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Bis[μ-chloro-dichlorobis(2,6-bis(4-amino-2-thiabutyl)-4-methylphenolato-(N,N^1,S,S^1,-μ-O))dicopper(II)-μ-Cl]; a dimer of dinuclear copper(II) complexes containing a novel pentadentate ligand

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Abstract

The di-hydrochloride salt of the N_2S_2O ligand, 2,6-bis(4-amino-2-thiabutyl)-4-methylphenol, $HL(HCl)_2$ reacts with $CuCl_2(H_2O)_2$ in methanol solution after treatment with KOH, to yield a dinuclear species of stoichiometry $[Cu_2LCl_3]$. Two dinuclear units of this complex are linked via long Cu–Cl and Cl–H–N interactions (Cu–Cl 3.270(3) Å; Cl–N 3.296(6), 3.526(6) Å) to yield a dimer in the solid state. Further hydrogen-bond interactions link these dimeric units into an infinite-chain structure along the z axis. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.657(3)$, $b = 16.647(5)$, $c = 8.845(2)$ Å and $\beta = 105.38(2)°$. The dinuclear unit contains a trigonal-bipyramidal and a square-pyramidal copper atom. The copper atoms are asymmetrically bridged by a phenolate oxygen and a chloride ion, with a Cu–Cu distance of 3.311(1) Å. Each copper atom has an additional chloride ligand. The compound was characterized by EPR, ligand field spectroscopy and magnetic measurements over the temperature range 6.3–290 K. The magnetic measurements indicate that there is a weak ferromagnetic interaction between the copper centers.

Introduction

Before the crystal structure of deoxy-hemocyanin was determined, it was believed that a phenolate group was a likely endogenous bridging ligand between the copper centers in the protein [1]. Consequently, phenolate-containing dicopper complexes have been investigated by many research groups [2, 3]. Some of these complexes exhibit magnetic and redox properties similar to that displayed by the active site of the dicopper-containing enzymes, hemocyanin and the polyphenol oxidases. The relevance of such compounds as models for hemocyanin has been demonstrated by Karlin, who showed that a phenoxo-bridged complex was able to bind dioxygen as a peroxide ion between two copper centers [3, 4]. As a result of such intensive studies, dicopper complexes that are able to interact with dioxygen and catalyze the oxidation of organic substrates have been discovered [2, 3]. For instance [5], recently the catalytic oxidation of hydroquinones and α-hydroxyketones using a phenolate-bridged dicopper complex has been reported. Dicopper, chloro-bridged complexes with amine-type ligands have also been proposed as active precursors in catalyzing the oxidation of 2,6-dimethylphenol to the corresponding polyphenyleneoxide, a polymer of considerable industrial interest [6]. The vast majority of phenolate-containing dinucleating ligands studied contain exclusively nitrogen-donor groups [2, 3]. Ligands incorporating sulfur donors as well as nitrogen donors are far less common [7].

Here we report the facile synthesis of a new pentadentate, dinucleating ligand, containing an endogenous phenolate group, together with amine and thioether donors. This dinucleating ligand belongs to a class of ligands introduced by Robson in the early 1970s [8]. The synthesis, X-ray crystal structure and magnetic properties of a dinuclear complex of this ligand are presented.

Experimental

All reagents and solvents were purchased from commercial sources and used as received unless otherwise stated. 2,6-Bis(hydroxymethyl)-4-methylphenol was prepared according to literature methods [9] and recrystallized from methanol prior to use. C, H and N analyses were performed by the University College, Dublin.

