Crystal and Molecular Structure and Magnetic Properties of a New μ-Oxalato Binuclear Copper(II) Complex containing Mepirizole *

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The crystal and molecular structure of the new μ-oxalato binuclear copper(II) complex $[(mpym)(H_2O)(NO_3)Cu(C_2O_4)Cu(NO_3)(H_2O)(mpym)]\cdot 2H_2O$ **1** [mpym = mepirizole = 4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine] has been determined by X-ray diffraction methods. It consists of discrete binuclear entities where the copper atoms lie in a strongly elongated octahedral environment, surrounded by two nitrogen atoms (one from each ring of a mepirizole molecule) and two oxygen atoms of the bridging oxalato group in the equatorial plane and oxygen atoms of water molecules and nitrate ions in the axial positions. The binuclear entities are not centrosymmetric and the difference in the ligand environments of the copper(II) ions induces an energy separation between the two magnetic orbitals large enough to weaken the antiferromagnetic interaction ($J = -142$ cm^{-1}) by approximately 60 cm^{-1} compared to that of symmetrical μ-oxalato binuclear copper(II) compounds. ESR, vibrational and electronic spectra are consistent with the above results.

As recently discussed,[1] there is a continuing effort devoted to the study of dinuclear copper(II) complexes because of their outstanding interest to both inorganic and bioinorganic chemists. With the aim of obtaining an improved insight into the understanding of the chemical and structural factors that govern the exchange coupling interactions, we have recently approached the study of low-dimensional magnetic systems containing Cu(mpym)X moieties bridged by X groups, where mpym is mepirizole [4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine], a biologically active pyrimidinepyrazole derivative which behaves as a bidentate ligand involving two nitrogen atoms, one for each ring, and X is a pseudohalide or one half of a bridging dianion such as oxalate, oxamidate or squarate (3,4-dihydroxycyclobut-3-ene-1,2-dionate, $C_4O_4^{2-}$). In this way, we have prepared and characterized several condensed systems including dimeric and linear-chain structures.[2-4] We report here the crystal and molecular structure and the magnetic properties of a new mepirizole-containing copper(II) oxalate dimer complex.

Results and Discussion

The compound $[(mpym)(H_2O)(NO_3)Cu(C_2O_4)Cu(NO_3)(H_2O)(mpym)]\cdot 2H_2O$ **1** was first obtained incidentally in attempts to synthesise mepirizole-containing μ-squarato-bridged copper(II) complexes. In a recent paper[4] a procedure to grow single crystals of $[Cu(mpym)(H_2O)(C_4O_4)]\cdot 2H_2O$ **2** was reported. When the resulting brown prismatic crystals of **2** were filtered from the mother-liquor and the remaining solution was allowed to stand at room temperature, besides more brown crystals, small green crystals formed within a few days. The IR spectrum of this new compound **1** did not exhibit any of the characteristic bands of the squarate anion. Instead, bands characteristic of the oxalato bridging group were identified. Furthermore, the analytical data for **1** correspond to the molecular formula $Cu_2(mpym)_2(C_2O_4)(NO_3)_2(H_2O)_4$. This was confirmed by a single-crystal X-ray analysis (see below) which indicates that **1** is a new mepirizole-containing oxalato-bridged copper(II) dimer.

All these observations reveal that the squarate groups have been oxidized to oxalate groups by ring breaking. Although the conversion of squaric acid into carbon dioxide and oxalic acid by nitric acid has been described,[5] no case of conversion of C_4O_4 into C_2O_4 has been reported so far in the relatively extensive literature about the preparation of squarato compounds using metal nitrates as source of the metal atom. However it seems reasonable to consider the nitrate anions as the oxidizing agent. Indeed, compound **1** has been obtained as a unique phase, in a reproducible way, by adding a controlled quantity of dilute nitric acid in the starting solution containing mepirizole, copper(II) nitrate and squarate anions (see Experimental section). Nevertheless, as recently reported[6,7] for related aromatic oxocarbons, the oxidation of $C_4O_4^{2-}$ anions can be photochemically induced. Such a mechanism cannot be ruled out in our case.

Crystal Structure.—The asymmetric unit consists of a non-centrosymmetric binuclear neutral entity $[(mpym)(H_2O)(NO_3)Cu(C_2O_4)Cu(NO_3)(H_2O)(mpym)]$ and two non-co-ordinated water molecules. A drawing of the dimer structure showing the labelling scheme is given in Fig. 1. Selected bond lengths and angles are reported in Table 1.

The planar oxalato group bridges the two copper atoms in the usual bis(bidentate) fashion: each copper atom is bound to two oxygen atoms from the two different carboxylic groups, with a copper–copper distance across the dimeric unit of 5.217 Å. Each copper atom is involved in a $CuN_2O_2O'O''$

* Mepirizole = 4-Methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine.

Supplementary data available (No. SUP 56840, 2 pp.): magnetic susceptibilities and moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: G = 10^{-4} T.

