyridine N-donors and one chloride. The coordination geometry of the two copper(II) ions is slightly different. One has a trigonal bipyramidal coordination with a τ parameter of 0.79. The τ -value is a geometric factor introduced to coordination chemistry by Addison *et al.* [33]. Its value can lie between 0 (perfect square pyramidal coordination)

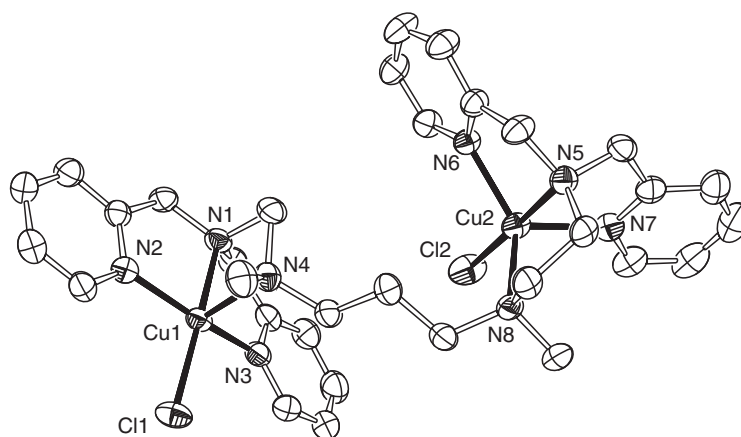


Figure 2. Molecular structure of the cation of $[\text{Cu}_2\text{Cl}_2(\text{L}^1)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. ORTEP plot with thermal ellipsoids set at 50% probability (hydrogens, solvent water, and perchlorate are not shown).

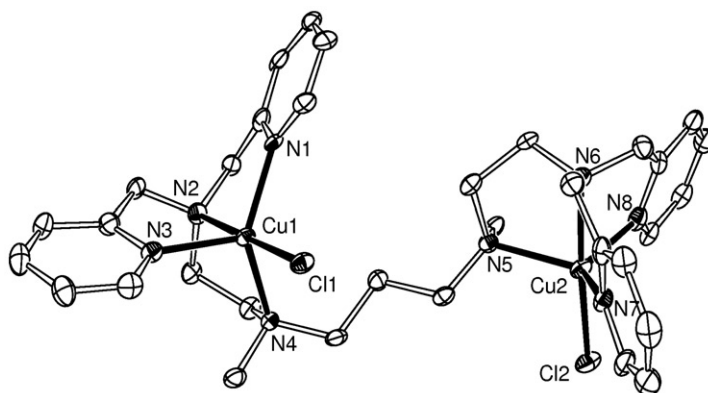


Figure 3. Molecular structure of the cation of $[\text{Cu}_2\text{Cl}_2(\text{L}^1)]\text{Cl}_2 \cdot 9\text{H}_2\text{O}$. ORTEP plot with thermal ellipsoids set at 50% probability (hydrogens, solvent water, and chlorides are not shown).

and 1 (perfect trigonal bipyramidal coordination). The other copper(II) ion has a square pyramidal geometry ($\tau = 0.27$), just as in the mononuclear copper(II) complexes $[\text{CuCl}(\text{Me}_2\text{uns-penp})]\text{ClO}_4$ and $[\text{CuCl}(\text{Me}_2\text{uns-penp})]\text{BPh}_4$ described previously [8, 10]. The crystal structure includes two non-coordinated perchlorates and one solvent water. The molecular structure of $[\text{Cu}_2\text{Cl}_2(\text{L}^1)](\text{ClO}_4)_2$ shows that in principle an intramolecular peroxido complex could form.

Furthermore, we succeeded in isolation and structural characterization of $[\text{Cu}_2\text{Cl}_2(\text{L}^1)](\text{Cl})_2$. The molecular structure of this complex is shown in figure 3. The crystallographic data and refinement parameters can be found in table 1; selected bond lengths and angles are reported in table 2.