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Synthesis of ligand, $HL(HCl)_2$

2,6-Bis(hydroxymethyl)-4-methylphenol (7.3 g, 43 mmol) and 2-aminoethanethiol hydrochloride (12.3 g, 108 mmol) were heated under reflux in glacial acetic acid (25 ml) for *c.* 2 h. The reaction mixture was cooled to room temperature, whereupon white crystals of the product, 2,6-bis(4-amino-2-thiabutyl)-4-methylphenol dihydrochloride, deposited. The solid was collected, washed with cold ethanol and dried *in vacuo* at 50 °C. Yield 13.9 g, 89%. $HL(HCl)_2$ could be recrystallized from ethanol. n.p. 176–178 °C. ^1H NMR data (d_6 DMSO): 2.16 (s, 3H, CH_3–), 2.65, 2.95 (m, 8H, NCH_2CH_2S), 3.75 (s, 4H, CH_2S), 6.92 (s, 2H, aromatic CH), 8.21 (br, s, 6H, NH_3Cl).

Synthesis of Cu_2LCl_3

To $HL(HCl)_2$, (1.3 g, 3.6 mmol) was added a methanolic solution of KOH (10 ml, 0.04 g KOH/ml). After *c.* 10 min heating the solution was gravity filtered to remove precipitated KCl. The free-ligand solution, obtained as described above was added to a boiling methanolic solution (25 ml) of $CuCl_2(H_2O)_2$ (1.4 g, 0.8 mmol) dropwise. The resultant black–brown solution was heated at boiling temperature for *c.* 10 min and then cooled to room temperature. The black crystals of Cu_2LCl_3 which deposited were collected, washed with copious amounts of methanol and dried *in vacuo* at 80 °C. Yield 1.4 g, 76%. *Anal.* Calc. for $C_{13}H_{21}Cl_3Cu_2N_2O_1S_2$: C, 30.09; H, 4.08; N, 5.40. Found: C, 29.68; H, 4.09; N, 5.24%.

Physical measurements

IR spectra from 4000–200 cm^{-1} were recorded as KBr pellets on a Perkin-Elmer 580 spectrometer. Diffuse reflectance spectra were recorded at room temperature in the range 28 000–5000 cm^{-1} on a Perkin-Elmer 330 spectrometer equipped with a data station, with MgO as a reference material. ^1H NMR spectra were recorded on a JNM-FX 200 spectrometer. All chemical shifts are recorded in ppm downfield from TMS. Electron paramagnetic resonance (EPR) spectra of the powdered complex at 77 K were recorded using a JEOL JES RE-2X spectrometer at X-band frequencies. A magnetometer model Manics DSM-8 equipped with a He continuous flow cryostat was used to measure magnetic susceptibilities over the temperature range 6.3–290 K. The observed susceptibilities were fitted to the theoretical expression for the susceptibility of a dinuclear species using the Bleaney–Bowers [10] expression (*vide infra*) by means of a non-linear least-squares SIMPLEX parameter optimization routine [11]. All parameters were independently varied during the fitting procedure.

Crystallographic data collection and refinement of the structure of Cu_2LCl_3

Black crystals of Cu_2LCl_3 grew directly from the reaction mixture, diluted four-fold with methanol, as described. Preliminary oscillation and Weissenberg photographs indicated that the crystal was stable and of suitable quality for an X-ray structural analysis. Crystal data are presented in Table 1. The crystal class was monoclinic; satisfactory structure solution and refinement was obtained in the space group $P2_1/c$. Intensity data were collected on an Enraf-Nonius CAD-4F diffractometer using Mo Kα radiation. The ω:2θ scan technique was employed to measure reflections up to a maximum Bragg angle of 27.5°. Accurate values of the unit cell parameters, together with their standard deviations were obtained from the accurate setting angles of 25 reflections. The intensities of 4915 reflections were measured, of which 4625 were unique and 2024 satisfied the $I > 2\sigma(I)$ criterion of observability. Three strong reference reflections measured every 5700 s of X-ray exposure time showed a *ca* 10% decrease in intensity during the period of the data collection. The data were corrected for Lorentz, polarization and absorption effects [12], but not for extinction.