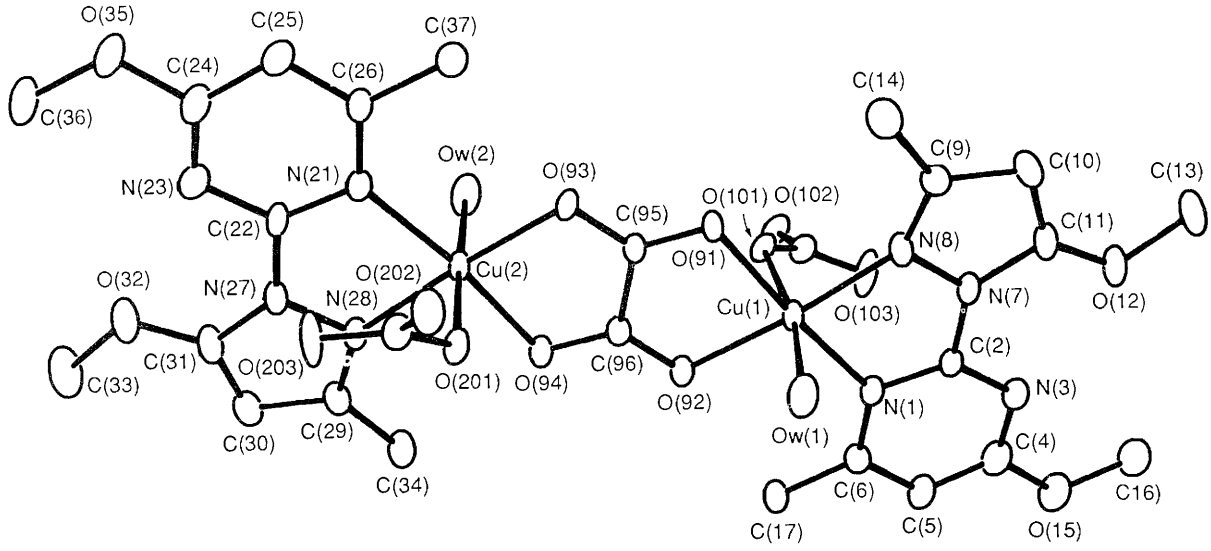

Fig. 1 Perspective view and atom numbering of complex **1**

chromophore, and lies in an elongated octahedral environment. As both chromophores are similar, with only small differences in bond lengths and angles, they will be described jointly for the sake of brevity. The equatorial co-ordination positions are occupied by two oxalate oxygen atoms and two nitrogen atoms of the mepirizole ligand, one from each ring as usual. The Cu–O and Cu–N distances range from 1.96 to 2.04 Å and are similar to those found in related complexes.[3] A water molecule and an oxygen atom belonging to a nitrate group occupy the apical positions at significantly different distances, larger than the equatorial ones. In both cases the axial H_2O–Cu–ONO_2 angle deviates somewhat from 180° [170.9 and 175.5° for Cu(1) and Cu(2) respectively]. The copper atoms are outside the equatorial planes towards the apical water molecules [0.122 Å for Cu(1) and 0.065 Å for Cu(2)]. The nitrate ions may be considered as semi-co-ordinated[8] to the central copper atom: the Cu–ONO_2 distances exceed the Cu–O(equatorial) ones by *ca.* 0.6 Å. Thus the co-ordination polyhedron around the copper(II) ions can be described as a tetragonally elongated octahedron (*i.e.* a '4 + 1 + 1' co-ordination mode); the tetragonality parameter[9,10] is $T = 0.85$ for Cu(1) and $T = 0.82$ for Cu(2).

In [(mpym)(NO_3)Cu(C_2O_4)Cu(NO_3)(H_2O)(mpym)]$_2$-[(mpym)(NO_3)Cu(C_2O_4)Cu(NO_3)(mpym)] **3**, a closely related compound,[3] three different co-ordination geometries are observed for the three crystallographically independent copper atoms. One of them lies in the same environment as the copper atoms of compound **1** and the co-ordination polyhedron displays the same '4 + 1 + 1' geometry with distortions of the same magnitude for chemically equivalent atoms.

All the relevant parameters for the mepirizole molecules and oxalato groups are in good agreement with the data previously obtained for related systems. As usually observed, the mepirizole molecules are close to planarity, the dihedral angles between the pyrazole and pyrimidine rings being 3.72 and 3.94° for the mepirizole molecules co-ordinated to Cu(1) and Cu(2) respectively. Moreover, the bite parameters of the mepirizole (bidentate) and oxalato [bis(bidentate)] ligands compare well with average values calculated from similar complexes (Table 2). In the same way, the two CO_2 groups of the C_2O_4 bridge exhibit a set of structural parameters which compare well with the observed values in other oxalato derivatives. In these respects, the r_1, r_2 and α parameters are in agreement with the relation proposed in ref. 15 for both carboxylato groups: $r_1 r_2 \cos(\alpha/2) = k \approx 0.73$ where r_1 and r_2 are the two C–O distances and α is the O–C–O angle. Values of k are 0.71 and 0.73 for the O(91)–C(95)–O(93) and O(92)–C(96)–O(94) groups respectively.

