Synthesis, Crystal Structure and Magnetic Properties of $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$ [Htidah = 1,1,6,6-tetrakis-(imidazol-2-yl)-2,5-diazahexane], a Unique Imidazolato- and Chloro-bridged Hexanuclear Copper(II) Compound†

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The novel hexanuclear copper(II) compound $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$ was obtained by the reaction of copper(II) chloride with the polyimidazole 1,1,6,6-tetrakis(imidazol-2-yl)-2,5-diazahexane (Htidah). This compound crystallizes in the monoclinic space group $P2_1/c$, with a = 7.915(5), b = 16.745(6), c = 20.954(8) Å, β = 95.41(4)°, Z = 2. The structure was solved using direct methods and refined on F by full-matrix least squares. Convergence was reached at R = 0.097 for 991 reflections with $I > 2\sigma(I)$. Structure analysis shows a complex molecule with six copper ions in three different co-ordination environments. The asymmetric unit, which comprises half a molecule, consists of a trinuclear subunit. In each subunit two copper ions are linked by an imidazolate anion, the Cu···Cu distance is 5.7226(8) Å. The two subunits are linked by four asymmetric copper to chloride to copper bridges, with Cu···Cu distances of 4.053(9) and 4.696(9) Å. The magnetic super-exchange interaction *via* the bridging imidazolate ligand seems to be the most important magnetic interaction in this molecule. A fit of the magnetic susceptibility *vs.* the temperature, in the 6–250 K range, shows a fair agreement for a dinuclear $S = \frac{1}{2}$ species, with an energy separation between the spin singlet ground state and the triplet excited state of 90 cm⁻¹.

Copper ions, as centres of the active site of metalloproteins, play an essential role in various biological processes.[1] In copper proteins, the copper ions are co-ordinated by donor atoms of the side chains of amino-acid residues. Except for the copper(I) metallothioneines, all the copper proteins studied so far contain one or more imidazole residues of histidine bound to the copper ion.

Imidazolate, the dehydronated form of imidazole, is involved in the active site of the mixed copper–zinc enzyme, superoxide dismutase. This protein occurs in mammals and catalyses the disproportionation of the harmful superoxide radical anion. Crystal structures of the bovine isoenzyme[2] and the human isoenzyme[3] show the imidazolate to bridge between the copper ion and the zinc ion, separating the metals by *ca.* 6.3 Å.

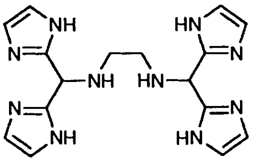
In the dinuclear copper protein haemocyanin, which functions as the dioxygen carrier for molluscs and arthropods, each copper ion is bound by three imidazole nitrogens. The crystal structure of both the oxy and deoxy form of *Limulus lyphemus* haemocyanin has been determined.[4] The Cu–Cu distance in the oxy form has been reported to be 3.55 Å and about 4.6 Å in the deoxy form. Oxyhaemocyanin is diamagnetic, due to the strong antiferromagnetic coupling between the two copper(II) ions ($-2J > 600$ cm^{-1}).[1]

Many model compounds have been synthesised with the aim of mimicking the active site of certain copper proteins.[5–7] However, the relation between the structure and the function of the active site of most copper proteins is not yet fully understood. The magnetic properties of imidazolato-bridged copper(II) compounds have been intensively studied and until now, a useful correlation between the structure and the magnitude of the exchange coupling[8] has not been established. The ligands most frequently used in modelling dinuclear Type 3 copper proteins appear to be pyrazoles and pyridines.[6,9] In the course of our research on copper co-ordination compounds, we have attempted to mimic both the structures and the properties of copper proteins by modelling the active site of these proteins with imidazole-containing ligands. To model the active site of haemocyanin, new ligands containing imidazole have been designed and synthesised.

