Structure and Magnetic Studies of a Two-dimensional Sheet-like Copper(II) Complex with Bridging Pyridine-4-carboxylate and *trans*-Oxamidate Ligands†

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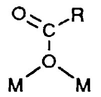
The complex polymer $[\{Cu_2L(pyca)(H_2O)\}_n][ClO_4]_n\cdot 2nH_2O$ [H_2L = *N,N'*-bis(2-aminoethyl)oxamide, Hpyca = pyridine-4-carboxylic acid] has been prepared and its magnetic properties and crystal structure determined. The crystals are monoclinic, space group $P2_1/c$, with a = 10.420(2), b = 13.118(2), c = 14.863(5) Å, β = 93.05(2)°, and Z = 4. The structure consists of a two-dimensional network of copper(II) ions bridged by the bis(tridentate) ligand L in *trans* conformation, and by pyridine-4-carboxylate where the carboxylate group is bonded to three different copper centres in a novel manner. The repeating asymmetric unit is a binuclear copper(II) fragment with one of the metal centres in an octahedral environment whereas the other is in a distorted square-based pyramidal geometry. From magnetic susceptibility measurements the complex was found to exhibit a strong antiferromagnetic coupling with $J = -486$ cm^{-1} and $\theta = -15$ K, due to the efficiency of the oxamidate and triatomic *anti-anti* carboxylate bridges in propagating antiferromagnetic exchange interaction between the copper(II) ions which are separated by about 5.2 and 6.9 Å, respectively.

Metal co-ordination polymers with low-dimensional structures have been actively investigated as molecular materials having unusual electrical, magnetic and optical properties.[1–5] In order to obtain such polymers with magnetic properties several strategies are possible. One is the reaction of metal ions with two different potentially bridging ligands to form one-dimensional alternating chains or two- or three-dimensional infinite networks.[3]

Carboxylate is a versatile anion which can bridge metal ions in mono- (**I**)[6–11] or tri-atomic [including *syn-syn* (**II**),[12] *syn-anti* (**III**)[13–18] and *anti-anti* (**IV**)[19] and mono- and bi-dentate (**V**)[20]] modes as shown. As expected on the basis of their respective geometries, the mono- and tri-atomic *syn-syn* conformations usually favour the formation of dinuclear complexes while the *anti-anti* and *syn-anti* triatomic conformations generally correspond to chain or layer compounds.[15,18] The magnetic properties resulting from their various structures is the most fascinating aspect of the chemistry of μ-carboxylato-copper(II) complexes. Although varieties of these complexes have been structurally and magnetically characterized, there are no examples of two-dimensional sheet-like copper(II) polymers in which the carboxylate groups present the novel bridging mode[20] **VI** (μ_3-carboxylate-*O,O'*) containing not only mono-atomic but also triatomic *syn-anti* and *anti-anti* types.



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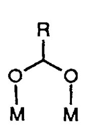

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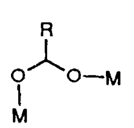

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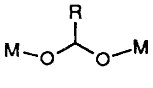

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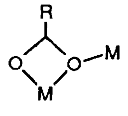

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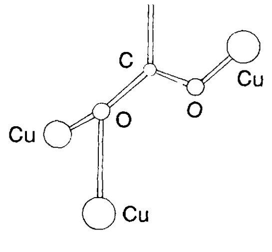

VI

Owing to their ready *cis-trans* conformational changes, *N,N'*-disubstituted oxamidates have played a key role in the design of polymetallic species hopefully exhibiting magnetic properties.[21] The bis(tridentate) character of these compounds in the *trans* conformation allows the formation of *trans*-oxamidato-bridged dinuclear copper(II) units which can be linked by anions such as azide,[22] cyanate[23] and acetate[7] to form one-dimensional alternating chains. In order to extend this work we considered higher-dimensionality complex polymers. For this purpose, carboxylate was chosen as secondary bridge. We report here the synthesis, crystal structure and magnetic behaviour of the first two-dimensional sheet-like copper(II) complex containing *trans*-oxamidate bridges and pyridine-4-carboxylate (pyca) ligands bridging in a novel μ_3-*O,O'* manner.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Experimental

