Synthesis, Structure and Properties of a Mononuclear and an End-On Double Azido-Bridged Copper(II) Complex Incorporating an N,N,N,O-Coordinating Tripodal Ligand

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The blue coloured complex $[Cu(HL)(H_2O)(ClO_4)]ClO_4{\cdot}H_2O{\cdot}MeOH$ ($\mathbf{1}{\cdot}H_2O{\cdot}MeOH$) has been synthesised in excellent yields by reacting $Cu(ClO_4)_2{\cdot}6H_2O$ with *N*,*N*-bis(2-methylpyridyl)(3,5-dimethyl-2-hydroxybenzyl)amine (HL) in methanol. The same reaction, when carried out in the presence of sodium azide, afforded a dark-blue complex of formula $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ (**2**). The crystal and molecular structures of the complexes have been solved. Variable-temperature magnetic susceptibility data in the range of 2–300 K for **2** reveal the existence of an antiferromagnetic interaction through an end-on azido linker. Temperature-dependent susceptibility studies for **2** were fitted using the Bleaney–Bowers expression, which led to the parameters $J = -3.2\ \mathrm{cm}^{-1}$, $g = 2.12$ and $R = 2.14 \times 10^{-4}$.

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Introduction

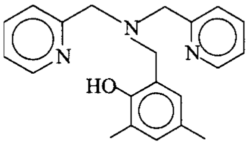
The existence of copper-containing enzymes and proteins and the potent biological activity of copper have increased recent interest in the coordination chemistry of copper with *O*,*N*-coordinating ligands.[1–6] It is well known that the azide ion inhibits the activity of metalloproteins,[1c,1d,1e,3e,7] thus metal azide complexes of such proteins have been studied extensively[8] in order to investigate the role of the metal ion in biological processes. The chemistry of azido-bridged copper(II) compounds has also received a great deal of attention for the understanding of magneto-structural correlations and for developing new functional-molecule-based materials.[9]

Among the many bridging ligands known, the azide ion can act not only as a monodentate ligand[10] but also link the metal ions in μ-1,1 (end-on) or μ-1,3 (end-to-end) bridging coordination modes, depending on the steric and electronic demands of the co-ligand. It has been widely found that the end-to-end bridging mode predominantly leads to antiferromagnetic coupling[11] and the end-on mode to ferromagnetic exchange;[12] instances of antiferromagnetic coupling in the case of end-on azido-bridged complexes are rare.[13] This has prompted us to undertake the task of designing diazido-bridged copper(II) species by using an *N*,*N*,*N*,*O*-coordinating tripodal ligand.

Here we describe the synthesis and characterisation of a mononuclear copper(II) species and a double asymmetric μ-1,1 azido-bridged Cu^{II} complex incorporating an *N*,*N*,*N*,*O*-coordinating tripodal ligand. The solid and solution structures of the complexes, as well as their properties, were probed by X-ray diffractometry and spectroscopic and electrochemical methods. The variable-temperature magnetic moment was measured for the dinuclear species.

Results and Discussion

The tripodal ligand HL is used in this present work; it was synthesised by a reported procedure.[14]



HL

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The stoichiometric reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with HL, in methanol, afforded the blue complex $[Cu(HL)(H_2O)(ClO_4)]ClO_4$ (**1**) in excellent yields. The same reaction, when carried out in the presence of an excess of sodium azide, yielded the dark-blue complex of formula $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ (**2**) [Equation (1)].

$$Cu(ClO_4){\cdot}6H_2O \xrightarrow[MeOH]{HL} [Cu(HL)(H_2O)(ClO_4)]ClO_4 \xrightarrow{N_3^-} [Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2 \quad (1)$$

In the IR spectra of complexes **1** and **2** the characteristic perchlorate stretches occur at $600\ cm^{-1}$ and $1100\ cm^{-1}$, respectively, and the hydrogen-bonded phenolic OH appears as a broad peak near $3250\ cm^{-1}$.[5c] The $Cu{-}N_3$ stretch is observed at $2100\ cm^{-1}$ in **2**.

In solution the complexes exhibit a relatively weak band in the 590 nm region of the UV/Vis spectrum. This transition is logically assigned as the ligand-field excitation.[15] An allowed intense band observed near 390 nm for complex **2** may be assigned as the $N_3^- \rightarrow Cu^{II}$ transition.[16]

All the complexes are electroactive at a platinum electrode in acetonitrile solution. Cyclic voltammetric reduction potential data are given in the Exp. Sect. and the voltammograms are shown in Figure 1. In both cases an anodic response occurs near 1.5 V, believed to be due to $Cu^{II}{\rightarrow}Cu^{III}$ oxidation; the oxidized complex is too reactive to survive for the cathodic scan. The complexes also display a quasireversible peak near 0.0 V corresponding to the Cu^{II}/Cu^{I} reduction couple. The low oxidation and reduction potentials for **2** compared to those of **1** may be due to the azide chelation.