The reaction of bis(imidazol-2-yl)nitromethane with diamines results in the formation of potential dinucleating ligands.[10–12] Using 1,1,6,6-tetrakis(imidazol-2-yl)-2,5-diazahexane (Htidah) not the expected dinuclear, but an unprecedented imidazolato- and chloro-bridged hexanuclear copper compound was obtained. In this paper the synthesis, crystal structure, spectroscopic and magnetic properties of this compound are discussed.

Experimental

Starting Materials and Syntheses.—All chemicals were commercially available, of sufficient purity, and were used



Htidah

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Fractional coordinates of the non-hydrogen atoms of $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.3752(7)	−0.2259(3)	0.4517(3)	C(12)	0.253(6)	−0.102(2)	0.362(2)
Cu(2)	0.3587(8)	−0.0810(3)	0.6059(3)	C(14)	0.136(6)	−0.208(2)	0.330(2)
Cu(3)	0.6148(8)	0.4193(3)	0.3857(3)	C(15)	0.079(6)	−0.156(3)	0.284(2)
Cl(4)	0.5394(14)	−0.3030(6)	0.5238(6)	C(22)	0.520(6)	−0.072(3)	0.425(2)
Cl(5)	0.1572(14)	−0.0620(6)	0.6882(5)	C(24)	0.725(6)	−0.143(2)	0.466(2)
Cl(6)	0.1924(15)	−0.1424(6)	0.5260(6)	C(25)	0.801(5)	−0.074(3)	0.459(2)
Cl(7)	0.7435(16)	0.5351(7)	0.3083(6)	C(32)	0.795(5)	0.269(2)	0.3539(19)
Cl(8)	0.7448(15)	0.4781(6)	0.4753(6)	C(34)	0.963(6)	0.349(2)	0.406(2)
O(61)	0.211(3)	−0.3174(15)	0.4446(12)	C(35)	1.058(5)	0.285(2)	0.393(2)
O(62)	0.409(3)	0.4857(15)	0.4007(14)	C(42)	0.534(6)	0.301(3)	0.282(2)
N(11)	0.172(4)	−0.088(2)	0.3014(16)	C(44)	0.381(5)	0.408(2)	0.256(2)
N(13)	0.242(4)	−0.176(2)	0.3746(17)	C(45)	0.358(5)	0.361(3)	0.207(2)
N(21)	0.669(4)	−0.0224(19)	0.4309(16)	C(51)	0.366(6)	−0.040(2)	0.391(2)
N(23)	0.548(5)	−0.144(2)	0.4469(17)	C(53)	0.289(5)	0.096(2)	0.351(2)
N(31)	0.948(4)	0.2355(19)	0.3583(15)	C(54)	0.369(5)	0.163(2)	0.323(2)
N(33)	0.799(5)	0.3406(19)	0.3767(16)	C(56)	0.641(5)	0.240(3)	0.3146(19)
N(41)	0.458(5)	0.297(2)	0.2214(16)	O(63)	0.539(3)	0.1593(16)	0.1546(13)
N(43)	0.501(5)	0.3730(19)	0.3066(18)	O(64)	0.124(3)	0.1681(15)	0.0748(13)
N(52)	0.408(4)	0.0327(19)	0.3582(17)	O(65)	0.860(3)	0.0538(15)	0.1676(13)
N(55)	0.535(4)	0.183(2)	0.3576(17)				

Table 2 Selected bond distances (Å) and angles (°) of the non-hydrogen atoms of $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$