Synthesis.— *N,N'*-Bis(2-aminoethyl)oxamide (H_2L) and its mononuclear complex [CuL]·$2H_2O$ were obtained according to the literature.[24]

$[\{Cu_2L(pyca)(H_2O)\}_n][ClO_4]_n \cdot 2nH_2O$. To a heated aqueous solution of [CuL]·$2H_2O$ (1 mmol, 30 cm^3) was added an aqueous solution of copper(II) perchlorate (1 mmol, 10 cm^3) with stirring. An aqueous solution of sodium pyridine-4-carboxylate (1 mmol, 20 cm^3) was added dropwise. After standing at room temperature for about 2 weeks, black-blue crystals were collected, yield 62% (Found: C, 25.00; H, 3.60; Cu, 22.00; N, 11.90. Calc. for $C_{12}H_{22}ClCu_2N_5O_{11}$: C, 25.10; H, 3.85; Cu, 22.15; N, 12.20%).

Physical Measurements.—Magnetic measurements on powder samples were carried out with a CAHN-2000 Faraday-type magnetometer in the temperature range 70–300 K. Correction for the diamagnetism of the compound was estimated from Pascal's constants to be -242×10^{-6} cm^3 mol^{-1}. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer.

Crystal Structure Determination.—The intensity data were collected at room temperature on a Rigaku AFC5R four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) by using the ω–2θ scan technique. Details of the crystal data, intensity collection and refinement are listed in Table 1. Intensity data were collected in the range 2θ 0–52°. The intensities were corrected for Lorentz-polarization and absorption effects. Of the 4199 measured independent reflections, 2040 were observed with $I \geqslant 3\sigma(I)$ and used for the structure refinement.

The structure calculations were performed using the TEXSAN program[25] on a Micro VAXII computer. The structure was solved by conventional heavy-atom methods and subsequently by Fourier-difference maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms (except those of the crystal water molecules) from the ΔF map were included with a common thermal parameter. In the course of locating the four oxygen atoms of perchlorate, seven possible positions were found from the Fourier-difference map, but six were lower than the normal one. So all were treated by full-matrix least-squares refinement, which indicated one of the four oxygen atoms [O(8)] with occupancy factor 1, while the other ones were scattered in six average positions with occupancy factor 0.5. The final least-squares refinement converged at $R(R')$ of 0.044 (0.053) [$w = 1/\sigma^2(F_o)$]. The atomic coordinates for the non-hydrogen atoms are listed in Table 2, and selected bond distances and angles in Table 3.

Table 1 Summary of crystal data, data collection and structure refinement

Formula	$C_{12}H_{22}ClCu_2N_5O_{11}$
M	574.88
Crystal size (mm)	0.10 × 0.20 × 0.50
System	Monoclinic
Space group	$P2_1/c$
a/Å	10.420(2)
b/Å	13.118(2)
c/Å	14.863(5)
β/°	93.05(2)
U/Å^3	2028.7(8)
Z	4
D_c/g cm^{-3}	1.88
μ(Mo-Kα)/cm^{-1}	23.00
F(000)	1168
No. unique reflections	4199
No. observed reflections [$I \geqslant 3\sigma(I)$]	2040
R	0.044
R'	0.053
No. of variables	308
Goodness of fit	1.25
Largest shift/e.s.d.	2.79
R_{int}	0.08
Residual/e Å^{-3}	0.50