As a whole (apical groups omitted), the dimeric entity is close to planarity: when a least-squares plane is fitted to the oxalato group and the co-ordinated nitrogen atoms the deviations are less than ±0.04 Å; however the Cu(1) and Cu(2) atoms are 0.13 and −0.07 Å outside this plane.

Each water molecule is involved in moderate hydrogen bonds as indicated by the values of the intermolecular O···O and H···O distances and of the corresponding O–H···O angles listed in Table 1. Both co-ordinated water molecules give two hydrogen bonds: one to the oxygen of a non-co-ordinated water molecule and the second to a non-co-ordinated oxygen of a nitrate ion of a different molecule. In addition each of the non-co-ordinated water molecules also gives a hydrogen bond to the co-ordinated oxygen of a nitrate group of the same molecule [note however that the Ow(3) molecule is a rather weak donor]. This hydrogen-bond pattern ensures the cohesion of the crystal lattice. All other intermolecular O···O and H···O distances are larger than those listed in Table 1.

Finally it should be pointed out that, in the nitrate anions, there is a slight but significant elongation of the co-ordinated N–O bond: this bond is about 4% larger than the remaining ones in the NO_3 group co-ordinated to Cu(1) and about 8% larger than the remaining ones in the NO_3 group co-ordinated to Cu(2).

Vibrational and Electronic Spectra.—The IR spectrum of compound **1** shows a broad absorption between 3200 and 3700 cm^{-1}, with a maximum at *ca.* 3440 cm^{-1}, assignable to the O–H stretching vibrations. The observed position of the ν(O–H) band is in agreement with the average O···O distance (see above) of the presumed hydrogen bonds.[16,17] In the 1700–400 cm^{-1} region the spectrum displays a large number of absorptions and, in some cases, the assignments are not unambiguous. Notwithstanding, the two strong absorptions observed at 1650 and 1360 cm^{-1} assigned to antisymmetric and symmetric O–C–O stretching modes are consistent with the presence of oxalate anions in a bis(bidentate) bridging mode.[18–20] On the other hand, the absorption frequencies assigned to the NO_3 groups are consistent with C_{2v} symmetry,[20,21] in agreement with their co-ordination to the metal atoms through an oxygen atom.

The diffuse reflectance spectrum is characterized by a very broad structure in the visible region, with a maximum at *ca.* 13 000 cm^{-1} and a shoulder at *ca.* 9000 cm^{-1} similarly to those previously reported for other *cis*-[CuN_2O_4] chromophores with a tetragonally distorted octahedral geometry (4 + 2 or 4 + 1 + 1 co-ordination modes, close to C_{2v} and C_s symmetry respectively).[9,22,23] Thus the higher-energy absorption is

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **1**

Cu(1) co-ordination sphere		Cu(2) co-ordination sphere	
Cu(1)–O(91)	2.007(5)	Cu(2)–O(94)	1.979(5)
Cu(1)–O(92)	2.011(7)	Cu(2)–O(93)	1.980(6)
Cu(1)–N(1)	2.032(6)	Cu(2)–N(21)	2.038(5)
Cu(1)–N(8)	1.957(7)	Cu(2)–N(28)	2.014(7)
Cu(1)–Ow(1)	2.243(7)	Cu(2)–Ow(2)	2.309(7)
Cu(1)–O(101)	2.635(8)	Cu(2)–O(201)	2.576(7)
O(91)–Cu(1)–O(92)	82.3(2)	O(94)–Cu(2)–O(93)	84.4(2)
O(91)–Cu(1)–N(1)	172.8(3)	O(94)–Cu(2)–N(21)	172.9(2)
O(91)–Cu(1)–N(8)	95.6(2)	O(94)–Cu(2)–N(28)	93.0(2)
O(91)–Cu(1)–Ow(1)	93.6(2)	O(94)–Cu(2)–Ow(2)	92.7(2)
O(91)–Cu(1)–O(101)	86.4(2)	O(94)–Cu(2)–O(201)	89.3(2)
O(92)–Cu(1)–N(1)	99.5(2)	O(93)–Cu(2)–N(21)	101.4(2)
O(92)–Cu(1)–N(8)	172.7(3)	O(93)–Cu(2)–N(28)	175.7(2)
O(92)–Cu(1)–Ow(1)	90.3(3)	O(93)–Cu(2)–Ow(2)	90.2(3)
O(92)–Cu(1)–O(101)	80.7(3)	O(93)–Cu(2)–O(201)	86.0(2)
N(1)–Cu(1)–N(8)	81.8(3)	N(21)–Cu(2)–N(28)	80.9(2)
N(1)–Cu(1)–Ow(1)	93.3(2)	N(21)–Cu(2)–Ow(2)	91.3(2)
N(1)–Cu(1)–O(101)	87.1(2)	N(21)–Cu(2)–O(201)	87.2(2)
N(8)–Cu(1)–Ow(1)	96.9(3)	N(28)–Cu(2)–Ow(2)	93.5(3)
N(8)–Cu(1)–O(101)	92.1(3)	N(28)–Cu(2)–O(201)	90.5(3)
Ow(1)–Cu(1)–O(101)	170.9(2)	Ow(2)–Cu(2)–O(201)	175.5(2)
Oxalato bridge			
C(95)–C(96)	1.504(10)		
O(91)–C(95)	1.233(10)	O(94)–C(96)	1.284(10)
O(92)–C(96)	1.246(8)	O(93)–C(95)	1.269(8)
O(91)–C(95)–O(93)	125.7(7)	O(94)–C(96)–O(92)	125.7(7)
O(91)–C(95)–C(96)	117.3(6)	O(94)–C(96)–C(95)	116.8(6)
O(93)–C(95)–C(96)	117.0(7)	O(92)–C(96)–C(95)	117.5(7)
Nitrate ions			
O(101)–N(100)	1.244(12)	O(201)–N(200)	1.260(10)
N(100)–O(102)	1.182(12)	N(200)–O(202)	1.151(13)
N(100)–O(103)	1.179(11)	N(200)–O(203)	1.182(12)
O(101)–N(100)–O(102)	120.1(8)	O(201)–N(200)–O(202)	119.0(8)
O(101)–N(100)–O(103)	124.3(9)	O(201)–N(200)–O(203)	119.8(9)
O(102)–N(100)–O(103)	115.4(9)	O(202)–N(200)–O(203)	121.2(9)
Hydrogen bonds			
Ow(1) · · · Ow(3)	2.854(9)	Ow(2) · · · Ow(4)	2.835(9)
Hw(11) · · · Ow(3)	2.05(1)	Hw(21) · · · Ow(4)	1.95(1)
Ow(1)–Hw(11) · · · Ow(3)	140.5(9)	Ow(2)–Hw(21) · · · Ow(4)	152(1)
Ow(1) · · · O(102^{I})	2.861(10)	Ow(2) · · · O(202^{II})	2.961(10)
Hw(12) · · · O(102^{I})	2.05(2)	Hw(22) · · · O(202^{II})	2.16(2)
Ow(1)–Hw(12) · · · O(102^{I})	141(1)	Ow(2)–Hw(22) · · · O(202^{II})	140(1)
Ow(3) · · · O(201)	2.825(10)	Ow(4) · · · O(101)	2.916(10)
Hw(32) · · · O(201)	2.52(3)	Hw(41) · · · O(101)	1.96(2)
Ow(3)–Hw(32) · · · O(201)	100(1)	Ow(1)–Hw(41) · · · O(101)	173(1)
Ow(3) · · · Ow(1)	2.854(9)		
Hw(31) · · · Ow(1)	2.53(3)		
Ow(3)–Hw(31) · · · Ow(1)	100(1)		