Cu(1)–N(13)	2.02(3)	Cu(2)–N(52)	2.09(3)	Cu(3)–N(33)	1.99(4)	Cu(3)–Cl(4a)	3.052(13)
Cu(1)–Cl(4)	2.295(13)	Cu(2)–Cl(5)	2.477(13)	Cu(3)–Cl(7)	2.782(14)	Cu(1) ··· Cu(2)	5.7226(8)
Cu(1)–O(61)	2.01(3)	Cu(2)–N(21)	1.90(3)	Cu(3)–O(62)	2.02(3)	Cu(1) ··· Cu(2a)	4.053(9)
Cu(1)–N(23)	1.95(4)	Cu(2)–N(55)	2.02(3)	Cu(3)–N(43)	1.97(4)	Cu(1) ··· Cu(3a)	4.696(9)
Cu(1)–Cl(6)	2.626(13)	Cu(2)–Cl(6a)	2.275(13)	Cu(3)–Cl(8)	2.278(14)	Cu(2) ··· Cu(3)	5.673(9)
Cl(4)–Cu(1)–Cl(6)	102.6(5)	N(13)–Cu(1)–N(23)	89.1(14)	N(21)–Cu(2)–N(55)	162.1(14)	O(62)–Cu(3)–N(33)	171.4(13)
Cl(4)–Cu(1)–O(61)	86.7(8)	Cl(5)–Cu(2)–Cl(6a)	101.8(5)	N(52)–Cu(2)–N(55)	82.4(13)	O(62)–Cu(3)–N(43)	92.1(14)
Cl(4)–Cu(1)–N(13)	167.8(10)	Cl(5)–Cu(2)–N(21)	96.2(10)	Cl(7)–Cu(3)–Cl(8)	91.0(4)	N(33)–Cu(3)–N(43)	86.6(15)
Cl(4)–Cu(1)–N(23)	94.2(11)	Cl(5)–Cu(2)–N(52)	107.7(10)	Cl(7)–Cu(3)–O(62)	93.0(8)	Cu(1)–Cl(4)–Cu(3a)	122.2(5)
Cl(6)–Cu(1)–O(61)	93.5(8)	Cl(5)–Cu(2)–N(55)	96.7(10)	Cl(7)–Cu(3)–N(33)	95.4(11)	Cu(1)–Cl(6)–Cu(2a)	113.3(5)
Cl(6)–Cu(1)–N(13)	88.8(10)	Cl(6a)–Cu(2)–N(21)	94.4(11)	Cl(7)–Cu(3)–N(43)	87.0(11)	Cu(1)–N(23)–N(21)	160(2)
Cl(6)–Cu(1)–N(23)	94.9(11)	Cl(6a)–Cu(2)–N(52)	150.5(10)	Cl(8)–Cu(3)–O(62)	86.7(9)	Cu(2)–N(21)–N(23)	147(2)
O(61)–Cu(1)–N(13)	88.3(12)	Cl(6a)–Cu(2)–N(55)	95.0(10)	Cl(8)–Cu(3)–N(33)	95.0(11)		
O(61)–Cu(1)–N(23)	171.2(13)	N(21)–Cu(2)–N(52)	81.8(13)	Cl(8)–Cu(3)–N(43)	177.6(11)		

without further treatment. Carbon, H and N determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland.

Htidah. To a solution of the hydrochloride salt of bis(imidazol-2-yl)nitromethane[10] (7 g, 31 mmol) in ethanol (45 cm^3) and sodium hydroxide solution (2 mol dm^{-3}, 30 cm^{-3}), ethylenediamine (0.92 g, 15 mmol) was added. The solution was stirred for 45 min during which time the product crystallized from the reaction mixture. After cooling to room temperature, the reaction mixture was filtered. The product was washed with water and ethanol and dried with diethyl ether. Yield 7.9 g, 74%. ^1H NMR (200 MHz, 1 mol dm^{-3} DLC, 25 °C, δ 0–10: δ 7.32 (s, 4 H, imidazole), 5.35 (s, 2 H, CH) and 2.67 (s, 4 H, CH_2).

$[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$. The poorly soluble solid Htidah (350 mg, 1 mmol) and a solution of $CuCl_2\cdot 2H_2O$ (510 mg, 3 mmol) in ethanol (60 cm^3, 96%) was stirred at 50 °C until the Htidah dissolved (15 min). From the filtered solution crystals started to grow after six weeks. After another two weeks the crystalline product was collected by filtration and washed with ethanol and dried in air. Yield 90 mg, 11.5% (Found: C, 24.70; H, 3.65; N, 16.75. Calc. for $C_{32}H_{58}Cl_{10}Cu_6N_{20}O_{10}$: C, 23.75; H, 3.60; N, 17.30%). This compound has been reproduced in several subsequent experiments.

