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Deprotonation and self-assembly of a symmetric oxamidate-bridged dinuclear copper(II) complex involving imidazole moieties

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A novel symmetrical bis-tetradentate Schiff base, H_4L, has been prepared from the condensation of H_2L' [*N*,*N*′-bis(3-aminopropyl)oxamide] with imidazole-2-carbaldehyde. This ligand reacts with copper(II) perchlorate in neutral medium to yield the dinuclear complex $[Cu_2(H_2L)][ClO_4]_2$, which has two non-deprotonated imidazolyl moieties. The crystal structure of this compound, solved by single-crystal X-ray diffraction, consists of planar centrosymmetric dinuclear copper(II) cations and two perchlorate anions. The copper(II) ions are bridged by an oxamidate group in *trans* conformation resulting in a copper–copper distance of 5.119 Å. Each copper(II) ion occupies an inner site of the dideprotonated ligand with a CuN_3O distorted square-planar environment, and bond distances of *ca.* 1.95 Å. In $[Cu_2(H_2L)][ClO_4]_2$, each copper(II) ion can additionally accept one donor atom in axial position. Under basic conditions, this donor atom is the deprotonated imidazolate nitrogen atom from another dinuclear $[Cu_2L]$ unit, giving rise, by a self-assembly process, to the formation of the polynuclear copper(II) complex $[(Cu_2L)_n]$. In this complex the copper(II) ions must be alternatively bridged by oxamidate and imidazolate groups. From magnetic susceptibility measurements, both $[Cu_2(H_2L)][ClO_4]_2$ and $[(Cu_2L)_n]$ were found to exhibit strong antiferromagnetic exchange coupling, with *J* values of −431 and −265 cm^{-1}, respectively.

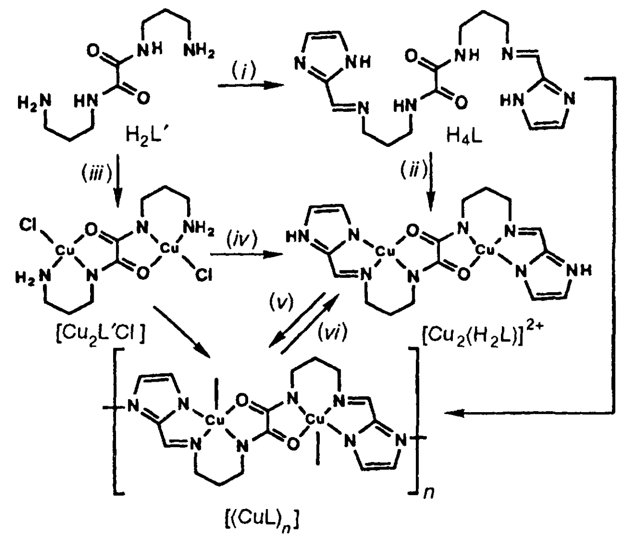
The synthesis of polymetallic co-ordination complexes, particularly those having two-, three-dimensional and supramolecular structures, is of current interest for inorganic chemists seeking to design new molecular materials with unusual magnetic and electrical properties.[1]

To prepare polynuclear metal complexes, two strategies are commonly followed: (*i*) the use of polynucleating ligands and (*ii*) the use of 'metal complexes as ligands'. As for the first method, from a literature survey it appears that the majority of the polynucleating ligands reported so far contain two or four equivalent co-ordination sites, which can be occupied by metal ions to afford di- and tetra-nuclear metal complexes, commonly of homonuclear nature.[2] The second strategy, which relies on the reaction of a metal complex containing potential donor groups with a metal ion or metal complex with empty co-ordination sites is more convenient to prepare heteropolynuclear species.

With the aim of obtaining more numerous and more complex systems that may represent new polymetallic magnetic models, we have designed a polynucleating ligand able to be involved successively in both strategies (*i*) and (*ii*).

The ligand H_4L, in a neutral medium, acts as a bis(tetradentate) N_3O to form the dinuclear cationic copper(II) complex $[Cu_2(H_2L)]^{2+}$, which, under basic conditions, can act as a 'ligand' and co-ordinate other metal ions through the two N-deprotonated imidazolyl groups (see Scheme 1).