Symmetry operations: I $1 - x, \frac{1}{2} + y, 2 - z$; II $-x, \frac{1}{2} + y, 1 - z$.

assigned to the overlap of the d_{xy}, d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$ transitions and the shoulder is assigned to the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition. In addition to the d–d structure band the spectrum displays a more intense band, centred at 24 000 cm^{-1}, assignable to a metal–ligand ($e_g \longrightarrow \pi^*$) transition.[24]

ESR Spectroscopy.—The ESR spectra of compound **1** (Fig. 2) are very similar to those exhibited by the previously reported μ-oxalato mepirizole-containing copper(II) dimers. At room temperature the spectrum consists of a single asymmetric derivative centred at $g = 2.212$ with a shoulder on the high-field side of the signal at 3440 G. In addition, a relatively weak $\Delta M_s = \pm 2$ transition can be observed at 1590 G ($g = 4.23$). Lowering the temperature of the sample to 110 K results in a

Table 2 Bite parameters for oxalato and mepirizole as bidentate ligands

	X–Cu–X (°)	d(X–X)/d(Cu–X)
X = N(1)/N(8)	81.8	1.32
X = N(21)/N(28)	80.9	1.30
X = O(91)/O(92)	82.3	1.32
X = O(93)/O(94)	84.4	1.35
Oxalate[a]	83.6	1.34
Mepirizole[b]	80.1	1.29

[a] Averaged from refs. 3, 11 and 12. [b] Averaged from refs. 3, 4, 11, 13 and 14.

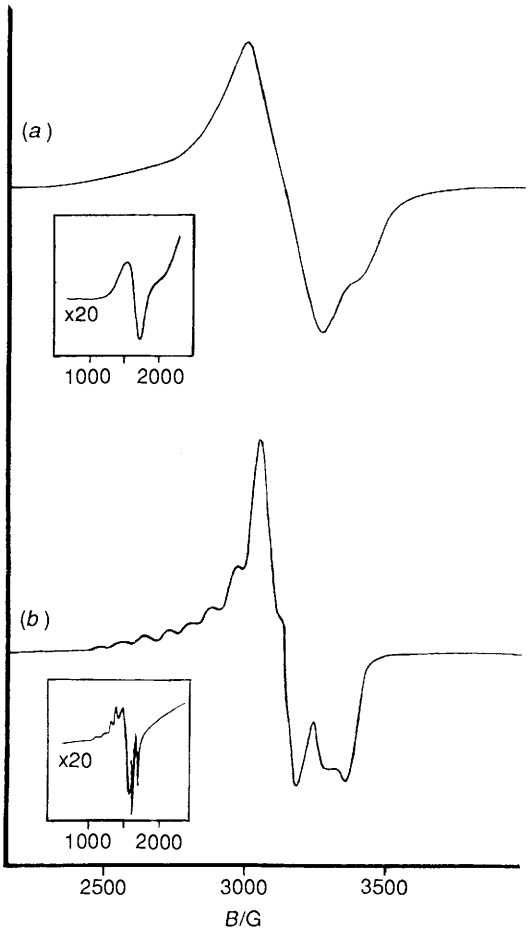

Fig. 2 X-Band polycrystalline ESR spectra of complex **1** at room temperature (*a*) and 110 K (*b*)