Table 2 Atomic positional parameters

Atom	x	y	z
Cu(1)	0.340 86(8)	0.056 53(6)	0.131 34(6)
Cu(2)	0.554 42(8)	0.413 52(6)	0.077 37(6)
Cl	1.006 0(3)	0.168 7(3)	0.374 8(2)
O(1)	0.492 2(5)	−0.446 3(3)	0.082 9(3)
O(2)	0.625 7(5)	−0.422 5(4)	0.202 4(3)
O(3)	0.378 1(5)	0.356 6(3)	0.087 8(4)
O(4)	0.521 0(5)	0.112 9(3)	0.114 3(3)
O(5)	0.710 3(6)	0.003 5(5)	0.022 1(4)
O(6)	0.781 2(9)	−0.025 5(7)	0.306 7(7)
O(7)	0.888 2(8)	−0.073 2(6)	0.152 8(6)
O(8)	1.136 2(8)	0.185(1)	0.383 3(9)
O(9)	0.934(2)	0.168(2)	0.446(1) *
O(10)	1.029(2)	0.068(1)	0.341(1) *
O(11)	0.953(3)	0.227(3)	0.305(2) *
O(12)	0.962(3)	0.254(3)	0.423(2) *
O(13)	0.964(3)	0.075(2)	0.430(2) *
O(14)	0.950(4)	0.166(4)	0.293(2) *
N(1)	0.150 1(6)	0.045 2(4)	0.157 0(4)
N(2)	0.292 1(6)	0.196 3(4)	0.108 4(4)
N(3)	0.606 4(6)	0.275 2(4)	0.098 5(4)
N(4)	0.744 7(6)	0.436 2(4)	0.074 7(4)
N(5)	0.402 6(6)	−0.086 4(4)	0.150 3(4)
C(1)	0.082 2(7)	0.126 3(6)	0.103 2(6)
C(2)	0.158 2(7)	0.222 7(5)	0.115 3(6)
C(3)	0.383 9(7)	0.259 1(5)	0.098 0(5)
C(4)	0.515 1(7)	0.209 5(5)	0.104 0(5)
C(5)	0.743 7(7)	0.254 7(5)	0.108 7(5)
C(6)	0.806 7(7)	0.355 7(6)	0.132 0(6)
C(7)	0.522 6(7)	−0.107 7(5)	0.176 6(5)
C(8)	0.571 7(7)	−0.204 9(5)	0.177 4(5)
C(9)	0.493 4(7)	−0.284 4(5)	0.151 1(4)
C(10)	0.365 2(7)	−0.263 4(5)	0.127 1(5)
C(11)	0.322 5(7)	−0.163 6(5)	0.127 8(5)
C(12)	0.543 4(7)	−0.393 0(5)	0.146 7(5)

* Refined with an occupancy factor of 0.5.

Table 3 Main bond distances (Å) and angles (°)

Cu(1)–N(2)	1.928(5)	Cu(1)–N(5)	1.998(6)
Cu(1)–O(4)	2.046(5)	Cu(1)–N(1)	2.049(6)
Cu(1)–O(2b)	2.492(5)	Cu(1)–O(5)	2.444(6)
Cu(2)–N(3)	1.915(5)	Cu(2)–O(1a)	1.953(4)
Cu(2)–O(3)	1.997(5)	Cu(2)–N(4)	2.008(6)
Cu(2)–O(1c)	2.444(5)	C(1)–C(2)	1.50(1)
O(1)–C(12)	1.273(9)	O(2)–C(12)	1.223(9)
O(3)–C(3)	1.289(8)	O(4)–C(4)	1.277(7)
N(1)–C(1)	1.487(9)	N(2)–C(3)	1.279(9)
N(2)–C(2)	1.447(9)	N(3)–C(4)	1.289(9)
N(3)–C(5)	1.456(9)	N(4)–C(6)	1.484(9)
N(5)–C(7)	1.319(9)	N(5)–C(11)	1.343(9)
N(2)–Cu(1)–N(5)	175.9(2)	N(2)–Cu(1)–O(4)	82.5(2)
N(2)–Cu(1)–N(1)	81.5(2)	N(5)–Cu(1)–O(4)	93.8(2)
N(5)–Cu(1)–N(1)	162.7(2)	O(4)–Cu(1)–N(1)	162.7(2)
O(2b)–Cu(1)–O(5)	166.5(2)	O(2b)–Cu(1)–N(2)	95.3(2)
O(5)–Cu(1)–N(2)	95.7(2)	O(2b)–Cu(1)–O(4)	90.1(2)
O(2b)–Cu(1)–N(5)	86.4(2)	O(5)–Cu(1)–O(4)	99.1(2)
O(5)–Cu(1)–N(5)	83.2(2)	O(2b)–Cu(1)–N(1)	84.8(2)
O(5)–Cu(1)–N(1)	89.1(2)	O(1c)–Cu(2)–N(3)	111.5(4)
O(1c)–Cu(2)–N(4)	95.7(2)	O(1a)–Cu(2)–O(1c)	80.0(2)
O(1c)–Cu(2)–O(3)	90.3(2)	C(6)–N(4)–Cu(2)	106.4(4)
N(3)–Cu(2)–O(1a)	167.2(2)	N(3)–Cu(2)–O(3)	83.5(2)
N(3)–Cu(2)–N(4)	82.7(2)	O(1a)–Cu(2)–O(3)	92.3(2)
O(1a)–Cu(2)–N(4)	101.1(2)	O(3)–Cu(2)–N(4)	166.1(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 consists of a two-dimensional array of copper(II) ions bridged by both oxamidate and pyridine-4-carboxylate; the former behaves as a bis(tridentate) ligand in *trans* conformation whereas the latter bridges four copper(II) centres and the carboxylate acts as a novel bridging group co-ordinating to three different copper(II) centres, spreading out along the *bc* plane to form an infinite network. A perspective view of the asymmetric unit together with the atom-labelling scheme and of one symmetry-related unit is depicted in Fig. 1. The array of infinite layers along the *a* axis is shown in Fig. 2.