The coordinates of the two copper atoms were obtained using direct methods [13]. The remaining non-hydrogen atoms were located on subsequent difference maps. The position of the sulfur atom, S(2) was disordered over two sites designated as S(2) and S(2A). Initially the site occupation factor of the isotropic atom was refined over two positions with *c.* 67% S(2) and 33% S(2A) occupancy. Refinement of the two sites of this atom was then continued anisotropically with the occupation factors at each site constrained. The struc-

TABLE 1. Crystallographic data for Cu_2LCl_3

Chemical formula	$C_{13}H_{21}N_2O_1S_2Cl_3Cu_2$
Molecular weight	518.89
Crystal system	monoclinic
a (Å)	11.657(3)
b (Å)	19.647(5)
c (Å)	8.845(2)
β (°)	105.38(2)
V (Å^3)	1953.1(8)
Space group	$P2_1/c$
Z	4
ρ_{calc} (g cm^{-3})	1.764
μ (cm^{-1})	26.95
Radiation λ (Å)	Mo Kα (0.71073)
T (K)	293
R ($R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$)	0.036
h range	−15 to +15
k range	0 to +25
l range	0 to +11
F(000)	1048

ture was refined by using the full-matrix least-squares procedure of SHELX-76 [14].

Unit weights were used for the least-squares refinement and at convergence the analysis of variance showed that a satisfactory weighting scheme had been employed. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were clearly visible in the difference maps and included in the scattering model at geometrically estimated positions, with common isotropic temperature factors applied to hydrogen atoms of a similar type. The parameters associated with all the non-hydrogen atoms of the structure converged such that the maximum shift/e.s.d. was 0.03. The maximum residual electron density was 0.48 e Å^{-3}. The scattering factors for the non-metal atoms were those collected by Sheldrick [14]. The values for copper which were corrected for real and imaginary dispersion effects were taken from the International Tables [12].

Results and discussion

Description of the structure of Cu_2LCl_3

The structure of Cu_2LCl_3 is shown in Fig. 1, together with the atomic labelling scheme employed. Final atomic positional parameters are given in Table 2. Selected bond distances and angles are given in Table 3 and 4, respectively. Each copper ion is five coordinate. The phenolate oxygen O(1) and a chloride Cl(1) bridge the two copper atoms. The Cu(1)-Cu(2) distance is 3.311(1) Å, and the angles within the bridge are Cu(1)-O(1)-Cu(2), 102.6(2)° and Cu(1)-Cl(1)-Cu(2), 81.3(1)°. The Cu(1), Cu(2), O(1), Cl(1) core is almost planar with an average deviation of 0.073(10) Å from the plane defined by these atoms. The phenolate oxygen is asymmetrically bound to the copper ions with bond lengths of 2.308(4) and 1.925(4) Å to Cu(1) and Cu(2), respectively. The bridging chloride is also asymmetrically bound with Cu(1)-Cl(1) = 2.323(2) Å and Cu(2)-Cl(1) = 2.735(2) Å. The atom Cl(1) is situated 3.270(3) Å from the $Cu(1)^{I}$ of the symmetry related molecule. The nitrogen atom, $N(1)^{I}$ is 3.296(6) Å from Cl(1) and 3.526(6) Å from Cl(3). These Cu-Cl and Cl-H-N

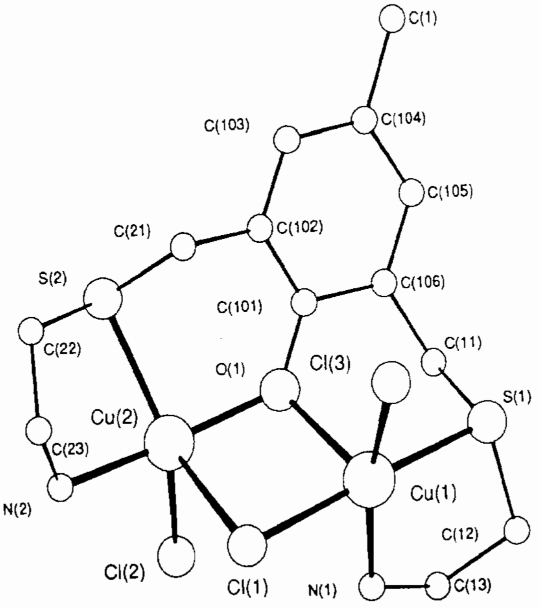

Fig. 1. The structure of Cu_2LCl_3 together with the atomic labelling employed. Hydrogen atoms have been omitted for clarity.