better resolved spectrum, showing several features associated with the triplet-state character of the dimer.[25–28] The half-field resonance ($\Delta M_s = 2$) exhibits a seven-line copper hyperfine splitting with an average hyperfine spacing $A = 70$ G, in agreement with the presence of exchange-coupled copper(II) ions.[29] With regard to the $\Delta M_s = \pm 1$ transition, the lowest-field resonance occurs at 2775 G, showing a seven-line copper hyperfine pattern similar to that of the $\Delta M_s = \pm 2$ resonances. No hyperfine splitting of the corresponding high-field signal is observed. Severe overlap of the individual lines in the $\Delta M_s = \pm 1$ region does not allow extraction of the principal components of the g tensor nor evaluation of the zero-field splitting parameter (D), which should be smaller than the linewidth ($D < 0.033$ cm^{-1}).

Magnetic Properties.—The room-temperature magnetic moment of complex **1** is below the value expected for single copper(II) ions, showing the presence of antiferromagnetic coupling. The magnetic susceptibility has been measured in the temperature range 360–5 K, affording the data deposited as SUP 56840 and displayed in Fig. 3.

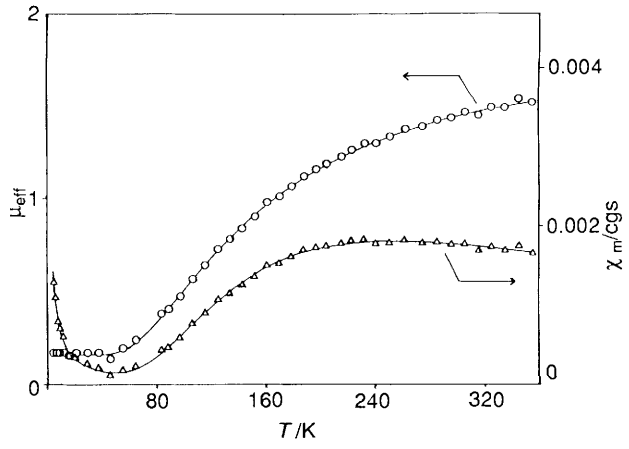

Fig. 3 Experimental molar magnetic susceptibility per binucler unit (△) and effective magnetic moment per copper(II) ion (○) *versus* temperature for complex **1**. The solid line represents the least-squares fit using equation (1)

The singlet–triplet energy gap ($2J$) was deduced from the least-squares fit of the experimental data to the temperature dependence of the molar magnetic susceptibility χ_M expressed according to the Bleaney–Bowers equation for isotropic exchange in a copper(II) dimer.[30] This equation has been modified to take into account admixture of paramagnetic impurity, according to ref. 25 [equation (1)], where the symbols

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

have their usual meaning and ρ is the fraction of non-coupled impurity, the molecular weight of which is assumed to be equal to that of the binuclear complex.

Since the diamagnetic correction is of the same order of magnitude as the uncorrected molar susceptibility, the uncertainty in the corrected values of χ_M is large, affording estimated J values reliable only within 5–10%.[31] The parameters obtained from the fit are $J = -142$ cm^{-1}, $g = 2.18$, $\rho = 2.5\%$ and $2N\alpha = 0$ together with the agreement factor[32] $R = 1.2 \times 10^{-2}$.

The co-ordination geometry around Cu(1) and Cu(2) is distorted octahedral (4 + 1 + 1 type, see above) and the $Cu(C_2O_4)Cu$ core has a flattened-chair conformation. The copper(II) unpaired electron is described by a d_{xy} type orbital pointing from the metal towards the four nearest neighbours in an antibonding fashion in both copper environments. However, since the structure of this dinuclear species is non-centrosymmetric, the core is not symmetrical, Kahn and co-workers[33] have established that for a symmetrical copper(II) binuclear complex the antiferromagnetic contribution J_{AF} to the exchange interaction may be expressed as $J_{AF} = -2S\Delta$, S being the overlap integral between the magnetic orbitals centred on the two transition-metal ions and Δ the energy separation between the two singly occupied molecular orbitals in the triplet state built from the magnetic orbitals. When the geometries of the ligand environments of the copper(II) ions of the binuclear complex are not strictly identical (which is the case for **1**) the binuclear complex is not symmetrical and the antiferromagnetic contribution must be expressed according to $J_{AF} = -2S(\Delta^2 - \delta^2)^{\frac{1}{2}}$, δ being the energy separation between the two magnetic orbitals.[34] The δ value and the corresponding decrease in the antiferromagnetic contribution J_{AF} that results from the lowering of the symmetry have been calculated by Girerd and co-workers[35] in the case of dithiooxamidato