X-Ray Methods and Structure Determination.—Crystal data, data collection and processing. $C_{32}H_{58}Cl_{10}Cu_6N_{20}O_{10}$, M = 1618.74, monoclinic, space group $P2_1/c$, a = 7.915(5), b = 16.745(6), c = 20.954(8) Å, β = 95.41(4)°, Z = 2, U = 2765(2) $Å^3$, D_c = 1.944 g cm^{-3}, μ(Mo-Kα) = 29.04 cm^{-1}, E(000) = 1628. Unit-cell parameters derived from the 25 SET4 setting angles in the range 5 < θ < 16°.

X-Ray data were collected for a tiny green block-shaped crystal (0.05 × 0.05 × 0.05 mm, glued on top of a glass fibre), obtained from the reaction mixture, on a CAD-4T/rotating anode [10 kW, monochromator, λ(Mo-Kα) = 0.710 73 Å, θ_{max} = 21.5°, 100 K]. A total of 2906 reflections were scanned of which 2681 were unique. Data were corrected for Lorentz polarization, for linear decay of 7%, but not for absorption. Atomic scattering factors and anomalous-dispersion corrections were taken from ref. 13.

Structure analysis and refinement. The structure was solved with SHELXS 86/TREF[14] and refined on F by full-matrix least squares (SHELX 76;[15] Cu and Cl anisotropic, C, N and O isotropic, H on calculated positions X–H 1.08 Å). No hydrogen atoms could be identified on the H_2O molecules. Convergence was reached at R = 0.097 [wR = 0.084, $w^{-1} = \sigma^2(F)$] for 991 reflections with $I > 2\sigma(I)$ and 225 parameters. The relatively high R factor is ascribed to the extreme smallness of the crystal. Fractional coordinates of the non-hydrogen atoms and selected bond lengths and angles are given in Tables 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Spectral and Magnetic Measurements.—Infrared spectra

(4000–200 cm^{-1}) were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE data station as Nujol mulls between KRS-5 discs or as KBr pellets. Ligand-field spectra of the solids (300–2000 nm) were recorded on a Perkin-Elmer 330 spectrophotometer equipped with a diffuse-reflectance attachment, using MgO as a reference. X-Band powder EPR spectra (variable temperature) were obtained on a JEOL RE2X electron spin resonance spectrometer using an ESR900 continuous-flow cryostat. Magnetic susceptibilities were measured in the temperature range 298–6 K with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *ca.* 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. Magnetic data were fitted by theoretical expressions by means of a Simplex routine.[16]

Results

The pattern of the absorption bands in the infrared spectrum of the copper compound strongly resembles that of the free ligand, indicating the presence of the ligand intact. Some of the ligand bands are split or shifted as a result of co-ordination. The diffuse-reflectance spectrum in the visible–near IR region shows a broad band, *ca.* 14.0 × 10^{3} cm^{-1}, which is in the usual range for copper(II) compounds.[17]

Crystal Structure.—The structure analysis shows a complex molecule with six copper ions in three different co-ordination environments (Fig. 1). The asymmetric unit consists of three copper ions, a uninegative tidah ligand, five chloride ions, two co-ordinated water ligands and three lattice water molecules. A dehydronated imidazole group bridges Cu(1) and Cu(2) [Cu(1)–N(23) 1.95(4) and Cu(2)–N(21) 1.90(3) Å]. The Cu(1) $\cdots$ Cu(2) distance is 5.7226(8) Å. The Cu(1) atom is co-ordinated by a bridging imidazolate nitrogen, an imidazole nitrogen, two bridging chloride ions, and an oxygen from a water molecule in a square-pyramidal geometry in contrast to the distorted trigonal bipyramidal environment of the Cu(2) atom, co-ordinated by the two amine nitrogens, the other nitrogen of the bridging imidazolate group and two chloride ions (one bridging). The Cu(3) atom, bonded to two imidazole nitrogens, a chloride ion and an oxygen from a water molecule as equatorial ligands, and by two chloride ions as weak axial ligands [Cu(3)–Cl(7) 2.782(14) and Cu(3)–Cl(4a) 3.052(13) Å, the latter bridging to Cu(1a)], forms a distorted octahedron. The two trinuclear units are linked by two asymmetric chloride bridges [Cl(6) and Cl(6a)], which separate Cu(1) and Cu(2a) by 4.053(9) Å, and two further bridges [Cl(4) and Cl(4a)], which separate Cu(1) and Cu(3a) by 4.696(9) Å. This compound is further stabilized by three intramolecular hydrogen bonds (Table 3).