The coordination geometry of both copper(II) ions can be best described as trigonal bipyramidal. Each copper ion is coordinated by two aliphatic, two pyridine N-donors and one chloride. The structural index parameters τ are 0.82 and 0.77. The crystal

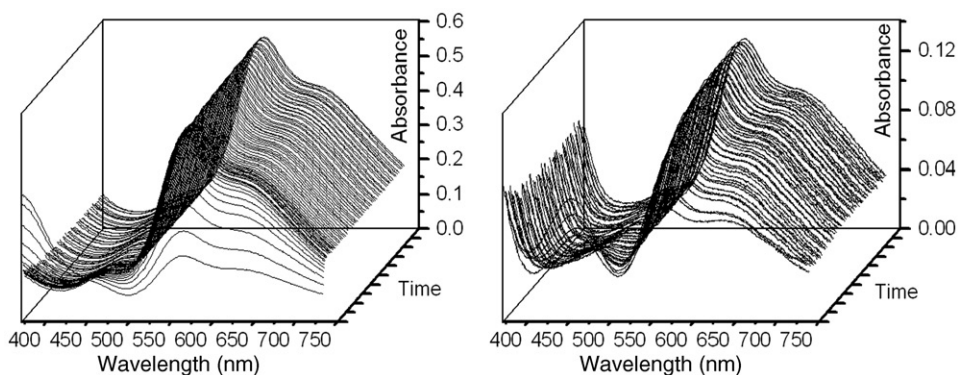


Figure 4. Time-resolved spectra for reaction of $[\text{Cu}_2(\text{L}^1)]^{2+}$ (left side) and $[\text{Cu}(\text{Me}_2\text{uns-penp})]^+$ (right side) with dioxygen in acetone at -39.1°C ($[\text{complex}] = 1.7 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{O}_2] = 1 \times 10^{-4} \text{ mol L}^{-1}$, total time = 0.1 s for $[\text{Cu}_2(\text{L}^1)]^{2+}$ and 0.6 s for $[\text{Cu}(\text{Me}_2\text{uns-penp})]^+$, integrations time = 0.002 s, and number of scans = 300 for $[\text{Cu}_2(\text{L}^1)]^{2+}$ and 50 for $[\text{Cu}(\text{Me}_2\text{uns-penp})]^+$).

structure includes two non-coordinated chlorides and nine solvent waters. The molecular structure of $[\text{Cu}_2\text{Cl}_2(\text{L}^1)]\text{Cl}_2$ is interesting because it demonstrates that additional, comparably strong ligands – the chlorides – do not bind once the coordination environment of the copper(II) is satisfied. It would not have been surprising if one donor arm of L^1 had been replaced by the counter ions present. Thus, it is clear that L^1 forms a quite stable copper(II) complex.

3.2. Reactivity of the binuclear copper(I) complex toward dioxygen

To investigate whether the binuclear copper(I) complex $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ forms a more stable peroxido complex compared to its mononuclear counterpart $[\text{Cu}(\text{Me}_2\text{uns-penp})]\text{BPh}_4$, we performed low-temperature stopped-flow studies with both complexes. $[\text{Cu}(\text{Me}_2\text{uns-penp})]\text{BPh}_4$ reacted with dioxygen in the same way as described previously for the same reaction using $[\text{Cu}(\text{Me}_2\text{uns-penp})]\text{PF}_6$. No influence of the different anions was observed. Time-resolved UV-Vis spectra for this reaction are shown on the right side of figure 4. In a very fast reaction, and according to scheme 2, the superoxide intermediate was formed as an unstable transient intermediate in a first step. In the spectra of figure 4, only its very fast decomposition reaction can be observed (decrease of the absorbance maximum at 410 nm), followed by formation of the expected peroxido complex, the second step in scheme 2 (with an increase in the absorbance maximum at 550 nm).

In contrast, the reaction of $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ with dioxygen immediately shows a very fast reaction to form the peroxido complex. Time-resolved UV-Vis spectra are shown on the left side of figure 4. No spectroscopic signature of a superoxido complex could be observed under the same reaction conditions as for $[\text{Cu}(\text{Me}_2\text{uns-penp})]\text{BPh}_4$ (only an increase in the absorbance maximum of the peroxido complex is observed). In principle, this is not unexpected and had been observed previously for other binuclear copper systems with a preorganized ligand [3–5, 20]. In a preorganized complex the rate determining step is the binding of dioxygen. Once it is bound, it will be immediately coordinated to the second copper ion in a much faster consecutive step. Therefore, only