Table 3 Fractional atomic coordinates with e.s.d.s in parentheses for complex **1**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.435 2(1)	1/4	0.894 59(5)	Cu(2)	0.106 0(1)	0.350 74(8)	0.603 51(5)
Ow(1)	0.545 2(8)	0.127 0(5)	0.837 6(4)	Ow(2)	−0.011 5(8)	0.479 4(5)	0.657 0(4)
Hw(1)	0.535(1)	0.114(1)	0.779 2(4)	Hw(21)	−0.007(1)	0.493(1)	0.715 1(4)
Hw(12)	0.603(1)	0.076 8(8)	0.868 7(8)	Hw(22)	−0.062(1)	0.530 5(8)	0.624 7(8)
N(1)	0.665 5(7)	0.272 7(5)	0.973 9(4)	N(21)	−0.122 1(7)	0.331 9(5)	0.521 0(4)
C(2)	0.660 2(8)	0.239 5(6)	1.049 9(4)	C(22)	−0.109 7(8)	0.367 3(6)	0.445 8(4)
N(3)	0.787 4(7)	0.243 5(6)	1.117 5(4)	N(23)	−0.236 4(8)	0.366 5(6)	0.378 7(4)
C(4)	0.931 4(9)	0.287 1(7)	1.105 8(6)	C(24)	−0.378 7(9)	0.323 7(6)	0.389 0(6)
C(5)	0.954 5(9)	0.325 4(7)	1.032 2(6)	C(25)	−0.410 7(9)	0.282 4(6)	0.462 7(6)
C(6)	0.818 6(8)	0.317 6(6)	0.964 1(5)	C(26)	−0.273 4(9)	0.290 3(6)	0.528 2(5)
N(7)	0.504 3(8)	0.196 0(5)	1.060 6(4)	N(27)	0.044 3(8)	0.411 9(5)	0.436 3(4)
N(8)	0.369 7(8)	0.188 5(5)	0.992 6(4)	N(28)	0.176 0(8)	0.418 0(5)	0.505 2(4)
C(9)	0.246 1(9)	0.138 5(6)	1.016 2(5)	C(29)	0.305 8(9)	0.468 8(5)	0.483 3(5)
C(10)	0.287 7(9)	0.110 1(7)	1.100 3(5)	C(30)	0.263 1(9)	0.496 3(6)	0.399 1(5)
C(11)	0.455 6(9)	0.148 5(6)	1.127 7(5)	C(31)	0.097 3(9)	0.462 1(6)	0.372 9(5)
O(12)	0.561 2(8)	0.144 7(5)	1.197 6(4)	O(32)	−0.011 1(8)	0.467 0(6)	0.300 6(4)
C(13)	0.498(1)	0.089 2(8)	1.260 2(6)	C(33)	0.056(1)	0.525 7(8)	0.239 6(7)
C(14)	0.085(1)	0.108 9(8)	0.960 9(6)	C(34)	0.472 6(9)	0.494 1(6)	0.541 3(5)
O(15)	1.067 9(7)	0.294 9(6)	1.170 7(4)	O(35)	−0.517 0(7)	0.316 9(5)	0.323 6(4)
C(16)	1.042 3(9)	0.249 9(8)	1.246 4(5)	C(36)	−0.490(1)	0.360 3(8)	0.246 4(5)
C(17)	0.841 6(8)	0.354 8(8)	0.881 9(5)	C(37)	−0.300 1(9)	0.249 1(8)	0.610 6(5)
N(100)	0.375 6(8)	0.453 6(6)	1.006 7(5)	N(200)	0.141 4(8)	0.151 8(6)	0.490 4(5)
O(101)	0.324 1(8)	0.409 1(6)	0.942 4(5)	O(201)	0.219 4(8)	0.199 8(5)	0.549 2(5)
O(102)	0.332 5(9)	0.530 7(6)	1.011 4(6)	O(202)	0.110 0(9)	0.076 7(6)	0.503 0(6)
O(103)	0.477(1)	0.426 1(7)	1.063 6(6)	O(203)	0.104(1)	0.184 0(7)	0.423 4(5)
O(91)	0.193 2(6)	0.238 4(5)	0.825 2(3)	Ow(3)	0.348 4(6)	0.078 7(5)	0.679 8(4)
O(92)	0.483 7(6)	0.326 8(5)	0.797 8(4)	Hw(31)	0.407 (1)	0.031 7(9)	0.715(1)
O(93)	0.053 4(6)	0.278 7(4)	0.700 1(3)	Hw(32)	0.433(1)	0.107(1)	0.649 2(9)
O(94)	0.343 3(6)	0.369 0(5)	0.671 5(3)	Ow(4)	0.119 1(7)	0.531 9(6)	0.823 0(4)
O(95)	0.186 7(8)	0.277 6(6)	0.757 7(5)	Hw(41)	0.195(1)	0.492(1)	0.859(1)
O(96)	0.351 6(8)	0.328 0(5)	0.741 8(5)	Hw(42)	−0.001 8(7)	0.526(1)	0.834(1)

binuclear copper(II) complexes. They showed that the decrease in J_{AF} estimated from extended-Hückel molecular orbital calculations is in good agreement with that estimated from the magnetic susceptibility measurements.