TABLE 2. Atomic positional coordinates with e.s.d. values in parentheses for Cu_2LCl_3

Atom	*x*	*y*	*z*
Cu(1)	0.1224(1)	0.4307(1)	0.0069(1)
Cu(2)	0.1933(1)	0.4300(1)	−0.3318(1)
S(1)	0.1561(2)	0.3376(1)	0.1802(3)
S(2)	0.3905(2)	0.4330(2)	−0.3531(3)
S(2A)	0.3762(5)	0.4913(3)	−0.2043(7)
Cl(1)	0.0758(2)	0.5161(1)	−0.1811(2)
Cl(2)	0.0260(2)	0.3684(1)	−0.4514(2)
Cl(3)	0.2635(2)	0.4939(1)	0.1696(2)
O(1)	0.2334(4)	0.3781(2)	−0.1403(5)
N(1)	−0.0309(5)	0.3858(3)	−0.1001(6)
N(2)	0.1694(5)	0.5018(3)	−0.4960(7)
C(1)	0.6700(8)	0.2689(6)	0.2277(15)
C(11)	0.2210(7)	0.2763(4)	0.0702(10)
C(12)	0.0029(6)	0.3107(3)	0.1322(8)
C(13)	−0.0576(7)	0.3191(4)	−0.0404(9)
C(21)	0.4493(8)	0.4437(7)	−0.1551(13)
C(22)	0.3814(7)	0.5226(5)	−0.4231(12)
C(23)	0.2620(7)	0.5545(4)	−0.4488(10)
C(101)	0.3384(6)	0.3547(3)	−0.0556(7)
C(102)	0.4481(6)	0.3804(4)	−0.0618(9)
C(103)	0.5519(7)	0.3526(4)	0.0271(9)
C(104)	0.5539(7)	0.3001(5)	0.1304(11)
C(105)	0.4451(8)	0.2768(4)	0.1432(11)
C(106)	0.3381(7)	0.3025(4)	0.0541(9)

TABLE 3. Interatomic distances (Å) with e.s.d. values in parentheses for Cu_2LCl_3

Cu(2)-Cu(1)	3.311(1)	S(1)-Cu(1)	2.352(2)
Cl(1)-Cu(1)	2.323(2)	Cl(3)-Cu(1)	2.250(2)
N(1)-Cu(1)	1.993(5)	S(2)-Cu(2)	2.357(3)
Cl(1)-Cu(2)	2.735(2)	Cl(2)-Cu(2)	2.301(2)
O(1)-Cu(2)	1.925(4)	N(2)-Cu(2)	1.990(6)
C(11)-S(1)	1.832(8)	C(12)-S(1)	1.801(7)
C(21)-S(2)	1.716(11)	C(22)-S(2)	1.860(10)
Cu(2)-Cl(3)	2.301(2)	Cu(1)-O(1)	2.308(4)
C(101)-O(1)	1.336(7)	C(13)-N(1)	1.477(8)
C(23)-N(2)	1.474(9)	C(106)-C(11)	1.500(10)
C(13)-C(12)	1.511(10)	C(102)-C(21)	1.494(12)
C(23)-C(22)	1.487(11)	C(102)-C(101)	1.389(9)
C(106)-C(101)	1.413(9)	C(103)-C(102)	1.369(10)
C(104)-C(103)	1.374(11)	C(1)-C(104)	1.527(11)
C(104)-C(105)	1.381(11)		