It is interesting that in the complex $[Cu_2(H_2L)]^{2+}$ each copper(II) atom can additionally accept one donor atom in axial position, increasing its co-ordination number from four to five. The donor atom can belong either to ligands such as azide or thiocyanate or under basic conditions to the deprotonated imidazolate group of another $[Cu_2(H_2L)]^{2+}$ unit. In the latter case, a self-assembly process occurs, giving rise to the polynuclear copper complex $[(Cu_2L)_n]$.



Scheme 1 (*i*) Imidazole-2-carbaldehyde, MeOH, reflux 1 h; (*ii*) $Cu(ClO_4)_2$, BuOH; (*iii*) $Cu(ClO_4)_2$, EtOH, water; (*iv*) imidazole-2-carbaldehyde, EtOH, 40 °C, few min, then $HClO_4$; (*v*) KOH; (*vi*) $HClO_4$

The formation of polynuclear copper(II) complexes by deprotonation and self-assembly of a mononuclear copper(II) precursor containing only one imidazolyl group has been previously reported.[3–6] However, to the best of our knowledge, no self-assembly process from a dinuclear copper(II) precursor containing two imidazolyl groups, such as $[Cu_2(H_2L)]^{2+}$, has been reported so far. The nature of the self-assembled polynuclear copper(II) complex will depend on the type of precursor. Thus, deprotonation of Cu–Him complexes leads to one-dimensional regular imidazolate-bridged polynuclear copper(II) complexes,[3–6] whereas $[Cu_2(H_2L)]^{2+}$ must generate

Table 1 Atomic coordinates (× 10^5) for the non-hydrogen atoms of $[Cu_2(H_2L)][ClO_4]_2$

Atom	*X/a*	*Y/a*	*Z/a*
Cu	12 589(5)	23 109(5)	4 996(4)
O(1)	−4 560(28)	15 318(29)	6 048(24)
N(1)	9 989(41)	41 424(37)	11 193(29)
N(2)	18 200(49)	62 542(41)	14 887(33)
C(1)	1 133(52)	49 214(53)	15 207(36)
C(2)	5 987(67)	62 312(53)	17 540(40)
N(3)	29 940(36)	31 648(39)	3 884(30)
C(3)	20 284(53)	49 829(54)	11 121(36)
N(4)	14 820(35)	6 351(34)	−2 641(26)
C(4)	31 221(51)	44 413(51)	6 925(37)
C(5)	40 056(43)	24 164(51)	−497(38)
C(6)	33 854(50)	14 867(52)	−9 618(40)
C(7)	26 425(43)	2 273(46)	−6 953(38)
C(8)	−5 505(42)	2 794(48)	2 599(32)
Cl(1)	33 717(14)	−1 575(15)	25 015(11)
O(2)	45 466(40)	6 348(43)	25 041(35)
O(3)	34 106(40)	−6 898(46)	35 137(30)
O(4)	22 746(41)	7 726(45)	22 087(29)
O(5)	33 355(45)	−12 101(36)	17 493(30)

an alternating copper(II) complex polymer, (–im–Cu–oxam–Cu–im–)$_n$ (where oxam and im represent oxamidate and imidazolate bridges, respectively).

This paper is concerned with the synthesis and magnetic properties of the oxamidate-bridged dinuclear copper(II) complex $[Cu_2(H_2L)][ClO_4]_2$ and the alternating oxamidate–imidazolate-bridged copper(II) complex polymer $[(Cu_2L)_n]$, which is obtained from $[Cu_2(H_2L)][ClO_4]_2$ by deprotonation and self-assembly. The crystal structure of $[Cu_2(H_2L)][ClO_4]_2$ is also reported.