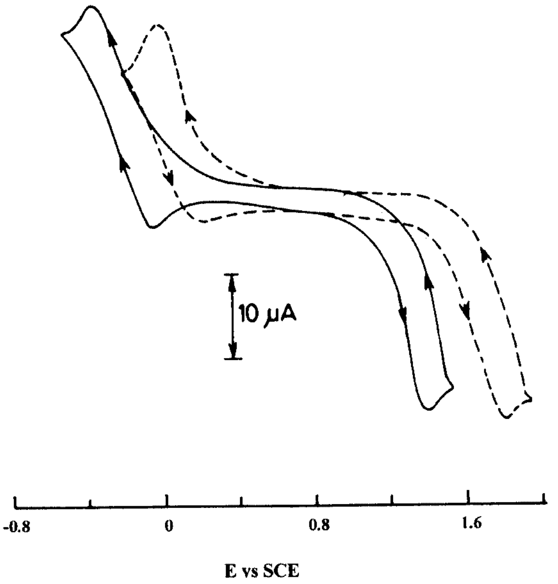


Figure 1. Cyclic voltammograms of ca. 10^{-3} M solutions of $[Cu(HL)(H_2O)(ClO_4)]ClO_4$ (----) and $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ (−) in acetonitrile

X-ray Crystallography

The crystal structures of $[Cu(HL)(H_2O)(ClO_4)]ClO_4{\cdot}H_2O{\cdot}MeOH$ ($\mathbf{1}{\cdot}H_2O{\cdot}MeOH$) and $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ (**2**) have been determined. Molecular views excluding the hydrogen atoms and the solvent molecules are shown in Figure 2 and 3, respectively. Selected bond parameters are listed in Table 1.

In both complexes the three nitrogen atoms of the tripodal ligand are disposed meridionally forming two five-membered chelate rings, whereas the phenolic oxygen atom is coordinated axially, forming a six-membered chelate ring. The two pyridine rings (NC_5H_5) of the ligand are planar (mean deviation about 0.02 Å) and the dihedral angle be-

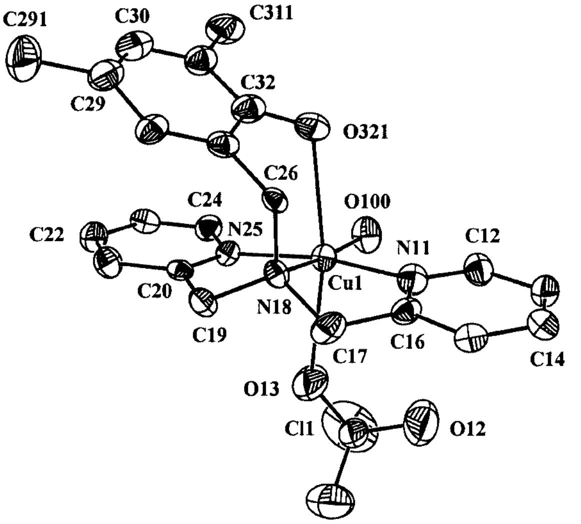


Figure 2. Perspective view and atom-labelling scheme for $[Cu(HL)(H_2O)(ClO_4)]ClO_4$ (**1**); all non-hydrogen atoms (excluding solvent molecules) are represented by 30% thermal probability ellipsoids

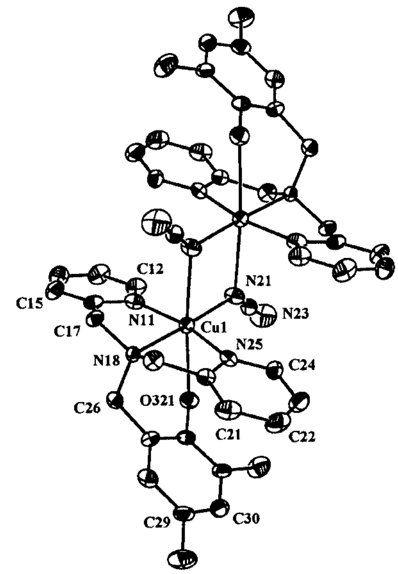


Figure 3. Perspective view and atom-labelling scheme of $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ (**2**): all non-hydrogen atoms (excluding perchlorate ions) are represented by 30% thermal probability ellipsoids

