Crystal Structure and Magnetic Properties of $[Cu(ox)(py)_2]$ (py = pyridine): a Ferromagnetic Oxalate-bridged Zigzag Chain Complex†

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The compound $[Cu(ox)(py)_2]$ (ox = oxalate, py = pyridine) was obtained as a breakdown oxidized product of $[Cu(epgly)_2]$ (Hepgly = *N*-2-ethylphenylglycine), and has been characterized by means of structural and magnetic measurements. The crystals are monoclinic, space group *C*2/*c*, with a = 14.088(3), b = 11.023(2), c = 8.689(2) Å, β = 92.23(3)° and Z = 4. The structure was solved and refined to R = 0.039 and R' = 0.040. The structure consists of $[Cu(py)_2]^{2+}$ units bridged sequentially by centrosymmetric oxalate anions to form zigzag polymeric chains parallel to the c axis, with a copper–copper distance of 5.463(1) Å. The copper ion is in distorted-octahedral environment and the equatorial co-ordination sites are occupied by N,N′ and O,O′ donors from two oxalate and two pyridine molecules at *ca.* 2.0 Å. Two weaker axial bonds are formed with O″ and O‴ atoms from two oxalate anions, with a O(1″)–Cu–O(1‴) angle of 162.9(1)°. From the magnetic susceptibility measurements, the complex is found to exhibit weak ferromagnetic exchange interaction between nearest-neighbour copper(II) ions.

Polynuclear metal complexes containing an oxalate bridging ligand (ox) have been widely studied during the last fifteen years, mainly because of the interesting magnetic properties that these may exhibit. Thus, it has been shown that oxalate may transmit strong antiferromagnetic coupling between paramagnetic centres in dinuclear copper complexes with copper–copper intramolecular separations larger than 5 Å.[1] Moreover, in this type of complex, the interaction can be tuned from 0 to 386 cm^{-1} by varying the nature of the terminal ligands.[2] The role of the oxalate anion as a bridging ligand however is not only restricted to dinuclear systems since a number of polynuclear oxalate-bridged complexes with tetranuclear and from one- to three-dimensional structures have been reported.[3–13] Some of these, of a heteronuclear nature, exhibit ferromagnetic exchange interactions generally as a consequence of the strict orthogonality of the magnetic orbitals on adjacent paramagnetic centres. Good examples of this type of behaviour are shown by the dinuclear complex $[(terpy)Cu(ox)VO(ox)(H_2O)]\cdot H_2O$[14] (terpy = 2,2′:6′,2″-terpyridine), the tetranuclear complex $[Cr\{(ox)NiL\}_3][ClO_4]_3$[7] (L = DL-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and the ferromagnets $\{[NBu_4][MCr(ox)_3]\}_x$[9] (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+}) with T_c varying from 6 to 14 K. Nevertheless, homonuclear one-dimensional systems such as $[Cu(ox)(mim)_2]$[6] (mim = 2-methylimidazole), $[NH_3C_3H_6NH_3][Cu(ox)_2]$[4] and $[Cu(ox)(bipy)]\cdot 2H_2O$[5] (bipy = 2,2′-bipyridine) have also been shown to exhibit ferromagnetic interactions.

This paper is devoted to a new example of a ferromagnetic oxalate-bridged zigzag chain copper complex $[Cu(ox)(py)_2]$ (py = pyridine), which was obtained from oxidation of the compound $[Cu(epgly)_2]$ (Hepgly = *N*-2-ethylphenylglycine) in the presence of pyridine.

Experimental

Preparation of $[Cu(ox)(py)_2]$.—A suspension of $[Cu(epgly)_2]$[15] (0.5 g, 1.19 mmol) in ethanol–water (20:1, 50 cm^3) was heated until boiling, then pyridine (10 cm^3) was added and refluxed for 10 min. The resulting blue solution was filtered to remove any residual solids and the filtrate allowed to stand at room temperature. After 2 d well developed blue crystals of the $[Cu(ox)(py)_2]$ complex were obtained (Found: C, 46.15; H, 3.25; Cu, 20.15; N, 9.20. Calc. for $C_{12}H_{10}CuN_2O_4$: C, 46.55; H, 3.25; Cu, 20.50; N, 9.05%).