The antiferromagnetic interaction afforded by the non-symmetrical co-ordination geometry of complex **1** ($J = -142$ cm^{-1}) is weaker than that achieved through the symmetrical co-ordination geometry of previously described μ-oxalato-bridged binuclear copper(II) complexes characterized by centro-symmetric molecular and crystal structures[3] but similar to that evaluated for unit 2A of $[(mpym)(NO_3)Cu(C_2O_4)Cu(NO_3)(H_2O)(mpym)]_2[(mpym)(NO_3)Cu(C_2O_4)Cu(NO_3)(mpym)]$ **3** which possesses a non-centrosymmetric structure characterized by a non-symmetrical $Cu(C_2O_4)Cu$ core.[3] It is worth noticing that the -133 cm^{-1} exchange integral indirectly evaluated for unit 2A of complex **3** is consistent with that presently obtained for complex **1**. In conclusion, the difference in the ligand environments of the copper(II) ions of **1** described in the crystal structure section is able to induce an energy separation between the two magnetic orbitals large enough to weaken the antiferromagnetic interaction by approximately 60 cm^{-1} compared to that of the symmetrical μ-oxalato-bridged binuclear copper(II) complexes.[3]

Experimental

Preparation of $[Cu_2(mpym)_2(H_2O)_4(C_2O_4)(NO_3)_2]$ **1**.—The mepirizole ligand (Daiichi Seiyaku Co. Japan) was purified by crystallization from a methanol solution. All other reagents were used as received. A disodium squarate solution was prepared by adding the required quantity of a titrated sodium hydroxide solution to a squaric acid solution. For the synthesis of the compound, dilute nitric acid (1%, 10 cm^3) was added to an aqueous mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (10 cm^3, 0.40 mmol), mepirizole (10 cm^3, 0.40 mmol) and $Na_2C_4O_4$ (10 cm^3, 0.20 mmol). The solution was allowed to stand at room temperature and green crystals of complex **1** formed after several days. They were separated by filtration and washed with a cold water–ethanol mixture (60:40) and stored in a desiccator over silica gel. The yield was 30% (Found: C, 33.0; H, 4.2; Cu, 14.3; N, 15.8. Calc. for $C_{24}H_{36}Cu_2N_{10}O_{18}$: C, 32.8; H, 4.1; Cu, 14.4; N, 15.9%).

Physical Measurements.—The IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range using a Philips Analytical SP 2000 spectrophotometer, diffuse reflectance electronic spectra with a Perkin-Elmer Lambda 9 uv/vis/near-IR spectrophotometer and ESR spectra with a Bruker ER 200D spectrometer equipped with a nitrogen cryostat. Variable-temperature (5–360 K) magnetic susceptibility data were obtained from a polycrystalline sample with a Faraday-type magnetometer equipped with continuous-flow Oxford Instruments cryostat; $HgCo(NCS)_4$ was used as the susceptibility standard. Experimental susceptibilities were corrected for the diamagnetism of the ligand[36] [χ(mepirizole) = -1.1×10^{-9} m^3 mol^{-1} [37]] and for the temperature-independent paramagnetism, estimated to be -7.5×10^{-10} m^3 mol^{-1} cgs per copper(II) ion.

X-Ray Structure Determination.—*Crystal data.* $C_{24}H_{36}Cu_2N_{10}O_{18}$, $M = 879.7$, monoclinic, space group $P2_1$, $a = 7.559(4)$, $b = 14.659(3)$, $c = 16.246(3)$ Å, $\beta = 98.6(2)°$, $U = 1780$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), $D_m = 1.62$ g cm^{-3} (flotation), $Z = 2$, $D_c = 1.64$, $F(000) = 904$, green block-like crystal 0.4 × 0.3 × 0.2 mm, μ(Mo-Kα) = 12.8 cm^{-1}.

Data collection and processing.[13] CAD4 diffractometer, ω–2θ mode with ω scan width = 1.1 + 0.35 tan θ, ω scan speed 0.9–8.2° min^{-1}, graphite-monochromated Mo-Kα radiation; 3505 unique reflections measured ($1.5 \leqslant \theta \leqslant 28°$, h, k, $\pm l$), three standard reflections monitored every 2 h, no decay observed, no absorption corrections because of small μ and block-shaped crystal, 3329 reflections with $I > 3\sigma(I)$. Space group $P2_1$ or $P2_1/m$ from systematic absences.