Table 1. Selected bond lengths (Å) and angles (°) for **1**·H_2O·MeOH and **2**

	1·H_2O·MeOH	**2**
Cu(1)−N(11)	1.949(10)	1.993(7)
Cu(1)−N(18)	2.051(8)	2.065(6)
Cu(1)−N(25)	1.975(8)	2.009(7)
Cu(1)−N(21)		1.972(7)
Cu(1)−N(21A)		2.563(8)
Cu(1)−O(13)	2.491(10)	
Cu(1)−O(100)	1.996(8)	
Cu(1)−O(321)	2.506(9)	2.578(9)
N(21)−N(22)		1.175(9)
N(22)−N(23)		1.154(10)
Cu···Cu		3.452(8)
N(11)−Cu(1)−N(18)	82.70(4)	81.70(3)
N(11)−Cu(1)−N(25)	164.50(4)	165.30(3)
N(18)−Cu(1)−N(25)	83.80(3)	83.50(3)
N(18)−Cu(1)−N(21)		177.10(3)
N(21)−Cu(1)−N(11)		97.70(3)
N(21)−Cu(1)−N(25)		97.00(3)
N(11)−Cu(1)−N(21A)		90.24(4)
N(18)−Cu(1)−N(21A)		95.42(5)
N(21)−Cu(1)−N(21A)		81.69(3)
N(25)−Cu(1)−N(21A)		91.34(5)
N(11)−Cu(1)−O(13)	89.67(5)	
N(18)−Cu(1)−O(13)	90.28(6)	
N(25)−Cu(1)−O(13)	82.84(4)	
N(11)−Cu(1)−O(100)	96.80(4)	
N(18)−Cu(1)−O(100)	174.70(3)	
N(25)−Cu(1)−O(100)	97.40(3)	
N(11)−Cu(1)−O(321)	101.45(6)	93.98(5)
N(18)−Cu(1)−O(321)	88.10(5)	87.16(6)
N(25)−Cu(1)−O(321)	85.62(4)	85.07(5)
N(21)−Cu(1)−O(321)		95.76(4)
N(21A)−Cu(1)−O(321)		175.34(6)
O(13)−Cu(1)−O(100)	95.12(6)	
O(13)−Cu(1)−O(321)	168.45(5)	
O(100)−Cu(1)−O(321)	86.70(6)	
Cu(1)−N(21)−Cu(1A)		98.31(8)
N(21)−N(22)−N(23)		177.00(10)

tween these two planes is 5.6° in **1**·H_2O·MeOH and 18.4° in **2**.

[Cu(HL)(H_2O)(ClO_4)]ClO_4·H_2O·MeOH (1·H_2O·MeOH)

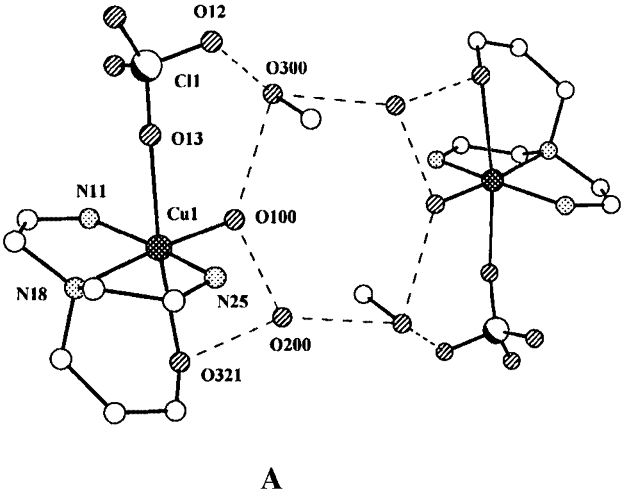
The structure of **1**·H_2O·MeOH consists of a monomeric [Cu(HL)(H_2O)(ClO_4)]ClO_4·H_2O·MeOH unit. The geometry around the metal centre of **1**·H_2O·MeOH appears to be distorted octahedral and is characterised by an O−Cu−O bond angle of 168.45°, which deviates significantly from the ideal value of 180°. In a distorted CuN_3O_3 octahedral environment, the fourth equatorial position *trans* to the tripodal nitrogen atom is occupied by the oxygen atom of a water molecule and the sixth axial position by the perchlorate oxygen atom. The copper atom is displaced by 0.01 Å towards the phenolic oxygen atom from the equatorial plane (mean deviation 0.105 Å) defined by N(11), N(18), N(25) and O(100). The three basal Cu−N bond lengths are unequal; the longest distance is the bond to the tripodal nitrogen and the shortest is that to the pyridine nitrogen. The latter is due to the sp^2 character of the pyridine nitrogen. The axial Cu−O and Cu−N bond lengths are longer because of the pseudo Jahn−Teller effect.

[Cu_2(HL)$_2$(μ-1,1-N_3)$_2$](ClO_4)$_2$ (2)