The different molecules are linked by intermolecular stacking of imidazole rings and by several hydrogen bonds (Table 3). Although no hydrogen atoms could be located on the water molecules, it is obvious from several short interatomic distances that these water molecules are involved in hydrogen bonding. Potential hydrogen bonds are listed in Table 3. In each asymmetric unit two imidazole rings stack to a ring in a neighbouring molecule (related by the symmetry operation $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$). The distance of the centroid of the ring containing N(13) to the least-squares plane through the ring containing N(41) is 3.32 Å. The dihedral angle is 11°.

EPR and Magnetic Properties.—The polycrystalline powder EPR spectrum of [$Cu_6(tidah)_2Cl_{10}(H_2O)_4$]·$6H_2O$, recorded at room temperature, is fairly broad, with an isotropic signal centred at $g = 2.12$. Variable-temperature EPR spectra were recorded in the range 298–6 K. At 30 K an anisotropic splitting is observed, resulting in an axial spectrum. This splitting at low

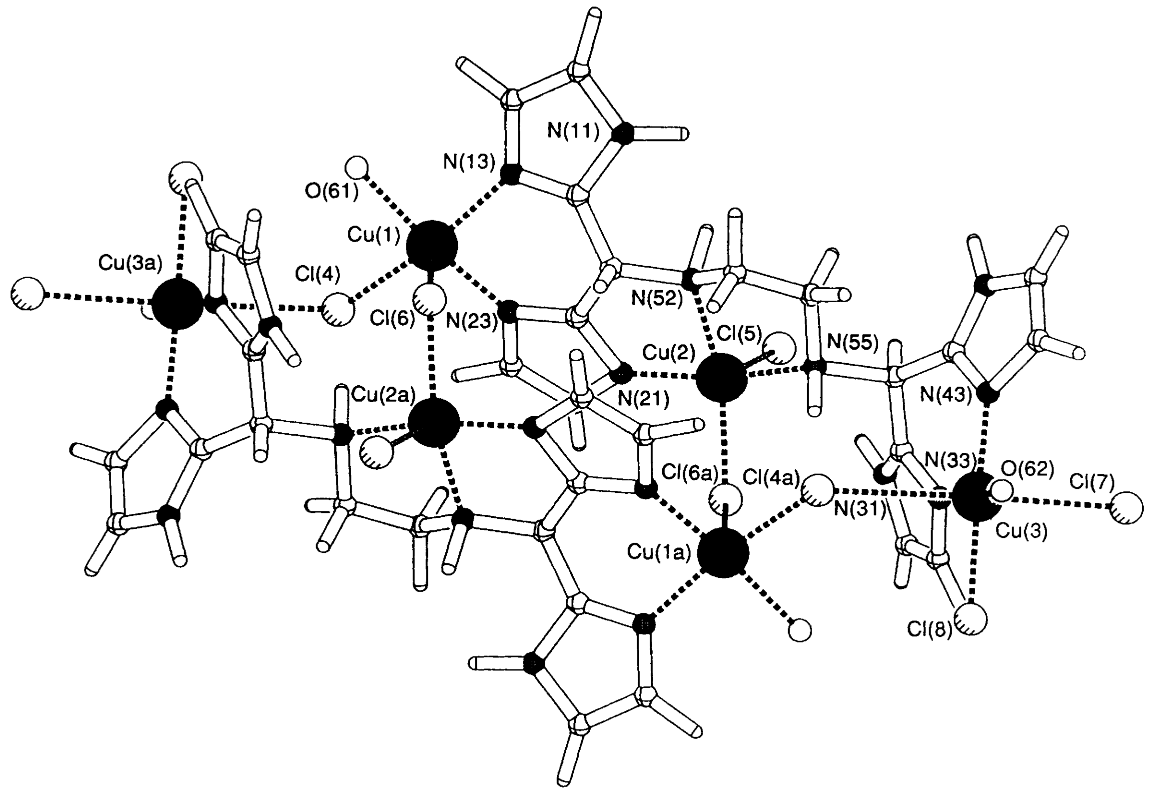


Fig. 1 Molecular structure of the hexanuclear copper compound [$Cu_6(tidah)_2Cl_{10}(H_2O)_4$]·$6H_2O$. Non-co-ordinated water molecules are omitted for clarity

Table 3 Intra- and inter-molecular hydrogen bonds (Å) in $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$