The repeating asymmetric unit contains two copper centres the geometries of which are not identical. Atom Cu(1) has an octahedral environment, whereas Cu(2) has a distorted square-based pyramidal surroundings. The equatorial plane of the Cu(1) centre is defined by atoms N(1), N(2) and O(4) of a *trans*-oxamidate group and N(5) from the pyridine ring of a pyridine-4-carboxylate ligand which is bound to three neighbouring centres Cu(1h), Cu(2c) and Cu(2d) (the first two axial, the third equatorial) through the two oxygen atoms [O(1) and O(2)] of its carboxylate group. The two axial co-ordination sites of Cu(1) are occupied, respectively, by O(5) of a crystal water and O(2b) from another carboxylate group which is bound to two other copper centres (one equatorial and the other axial). The largest deviation from the least-squares plane through N(1),N(2),O(4),N(5) is 0.0907 Å at N(2), and Cu(1) lies 0.0495 Å out of this plane. The basal plane of Cu(2) is comprised of atoms N(3), N(4) and O(3) from a *trans*-oxamidate group, and O(1a) from a carboxylate group which is axially bonded to the next two copper centres. The apical position is occupied by atom O(1c) from another carboxylate which co-ordinates to two other neighbouring centres Cu(2e) and Cu(1f) (the first equatorial, the second axial). The largest deviation from the least-squares basal plane through N(3),N(4),O(3),O(1a) is 0.0971 Å at N(3), and atom Cu(2) is displaced out of this plane toward axial O(1c) atom by 0.1219 Å.

The carboxylate group of each pyridine-4-carboxylate bridges three different copper centres in a novel way in which it assumes three types of bridging,[15] *i.e.* monoatomic, triatomic *anti-anti* and triatomic *anti-syn*, which link the *trans*-oxamidato-bridged dimers to give an infinite two-dimensional network. The three Cu–O bond distances involving each carboxylate group are not identical with the shorter one in equatorial position [Cu(2d)–O(1) 1.953(4) Å] and the longer two in axial sites [Cu(1h)–O(2) 2.492(5) and Cu(2c)–O(1) 2.444(6) Å]. The four-membered Cu_2O_2 bridging unit [Cu(2),O(1a),Cu(2e),O(1c)] is approximately planar, forming a dihedral of 80.1° with the Cu(2) co-ordination plane [N(3),N(4),O(1a),O(3)]. The Cu–O–Cu bridging angle (100.0°) together with the out-of-plane [2.444(6) Å] and in-plane [1.953(4) Å] Cu–O distances are similar to those reported for the other complexes.[6–11] The bridging pathway Cu(2d)–O(1)–C(12)–O(2)–Cu(1h) in *syn-anti* mode is asymmetric not only in its conformation but also with respect to the Cu–O bond lengths with Cu(2d)–O(1) in equatorial position whereas Cu(1h)–O(2) is axial. On the contrary, the *anti-anti* bridging unit Cu(2c)–O(1)–C(12)–O(2)–Cu(1h) is symmetric not only in its conformation, but also in the Cu–O distances with both Cu(2c)–O(1) and Cu(1h)–O(2) in axial sites, and is symmetric in the Cu–O–C bridging angles with Cu(2c)–O(1)–C(12) [133.1(4)°] and Cu(1h)–O(2)–C(12) [139.6(4)°] being almost equivalent. The copper–copper separations through the monoatomic, triatomic *anti-anti* and *anti-syn* carboxylato bridges are 3.383 [Cu(2d) • • • Cu(2c)], 6.891 [Cu(1h) • • • Cu(2c)] and 4.791 Å [Cu(1h) • • • Cu(2d)], respectively.