Experimental

Preparation of the ligands

The ligand *N,N'*-bis(3-aminopropyl)oxamide (H_2L'), was obtained according to the literature,[7] but using diethyl ether instead of light petroleum as solvent. Yield: 90%. ^{1}H NMR [$(CD_3)_2SO$]: δ 1.62 (q, 4 H, CCH_2C), 2.63 (t, 4 H, CH_2NH_2), 3.29 (qnt, 4 H, CH_2NH), 3.31 (br, 4 H, NH_2) and 8.93 (t, 2 H, NHCO).

H_4L. Imidazole-2-carbaldehyde (0.021 mol, 2.02 g) was added to a suspension of H_2L' (0.01 mol, 2.02 g) in methanol (80 cm^3). The mixture was stirred and heated at reflux for 1 h. The resulting yellow solution was filtered, to remove any insoluble material present, and allowed to stand at 0 °C for 1 day. The yellow pale powder which formed was filtered off, washed with methanol and diethyl ether, and air dried. Yield: 85%. Analytical data (C, H, N) were in accord for the anhydrous ligand. ^{1}H NMR [$(CD_3)_2SO$]: δ 1.82 (q, 4 H, CCH_2C), 3.21 (m, 4 H, CH_2NH), 3.55 (t, 4 H, NCH_2), 7.12 (s, 4 H, CH=CH), 8.17 (s, 2 H, HC=N) and 8.85 (t, 2 H, NHCO).

Preparation of the complexes

$[Cu_2(H_2L)][ClO_4]_2$. An ethanolic solution of copper(II) perchlorate (2.1 mmol, 0.778 g) was slowly added to a suspension of H_4L (1 mmol, 0.358 g) in butanol (50 cm^3). The mixture was stirred for a few min and then a blue-violet precipitate appeared, which, after 30 min of additional stirring, was filtered off, washed with ethanol and diethyl ether and air-dried; yield, 80%. Suitable crystals for X-ray analysis were obtained by evaporation of a methanol–water (4:1) solution of the complex at room temperature (Found: C, 28.1; H, 3.1; N, 16.1. Calc. for $C_{16}H_{20}Cl_2Cu_2N_8O_{10}$: C, 28.2; H, 2.9; N, 16.4%).

This complex can also be prepared from the condensation of the complex $[Cu_2(trans\text{-}L')Cl_2(H_2O)_2]$[8] with imidazole-2-carbaldehyde as follows: imidazole-2-carbaldehyde (2 mmol, 0.192 g) was added to a stirred suspension of $[Cu_2(trans\text{-}L')Cl_2(H_2O)_2]$ (1 mmol, 0.434 g) in ethanol (40 cm^3). The mixture was heated at 40 °C for a few min and then perchloric acid (0.6 cm^3, 70%) was added, whereupon the colour changed from green to blue, and a blue-violet powder corresponding to the complex $[Cu_2(H_2L)][ClO_4]_2$ appeared, which was filtered off, washed with ethanol, diethyl ether and air dried.

$[(Cu_2L)_n]$. The ligand H_4L (1 mmol, 0.358 g) was dissolved in methanol–water (4:1, 50 cm^3) containing potassium hydroxide (4.1 mmol, 0.230 g). To the filtered solution was added copper(II) perchlorate (2 mmol, 0.741 g) dissolved in water (20 cm^3), resulting in the immediate precipitation of a green powder, which, after 10 min, was filtered off, washed with methanol and diethyl ether and air-dried; yield, 91% (Found: C, 39.9; H, 3.9; Cu, 26.1; N, 23.1. Calc. for $C_{16}H_{18}Cu_2N_8O_2$: C, 39.9; H, 3.7; Cu, 26.4; N, 23.3%).

This complex can also be prepared by the addition of a base, such as KOH or triethylamine, to an aqueous or methanolic solution, respectively, of $[Cu_2(H_2L)][ClO_4]_2$. A green powder of $[(Cu_2L)_n]$ immediately precipitated. On the other hand, addition of perchloric acid to an ethanolic suspension of $[(Cu_2L)_n]$ after short stirring yields a blue solution from which $[Cu_2(H_2L)][ClO_4]_2$ precipitates.