X-Ray Data Collection and Structure Determination of $[Cu(ox)(py)_2]$.—A tabular blue crystal (0.46 × 0.46 × 0.13 mm) was selected for single-crystal X-ray diffraction analysis. Data collection was performed at 295 K with a Siemens-Stoe AED-2 four-circle diffractometer using monochromatized Mo-Kα radiation (λ = 0.710 69 Å). The unit-cell parameters were obtained from least-squares refinement of 25 well centred reflections ($25 > 2\theta > 35°$) scanned in the positive and in the negative ω region.

Intensity data were collected by ω–2θ scan mode ($3 < 2\theta < 60°$, $-18 \leqslant h \leqslant 18$, $-14 \leqslant k \leqslant 14$, $-11 \leqslant l \leqslant 11$). 6625 Reflections were measured, 2052 of which with $F > 6\sigma(F)$ were considered to have observable intensity and were used in the structure analysis. The intensities of four check reflections measured every 120 min showed only statistical variation. The data were corrected for Lorentz-polarization effects and for absorption.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, eV $\approx 1.60 \times 10^{-19}$ J.

Crystal data. $C_{12}H_{10}CuN_2O_4$, $M = 309.8$, monoclinic, space group $C2/c$, $a = 14.088(3)$, $b = 11.023(2)$, $c = 8.689(2)$ Å, $\beta = 92.23(3)°$, $U = 1348.4(5)$ Å^3, $Z = 4$, $D_c = 1.526$ g cm^{-3}, $F(000) = 628$, μ(Mo-Kα) = 1.631 mm^{-1}.

The structure was solved by a combination of the Patterson method and Fourier techniques and refined by full-matrix least squares using the SHELXTL PLUS program package[16] on a MicroVAX II computer. In the final refinement all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were observed and the recalculated positions refined isotropically.

The function minimized was $\Sigma w(\Delta F)^2$ where $w = 1/\sigma_F^2$, resulting in a final $R = \Sigma||F_o| - |F_c||/|F_o|$ value of 0.039 and $R' = \Sigma(|F_o| - |F_c|)w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}} = 0.040$. The goodness-of-fit ratio was 1.53 for 88 parameters. Atomic coordinates for the non-hydrogen atoms are listed in Table 1.

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

Results and Discussion

The reaction of a water–ethanol suspension of $[Cu(epgly)_2]$ with pyridine surprisingly leads to a complex of empirical formula $[Cu(ox)(py)_2]$. Its IR spectrum exhibits features characteristic of the co-ordination of oxalate and pyridine. Since the bands attributable to oxalate at 1665 [ν_{asym}(CO)], 1357, 1306 [ν_{sym}(CO)] and 799 cm^{-1} [δ(OCO)] compare well with those reported for bis(bidentate) oxalato copper(II) compounds,[1,7] the complex $[Cu(ox)(py)_2]$ is expected to exhibit a polynuclear structure.

The compound presumably arises from the breakdown of an oxidized product of the *N*-2-ethylphenylglycinate anion. For the formation of the oxalate anion a mechanism analogous to the well known oxidative deamination of α-amino acids might be proposed. Thus, oxidation by molecular oxygen of epgly would lead to an α-imino acid, which after hydrolysis and subsequent oxidation by molecular oxygen would give rise to the oxalate anion. Given that all attempts to obtain the compound $[Cu(ox)(py)_2]$ directly from the oxalate–copper(II)–pyridine system were unsuccessful, the formation of oxalate must occur without breakdown of the glycinate-*O*–copper(II) bond (see Scheme 1).

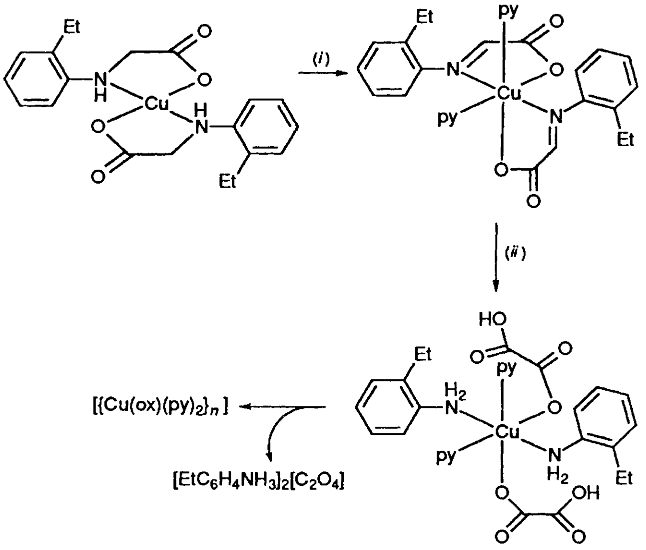
Although the role of the pyridine remains unclear, it co-ordinates to copper(II) and dissolves the complex $[Cu(epgly)_2]$ which might favour the oxidative-deamination process.

