Magnetic Properties and Crystal Structure of a Linear-chain Copper(II) Compound with Bridging Chloride and Oxamidate Ligands†

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The compound [$Cu_2(L)Cl_2$] [H_2L = *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamide] has been prepared and characterized by means of structural and magnetic measurements. The crystals are triclinic, space group $P\bar{1}$, with a = 6.630(1), b = 7.443(1), c = 9.702(1) Å, α = 95.38(1), β = 102.72(1), γ = 101.12(1)° and Z = 2. The structural unit comprises one independent copper ion bonded to one half of a *trans*-oxamidate ligand and one chloride ion. Two centres of symmetry lead to a polymeric molecule. The copper ions are in distorted square-pyramidal environments and the basal co-ordination sites are occupied by O,N,N' donors from the *trans*-oxamidate ligand and by a chloride ion. The fifth contact occurs with the chloride ion of an adjacent asymmetric unit. The nearest-neighbour Cu ··· Cu distance is 3.2989(9) Å and a remarkably acute angle is found at the bridging chloride[79.02(3)°]. The magnetic properties of the compound are well reproduced by the dimer model with pairwise interactions, owing to the overwhelming importance of the oxamidate bridge in determining the exchange coupling interactions [J = 409(3) cm^{-1}]. The EPR spectra, however, indicate that the compound intimately behaves as an alternating chain.

The copper(II) complex [CuL] [H_2L = *N,N'*-bis(3-amino-2,2-dimethylpropyl)oxamide], which contains the oxamidate group in the *cis* conformation, has been found to act as a bidentate paramagnetic ligand toward transition-metal[1,2] and rare-earth[3] cations, yielding tri-[1-3] and tetra-nuclear[1] complexes. In particular, [CuL] was found to yield trinuclear complexes with copper(II) nitrate,[1] nickel(II) perchlorate[2] and gadolinium(III) nitrate,[3] the central metal ion being four-, six- and eight-co-ordinated, respectively. The two pairs of oxamidate oxygens, defining a square-planar environment in the copper(II) trimer, are *cis* in the nickel(II) and gadolinium(III) trinuclear complexes, the remaining co-ordination sites of the central metal ion being occupied by water molecules.

The versatility of [CuL] as a starting material for the design of oligo- and poly-nuclear complexes is enhanced by the possible *cis–trans* isomerization of the oxamidate group. In the *trans* conformer an equatorial co-ordination site on the central copper(II) ion becomes vacant and, provided that suitable co-ligands are present, the resulting complex may be a convenient building block for polynuclear compounds.[4] However, it has been found that both the *cis* and *trans* isomers may be present within the same oligonuclear complex. In fact, when [CuL] was treated with copper(II) nitrate both the trinuclear species already described and a tetranuclear complex were formed in the same lattice.[1] The structure of the latter comprises a central Cu^{II}(*trans*-oxamidate)Cu^{II} moiety and two molecules of [CuL] as external ligands, the inner copper(II) atoms being five-co-ordinated.

We have previously reported the crystal structure and magnetic properties of a polynuclear copper(II) complex [$\{Cu_2(L)(O_2CMe)_2\}_n$] obtained from the reaction of [CuL] with copper(II) acetate. It consists of infinite alternating linear chains of copper(II) atoms bridged by *trans*-oxamidate and acetate ligands.[4]

We have now observed that the reaction of [CuL] with copper(II) chloride yields a structurally similar polynuclear complex, [$Cu_2(L)Cl_2$], the crystal and molecular structure and the magnetic properties of which are reported herein.

Experimental

All chemicals were reagent grade and used as received. The copper(II) complex [CuL] (1 mol), prepared as previously reported[2] and suspended in water (30 cm^3), was treated under stirring with solid copper(II) chloride dihydrate (1 mol). The green solution was filtered and left under vacuum over P_2O_5. Within a couple of days blue crystals of [$Cu_2(L)Cl_2$] were formed. [Found: C, 31.80; H, 5.40; N, 12.25. Calc. for $C_{12}H_{24}Cl_2Cu_2N_4O_2$: C, 31.70; H, 5.30; N, 12.35%).