Physical measurements

Microanalyses and infrared spectra and the magnetic susceptibility measurements were performed as previously described.[9] Proton NMR spectra of the ligands were recorded on a Bruker AM-300 spectrometer. All ^{1}H chemical shifts are given in ppm *versus* $SiMe_4$ using $(CD_3)_2SO$ as solvent.

X-Ray data collection and structure determination of $[Cu_2(H_2L)][ClO_4]_2$

Single-crystal data collection was performed at ambient temperature with a Siemens R3m/V diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation. A violet crystal of this compound with dimensions 0.304 × 0.266 × 0.152 mm was used. The unit cell parameters were calculated by least-squares refinement of 25 carefully centred reflections ($25 < 2\theta < 35°$). The compound crystallizes in the monoclinic system, space group $P2_1/c$, with a = 10.242(1), b = 9.515(1) and c = 12.976(2) Å, β = 102.92(3)°, U = 1232.6(5) Å^3, Z = 4, D_c = 1.839 g cm^{-3} and μ(Mo-Kα) = 2.011 mm^{-1}. A total of 3900 reflections were collected ($2\theta_{max}$ = 60°, h = 0–14, k = 0–13, l = −18 to 18), giving 3593 unique reflections of which 1780 were considered as observed with $|F| > 3\sigma(F)$. Intensities of three checked reflections measured after every 90 min showed only statistical fluctuations during the course of the data collection. The data were corrected for Lorentz-polarization effects, for dispersion and for absorption.

The structure was solved by the Patterson method by using the SHELXTL PLUS program.[10] In the final refinements, all non-hydrogen atoms were refined anisotropically. Some hydrogen [C(2)–H(2A), N(2)–H(2B) and C(6)–H(6A)] were located in difference Fourier maps, and were refined isotropically. The remaining hydrogen atoms bonded to carbons were placed at their calculated positions (C–H 0.96 Å) and were refined at the final cycle. The function minimized was $\Sigma w(\Delta F)^2$ [$1/w = \sigma^2(F_o)$], resulting in a final $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ value of 0.063 (R' = 0.035). Atomic coordinates for the non-hydrogen atoms are listed in Table 1. Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

The ligand H_2L' has been widely used by inorganic chemists due to its ability to yield bridged-oxamidate polynuclear copper(II) complexes.[11] The dianionic form L′ can adopt *cis* or *trans* conformation: in the *cis* conformation, the ligand displays two different co-ordination sites: (*i*) an inner N_4 site, which can be occupied by a copper(II) ion giving rise to the mononuclear complex [Cu(*cis*-L′)], and (*ii*) an outer O_2 site, that can co-ordinate, in a second step, another metal ion, yielding a polynuclear metal complex. However, when L′ adopts the *trans* conformation, two identical N_2OX (X is a donor atom from an external ligand) co-ordination sites are formed so that the ligand can accommodate two copper(II) ions to afford the dinuclear complexes $[Cu_2(trans\text{-}L')X_2]$. Some complexes of this type have been prepared with 2,2′-bipyrimidine,[12] pyrimidine,[13,14] 4,4′-bipyridine,[14] cyanate,[15] imidazole[16] and azide.[16,17]

Recently, it has been shown that the NH_2 groups of the N,N′-disubstituted oxamides can be condensed with an aldehyde, such as salicylaldehyde, to yield new binucleating ligands.[18] This is of great interest for generating, from H_2L', and depending on the choice of the aldehyde reagent, new ligands designed for a particular problem. Using this procedure, condensation of H_2L' and imidazole-2-carbaldehyde (Scheme 1) leads to a new symmetric ligand, H_4L, containing two N_3O inner sites. This ligand reacts with copper(II) perchlorate in 1 : 2 molar ratio to afford the dinuclear complex $[Cu_2(H_2L)][ClO_4]_2$, which shows a high solubility in methanol and water. This complex, after deprotonation, can act as a ligand for the copper(II) ions of a neighbouring $[Cu_2(H_2L)]^{2+}$ unit, giving rise, in a self-assembly process, to a polynuclear copper(II) complex. Thus, the addition of KOH to an aqueous solution of $[Cu_2(H_2L)][ClO_4]_2$ immediately produces a green precipitate of the complex $[(Cu_2L)_n]$, which is insoluble in water and organic solvents. It should be noted, as indicated in the Experimental section, that this complex and its precursor can be reversibly interconverted by adjustment of pH.