(*a*) Observed

N(55) ··· Cl(4a)	3.29(4)	N(52) ··· Cl(7^{III})	3.58(4)
N(31) ··· Cl(5a)	3.15(3)	N(52) ··· N(11)	2.93(5)
N(11) ··· Cl(7^{III})	3.20(4)	O(63) ··· N(41)	2.80(4)

(*b*) Potential

O(61) ··· O(64^{II})	2.66(3)	O(63) ··· O(65)	3.09(3)
O(61) ··· Cl(4)	2.96(3)	O(63) ··· O(62^{III})	3.17(4)
O(61) ··· O(63^{III})	3.03(4)	O(64) ··· O(65^{I})	3.55(4)
O(61) ··· Cl(8a)	3.17(3)	O(64) ··· Cl(7^{III})	2.66(3)
O(61) ··· Cl(6)	3.40(3)	O(65) ··· Cl(5a)	3.04(4)
O(62) ··· Cl(8)	2.96(3)	O(65) ··· O(62^{III})	2.70(4)
O(62) ··· Cl(8^{V})	3.03(3)	O(65) ··· Cl(7^{IV})	3.15(3)
O(62) ··· Cl(4a)	3.45(3)		

Atoms related by the symmetry operations: I $x-1, y, z$; II $-x, \frac{1}{2}+y, \frac{1}{2}-z$; III $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; IV $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; V $1-x, 1-y, 1-z$.

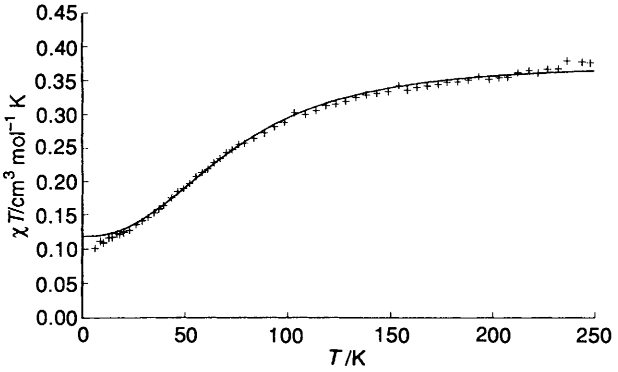
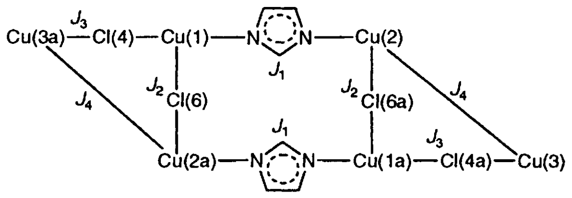


Fig. 2 χT *vs.* T curves for $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$. The solid line represents the calculated curve ($-2J_1 = 90$ cm^{-1}, J_2–J_4 are assumed to be zero, $g_1 = 2.15$, $\theta = -3$ K and $g_2 = 2.00$)



Scheme 1 Possible magnetic-exchange pathways of $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$

temperature is probably caused by the magnetically isolated copper ion [Cu(3)].