Magnetic and EPR Measurements.—Magnetic susceptibilities of powdered samples were measured in the range 12–280 K in a field of 4 T with a Métronique Ingénierie MS03 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.[5] The EPR spectra of polycrystalline powders were recorded at various temperatures in the range 4.2–280 K with a Varian E9 spectrometer at X-band frequency equipped with an Oxford Instruments ESR9 liquid-helium continuous flow cryostat.

Crystal-structure Determination.—Blue crystals of [$Cu_2(L)Cl_2$], consisting of well shaped individuals, were obtained by slow crystallization of the reaction mixture. X-Ray data were collected on an automated Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å).

Crystal data. $C_6H_{12}ClCuN_2O$, M = 227.17, triclinic, space group $P\bar{1}$, a = 6.630(1), b = 7.443(1), c = 9.702(1) Å, α = 95.38(1), β = 102.72(1), γ = 101.12(1)°, U = 453.6(3) $Å^3$, Z = 2, D_c = 1.66 (D_m = 1.65 by flotation) g cm^{-3}, $F(000)$ = 232, μ(Mo-Kα) = 20.8 cm^{-1}, crystal dimensions *ca.* 0.25 × 0.30 × 0.20 mm.

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

Unit-cell parameters were derived by least-squares fitting to the setting angles of 25 intense reflections in the range θ 7–14°. The intensity data were collected at room temperature with the ω–2θ scan technique, in the range 2–35°, at a scan speed range of 0.9–5.5° min^{-1}, with a scan width 0.8° + 0.35 tan θ. Two standard reference reflections were measured at 3 h intervals. No significant changes in intensity were observed. Of 4194 collected reflections, 1251 had $I > 3.0\sigma(I)$ (after merge $R = 0.013$); the number of parameters was 138. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the Ψ scan, was applied[6] (maximum, minimum transmission factors = 0.99, 0.97).

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares calculations, minimizing $\Sigma w(|F_o| - |F_c|)^2$. All non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms, located in ΔF maps, were refined isotropically with fixed thermal parameters 1 Å^2 greater than those of the attached carbon or nitrogen atoms.

This model converged at $R = 0.026$ and $R' = 0.028$, $w = 0.9/[\sigma^2(F) + 0.001F_o{}^2]$, the residual electron density in the final Fourier difference map being 0.28–0.30 e Å^{-3}. Complex neutral-atom scattering factors[7] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76[8] program package and the ORTEP[9] plotting program. Final fractional coordinates for the non-hydrogen atoms are given in Table 1, selected bond distances and angles in Table 2.

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

Results and Discussion

Crystal Structure.—The structure of $[Cu_2(L)Cl_2]$ consists of infinite zigzag chains of copper atoms bridged by *trans*-oxamidate and chloride ligands. An analysis of the crystal packing reveals no features of chemical relevance.

A view of the asymmetric unit and of four symmetry related units is shown in Fig. 1. Two inversion centres relate adjacent chloride-bridged [Cu ··· Cu″ 3.2989(9) Å] and oxamidate-bridged [Cu ··· Cu′ 5.212(1) Å] copper atoms, the first corresponding to the geometrical centre of the $Cu_2(\mu\text{-}Cl)_2$ moiety and the second lying in the middle of the C(1) ··· C(1′) bond of the oxamidate ligand. The copper(II) atoms zigzag down the chain with a remarkably acute Cu″ ··· Cu ··· Cu′ angle of 120.30(3)°.[10]

A distorted square-pyramidal geometry is formed around each copper atom by two chlorine atoms (Cl and Cl″) in basal and apical co-ordination sites, respectively, and by three basal oxamidate donor atoms [N(1), N(2) and O(1′)]. The copper atom is displaced out of the basal least-squares plane, toward the apical chlorine, by 0.111 Å. The Cu–Cl″ vector forms an angle of 85.3° with the basal plane and a dihedral angle of 92.6° is formed between the CuClCu″Cl″ and basal planes.

The *trans*-oxamidate dianion, which is essentially flat, forms two chelate rings with each copper atom. The constraints imposed by the five-membered ring, which involves the almost perfectly planar O(1)C(1)N(2)O(1′)C(1′)N(2′) moiety (maximum deviation from the least-squares plane 0.004 Å), are reflected by the O(1′)–Cu–N(2) angle [84.5(1)°]. The six-membered ring exhibits a half-chair conformation in which C(3) is out of the plane described by the other five atoms (0.67 Å). The oxamidate plane and the basal plane are essentially parallel.