The IR spectra of the complexes $[Cu_2(H_2L)][ClO_4]_2$ and $[(Cu_2L)_n]$ do not show the N–H amide band appearing at 3292 cm^{-1} for the free ligand. This is in accordance with the co-ordination of the oxamide group to the copper(II) ions in a dideprotonated form in both complexes. Moreover, the IR spectrum of $[Cu_2(H_2L)][ClO_4]_2$ exhibits two ν(N–H) imidazole bands at *ca.* 3150 cm^{-1}. These bands are absent from the IR spectrum of the complex $[(Cu_2L)_n]$, indicating that both imidazolic groups are deprotonated in this compound. Finally, only the IR spectrum of $[Cu_2(H_2L)][ClO_4]_2$ exhibits the characteristic ν_3 and ν_4 (Cl–O) modes (1060 and 625 cm^{-1}) of perchlorate anions. These spectral features are in accord with the molecular structure of $[Cu_2(H_2L)][ClO_4]_2$ described below.

Crystal structure of $[Cu_2(H_2L)][ClO_4]_2$

The structure of this complex consists of centrosymmetric dinuclear copper(II) cations and two perchlorate anions. A perspective view of the molecular structure with the atomic numbering scheme is shown in Fig. 1. Selected intramolecular bond distances and angles are listed in Table 2.

Within the dinuclear molecules, crystallographically equivalent copper(II) ions are bridged by an oxamidate group in *trans* conformation resulting in a copper–copper distance of 5.119 Å. The centre of inversion is located at the middle of the C(8)–$C(8^I)$ bond of the oxamidate group (I: $-x$, $-y$, $-z$). Each copper(II) ion occupies an inner site of the dideprotonated ligand with a CuN_3O distorted square-planar environment, and bond distances of *ca.* 1.95 Å. The bis(tetradentate) behaviour of H_2L results in the formation of two five- and one six-membered ring around each copper atom.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_2(H_2L)][ClO_4]_2$

Cu–N(1)	1.962(4)	Cu–N(3)	1.988(4)
Cu–N(4)	1.918(3)	Cu–O(1)	1.939(3)
Cu–O(4)	2.676	C(8)–O(1)	1.269(5)
$C(8^I)$–N(4)	1.292(6)	C(8)–$C(8^I)$	1.533(9)
N(1)–Cu–N(3)	82.7(2)	N(1)–Cu–N(4)	173.2(2)
N(1)–Cu–O(1)	95.9(2)	N(3)–Cu–N(4)	95.2(2)
N(3)–Cu–O(1)	178.3(1)	N(4)–Cu–O(1)	86.2(1)
O(1)–C(8)–$N(4^I)$	129.0(4)	C(8)–O(1)–Cu	109.5(3)
$C(8^I)$–N(4)–Cu	112.6(3)	Cu–N(4)–C(7)	127.9(3)

I: $-x$, $-y$, $-z$.

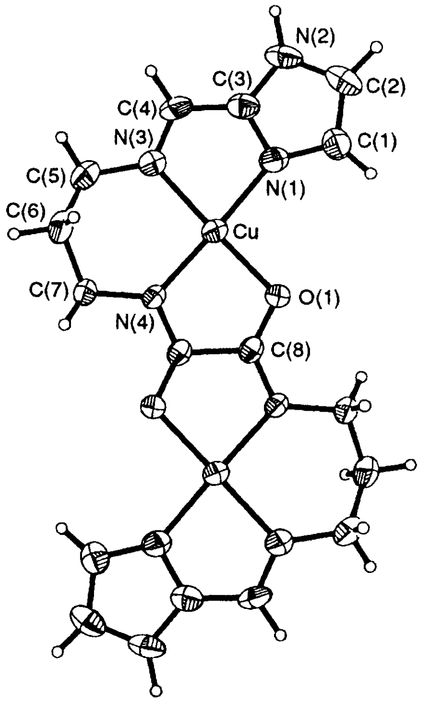


Fig. 1 A perspective view of the centrosymmetric dinuclear cation $[Cu_2(H_2L)]^{2+}$. Perchlorate anions are omitted for clarity