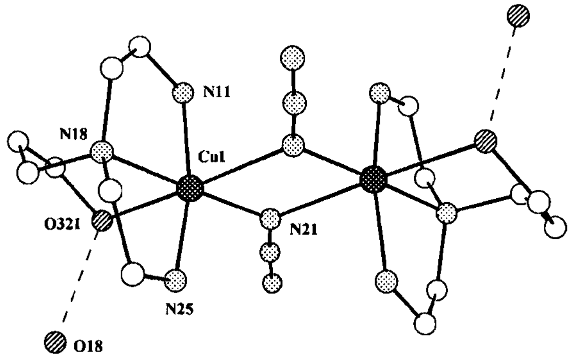
Two centrosymmetrically related Cu(HL)(μ-1,1-N_3) units are linked by the azide ion in an end-on fashion forming a doubly asymmetric bridged dimeric complex. The coordination geometry around the copper ion is distorted octahedral. Four nitrogen atoms (two pyridine, one tripodal and one azide nitrogen) form the square plane (mean deviation 0.023 Å) and the copper atom is displaced by 0.026 Å towards the coordinated phenolic oxygen atom from this plane. The remaining apical position of the octahedron is occupied by the bridging azide nitrogen atom of the other unit. The Cu−N distances and N−Cu−N bond angles in the basal plane range from 1.972 Å to 2.065 Å and 97.0° to 177.1° respectively. The long axial Cu−N (ca. 2.563 Å) distance can be attributed to a pseudo Jahn−Teller distortion. The intra-dimer Cu···Cu bond length is 3.452 Å. The azide ion is quasilinear, with an N−N−N bond angle of 177.0(10)°; the N−N bond lengths are 1.175(9) Å and 1.154(10) Å, respectively. In the end-on bridging moiety, the Cu−N−Cu bond angle is 98.31(8)°.

Hydrogen Bonding

In complex **1**·H_2O·MeOH the coordinated water molecule, the oxygen atom of the coordinated perchlorate ion and the phenolic oxygen atom of the ligand are extensively involved in hydrogen bonding with lattice water and methanol molecules. The lattice water molecule is held by water(lattice)···water(coordinated) [O···O = 2.718(14) Å] and water(lattice)··· oxygen(phenolic) [2.883(12) Å] hydrogen bonds. The methanol molecule in the lattice is also engaged in such bonding with the oxygen atom of the coordinated perchlorate ion and the coordinated water molecule, with O···O bond lengths of 2.831(13) Å and 2.782 (12) Å, respectively. The most striking feature is that two such molecules are linked by water···methanol hydrogen bonds [2.713(12) Å] forming a six-membered ring as depicted in



A



B

A. In the case of **2** the oxygen atom of the perchlorate ion is hydrogen bonded to the phenolic oxygen atom, with an O···O bond length of 2.650(10) Å as depicted in **B**.

Magnetic Studies

Variable-temperature magnetic susceptibility measurements were performed in the range of 2−300 K. The plot of $\chi_M T$ versus T for complex **2** is shown in Figure 4.

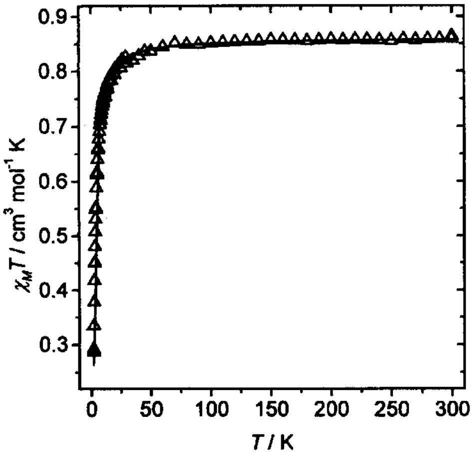


Figure 4. $\chi_M T$ versus T for **2**; open points are the experimental data and the solid line represents the best fit obtained

In **2**, the magnetic data are for two copper(II) ions as the complex is a dinuclear system. The experimental $\chi_M T$ value at 300 K is 0.86 emu·cm^{-1}·K, as expected for two quasi-isolated spin doublets. This value remains almost constant up to 50 K but decreases rapidly to 0.28 emu·cm^{-1}·K at 2 K. This feature is characteristic of a weak antiferromagnetic interaction. The reduced molar magnetisation at 2 K (Figure 5) clearly corroborates that the antiferromagnetic coupling is very small.

The magnetic susceptibility data were fitted by applying the Bleaney−Bowers formula with the Hamiltonian[9d]

$$H = -JS_1 \cdot S_2$$

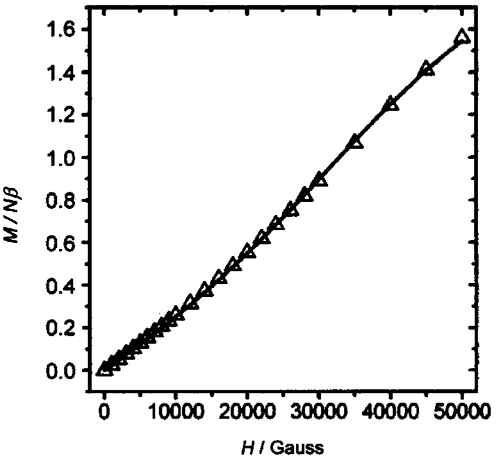


Figure 5. Plot of the reduced magnetisation, $M/N\beta$, versus H for **2**; open points are the experimental data and the solid line represents the best fit obtained.