The magnetic behaviour of this compound is shown in Fig. 2 in the form of a χT *vs.* T plot, χ being the magnetic susceptibility per copper(II) ion and T the temperature. At 292 K, $\chi T = 0.382$ cm^3 K mol^{-1}, which is about the value expected for a single, uncoupled copper(II) ion. The value of χT decreases upon cooling, reaching a value of 0.101 cm^3 K mol^{-1} at 6.2 K. This behaviour is characteristic for compounds having an overall antiferromagnetic interaction between the metal ions, which is also illustrated by the θ value of -70 K obtained from the $1/\chi$ *vs.* T plot, in the temperature range 250–6 K. To interpret the magnetic data, the possible magnetic-exchange pathways have to be examined. Scheme 1 shows the possibility of magnetic interaction between four pairs of copper(II) ions. It appears that Cu(3) can be regarded as being magnetically isolated from the other copper ions, since Cu(3) is more than 3 Å away from the bridging Cl(4a) ligand ($J_3 = 0$) and Cu(3) is not directly linked to Cu(2) ($J_4 = 0$). Antiferromagnetic interaction between Cu(1) and Cu(2a) through the chloride bridges is also expected to be rather weak, because the magnetic orbitals on the linked copper ions are unfavourably oriented for overlap, as Cl(6) is axial co-ordinated to Cu(1). Moreover the distance between Cu(1) and Cu(2a) of 4.053(9) Å is rather long, so J_2 will be negligible. In contrast, magnetic super-exchange interaction *via* a bridging imidazolate ligand is known to be relatively strong.[18] It is concluded from the two short copper–imidazolate distances [Cu(1)–N(23) 1.95(4) and Cu(2)–N(21) 1.90(3) Å] that on both copper(II) ions the magnetic orbitals are directed in such a way that a considerable electron delocalization occurs over the imidazolate nitrogens. Therefore, an antiferromagnetic interaction is expected between Cu(1) and Cu(2). These considerations lead to expression (1) to describe the magnetic

$$\chi_M = \left(\frac{2}{3}\right)\frac{2N\beta^2{g_1}^2}{k(T-\theta)}\,\frac{1}{3+\exp(-2J_1/kT)} + \left(\frac{1}{3}\right)\frac{N\beta^2{g_2}^2}{3kT}S(S+1) \qquad (1)$$

behaviour of this hexanuclear cluster. The first term is the modified Bleaney–Bowers form of the Van Vleck equation for exchange-coupled pairs of $S = \frac{1}{2}$ ions[19] and $2J$ is the singlet–triplet energy gap defined by the phenomenological spin Hamiltonian, $\hat{H} = (\frac{2}{3})[-2J_1\hat{S}_{Cu(1)}\cdot\hat{S}_{Cu(2)}]$, with quantum-spin operators $\hat{S}_{Cu(1)}$ and $\hat{S}_{Cu(2)}$. The parameter θ accounts for intercluster exchange. The second term describes the magnetic behaviour for the isolated $S = \frac{1}{2}$ ion Cu(3), given by the Curie law. A very good fit has been obtained for the parameters $-2J_1 = 90$ cm^{-1}, $g_1 = 2.15$, $\theta = -3$ K and $g_2 = 2.00$, as depicted in Fig. 2.