The four atoms of the co-ordination plane are almost coplanar with deviations from the least-squares plane < 0.045 Å. The copper(II) ion deviates 0.068 Å toward the O(4) oxygen atom belonging to a semi-co-ordinated perchlorate anion at 2.676 Å. The oxamidato bridge is also planar and forms a dihedral angle of 5.7° with the N_3O co-ordination plane, so that the whole centrosymmetric cation can be considered as planar. The dinuclear molecules are connected by hydrogen bonds involving the imidazole N(2)–H(2B) and the oxygen atom $O(5^{II})$ from a perchlorate anion, with a N(2)–$O(5^{II})$ (II: x, $y + 1$, z) distance of 2.848 Å. This interaction gives rise to an infinite zigzag chain running along the *b* axis (Fig. 2).

All attempts to grow suitable crystals of $[(Cu_2L)_n]$ for X-ray analyses were unsuccessful. Nevertheless, given that both complexes, $[(Cu_2L)_n]$ and $[Cu_2(H_2L)][ClO_4]_2$, are involved in an acid–base equilibrium (Scheme 1), it is reasonable to assume that: (*i*) the dinuclear unit in the structure of $[Cu_2(H_2L)][ClO_4]_2$ should also be present in $[(Cu_2L)_n]$ and (*ii*) the deprotonation of $[Cu_2(H_2L)][ClO_4]_2$ induces the co-ordination of the N-imidazolate atoms at axial positions of the copper(II) ions of neighbouring dinuclear units, so that these are assembled to yield a complicated two-dimensional polymetallic network, as proposed in Scheme 2.

On the other hand, $[Cu_2(H_2L)][ClO_4]_2$ can also be obtained by another route which relies on the template effect. Indeed, from the reaction between the dinuclear complex $[Cu_2(trans\text{-}L')Cl_2]$ and imidazole-2-carbaldehyde in the presence