TABLE 4. Bond angles (°) with e.s.d. values in parentheses for Cu_2LCl_3

S(1)–Cu(1)–Cu(2)	123.2(1)	Cl(1)–Cu(1)–S(1)	174.4(1)
Cl(3)–Cu(1)–Cu(2)	105.4(1)	Cl(3)–Cu(1)–S(1)	92.6(1)
Cl(3)–Cu(1)–Cl(1)	92.9(1)	O(1)–Cu(1)–Cu(2)	34.6(1)
O(1)–Cu(1)–S(1)	89.9(1)	O(1)–Cu(1)–Cl(1)	88.8(1)
O(1)–Cu(1)–Cl(3)	100.6(1)	N(1)–Cu(1)–Cu(2)	88.6(2)
N(1)–Cu(1)–S(1)	86.5(2)	N(1)–Cu(1)–Cl(1)	88.3(2)
N(1)–Cu(1)–Cl(3)	163.6(2)	N(1)–Cu(1)–O(1)	95.7(2)
S(2)–Cu(2)–Cu(1)	123.7(1)	Cl(1)–Cu(2)–S(2)	130.4(1)
Cl(2)–Cu(2)–Cu(1)	91.9(1)	Cl(2)–Cu(2)–S(2)	134.6(1)
Cl(2)–Cu(2)–Cl(1)	94.4(1)	O(1)–Cu(2)–S(2)	94.0(1)
O(1)–Cu(2)–Cl(1)	86.3(1)	O(1)–Cu(2)–Cl(2)	96.0(1)
N(2)–Cu(2)–Cu(1)	129.6(2)	N(2)–Cu(2)–S(2)	82.8(2)
N(2)–Cu(2)–Cl(1)	85.8(2)	N(2)–Cu(2)–Cl(2)	95.8(2)
N(2)–Cu(2)–O(1)	166.3(2)	C(11)–S(1)–Cu(1)	100.7(3)
C(12)–S(1)–Cu(1)	95.2(2)	C(12)–S(1)–C(11)	101.9(3)
C(21)–S(2)–Cu(2)	93.2(4)	C(22)–S(2)–Cu(2)	94.5(3)
C(22)–S(2)–C(21)	101.3(6)	Cu(2)–Cl(1)–Cu(1)	81.3(1)
Cu(2)–O(1)–Cu(1)	102.6(2)	C(101)–O(1)–Cu(1)	113.9(4)
C(101)–O(1)–Cu(2)	130.4(4)	C(13)–N(1)–Cu(1)	118.1(5)
C(23)–N(2)–Cu(2)	109.9(5)	C(106)–C(11)–S(1)	109.9(5)
C(13)–C(12)–S(1)	112.0(5)	C(12)–C(13)–N(1)	111.8(6)
C(102)–C(21)–S(2)	113.7(9)	C(23)–C(22)–S(2)	114.7(6)
C(22)–C(23)–N(2)	109.4(7)	C(102)–C(101)–O(1)	124.7(6)
C(106)–C(101)–O(1)	117.8(6)	C(106)–(C101)–C(102)	117.4(6)
C(101)–C(102)–C(21)	117.8(7)	C(103)–C(102)–C(21)	120.8(7)
C(103)–C(102)–C(101)	121.0(7)	C(104)–C(103)–C(102)	122.5(7)
C(103)–C(104)–C(1)	122.2(8)	C(105)–C(104)–C(1)	121.1(9)
C(105)–C(104)–C(103)	116.7(7)	C(106)–C(105)–C(104)	122.8(8)
C(101)–C(106)–C(11)	118.8(6)	C(105)–C(106)–C(11)	121.8(7)
C(105)–C(106)–C(101)	119.4(7)		