The Cu–O and Cu–N bond distances compare well with those observed in other oxamidate compounds,[1–4,11] the amide nitrogen N(2) giving rise to the strongest interaction with the copper(II) ion. The apical and equatorial Cu–Cl bond lengths are, as expected, markedly different from each other [2.866(1) and 2.268(1) Å, respectively] and are in the range usually found for di-μ-chloro-bridged copper(II) compounds.[12–14]

Table 1 Final positional parameters with estimated standard deviations (e.s.d.s) in parentheses for $[Cu_2(L)Cl_2]$

Atom	*x*	*y*	*z*
Cu	0.140 99(7)	0.197 86(6)	0.476 47(5)
Cl	0.272 6(2)	0.031 4(1)	0.645 2(1)
O(1)	−0.027 5(4)	0.667 1(3)	0.384 2(3)
N(1)	0.232 2(6)	0.052 6(5)	0.330 3(4)
N(2)	0.098 3(5)	0.399 4(4)	0.366 7(3)
C(1)	0.020 0(5)	0.521 3(4)	0.429 0(4)
C(2)	0.191 3(7)	0.101 1(5)	0.183 6(4)
C(3)	0.271 3(6)	0.305 8(5)	0.175 6(4)
C(4)	0.499 3(7)	0.377 0(7)	0.264 2(6)
C(5)	0.258 4(9)	0.323 3(7)	0.018 1(5)
C(6)	0.126 6(7)	0.421 8(6)	0.223 5(4)

Table 2 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[Cu_2(L)Cl_2]$

Cu–Cl	2.268(1)	Cu–O(1′)	1.972(3)
Cu–N(1)	1.972(4)	Cu–N(2)	1.949(3)
Cu–Cl″	2.866(1)	Cu ··· Cu′	5.212(1)
Cu ··· Cu″	3.2989(9)		
O(1′)–Cu–Cl	90.28(8)	N(1)–Cu–Cl	90.9(1)
N(2)–Cu–Cl	162.59(8)	O(1′)–Cu–N(1)	175.6(1)
O(1′)–Cu–N(2)	84.5(1)	N(2)–Cu–N(1)	95.5(1)
Cl–Cu–Cl″	100.98(3)	O(1′)–Cu–Cl″	90.16(7)
N(1)–Cu–Cl″	85.5(1)	N(2)–Cu–Cl″	95.63(8)
Cu–Cl–Cu″	79.02(3)	Cu″ ··· Cu ··· Cu′	120.30(3)

(′) = $-x, 1-y, 1-z$; (″) = $-x, -y, 1-z$.

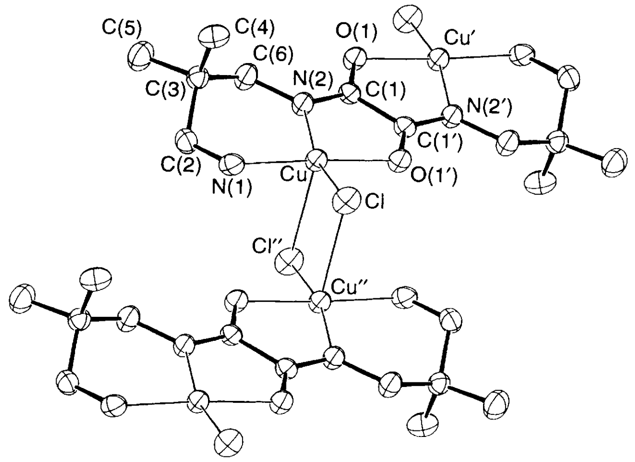

Fig. 1 ORTEP view of $[Cu_2(L)Cl_2]$ showing the atom numbering scheme and thermal motion ellipsoids (50%). The hydrogen atoms have been omitted for clarity

One geometrical feature of the di-μ-chloro bridge deserves comment. The Cu–Cl–Cu″ angle [79.02(3)°] has a remarkably small value. Typical values observed in di-μ-chloro-bridged copper(II) complexes range from 86 to 101° in dimeric compounds and from 88 to 145° in linear-chain compounds.[12–14] Correspondingly, the Cu ··· Cu″ distance [3.2989(9) Å], which is similar to that observed by us in the analogous di-μ-acetate-bridged polymer,[4] is very short.[12–14] We suggest that crystal-packing requirements are responsible for the remarkable compression of the di-μ-chloro bridge.