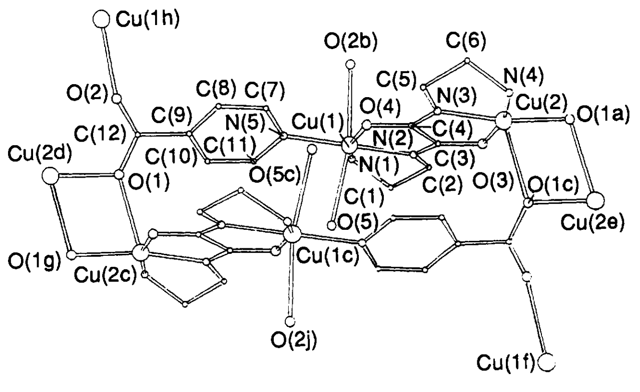


Fig. 1 A perspective view of the two symmetry-related asymmetric units

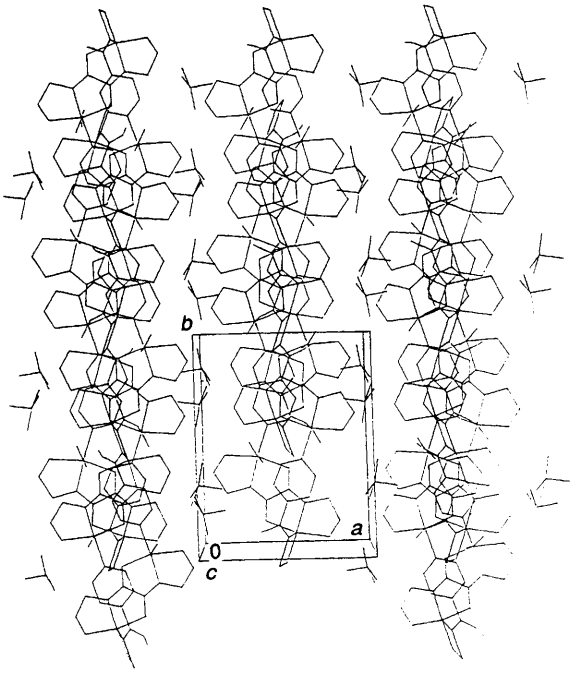


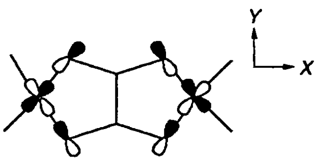
Fig. 2 A view of the crystal packing down the *a* axis