interactions link dinuclear units, as shown in Fig. 2, thereby forming dimers of dinuclear units [15]. In addition, there is a further intermolecular hydrogen bond, between N(2) and Cl(3)^{III} of 3.420(6) Å, so that the dimeric units are linked to form an infinite chain structure as shown in Fig. 3. The important hydrogen intermolecular contacts are listed in Table 5. The Cu(1)–Cu(1)^{I} distance is 3.923(2) Å. The other donors to each copper ion are the thioether sulfur atom and an amine nitrogen, both provided by the pendant arms of the ligand L^-, together with an additional chloride ligand. Addison *et al.* [16] have proposed a structural index, τ which distinguishes between square-pyramidal and trigonal-bipyramidal geometries, defined as $\tau = (\beta - \alpha)/60$, where α and β are the largest coordination angles, excluding the axial donor. In a perfect square-pyramidal geometry, $\tau = 0$, whereas for a perfect trigonal-bipyramidal geometry, $\tau = 1$. On the basis of this structural criterion, Cu(I) is described as distorted square-pyramidal with $\tau = 0.18$. The atoms, N(1), Cl(1), Cl(3) and S(1) define the basal plane of the square pyramid, from which Cu(1) is situated 0.348(17) Å towards the apical oxygen O(1). For Cu(2), $\tau = 0.52$ and therefore the coordination geometry cannot be determined straightforwardly. The bond angles around Cu(2) suggest that the copper coordination sphere may be tentatively described as distorted trigonal-bipyramidal. The axis of the bipyramid passes through N(2) and O(1) and the equatorial plane comprises S(2), Cl(1) and Cl(3). The extreme flexibility of the pendant sidearms is highlighted by the fact that the sulfur atoms S(1) and S(2) are situated −1.72(4) Å and 1.07(3) Å, respectively, from the mean plane defined by the atoms C(101–C(106) in the central aromatic ring. The phenolate oxygen is 0.03(3) Å from this aromatic ring.

Latour and co-workers [7] have described a discrete dicopper complex of 2,6-bis[4-(2-benzimidazolyl)-2-thiabutyl]-4-methylphenol. This complex is very similar to the one described here; the copper atoms have different coordination geometries, one is trigonal-bipyramidal and the other square-pyramidal, each copper has an additional chloride ligand and the copper atoms are bridged by a phenolato oxygen and a chloride ligand. The Cu–Cu separation of 3.255(1) Å is slightly shorter than that observed in Cu_2LCl_3. Unlike in Cu_2LCl_3, the chloride and phenolato oxygen bridge the copper atoms symmetrically. The angles at the bridging chloride and oxygen are significantly larger than those observed in Cu_2LCl_3, by *c.* 4.8 and 10.8°, respectively. The aliphatic amines, compared with the benzimidazole sidearms allow H-bond interactions between dinuclear units in Cu_2LCl_3.

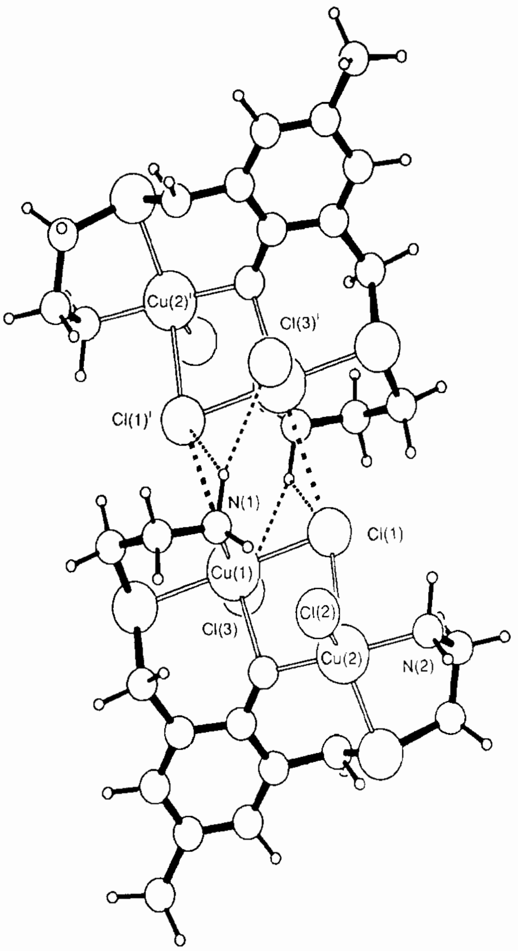

Fig. 2. The linking of dinuclear units of Cu_2LCl_3 via intermolecular contacts, (shown as dashed lines) to form a tetranuclear complex. I: (2−*x*, −*y*, 1−*z*).