The formation of oxalate-bridged polynuclear chain copper(II) complexes from the oxidation of a suitable precursor, which seems to occur in our case, has been previously reported. Thus, by using either molecular oxygen or hydrogen peroxide and ascorbic acid, the compounds disodium *catena*-bis(oxalato)cuprate(II) dihydrate[3] and bis[diethyl(2-hydroxyethyl)ammonium] *catena*-μ-tris[oxalato(2$^-$)-O^1, O^2: O^3, O^4]-dicuprate(II),[8] respectively, were obtained.

Table 1 Atomic coordinates (× 10^4) for $[\{Cu(ox)(py)_2\}_n]$

Atom	*x*	*y*	*z*
Cu	0	1502(1)	2500
O(1)	791(1)	−1197(2)	−214(2)
O(2)	787(1)	214(2)	1590(2)
N(1)	891(2)	2764(2)	1688(3)
C(1)	453(2)	−287(3)	391(3)
C(2)	1755(2)	2918(3)	2329(4)
C(3)	2404(3)	3728(4)	1761(5)
C(4)	2162(3)	4370(4)	476(6)
C(5)	1284(3)	4209(4)	−209(6)
C(6)	668(2)	3401(4)	428(5)

Crystal Structure of $[Cu(ox)(py)_2]$.—The structure of this compound consists of $[Cu(py)_2]^{2+}$ units bridged sequentially by centrosymmetric oxalate anions to form zigzag polymeric chains parallel to the *c* axis, with a copper–copper distance of 5.463(1) Å. The oxalate ligands occupy centres of symmetry



Scheme 1 (*i*) Pyridine, dioxygen; (*ii*) water, dioxygen

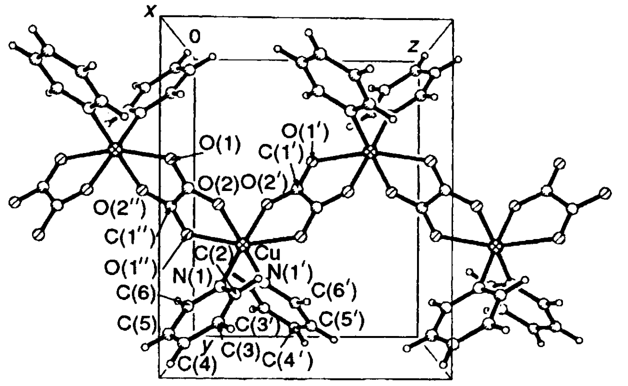


Fig. 1 A perspective view of the $[Cu(ox)(py)_2]$ chain

Table 2 Selected bond distances (Å) and angles (°) of $[\{Cu(ox)(py)_2\}_n]$

Cu–O(2)	1.985(2)	C(1)–O(1)	1.236(3)
Cu–O(1″)	2.264(2)	C(1)–C(1″)	1.557(5)
Cu–N(1)	2.020(3)	C(2)–C(3)	1.384(6)
N(1)–C(2)	1.329(4)	C(4)–C(3)	1.355(7)
N(1)–C(6)	1.328(5)	C(4)–C(5)	1.363(6)
O(2)–C(1)	1.255(3)	C(6)–C(5)	1.375(6)
O(2)–Cu–N(1)	89.4(1)	Cu–O(2)–C(1)	116.7(2)
N(1)–Cu–N(1′)	93.0(1)	Cu–N(1)–C(2)	120.8(2)
O(2′)–Cu–O(1″)	88.8(1)	C(1)–O(1)–Cu″	108.0(2)
O(2′)–Cu–O(1‴)	78.9(1)	N(1)–C(2)–C(3)	122.7(3)
O(1″)–Cu–O(1‴)	162.9(1)	N(1)–C(6)–C(5)	122.7(3)
O(2)–Cu–O(2′)	88.6(1)	C(6)–N(1)–C(2)	117.5(3)
O(2′)–Cu–N(1′)	89.4(1)	O(2)–C(1)–O(1)	124.9(2)
N(1)–Cu–O(1″)	95.0(1)	O(1)–C(1)–C(1″)	117.9(3)
O(2)–Cu–O(1″)	78.9(1)	O(2)–C(1)–C(1″)	117.2(3)
N(1)–Cu–O(2′)	175.2(1)	C(2)–C(3)–C(4)	118.8(4)
N(1′)–Cu–O(1″)	96.7(1)	C(3)–C(4)–C(5)	119.2(4)
Cu–N(1)–C(6)	121.4(2)	C(6)–C(5)–C(4)	119.0(4)