The deprotonated ligand L adopts the *trans* conformation forming two five-membered chelate rings at each copper ion. The bond distances for Cu(1)–N(2) [1.928(5)] and Cu(2)–N(3) [1.915(5) Å], shorter than those of Cu(1)–N(1) and Cu(1)–O(4) [2.049(6) and 2.046(5) Å], and Cu(2)–N(4) and Cu(2)–O(3) [2.008(6) and 1.997(5) Å], accord with those found in other oxamidato-bridged copper(II) complexes.[26–28] The significant shortening of Cu(1)–N(2) and Cu(2)–N(3) is consistent with the strong basicity of the deprotonated amide nitrogen atoms. The three atoms around N(2) [Cu(1), C(2) and C(3)] and N(3) [Cu(2), C(4) and C(5)] lie in a plane, respectively, with bond angles of 117.5(4), 116.3(5) and 125.8(6)° for C(2)–N(2)–Cu(1), C(3)–N(2)–Cu(1) and C(3)–N(2)–C(2), and of 117.3(4), 116.2(5) and 126.4(6)° for C(5)–N(3)–Cu(2), C(4)–N(3)–Cu(2) and C(4)–N(3)–C(5), respectively. This fact together with the bond distances and planarity of the oxamidato bridge reveals that N(2) and N(3) are sp^2 hybridized and the π electrons of C(3)–N(2) and C(4)–N(3) are delocalized to form a conjugated system. The co-ordination planes of the two copper centres [N(1),N(2),O(4),N(5) and N(3),N(4),O(1a),O(3) for Cu(1) and Cu(2), respectively], forming a dihedral of 8.6° to each other, have dihedral angles of 29.5 and 21.7°, respectively, with the ring plane [N(5),C(7),C(8),C(9),C(10),C(11)] of the pyridine-4-carboxylate ligand. The copper–copper distances through the L and pyridine-4-carboxylate bridges are 5.265 for Cu(1) • • •

Cu(2) and 8.771, 7.014 and 8.076 Å for Cu(1) ··· Cu(2d), Cu(1) ··· Cu(2c) and Cu(1) ··· Cu(1h), respectively.

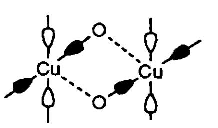
EPR Spectra and Magnetic Data.—The EPR spectrum recorded at room temperature shows an asymmetric feature at $g = 2.05$ and no signal at half-field. It does not change on lowering the temperature, simply decreasing in intensity with no hyperfine splitting.

The temperature dependence of the magnetic moment per copper atom of $[\{CuL(pyca)(H_2O)\}_n][ClO_4]_n \cdot 2nH_2O$ in the form μ_{eff} *vs.* T is shown in Fig. 3. The μ_{eff} for each copper atom at 300 K is only 1.03 μ_B, much lower than the value for a paramagnetic copper(II) ion. This fact together with the smooth decrease in μ_{eff} with T reveals that a strong antiferromagnetic exchange at temperature higher than 300 K is operative between the copper atoms. Since the molar susceptibility at low temperature is close to the Pascal's constant used for diamagnetic correction, the susceptibility was only measured up to 70 K. From the structure of the complex several different exchange pathways are possible. Oxamidato bridges are known to have a remarkable efficiency in propagating a strong antiferromagnetic interaction between two metal centres in elongated tetragonal surroundings with an almost coplanar basal plane. In such surroundings the magnetic orbitals centred on the copper(II) ions are as shown in **VII**. They point from the metal toward the four nearest neighbours and overlap either side of the bridge, which favours a strong antiferromagnetic interaction,[29] with $|J| > 300$ cm^{-1}. On the other hand, the Cu ··· Cu [Cu(1) ··· Cu(2c), Cu(1) ··· Cu(2d) and Cu(1) ··· Cu(1h)] separation through the pyridine-4-carboxylate (both pyridine ring and carboxylate) bridge is so large that the magnetic orbitals on the two neighbouring copper ions cannot overlap effectively, so the magnetic exchange transmitted by this bridge is expected to be very small[30,31] and negligible.



VII

For the carboxylate group bridge the situation is very complicated, and the most interesting aspect of the chemistry of μ-carboxylato-copper(II) complexes may be the versatility of their magnetic properties. On the one hand, in complexes with monoatomic carboxylate bridges in which the copper centres are bridged through two co-ordinated oxygen atoms of the carboxylate anions, with each bridging oxygen simultaneously occupying an equatorial position on one copper atom and an apical position on the other copper atom, the exchange interaction is very small and negligible,[6–11,32,33] for the relative orientations of the two magnetic orbitals are particularly unfavourable for transmitting electronic effects between two copper(II) ions, see **VIII**. On the other hand, when the carboxylate group bridges copper ions in a triatomic way the exchange coupling is largely determined by the conformation of the bridge and the interaction between the d orbitals of the metal and the bridge. In complexes where the metal ions are bridged in a *syn-syn* manner the exchange-coupling constant is large and antiferromagnetic; the carboxylate groups interact directly with the $d_{x^2-y^2}$ orbitals of the copper ions.