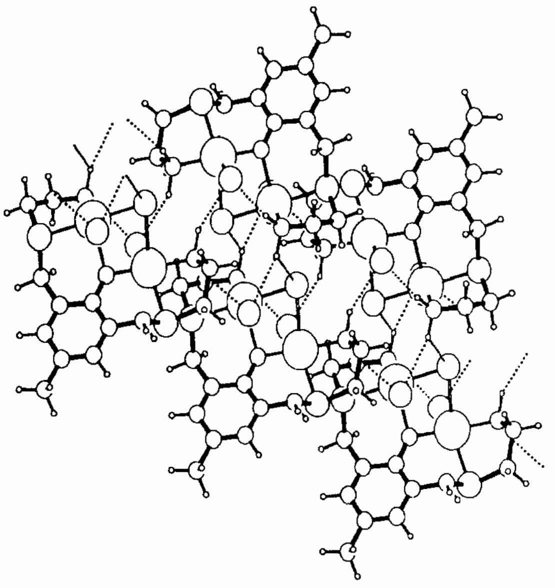

Fig. 3. An overview of the important contacts, (shown as dashed lines) that link the dimeric units to form an infinite chain in the *z* direction.

TABLE 5. Important hydrogen intermolecular contacts (Å) with e.s.d. values in parentheses for Cu_2LCl_3

A–H···B	H···B (Å)	A···B (Å)
N(2)–H(N2)···Cl(2)″	2.429(6)	3.368(6)
N(1)–H(N11)···Cl(1)′	2.680(6)	3.296(6)
N(1)–H(N11)···Cl(3)′	2.485(6)	3.526(6)
N(2)–H(N21)···Cl(3)‴	2.498(6)	3.420(6)

′: (2-*x*, -*y*, 1-*z*); ″: (2-*x*, -*y*, 2-*z*); ‴: (*x*, *y*, *z*+1).

Magnetic and spectral measurements

The magnetic properties of Cu_2LCl_3 are illustrated in Figs. 4 and 5, in the form of $1/\chi_{Cu}$ versus T, and $\chi_{Cu}T$ versus T, respectively, over the range 6–290 K. As noted in the X-ray crystallographic description of Cu_2LCl_3 the Cu_2OCl core is almost planar. In dicopper complexes with bridging ligands such as Cl^-, OH^- and phenolato oxygens, antiferromagnetism is commonly observed with such planar systems. It is believed that the interaction is via a superexchange mechanism mediated by the bridging ligand orbitals [17]. The magnetic behaviour of the title compound behaves differently and the susceptibilities are Curie-like in the range 300–20 K. In fact a fit of the $\chi_{Cu}T$ values was possible (300–20 K range) with a very weak ferromagnetic exchange showing $J=1.5(5)$ cm^{-1} for $g=2.01(3)$. Below 20 K the curve of $\chi_{Cu}T$ shows a small increase from 4.0×10^{-1} to 5.1×10^{-1} K mol^{-1} cm^3 at 6 K. The additional ferromagnetic interaction at low T between the copper centres is the result of an overall effect. Exchange can be considered to consist of an antiferromagnetic and a ferromagnetic contribution [17]. Clearly, the competition between the antiferromagnetic and ferromagnetic interactions for this compound leads to a small overall ferromagnetic interaction between the copper(II) centers. In Cu_2LCl_3, Cu(2) has a trigonal-

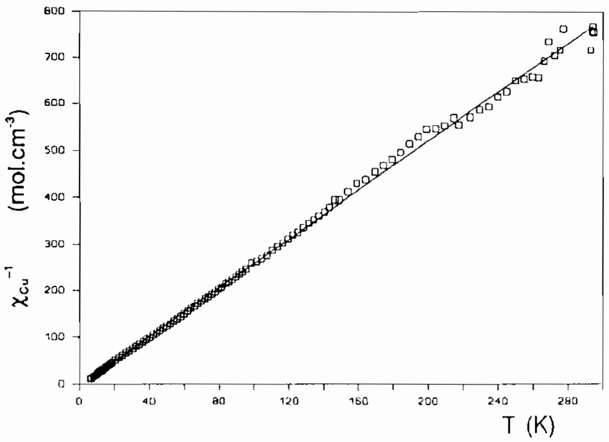

Fig. 4. A plot of temperature dependence of χ_{Cu}^{-1}. The solid line is that calculated using the parameters given in the text.