Primed, doubly primed and triply primed atoms are related by $-x, y, \frac{1}{2} - z$; $1 - x, 1 - y, -z$; and $x, 1 - y, \frac{1}{2} + z$ respectively.

whereas the copper atoms lie on two-fold axes. A portion of the infinite chain is given in Fig. 1 together with the atomic labelling scheme. Selected bond lengths and angles are listed in Table 2.

The co-ordination environment around the copper ions can be better described as a distorted octahedron. Four short bonds of *ca.* 2.0 Å are formed with the atoms N(1) and N(1′) (related by $-x, y, \frac{1}{2} - z$) from the two pyridine molecules and O(2) and O(2′) from two oxalate anions. These atoms, which are reasonably planar [maximum deviation from the least-squares plane 0.076(2) Å], define the equatorial plane, in which the co-ordination angles around the copper atom are close to 90°. The axial co-ordination sites are occupied by the oxalate oxygen atoms O(1″) (related by $1 - x, 1 - y, -z$) and O(1‴) ($x, 1 - y, \frac{1}{2} + z$) at a longer distance. The axial and equatorial oxygen–copper bond lengths, as expected, are markedly different from each other [1.985(2) and 2.264(2) Å, respectively] and are in the range found for other oxalate-bridged copper(II) complexes.[5,8] Owing to the small O(2)–Cu–O(1″) bite angle of the asymmetrically co-ordinated oxalate anion [78.9(1)°], the O(1″)–Cu–O(1‴) angle of 162.9(1)° is significantly reduced from 180°. The oxalate ligand is planar and forms a dihedral angle of 80.79(5)° with the equatorial co-ordination plane.

There are no unusual bond lengths and angles in the oxalate and pyridine molecules and the latter are twisted 73.5(1)° away from the co-ordination plane in order to relieve close interligand contacts.

The interaction between neighbouring chains is of van der Waals type, the minimum interchain copper Cu···Cu‴ ($-\frac{1}{2} - x, \frac{1}{2} - y, -z$) distance being 8.423(2) Å.

Finally, it should be pointed out that the whole structure of [Cu(ox)(py)$_2$] is very similar to that reported by Hathaway and co-workers[5] for the analogous complex [Cu(ox)(bipy)]·2H$_2$O.

Electronic and Magnetic Properties.—The electronic reflectance spectrum of [Cu(ox)(py)$_2$] exhibits two bands at 9100 and 14 285 cm^{-1}, consistent with the elongated tetragonal distortion of the CuN$_2$O$_4$ chromophore.[18] The energies of these bands are comparable to those observed at 9300 and 14 500 cm^{-1} for the analogous complex [Cu(ox)(bipy)]·2H$_2$O.[5]

The polycrystalline X-band spectrum of [Cu(ox)(py)$_2$] at room temperature looks like that expected for a copper(II) ion in a $d_{x^2-y^2}$ ground state. The two main features are attributable to parallel ($g_\parallel = 2.29$) and perpendicular ($g_\perp = 2.09$) components of an axial spectrum. Moreover, several signals of low intensity are discernible between these two main features, which increase in intensity as the temperature is lowered. In a previous study we observed an analogous overall temperature dependence of the EPR spectra for the *syn-anti* carboxylate copper(II) ferromagnetic chain [CuL(H$_2$O)][19] [H$_2$L = 5-(2-carboxyphenylazo)-1,3-dimethyl barbituric acid]. Nevertheless, to explain these data a single-crystal study is needed.

The temperature dependence of the magnetic susceptibility per copper atom of [Cu(ox)(py)$_2$] in the form μ_{eff} *vs.* T is shown in Fig. 2. When the temperature is lowered μ_{eff} increases steadily from a value of 1.85 μ_B at 250 K to a value of 2.15 μ_B at 2 K. This magnetic behaviour indicates the existence of weak but definite ferromagnetic exchange interaction between the copper ions.