The best-fit parameters obtained are $J = -3.2 \pm 0.1$ cm^{-1}, $g = 2.12 \pm 0.01$ and $R = 2.1 \times 10^{-4}$. Very similar J and g values were obtained by a full-diagonalisation from the curve of the magnetisation at 2 K. In this case, the best-fit parameters are $J = -3.0 \pm 0.1$ cm^{-1}, $g = 2.12 \pm 0.01$ and $R = 5.1 \times 10^{-5}$. Thus, the two methods give almost identical results. It is well documented that end-on double azido-bridged copper(II) dimers are usually ferromagnetic[12] but here the measurement clearly indicates that the coupling between the two Cu^{II} ions is antiferromagnetic which is very unusual.

In copper(II) systems with an end-on coordination of the azide ion, the exchange interaction will be strong when the magnetic orbitals involved are of the $d_{x^2-y^2}$ type. However, a low magnetic coupling should be expected when the interaction is between axial-equatorial coordination sites because the atomic orbitals involved are $d_{x^2-y^2}$ and d_{x^2} respectively. In complex **2**, the nitrogen atom of the unsymmetrically bridged azide ion belongs to the basal plane of one copper ion and also occupies one elongated apical position of the other metal centre. An exactly analogous situation occurs for the other centrosymmetrically related azide bridge. Consequently, the interaction between the magnetic orbitals is expected to be very weak, leading to a small exchange-coupling parameter. Moreover, the Cu−N(apical) bond is significantly longer than the distance required for a ferromagnetic interaction.[17] These two factors are most probably responsible for the weak antiferromagnetic coupling.

EPR Spectra

Both complexes show axial EPR spectra typical for monomeric copper(II) species with a $d_{x^2-y^2}$ ground-state doublet ($g_{\|} > g_{\perp} > 2.0$) in the solid state and in solution.[18] The spectroscopic data are listed in Table 2. From the spectrum of **2** it is clear that there is no significant interaction between the copper centres (Figure 6) in the solid state. The EPR spectra of **1**·H$_2$O·MeOH and **2** are practically identical with very similar $g_{\|}$ (range = 2.219−2.234), $g_{\perp}$ (range = 2.039−2.042) and $A_{\|}$ (range = 171−176 G) values.

Table 2. X-Band EPR data for 1·H_2O·MeOH and 2((Author: There appears to be data missing from this table. Please check))

	Matrix	g_{av}	A_{av} (G)	$g_{\|}$	$g_{\perp}$	$A_{\|}$ (G)
1·H_2O·MeOH	DMF/toluene, 77 K	2.122	120	2.235	2.042	171
	solid, 77 K					
	DMF/toluene, 77 K	2.115	120	2.219	2.039	175
2	solid, 77 K					

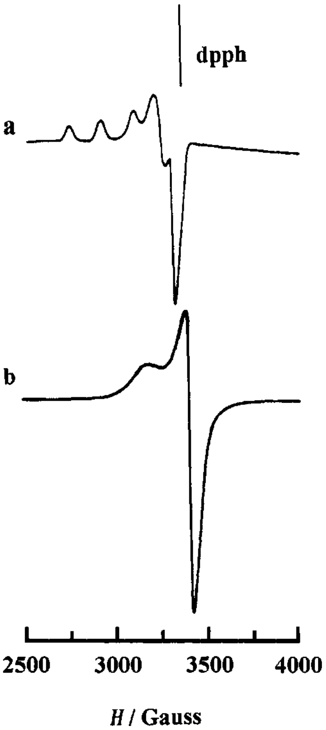


Figure 6. X-band EPR spectra of (a) $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ in DMF/ toluene at 77 K, and (b) $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ in the solid state at 77 K; instrument settings: power 30 db; modulation 100 kHz; sweep centre 3200 G

Conclusions

The synthesis and structural characterisation of copper(II) complexes incorporating *N*,*N*-bis(2-methylpyridyl)(3,5-dimethyl-2-hydroxybenzyl)amine (HL) has been successfully achieved. The parent species $[Cu(HL)(H_2O)(ClO_4)]ClO_4$ was prepared by the reaction of HL with $Cu(ClO_4)_2$·$6H_2O$ in methanol. This complex reacts with sodium azide to afford the complex $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$. To the best of our knowledge $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ is the first example of an end-on diazido-bridged octahedral copper(II) complex showing antiferromagnetic character. A search for new copper(II) complexes with different tetradentate ligand systems is in progress.

Experimental Section

Materials: All the starting chemicals were analytically pure and used without further purification. The ligands were prepared according to the literature procedure.[14]

Caution! *Perchlorate salts are highly explosive, and should be handled with care and in small amounts.*

Physical Measurements: UV/Vis spectra were recorded on a Perkin−Elmer LAMBDA EZ-301 spectrophotometer and IR spectra were measured with a Perkin−Elmer L-0100 spectrometer. Electrochemical measurements were performed on acetonitrile solutions of the complexes on a CH 620 A electrochemical analyzer using a platinum electrode. Tetraethylammonium perchlorate (TEAP)[19] was used as the supporting electrolyte and the potentials are referenced to the standard calomel electrode (SCE) without junction correction. EPR spectra were recorded on a Varian E-109C X-band spectrometer. Magnetic measurements were carried out on polycrystalline samples with a Quantum Design MPMS XL SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 3 K. The diamagnetic corrections were evaluated from Pascal's constants. Elemental analyses (C, H, N) were performed on a Perkin−Elmer 2400 Series II elemental analyzer.

