Crystal and Molecular Structure and Properties of the First Characterized Copper(II) One-dimensional Polymer containing Mepirizole [4-Methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine]†

Matilde Benetó,[a] Lucia Soto,[a] Julia García-Lozano,*[,a] Emilio Escrivá,[a] Jean-Pierre Legros[b] and Françoise Dahan[b]

[a] *Departament de Quimica Inorgánica, Facultat de Farmacia, Universitat de Valencia, Avda Blasco Ibañez 13, 46010, Valencia, Spain*

[b] *Laboratoire de Chimie de Coordination du CNRS, Unité nº 8241, liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205, route de Narbonne, 31077 Toulouse Cedex, France*

The crystal and molecular structure of the complex $[Cu(mpym)(H_2O)(C_4O_4)]\cdot 2H_2O$ [mpym = mepirizole = 4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine] has been determined by X-ray methods. It crystallizes in the orthorhombic space group *Pbcn*, with $Z = 8$, $a = 18.592(3)$, $b = 14.723(2)$ and $c = 13.755(3)$ Å, $R = 0.053$ and $R' = 0.070$ for 2697 reflections. The structure comprises infinite chains parallel to [001] built up of 1-bis(monodentate) squarate-O^1O^3 C_4O_4 anions bridging $[Cu(mpym)(H_2O)]^{2+}$ units. The copper(II) ions display distorted trigonal-bipyramidal geometry. Both electronic and ESR spectra are indicative of an essentially d_{z^2} ground state for the Cu^{II}. No exchange coupling has been detected down to 4.2 K by means of magnetic susceptibility measurements. This feature is discussed on the basis of the relative orientation of the co-ordination polyhedron around the metallic atom and the bridging ligand.

The study of the interactions between paramagnetic centres in condensed systems has recently become an active area of co-ordination chemistry. In particular, significant progress has been made in the understanding of the exchange interaction through extended bridging ligands. On the other hand, co-ordination chemistry offers a great flexibility in the design of materials with particular properties (structural and/or magnetic dimensionality, strength and range of interactions, *etc.*).[1] In a previous paper[2] we have structurally and/or magnetically characterized a set of copper(II) oxalato and oxamido complexes, containing binuclear units (mpym)Cu(A)Cu(mpym), where H_2A = oxalatic and/or oxamide and the terminal ligand mpym is mepirizole [4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine], a biologically active pyrimidine–pyrazole derivative. The latter acts as a bidentate ligand through two nitrogen atoms, one from each ring, with significant steric hindrance in the formation of metal complexes.[2,3]

Our current interest is focused on the design and characterization of new polynuclear systems containing $[ML]^{m+}$ (M = 3d ion) entities, where L is a bi-tri-dentate ligand such as pyrimidine–pyrazole and related heterocyclic systems which play an outstanding role in several biological processes. To progress on this subject, we are now developing the study of interactions between $[Cu(mpym)]^{2+}$ entities and the dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione, $C_4O_4^{2-}$, commonly referred to as squarate (sq) anion. The latter cyclic oxocarbon system has been shown to exhibit a wide variety of co-ordination modes[4–9] toward 3d ions. In this paper we report the structure and properties of a new copper(II) complex polymer formed by using squarato-O^1O^3 groups as bridging ligands.

Results and Discussion

Crystal Structure.—Fig. 1 shows a perspective view of the repeat unit and the atom numbering scheme, and Fig. 2 a projection of the chain structure onto the *ac* plane. Interatomic bond distances and angles are given in Table 1. The structure is made of infinite chains parallel to [001] built from $[Cu(mpym)(H_2O)]^{2+}$ units bridged by squarate anions which act in a O^1O^3 bis(monodentate) fashion. Adjacent chains interact through van der Waals contacts and weak hydrogen bonds. The copper(II) ion is five-co-ordinated by the N(3) atom of the pyrazole ring, two oxygen atoms O(1) and O(3^I) belonging to different $C_4O_4^{2-}$ groups, the N(1) atom of the pyrimidine ring, and a water molecule Ow(1). The Cu–Ow(1) distance [1.935(3) Å] is