In keeping with the structure, the magnetic susceptibility data were analysed with equation (1) for a linear chain of Heisenberg

$$\chi_m = Ng^2\mu_B^2\left(\frac{1 + a_1k + a_2k^2 + a_3k^3 + a_4k^4 + a_5k^5}{1 + b_1k + b_2k^2 + b_3k^3 + b_4k^4}\right)^{\frac{2}{3}} \quad (1)$$

coupled $S = \frac{1}{2}$ atoms, based on the high-temperature Padé expansion, reported by Baker *et al.*[20] where $k = J/2k_BT$ and a_i and b_i are expansion coefficients. The best-fit parameters for the data are $J = 0.67$ cm^{-1}, $g = 2.09$ and $R = 1 \times 10^{-4}$. The ferromagnetic exchange coupling is consistent with the structure of [Cu(ox)(py)$_2$] and can be understood by using the same arguments as for the structurally analogous [Cu(ox)(bipy)]·2H$_2$O, which is also ferromagnetic with an evaluated exchange integral of 1.22 cm^{-1}. In our complex, the $d_{x^2-y^2}$ orbital, which contains the unpaired electron, lies in the O(2), O(2′), N(1), N(1′) equatorial plane, so that the spin density on the copper atom can be delocalized to the neighbouring copper atom through two σ pathways. The first, Cu″–O(1)–C(1)–C(1″)–O(1″)–Cu [or Cu–O(2)–C(1)–C(1″)–O(2″)–Cu″], involving either two axial (d_{z^2} direction) or two equatorial ($d_{x^2-y^2}$ direction) positions on the copper atom, mediates an antiferromagnetic exchange interaction. Nevertheless, because this pathway is rather extended, a very weak interaction is expected. In the second pathway, Cu″–O(1)–C(1)–O(2)–Cu [or Cu″–O(2″)–C(1″)–O(1″)–Cu], the O(1) and O(2) [or O(1″) and O(2″)] oxygen atoms occupy axial and equatorial positions on adjacent copper atoms, respectively, thus involving orthogonal orbitals ($d_{x^2-y^2}$ and d_{z^2}) and causing a ferromagnetic interaction. This second pathway, which is less extended than the first, must determine the overall magnetic behaviour observed for the complex. It should be pointed out that an extended-Hückel molecular orbital (EHMO) calculation recently performed on the model compound [Cu$_2$(NH$_3$)$_8$(ox)]$^{2+}$,[9] which has a geometry analogous to that of [Cu(ox)(bipy)]·2H$_2$O,[5] revealed an energy gap between the highest occupied and lowest unoccupied molecular orbitals of only 0.02 eV. This value is small enough to lead to an antiferromagnetic contribution lower than the ferromagnetic one, in agreement with the experimental result. Since the O(1)–Cu–O(1″) axis is bent, which causes mixing of d_{z^2} with $d_{x^2-y^2}$, the orthogonality is not strictly preserved and this ultimately leads to a small J value.

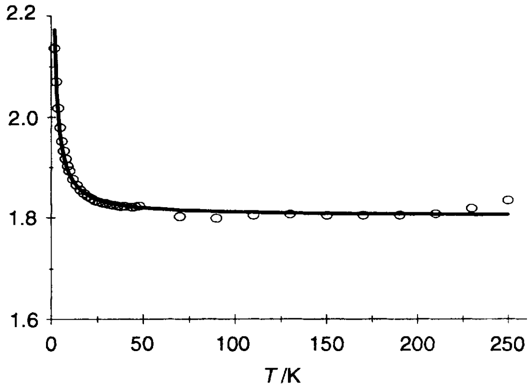


Fig. 2 Temperature dependence of μ_{eff} for [Cu(ox)(py)$_2$] (○). The solid line is generated from the best-fit magnetic parameters

The fact that [Cu(ox)(py)$_2$] shows a weaker ferromagnetic interaction than the related complex [Cu(ox)(bipy)]·2H$_2$O, despite the lower O(1″)–Cu–O(1‴) bond angle for the latter, seems to indicate that additional stuctural parameters should be taken into consideration for determining the magnitude of J. However, the difference in the magnitudes of the J values of [Cu(ox)(py)$_2$] and [Cu(ox)(bipy)]·2H$_2$O is too small for it to be ascribed to the effect of a particular structural factor. In order to obtain a correlation between the magnetic properties and the structure more examples of this kind of complex are needed. Further work along these lines is in progress.

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