$[Cu(HL)(H_2O)(ClO_4)]ClO_4$ (1): HL (0.168 g, 0.5 mmol) was added to a solution of copper(II) perchlorate hexahydrate (0.186 g, 0.5 mmol) in methanol (10 mL) and the resulting blue solution was stirred for 0.5 h at room temperature. Slow evaporation of the solution yielded a blue, crystalline product. Yield: 0.210 g (70%). $C_{21}H_{25}ClCuN_3O_{10}$ (610.5): calcd. C 42.32, H 4.20, N 7.05; found C 42.08, H 4.04, N 6.94. UV/Vis (CH_3CN): λ_{max} (ε) = 590 nm (107 $M^{-1}cm^{-1}$). IR (KBr): $\nu(ClO_4^-)$ 1100, 620; ν(OH) 3250 cm^{-1}. E_{pa} (Cu^{III}/Cu^{II} couple): 1.8 V (irr.); $E_{1/2}$ (Cu^{II}/Cu^{I} couple): 0.15 V (ΔE_p, 200 mV).

$[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ (2): HL (0.168 g, 0.5 mmol) and sodium azide (0.046 g, 0.7 mmol) were added to a methanolic solution (10 mL) of copper(II) perchlorate hexahydrate (0.186 g, 0.5 mmol). The resulting blue solution was stirred for 0.5 h at room temperature. Slow evaporation of the solution yielded a blue, crystalline product. Yield: 0.140 g (70%). $C_{21}H_{23}N_6ClCuO_5$ (538.44): calcd. C 46.84, H 4.28, N 15.61; found C 46.56, H 4.12, N 15.44. UV/Vis (CH_3CN): λ_{max} (ε) = 392 nm (2368 $M^{-1}cm^{-1}$), 590 (293). IR (KBr): $\nu(N_3^-)$ 2100; $\nu(ClO_4^-)$ 1100, 640; ν(OH) 3240 cm^{-1}. E_{pa} (Cu^{III}/Cu^{II} couple): 1.5 V (irr.); $E_{1/2}$ (Cu^{II}/Cu^{I} couple): −0.2 V (ΔE_p, 200 mV).

Crystallographic Studies: Crystals of $[Cu(HL)(H_2O)(ClO_4)]ClO_4$ and $[Cu_2(HL)_2(\mu\text{-}1,1\text{-}N_3)_2](ClO_4)_2$ were grown by slow evaporation of the solvents from their methanolic solution. Data were measured with Mo-K_α radiation using an MA Research Image Plate System. The crystals were positioned 70 mm from the Image Plate. 100 Frames were measured at 2° intervals with a counting time of 5 min. Data analyses were carried out with the XDS program[20] and the structures were solved by direct methods with the Shelx-86 program.[21] Non-hydrogen atoms were refined with anisotropic thermal parameters. One of the perchlorate ions of complex **1**·H_2O·MeOH and that of **2** are highly disordered. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2-times those of the atom to which they are attached. Empirical absorption corrections were applied using DIFABS[22] and the structures were refined on F^2 using Shelxl.[23] Significant crystal data are given in Table 3.
CCDC-240990 (for **1**·H_2O·MeOH) and -240991 (for **2**) contain the supplementary crystallographic data for this paper. The CIF files

for [Cu(L^1)(N_3)(ClO_4)], [Cu(L^2)(N_3)(ClO_4)]$_2$ and [Cu(L^3)(N_3)]$_n$-(ClO_4)$_n$ have also been deposited. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure-refinement parameters for **1**·H_2O·MeOH and **2**

	1·H_2O·MeOH	**2**
Formula	$C_{22}H_{28}Cl_2N_3O_{12}Cu$	$C_{21}H_{23}ClN_6O_5Cu$
Mol. mass	660.5	538.44
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	8.360(11)	8.185(9)
b (Å)	21.690(2)	12.573(14)
c (Å)	15.256(17)	22.70(2)
β (°)	92.272(10)	90.913(10)
V (Å^3)	2765(6)	2336(4)
Z	4	4
$D_{calcd.}$, [mg m^{-3}]	1.547	1.531
μ(Mo-K_α) (mm^{-1})	1.046	1.095
θ (°)	2.61 to 25.79	1.85 to 26.11
Measured reflections	7872	3996
Unique reflections (R_{int})	4000/ 0.1025	3996/ 0.0000
Temperature (K)	293	293
$R1$,[a] $wR2$[b][$I > 2\sigma(I)$]	0.1029, 0.2330	0.0976, 0.2601
GOF on F^2	1.059	1.057