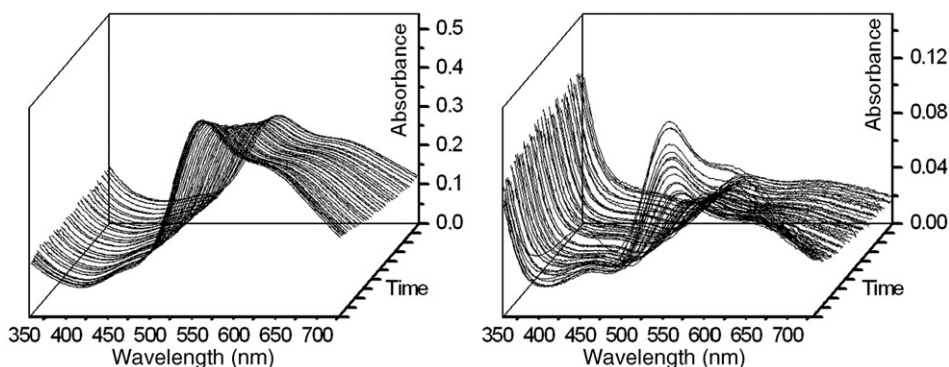


Figure 5. Time-resolved spectra for reaction of $[\text{Cu}_2(\text{L}^1)]^{2+}$ (left side) and $[\text{Cu}(\text{Me}_2\text{uns-penp})]^+$ (right side) with dioxygen in acetone at -6.3°C ($[\text{complex}] = 1.7 \times 10^{-4} \text{ mol L}^{-1}$, $[\text{O}_2] = 1 \times 10^{-4} \text{ mol L}^{-1}$, total time = 40 s, integrations time = 0.002 s, and number of scans = 200).

the spectroscopic signature of the final product complex is visible. However, for $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ this reactivity was not obvious, because of its crystal structure reported above, offering alternative possible reaction pathways. The results from our measurements, however, demonstrate that this complex is – at least partially – the preorganized copper(I) complex in solution we wanted to prepare. Otherwise, we should have been able to observe at least traces of the formation of a superoxido complex.

From the spectral comparison in figure 4 we could not detect whether we actually stabilized the formed peroxido complex. Nevertheless, this could be investigated at higher temperatures. A comparison of the two complexes is shown in figure 5. Looking at the right side of this figure it becomes obvious that the peroxido complex $[(\text{Me}_2\text{uns-penp})\text{CuO}_2\text{Cu}(\text{Me}_2\text{uns-penp})](\text{BPh}_4)_2$, from two mononuclear units, is less stable than the preorganized binuclear peroxido complex with the ligand L^1 . The peroxido complex on the left side in figure 5 is much more persistent than the one on the right side under the reaction conditions applied.

Unfortunately, the observed increased stability of the copper peroxido complex with L^1 as ligand has proven not to be significantly different from the copper peroxido complex formed by the two mononuclear units with the ligands $\text{Me}_2\text{uns-penp}$. Therefore, we did not perform a more detailed kinetic analysis of the reaction of $[\text{Cu}_2(\text{L}^1)](\text{BPh}_4)_2$ with dioxygen as we had done with the $\text{Me}_2\text{uns-penp}$ system [8].

4. Summary and conclusion

In this study, we described the synthesis and characterization of copper(I) and copper(II) complexes of the new binucleating ligand L^1 . While the crystal structures of the reported copper(II) complexes were obtained as expected, the molecular structure of the copper(I) complex showed unexpected coordination behavior. However, in solution the copper(I) complex reacts as expected, and in comparison with the related

species formed from mononuclear complex units, a slightly thermally more stable copper peroxido complex is formed.

Despite the disappointment regarding the stability of the copper L¹ peroxido complex, the study described herein helped us to find a way to significantly stabilize copper peroxido complexes with the tetradentate tripodal ligands tmpa, Me₂uns-penp, Me₄apme, and Me₆tren in the solid state [7].

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC-764026 for [Cu₂Cl₂(L¹)](ClO₄)₂ · H₂O, CCDC-766046 for [Cu₂(L¹)](BPh₄)₂ and CCDC-766047 for [Cu₂Cl₂(L¹)]Cl₂ · 9H₂O. Copies of the data can be obtained, free of charge from The CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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