Discussion

In $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$, the isotropic exchange coupling constant ($-2J$) is 90 cm^{-1}. However, it should be noted that other possible exchange pathways (other than *via* the imidazolate bridge) have been neglected. Thus, this value must be considered as the upper value of $-2J$ for the interaction *via* the imidazolate. This exchange coupling constant is in the range (*i.e.* 38–163 cm^{-1})[8,20,21] found for other imidazolato-bridged copper(II) complexes. The magnitude of the antiferromagnetic coupling in imidazolato-bridged copper(II) compounds is determined by the extent of overlap of the magnetic orbitals situated on the copper(II) ions. A number of studies have been undertaken to analyse which structural parameters determine the effectiveness of the super-exchange pathway.[8,12,18,20–23] Clearly, when the super-exchange is mediated by a bridging imidazolate ligand, the relative orientations of the copper co-ordination and imidazolate ring need to be considered, yet several attempts to correlate the magnetic and structural data for imidazolato-bridged complexes have failed. An important point of controversy is whether the π and/or the σ orbitals on the imidazolate constitute the exchange pathway.[8,21,22] Furthermore, it has been suggested that not only the copper–imidazolate overlap is of importance, the overlap of the orbitals of the other atoms in the co-ordination sphere of the bridged copper(II) ions might have a considerable effect on the exchange pathway.[8,21]

The analysis of the magnitude of the isotropic exchange constant for $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]\cdot 6H_2O$ is further complicated by the high asymmetry of the bridging imidazolate. This asymmetry is reflected in the two Cu(1)–N(23)–N(21) 160(2) and Cu(2)–N(21)–N(23) 147(2)° angles [N(21) and N(23) being the imidazolate nitrogens]. Moreover, the co-ordination geometries around Cu(1) and Cu(2) are entirely different. The $d_{x^2-y^2}$ magnetic orbital of Cu(1) lies in the square-pyramidal basal plane formed by N(13), N(23), O(61) and Cl(4), 22.6(19)° to the bridging imidazolate ring. The Cu(1) atom is 0.18(11) Å from the basal plane and directed towards

Cl(6). The Cu(2) atom is co-ordinated in a distorted trigonal-bipyramidal geometry, which complicates the assignment of a magnetic orbital to Cu(2). This implies that the relative orientation of the Cu(2) magnetic orbital towards the imidazolate ring cannot be determined. Due to the high asymmetry of this compound and the resulting uncertainty in the orientation of the copper(II) magnetic orbitals, a quantitative interpretation of the magnetic data in view of the structural data is therefore impossible.

In $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]{\cdot}6H_2O$ the imidazolate separates the two copper ions by a relatively small distance [5.7226(8) Å]. The smallest distance ever found for an imidazolato-bridged copper(II) compound is 5.6619(7) Å in $[\{Cu(pmdien)\}_2(2\text{-}mim)][ClO_4]_3$ (pmdien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, 2-Hmim = 2-methylimidazole).[24] The copper–zinc distance in bovine superoxide dismutase is reported to be *ca.* 6.3 Å.[2]

In the copper(II) complex $[Cu(dpma)_2][ClO_4]_2$ of the tridentate ligand di-2-pyridylmethanamine (dpma)[25] the copper ion is co-ordinated by all three nitrogen donors of the ligand. Its crystal structure revealed that considerable steric strain results from this co-ordination, elongating one of the Cu–N(pyridine) bonds to as much as 2.536(6) Å. The ligand bites in Htidah are comparable to those in dpma. The smaller ring size and ring angles of imidazole compared to pyridine makes double tridentate co-ordination in tidah co-ordination compounds impossible.

Conclusion

Although $[Cu_6(tidah)_2Cl_{10}(H_2O)_4]{\cdot}6H_2O$ cannot serve as a model for dinuclear copper proteins, efforts to model the active site have resulted in a very interesting hexanuclear co-ordination compound. One of the four imidazole groups of the Htidah ligand is spontaneously dehydronated during the complexation reaction which results in an unprecedented compound with a unique architecture.

The analysis of the magnetic data in view of the structural parameters is complicated by the high asymmetry of the imidazolate bridge and the difference in co-ordination environment of the bridged copper ions. The energy separation between the singlet ground state and the triplet excited state of 90 cm^{-1}, however, is fairly large.

Further investigations with ligands containing the bis(imidazol-2-yl)methane unit to obtain dinuclear copper complexes are in progress.

Acknowledgements

We thank Mrs. P. Slangen for her assistance with the magnetic susceptibility measurements. We thank the Foundation for Chemical Research in the Netherlands (SON) for financial support.

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Received 16*th July* 1993; *Paper* 3/04178F