[a] $R1 = |F_o| - |F_c|/|F_o|$. [b] $wR2 = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

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[1] [1a] F. A. Cotton, G. Wilkinson, C. A. Murillo, *Advanced Inorganic Chemistry*, Wiley, New York, **1999**. [1b] M. E. Cuff, K. I. Miller, K. E. van Holde, W. A. Hendrickson, *J. Mol. Biol.* **1998**, *278*, 855. [1c] E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.* **1996**, *96*, 2563. [1d] N. Kitajima, Y. Moro-oka, *Chem. Rev.* **1994**, *94*, 737. [1e] K. A. Magnus, H. Ton-That, J. E. Carpenter, *Chem. Rev.* **1994**, *94*, 727. [1f] N. Kitajima, *Adv. Inorg. Chem.* **1992**, *39*, 1.

[2] [2a] R. H. Holm, P. Kennepohl, E. I. Solomon, *Chem. Rev.* **1996**, *96*, 2239. [2b] E. T. Adam, *Adv. Protein Chem.* **1991**, *92*, 145. [2c] S. K. Chapman, *Perspectives on Bioinorganic Chemistry* (Eds.: R. W. Hay, J. R. Dilworth, K. B. Nolan), JAI Press, London, **1991**, p. 95.

[3] [3a] K. D. Karlin, A. D. Zuberbhuler, in *Bioinorganic Catalysis*, 2nd. ed. (Eds.: J. Reedijk, E. Bouwman), Marcel Dekker, New York, **1999**, p. 469. [3b] H. C. Liang, M. Dahan, K. D. Karlin, *Curr. Opin. Chem. Biol.* **1999**, *3*, 168. [3c] S. Fox, K. D. Karlin, in *Active Oxygen in Biochemistry* (Eds.: J. S. Valentine, C. S. Foote, A. Greenberg, J. F. Liebman), Blackie Academic and Professional, Glasgow, Scotland, **1995**, p. 188. [3d] K. D. Karlin, N. Wei, B. Jung, S. Kaderli, P. Niklaus, A. D. Zuberbuehler, *J. Am. Chem. Soc.* **1993**, *115*, 9506. [3e] *Bioinorganic Chemistry of Copper* (Eds.: K. D. Karlin, Z. Tyekler), Chapman & Hall, New York, **1993**. [3f] K. D. Karlin, *Science* **1993**, *261*, 701.

[4] [4a] S. Schindler, *Eur. J. Inorg. Chem.* **2000**, 2311. [4b] D. E. Wilcox, *Chem. Rev.* **1996**, *96*, 2435. [4c] A. L. Feig, S. J. Lippard, *Chem. Rev.* **1994**, *94*, 759. [4d] E. I. Solomon, F. Tuczek, D. E. Root, C. A. Brown, *Chem. Rev.* **1994**, *94*, 827. [4e] T. N. Sorell, *Tetrahedron* **1989**, *45*, 3.

[5] [5a] B. K. Santra, P. A. N. Reddy, M. Nethaji, A. R. Chakravarty, *J. Chem. Soc., Dalton Trans.* **2001**, 3553. [5b] M. Schatz, M. Becker, F. Thaler, F. Hampel, S. Schindler, R. R. Jacobson, Z. Tyeklár, N. N. Murthy, P. Ghosh, Q. Chen, J. Zubieta, K. D. Karlin, *Inorg. Chem.* **2001**, *40*, 2312. [5c] S. Torelli, C. Belle, I. Gautier-Luneau, J. L. Pierre, E. Saint-Aman, J. M. Latour, L. Le Pape, D. Luneau, *Inorg. Chem.* **2000**, *39*, 3526. [5d] H. Decker, R. Dillinger, F. Tuczek, *Angew. Chem. Int. Ed.* **2000**, *39*, 1591. [5e] A. G. Blackman, W. B. Tolman, *Structure and Bonding: Metal Oxo and Metal Peroxo Species* (Ed.: B. Meunier), Springer, Berlin, **2000**, vol. 97, pp. 179. [5f] L. L. Koh, J. O. Ranford, W. T. Robinson, J. O. Svensson, A. L. C. Tan, D. Wu, *Inorg. Chem.* **1996**, *35*, 6466.

[6] [6a] R. C. Holz, J. M. Bradshaw, B. Bennett, *Inorg. Chem.* **1998**, *37*, 1219 and references cited therein. [6b] J. Reim, B. Krebs, *J. Chem. Soc., Dalton Trans.* **1997**, 3793. [6c] Y.-H. Chung, H.-H. Wei, H.-Y. Liu, G.-H. Lee, Y. Wang, *J. Chem. Soc., Dalton Trans.* **1997**, 2825. [6d] W. Kaim, J. Rall, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 43. [6e] J. Ling, L. P. Nestor, R. S. Czernuszewicz, T. G. Spiro, R. Fraczkiewicz, K. D. Sharma, T. M. Loehr, J. Sanders-Loehr, *J. Am. Chem. Soc.* **1994**, *116*, 7682. [6f] K. Lerch, *Life Chem. Rep.* **1987**, *5*, 221.