Magnetic and EPR Data.—The behaviour of χ_mT as a function of T, where χ_m is the magnetic susceptibility of $[Cu_2(L)Cl_2]$ per copper(II) atom and T is the absolute temperature, is shown in Fig. 2. The room-temperature χ_mT value (*ca.* 0.30 cm^3 K mol^{-1}), which is much lower than expected

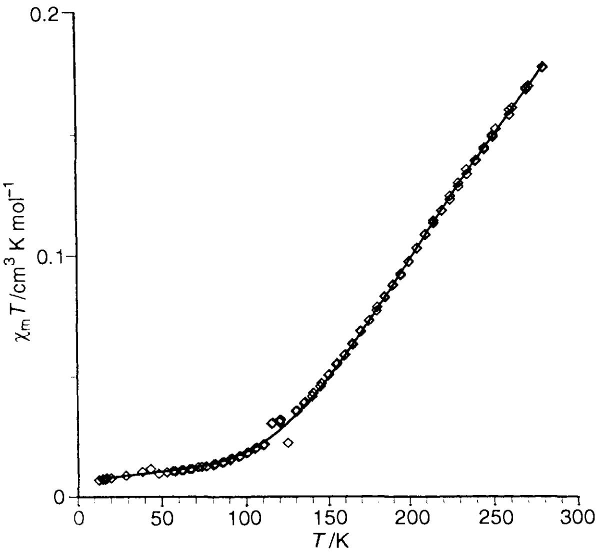

Fig. 2 Plot of $\chi_m T$ *versus* T for $[Cu_2(L)Cl_2]$. The solid line represents the best fit (see text)

for uncorrelated copper(II) ions (0.75 cm^3 K mol^{-1} with $g = 2$), and the smooth decrease of $\chi_m T$ and χ_m with T over the whole temperature range explored clearly prove that a strong antiferromagnetic coupling is operating between the copper(II) ions. This hypothesis is also supported by the polycrystalline powder EPR spectra of $[Cu_2(L)Cl_2]$. The room-temperature spectrum indicates an axial g tensor, with $g_\perp = 2.08$ and $g_\parallel = 2.24$. The signal intensity decreases on lowering the temperature, and no signal is observed below 120 K, pointing to a diamagnetic ($S = 0$) electronic spin ground state. No half-field transitions, nor hyperfine splittings are observed (see below).

The molecular structure of $[Cu_2(L)Cl_2]$ suggests the scheme shown below for the magnetic exchange interactions,

$$---(\mathrm{Cu}_{m-1} \overset{J}{—} \mathrm{Cu}_m \overset{J'}{—} \mathrm{Cu}_{m+1})---$$

where J and J' are the exchange coupling constants *via* the oxamidate and chloride bridges, respectively. The spin Hamiltonian for the resulting alternating chain[15,16] is given by equation (1), where $\alpha = J'/J$ is the alternation parameter.

$$\mathscr{H} = J \sum_{m=1}^{n/2} (S_{2m} \cdot S_{2m-1} + \alpha S_{2m} \cdot S_{2m+1}) \qquad (1)$$

Coupling constants as large as 400–500 cm^{-1} have been found in di-[11,17] and poly-nuclear[4] copper(II) complexes containing a *trans*-oxamidate bridge with similar co-ordination geometry. On the other hand, both the sign and the strength of the coupling occurring through bridging chloride ions in di- and poly-nuclear copper(II) complexes depend critically on the structural parameter Φ/R_0, where Φ is the Cu–Cl–Cu angle (in °) and R_0 is the out-of-plane Cu–Cl bond length (in Å).[12] Although recently criticized from a physical standpoint,[13] the established empirical correlation between J' and Φ/R_0 leads to the conclusion that, in the present case ($\Phi = 79.02°$, $R_0 = 2.866$ Å, $\Phi/R_0 = 27.6°$ Å^{-1}) an antiferromagnetic coupling is expected and a J' value in the range 5–20 cm^{-1} is predicted. Unfortunately, as a result of the large expected value of J, the available expressions of χ_m as a function of T, J and α[16] are not applicable, since they hold only for $kT/J > 0.5$. Even if this were not the case, their reliability for very low values of α (0.01–0.05) is doubtful. However, some simplification may be introduced owing to the predicted overwhelming importance of the oxamidate bridge in determining the exchange interactions between the copper(II) ions. In fact, the low expected value of the alternation parameter α in equation (1) suggests that the dimer model with pairwise interactions may be used at a good approximation and that the spin Hamiltonian (1) may be conveniently rewritten as equation (2).