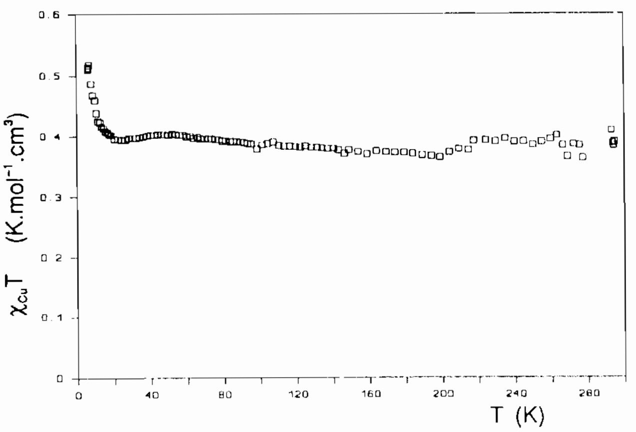

Fig. 5. Plot of temperature dependence of $\chi_{Cu}T$, illustrating the ferromagnetic interaction visible below 19 K.

bipyramidal based geometry and so the unpaired electron resides primarily in the d(z^2) orbital pointed along the N(2)–Cu(2)–O(1) bond. For Cu(1), the square-pyramidal geometry suggests the unpaired electron is localized in a d(x^2–y^2) orbital in the basal plane of the square pyramid defined by the atoms S(1), Cl(3), Cl(1) and N(1). The magnetic orbitals are therefore not aligned favourably for antiferromagnetic exchange through orbital overlap of the copper(II) ions. Even though one could possibly also consider a Cu(1)–Cu(1)$^{\mathrm{I}}$ exchange through Cu(1)–Cl(1)–Cu(1)$^{\mathrm{I}}$ (the Cu(1)–Cl(1)–Cu(1)$^{\mathrm{I}}$ bond angle is 87.3(3)°) no attempt was made to fit the data to a tetranuclear model, since reasonable fit parameters were obtained using the simpler dinuclear model. Moreover such an interdimer interaction, if present at all, would be expected to be small considering the quite large Cu(1)–Cu(1)$^{\mathrm{I}}$ separation of 3.923(2) Å.

The EPR spectrum of Cu_2LCl_3 at 77 K is broad and isotropic with $g_{iso} = 2.10$. Cu_2LCl_3 is only soluble in solvents such as dmf. From frozen solution EPR spectra at 77 K it appears that the copper is extracted from the complex and that the dinuclear structure is disrupted. This is probably because the thioether sulfur atoms are weak donors. The Vis–NIR spectrum of the complex (diffuse reflectance) is dominated by a large, broad absorption centered at 12 500 cm^{-1}. Since the color of solid Cu_2LCl_3 is black we believe that the absorption is a charge-transfer band. Broad charge-transfer bands of low energy are commonly observed with sulfur-containing ligands, which often mask d–d transitions [18].

Conclusions

It is interesting to note that attempts to synthesize other solid dicopper complexes of the ligand L$^-$ with various other exogenous bridging species such as Br$^-$, $CH_3(C_6H_4)S^-$, OH$^-$, N_3^-, etc. failed. No pure, discrete compounds could be isolated from reactions with these ligands, although the reaction containing Cl$^-$ is entirely reproducible. We presume that the crystal packing and hydrogen-bonding interactions between dinuclear units have an important effect on the stability of the complex obtained. The extreme insolubility of Cu_2LCl_3 and its decomposition in solution, mentioned above, make this complex unsuitable for catalyzing the oxidation of 2,6-dimethylphenol.

Supplementary material

Tables of anisotropic thermal parameters, hydrogen parameters, and a list of structure factors (9 pages) are available from the authors.

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