[7] [7a] T. G. Spiro, *Copper Proteins*, Wiley, New York, **1981**. [7b] B. Reinhammer, *Copper Proteins and Copper Enzymes*, CRC, Boca Raton, FL, **1984**, vol. 3, pp. 1−35. [7c] E. I. Solomon, M. J. Baldwin, M. D. Lowery, *Chem. Rev.* **1992**, *92*, 521. [7d] E. I. Solomon, *Metal Clusters in Proteins* (Ed.: L. Que), American Chemical Society, Washington D.C., **1988**, pp. 116. [7e] M. Trémolières, J. G. Bieth, *Phytochemistry* **1984**, *23*, 501. [7f] A. Rompel, H. Fisher, K. Büldt-Karentzopoulos, D. Miewes, F. Zippel, H. F. Nolting, C. Hermes, B. Krebs, H. Witzel, *J. Inorg. Biochem.* **1995**, *59*, 715.

[8] [8a] J. L. Cole, P. A. Clark, E. I. Solomon, *J. Am. Chem. Soc.* **1990**, *112*, 9534. [8b] J. L. Cole, L. Avigliano, L. Morpurgo, E. I. Solomon, *J. Am. Chem. Soc.* **1991**, *113*, 9080.

[9] [9a] P. Manikandan, R. Muthukumaran, K. R. Justin Thomas, B. Varghese, G. V. R. Chandramouli, P. T. Manoharan, *Inorg. Chem.* **2001**, *40*, 2378. [9b] K.-S. Bürger, P. Chaudhuri, K. Weighardt, *Inorg. Chem.* **1996**, *35*, 2704. [9c] *Magnetism: A Supramolecular Function* (Ed.: O. Kahn), NATO ASI Series, No. C484; Kluwer Academic Publishers, Dordrecht, The Netherlands, **1996**. [9d] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, **1993**. [9e] *Magnetism: Molecules to Materials* (Eds.: J. Miller, M. Drilon), Wiley-VCH, Weinheim, **2002**.

[10] R. Kurtaran, C. Arici, S. Durmu, D. Ülkü, O. Atakol, *Anal. Sci.* **2003**, *19*, 335.

[11] [11a] Y. Agnus, R. Louis, J. P. Gisselbrecht, R. Weiss, *J. Am. Chem. Soc.* **1984**, *106*, 93. [11b] V. Mckee, M. Zvagulis, J. V. Dagdigian, M. G. Patch, C. A. Reed, *J. Am. Chem. Soc.* **1984**, *106*, 4765.

[12] [12a] O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin, Y. Jeannin, *Inorg. Chem.* **1983**, *22*, 2877. [12b] J. Comarmond, P. Plumere, J. M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn, I. Morgenstern-Badarau, *J. Am. Chem. Soc.* **1982**, *104*, 6330. [12c] I. B. Waksman, M. L. Boillot, O. Kahn, S. Sikorav, *Inorg. Chem.* **1984**, *23*, 4454. [12d] J. Cabrero, C. de Graaf, E. Bordas, R. Caballol, J.-P. Malrieu, *Chem. Eur. J.* **2003**, *9*, 2307.

[13] [13a] M. Sinha Ray, A. Ghosh, R. Bhattacharya, G. Mukhopadhyay, M. G. B. Drew, J. Ribas, *Dalton Trans.* **2004**, 252. [13b] S. Koner, S. Saha, T. Mallah, K.-I. Okamoto, *Inorg. Chem.* **2004**, *43*, 840.

[14] R. Kannappan, R. Mahalakshmy, T. M. Rajendiram, R. Venk-

atesan, P. Sambasiva Rao, *Proc. Indian Acad. Sci. (Chem. Sci.)* **2003**, *115*, 1–14.
[15] J. M. Rowland, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **2000**, *39*, 5326.
[16] M. E. Winkler, K. Lerch, E. I. Solomon, *J. Am. Chem. Soc.* **1981**, *103*, 7001.
[17] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, *120*, 11122.
[18] B. J. Hathaway, *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon Press, Oxford, U. K., **1987**, vol. 5, p. 668.
[19] G. K. Lahiri, S. Bhattacharya, B. K. Ghosh, A. Chakravorty, *Inorg. Chem.* **1987**, *26*, 4324.
[20] W. Kabsh, *J. Appl. Crystallogr.* **1988**, *21*, 916.
[21] G. M. Sheldrick, *SHELXL-86, Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[22] N. Walker, D. Stuart, DIFABS program, *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
[23] G. M. Sheldrick, *SHELXL*; University of Göttingen, **1993**.

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