$$\mathscr{H} = JS_1 \cdot S_2 \qquad (2)$$

For $S_1 = S_2 = \frac{1}{2}$, the Hamiltonian (2) leads to the Bleaney–Bowers expression (3)[18] in which corrections for the presence of a small amount ρ of a paramagnetic impurity obeying the Curie law over the temperature range explored and for temperature independent paramagnetism have been introduced.

$$\chi_m T = (Ng^2\mu_B{}^2/3k)[1 + \tfrac{1}{3}\exp(J/kT)](1 - \rho) + (Ng^2\mu_B{}^2/4k)\rho + N\alpha' T \qquad (3)$$

$$g = \langle g^2 \rangle^{\frac{1}{2}} = [\tfrac{1}{3}(2g_\perp{}^2 + g_\parallel{}^2)]^{\frac{1}{2}} \qquad (4)$$

The least-squares best fit of expression (3) to the experimental data, with g fixed at 2.13 on the basis of the EPR findings and of expression (4), yields $J = 409(3)$ cm^{-1}, $\rho = 0.015(1)$ and $N\alpha' = 77(7) \times 10^{-6}$ cm^3 mol^{-1}. As may be seen in Fig. 2, the agreement between the experimental points and the theoretical curve is excellent.

The positive and large value of the exchange coupling constant J agrees with the absence of any magnetic susceptibility maximum in the temperature range examined: in fact, a maximum is expected at $T_{max} = \frac{5}{8} J/k = 368$ K, much higher than those explored.[19]

The absence of half-field transitions and hyperfine splittings in the polycrystalline powder EPR spectra of $[Cu_2(L)Cl_2]$, however, indicates that, as previously reported for the alternating *trans*-oxamidate/acetate bridged linear chain,[4] significant exchange narrowing effects are present and that the compound intimately behaves as a alternating chain, the dimer model thus being only a first-order good approximation.[11,17]

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References

1 V. G. Albano, C. Castellari, A. C. Fabretti and A. Giusti, *Inorg. Chim. Acta*, 1992, **191**, 213.
2 A. C. Fabretti, A. Giusti, V. G. Albano, C. Castellari, D. Gatteschi and R. Sessoli, *J. Chem. Soc., Dalton Trans.*, 1991, 2133.
3 C. Benelli, A. C. Fabretti and A. Giusti, *J. Chem. Soc., Dalton Trans.*, 1993, 409.
4 A. Bencini, C. Benelli, A. C. Fabretti, G. C. Franchini and D. Gatteschi, *Inorg. Chem.*, 1986, **25**, 1063.
5 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **30**, 203.
6 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
7 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99–101.
8 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, 1976.
9 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
10 M. M. Olmstead, W. K. Musker, L. W. Ter-Haar and W. E. Hatfield, *J. Am. Chem. Soc.*, 1982, **104**, 6627.
11 A. Bencini, M. Di Vaira, A. C. Fabretti, D. Gatteschi and C. Zanchini, *Inorg. Chem.*, 1984, **23**, 1620.

12 W. E. Hatfield, in *Magneto-Structural Correlations in Exchange Coupled Systems*, eds. R. D. Willett, D. Gatteschi and O. Kahn, D. Reidel, Dordrecht, 1985, p. 567 and refs. therein.
13 M. T. Garland, J.-Y. Saillard and E. Spodine, *J. Crystallogr. Spectrosc. Res.*, 1992, **22**, 467.
14 P. Alemany and S. Alvarez, *Chem. Mater.*, 1990, **2**, 723.
15 W. Duffy and K. P. Barr, *Phys. Rev.*, 1968, **165**, 647.
16 J. W. Hall, W. E. Marsh, R. R. Weller and W. E. Hatfield, *Inorg. Chem.*, 1981, **20**, 1033.
17 A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, A. C. Fabretti and G. C. Franchini, *Inorg. Chim. Acta*, 1984, **86**, 169.
18 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.
19 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, 1986, p. 76.

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