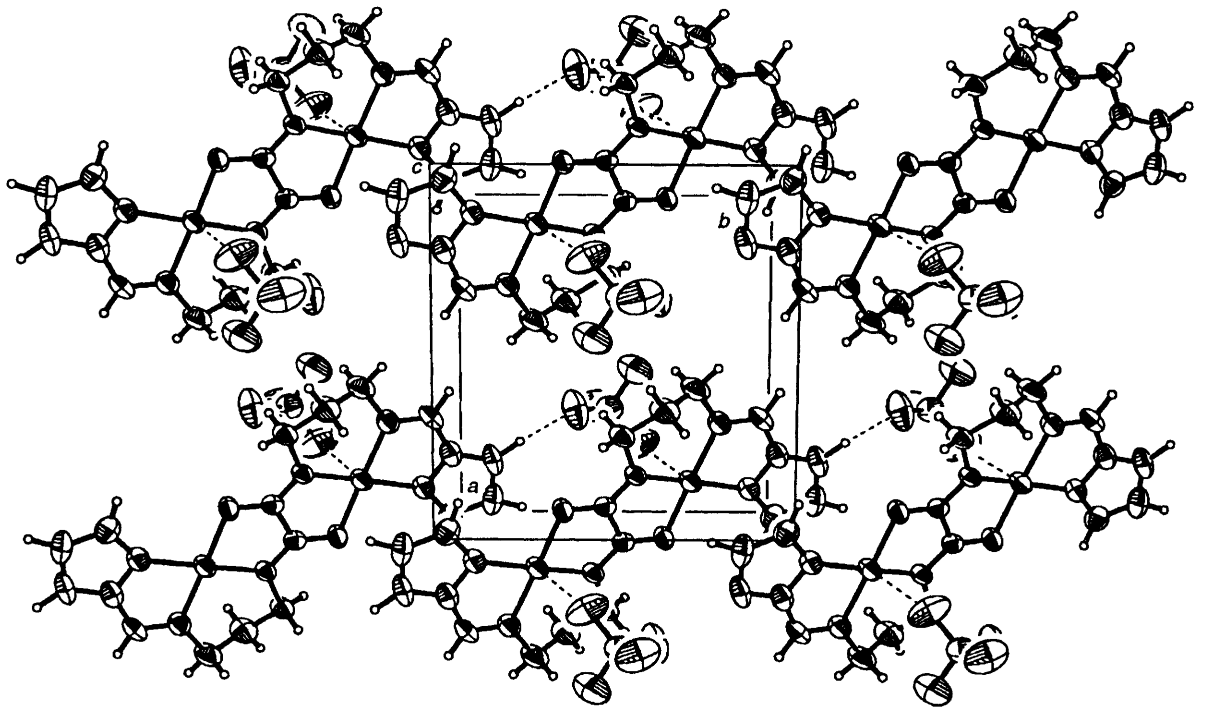
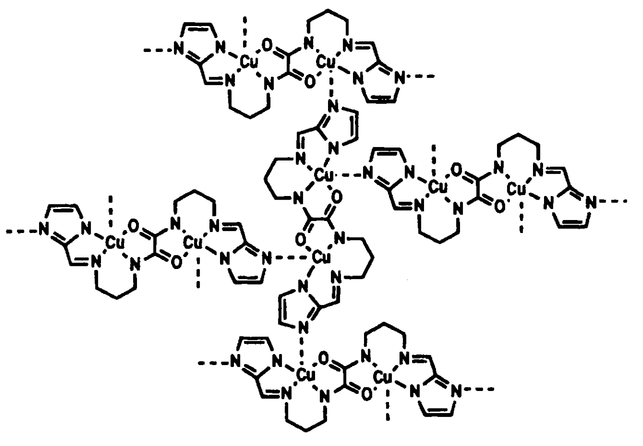


Fig. 2 A view of the molecular packing of $[Cu_2(H_2L)][ClO_4]_2$ down the *a* axis



Scheme 2 Proposed structure of $[(Cu_2L)_n]$

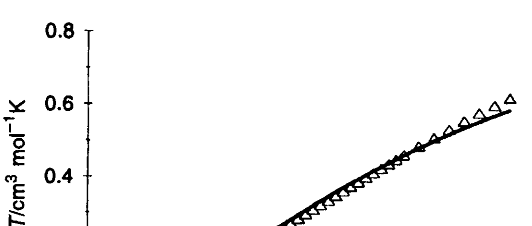


Fig. 3 Temperature dependences of $\chi_M T$ for $[(Cu_2L)_n]$ (△) and $[Cu_2(H_2L)][ClO_4]_2$ (○). Solid lines were generated from the best-fit magnetic parameters

of perchloric acid, the complex $[Cu_2(H_2L)][ClO_4]_2$ can be isolated (Scheme 1). It seems that acid or base is required to induce the condensation reaction (*e.g.* $HClO_4$ or KOH, NEt_3), since, in their absence, reaction does not take place. However, use of base causes not only condensation but also deprotonation and the self-assembly process, ultimately leading to the polynuclear complex $[(Cu_2L)_n]$.

It should be pointed out that, as far as we know, the condensation of imidazole-2-carbaldehyde with a metal complex containing free NH_2 groups always leads to deprotonated species.[19] However, our results seem to indicate that the preparation of non-deprotonated species can be achieved in acidic media.

Magnetic properties

The temperature variation of $\chi_M T$ for the complexes $[Cu_2(H_2L)][ClO_4]_2$ and $[(Cu_2L)_n]$ is shown in Fig. 3. The room-temperature $\chi_M T$ values (per dinuclear molecule) of 0.23 and 0.61 $cm^3\,mol^{-1}$ K, respectively are lower than those expected for two isolated copper(II) ions, clearly indicating that a strong antiferromagnetic exchange coupling is operative between the copper(II) ions in both compounds, but with different *J* values. This is also apparent from a consideration of the temperature dependences of $\chi_M T$. Thus, as the temperature is lowered, the product $\chi_M T$ for the complex $[Cu_2(H_2L)][ClO_4]_2$ steadily decreases to zero at *ca.* 75 K, whereas for $[(Cu_2L)_n]$, $\chi_M T$ gradually decreases reaching a quasiplateau at *ca.* 50 K and then decreases again approaching almost zero at 5 K.