VIII

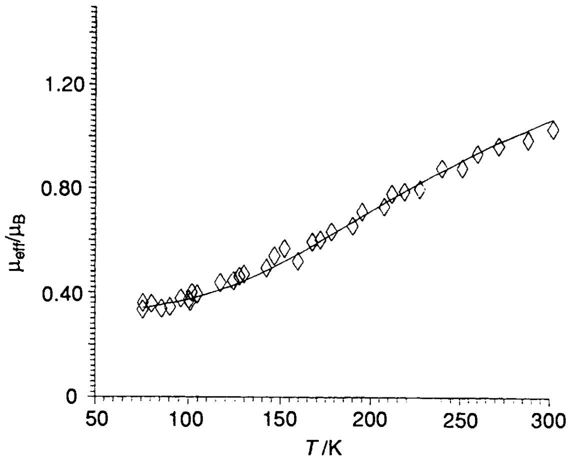
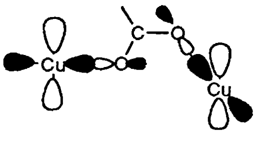
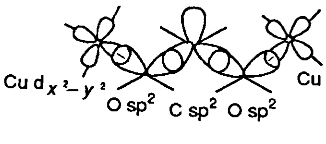


Fig. 3 Experimental (◇) and calculated (—) temperature dependence of μ_{eff}

In complexes containing *syn-anti* bridges the magnitudes of the exchange-coupling constants are much smaller than those for *syn-syn*-bridged complexes and the exchange is usually weakly ferromagnetic with $|J| < 5$ cm^{-1}. Owing to the asymmetry of the *syn-anti* Cu–O–C–O–Cu bridging network, the contributions of the 2p orbitals belonging to the magnetic orbitals centred on Cu are unfavourably oriented to give a strong overlap[17] as shown in **IX**. On the contrary, when the triatomic bridging network Cu–O–C–O–Cu is of the *anti-anti* type the carboxylate group can provide a relatively efficient exchange pathway **X**, resulting in an antiferromagnetic interaction with $|J|$ about 20 cm^{-1}.[19]



IX



X

Since monoatomic carboxylate groups do not transmit magnetic exchange, whereas triatomic *anti-syn* and *anti-anti* groups propagate weak ferromagnetic ($|J| < 5$ cm^{-1}) and antiferromagnetic ($|J|$ about 20 cm^{-1}) coupling, respectively, we attempted to simplify the magnetic system to two-dimensional sheets of interacting dimers, CuLCu, on the assumption that the exchange through the carboxylate groups is interdimeric in a molecular field approach. So it should be possible to interpret the data with a simple modified Bleaney–Bowers equation (1), taking into account the intermolecular interactions and the percentage of paramagnetic impurities ρ which exhibit a Weiss constant θ. The least-squares fit of all

$$\chi_M = \frac{2N\beta^2g^2}{K(T-\theta)}\left[3 + \exp\left(-\frac{J}{KT}\right)\right]^{-1}(1-\rho) + \frac{Ng^2\beta^2}{2K(T-\theta)}\rho + 2N_\alpha \qquad (1)$$

experimental data by equation (1) led to $g = 2.09$, $J = -486$ cm^{-1}, $\rho = 0.0285$ and $\theta = -15$ K, with an agreement factor $R = \Sigma(\mu_{obs} - \mu_{calc})^2 / \Sigma(\mu_{obs})^2$ of 1.2×10^{-3}. The curve calculated with these parameters gives a satisfactory fit to the experimental points as shown in Fig. 3. The negative value of θ reveals that the triatomic *anti-anti* bridges exert an antiferromagnetic contribution, which is not totally compensated by the weak ferromagnetic contribution from the triatomic *anti-syn* bridges. However, the magnitude of the resulting antiferromagnetic interaction is less pronounced than in other similar complexes with triatomic *anti-anti* carboxylate bridges transmitting antiferromagnetic exchange.[19]

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