Structure analysis and refinement. Direct methods[38] followed by standard full-matrix least-squares refinements and Fourier procedures.[39] Attempts to solve and refine the structure in the centrosymmetric space group $P2_1/m$ failed; calculations were carried out assuming the non-centrosymmetric space group $P2_1$, no correlation between parameters being noticed. The absolute configuration could not be determined for the refinements of both enantiomers were not significantly different. All hydrogen atoms were located on Fourier difference maps, but idealized, unrefined positions and arbitrary isotropic thermal parameters were used for organic hydrogen atoms; positional parameters of hydrogen atoms of the water molecules were refined along with a common isotropic thermal parameter. Unit weights gave satisfactory agreement analyses ($S = 1.3$). Final R and R' values were 0.046 and 0.047. Scattering factors and anomalous dispersion terms were taken from ref. 40. Calculations were performed on a microVAX 3400 DEC computer. Atomic coordinates are listed in Table 3.

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

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References

1 G. Christou, S. P. Perlepes, E. Libby, K. Folting, J. C. Huffman, R. J. Webb and D. N. Hendrickson, *Inorg. Chem.*, 1990, **29**, 3657 and refs. therein.
2 M. Beneto, J. Garcia, L. Soto, J. V. Folgado and E. Escriva, *Polyhedron*, 1989, **8**, 1523.
3 L. Soto, J. Garcia, E. Escriva, J.-P. Legros, J.-P. Tuchagues, F. Dahan and A. Fuertes, *Inorg. Chem.*, 1989, **28**, 3378.
4 M. Beneto, L. Soto, J. García-Lozano, E. Escrivá, J.-P. Legros and F. Dahan, *J. Chem. Soc., Dalton Trans.*, 1991, 1057.
5 R. West, H. N. Niu and M. Ito, *J. Am. Chem. Soc.*, 1963, **85**, 2584.
6 D. Deguenon, Ph.D. Thesis, Toulouse, 1990.
7 D. Deguenon, G. Bernardinelli, J.-P. Tuchagues and P. Castan, *Inorg. Chem.*, 1990, **29**, 3031.
8 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1985, vol. 5, p. 604 and refs. therein.
9 W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, B. Hathaway and P. O'Brien, *J. Chem. Soc., Dalton Trans.*, 1982, 1117.
10 B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55 and refs. therein; B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.
11 J. Suarez-Varela, L. Soto, J.-P. Legros, C. Esteve and J. Garcia, *Polyhedron*, 1988, **7**, 229.
12 X. Solans, M. Aguilo, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775 and refs. therein.
13 L. Soto, J.-P. Legros, M. C. Molla and J. Garcia, *Acta Crystallogr., Sect. C*, 1987, **43**, 834.
14 M. C. Molla, J. Garcia, J. Borras, C. Foces-Foces, F. H. Cano and M. Martinez-Ripoll, *Transition Met. Chem.*, 1985, **10**, 460.
15 P. W. Borthwick, *Acta Crystallogr., Sect. B*, 1980, **36**, 628.
16 M. Falk and O. Knop, in *Water: a Comprehensive Treatise*, ed. Franks, Plenum, New York, 1973, vol. 2, p. 103.
17 K. Nakamoto, M. Marghoses and P. E. Rundle, *J. Am. Chem. Soc.*, 1955, **77**, 6480.
18 N. F. Curtis, *J. Chem. Soc. A*, 1968, 1584.
19 L. J. Bellamy and A. J. Owen, *Spectrochim. Acta, Part A*, 1969, **25**, 329.
20 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.
21 M. R. Rosenthal, *J. Chem. Educ.*, 1973, **50**, 331.
22 E. Escriva, A. Fuertes and D. Beltran, *Transition Met. Chem.*, 1984, **9**, 184.
23 A. Fuertes, E. Escriva, C. Munoz, J. Alamo, A. Beltran and D. Beltran, *Transition Met. Chem.*, 1987, **12**, 62.
24 A. B. P. Lever, *J.Chem. Educ.*, 1974, **51**, 612.
25 Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.*, 1985, **24**, 4063.
26 A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, A. C. Fabretti and G. Franchini, *Inorg. Chim. Acta*, 1984, **86**, 169.
27 T. R. Felthouse, E. J. Laskowski and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 1077.
28 D. Sonnenfroh and R. W. Kreilick, *Inorg. Chem.*, 1980, **19**, 1259.
29 C. P. Slichter, *Phys. Rev.*, 1955, **99**, 479.
30 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **266**, 95.
31 C. O'Connor, *Prog. Inorg. Chem.*, 1982, **20**, 203.
32 A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, *Inorg. Chem.*, 1972, **11**, 2884.
33 O. Kahn and B. Briat, *J. Chem. Soc., Faraday Trans. 2*, 1976, 268, 1441; J.-J. Girerd, M.-F. Charlot and O. Kahn, *Mol. Phys.*, 1977, **34**, 1063.
34 P. Tola, O. Kahn, C. Chauvel and H. Coudanne, *Nouv. J. Chim.*, 1977, **1**, 467.
35 J.-J. Girerd, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem.*, 1978, **17**, 3034; C. Chauvel, J.-J. Girerd, Y. Jeannin, O. Kahn and G. Lavigne, *Inorg. Chem.*, 1979, **18**, 3015.
36 K. Burger, *Coordination Chemistry, Experimental Methods*, Butterworths, London, 1973.
37 M. C. Molla, D. Thesis, Universitat de Valencia, 1985.
38 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingen, 1986.
39 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
40 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99–102 and 148–151.

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