According to the crystal structure, the magnetic data for $[Cu_2(H_2L)][ClO_4]_2$ were fitted to the Bleaney–Bowers equation. From the best fit (Fig. 3), a *J* value of $-431\ cm^{-1}$ was obtained with $g = 2.0$. This *J* value is of the same order as those observed for other *trans*-oxamidate-bridged dinuclear copper(II) complexes (*ca.* 500 cm^{-1})[12–17] and is consistent with the remarkable ability of the oxamidate bridge to transmit an exchange interaction between copper(II) ions.

For $[(Cu_2L)_n]$, taking into account the proposed structure (see Scheme 2), two different exchange pathways are possible: (*i*) Cu–oxam–Cu (through the *trans*-oxamidate group) and (*ii*) Cu–im–Cu (through the imidazolate group). The oxamidate bridge, as observed in $[Cu_2(H_2L)][ClO_4]_2$, propagates the antiferromagnetic exchange interaction very effectively whereas the imidazolate bridge is less efficient, with $|J|$ varying up to *ca.* 100 cm^{-1}.[20] Nevertheless, when the imidazolate bridging group co-ordinates one of the copper(II) atoms at axial position, as must occur in $[(Cu_2L)_n]$, much more feeble exchange interactions ($2J$ *ca.* -1.8 to $-15\ cm^{-1}$) have been observed.[3-6] Therefore, from the magnetic point of view, the structure proposed for $[(Cu_2L)_n]$ may be considered as a two-dimensional network of weakly interacting dinuclear copper(II) complexes and then a modified Bleaney–Bowers equation, which takes into account the intermolecular exchange interactions (θ), may be used as a good approximation to analyse the magnetic data, equation (1).

$$\chi_M = (2N\beta^2g^2)/k(T-\theta)\,[3+\exp(-J/kT)]^{-1}(1-\rho) + [Ng^2\beta^2/2k(T-\theta)]\rho + 2N\alpha \quad (1)$$

In this equation ρ represents a small amount of paramagnetic impurity which exhibits a Weiss constant θ to take phenomenologically into account the decrease of μ_{eff} at low temperature.

The best fit of the susceptibility data by this equation was found with $J = -265\ cm^{-1}$, $g = 2.0$, $\theta = -7.5$ K and $\rho = 0.14$. The calculated curve fits the experimental points satisfactorily as shown in Fig. 3. The lower value of J in $[(Cu_2L)_n]$ compared to that of $[Cu_2(H_2L)][ClO_4]_2$ is a consequence of the co-ordination of the *N*-imidazolate in axial position, which could confer some trigonal-bipyramidal character to the resulting CuN_4O chromophore and decrease the overlap of the magnetic orbitals.

Similar magnetic behaviours have been observed for two-dimensional copper(II) complexes containing bridging *trans*-oxamidate in conjunction with other bridging ligands, such as pyrimidine,[13,14] 4,4′-bipyridine[14] or acetate,[21] which transmit the exchange magnetic interaction less efficiently than the former.

Conclusion

We have shown in this work that it is possible to prepare and isolate a bridged-oxamidate dinuclear copper(II) complex in which two non-deprotonated 2-imidazolyl groups are present. The interest of this complex lies in its ability to afford, by deprotonation and self-assembly, a polymer in which the copper(II) ions must be alternatively bridged by oxamidate and imidazolate groups. In this sense, a similar route can be used to prepare alternating heterobimetallic polynuclear complexes of the type $[M\text{–}im\text{–}Cu\text{–}oxam\text{–}Cu\text{–}im\text{–}M]_n$. Work along such lines is in progress.

Acknowledgements

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