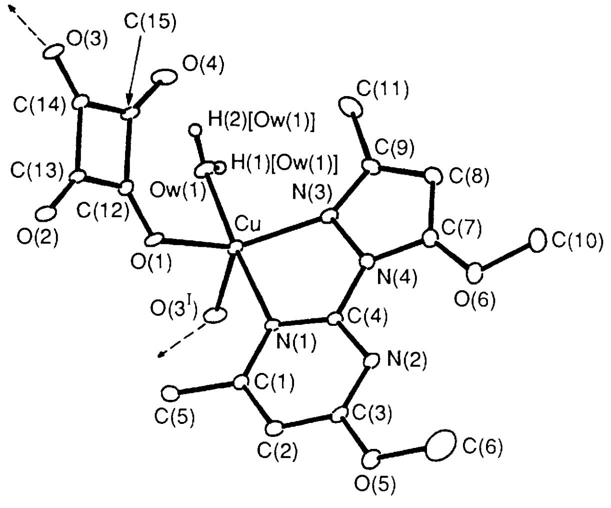

Fig. 1 Perspective view and atomic numbering of $[Cu(mpym)(H_2O)(C_4O_4)]\cdot 2H_2O$. Symmetry operation: I $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected bond lengths (Å) and angles (°) for [Cu(mpym)(H_2O)(C_4O_4)]·$2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Copper co-ordination sphere

Cu–Ow(1)	1.935(3)	Ow(1)–Cu–O(1)	90.3(1)	O(1)–Cu–N(3)	134.3(1)
Cu–N(1)	2.019(4)	Ow(1)–Cu–N(1)	175.9(1)	O(1)–Cu–O(3^{I})	109.5(1)
Cu–O(3)	2.108(1)	Ow(1)–Cu–N(3)	96.2(1)	N(1)–Cu–N(3)	79.7(1)
Cu–O(1)	1.999(3)	Ow(1)–Cu–O(3^{I})	92.0(1)	N(1)–Cu–O(3^{I})	89.4(1)
Cu–N(3)	2.032(4)	O(1)–Cu–N(1)	92.8(1)	N(3)–Cu–O(3^{I})	115.4(1)

Mepirizole molecule

N(1)–C(1)	1.370(6)	C(4)–N(4)	1.392(6)	C(1)–N(1)–C(4)	116.1(4)	N(1)–C(4)–N(4)	115.4(4)
C(1)–C(2)	1.349(6)	N(3)–N(4)	1.380(5)	N(1)–C(1)–C(2)	120.1(4)	C(4)–N(4)–N(3)	117.5(3)
C(2)–C(3)	1.401(7)	N(4)–C(7)	1.381(6)	N(1)–C(1)–C(5)	119.0(4)	C(4)–N(4)–C(7)	133.0(4)
C(3)–N(2)	1.318(6)	C(7)–C(8)	1.353(7)	C(2)–C(1)–C(5)	120.9(4)	N(3)–N(4)–C(7)	109.6(4)
N(2)–C(4)	1.323(6)	C(8)–C(9)	1.378(7)	C(1)–C(2)–C(3)	118.3(4)	N(4)–C(7)–C(8)	106.8(4)
C(4)–N(1)	1.324(5)	C(9)–N(3)	1.341(6)	C(2)–C(3)–N(2)	122.5(4)	N(4)–C(7)–O(6)	119.0(4)
C(1)–C(5)	1.506(6)	C(7)–O(6)	1.329(6)	C(2)–C(3)–O(5)	118.1(4)	C(8)–C(7)–O(6)	134.2(4)
C(3)–O(5)	1.330(6)	O(6)–C(10)	1.447(6)	N(2)–C(3)–O(5)	119.4(4)	C(7)–O(6)–C(10)	114.6(4)
O(5)–C(6)	1.452(7)	C(9)–C(11)	1.468(8)	C(3)–O(5)–C(6)	118.5(4)	C(7)–C(8)–C(9)	107.6(5)
				C(3)–N(2)–C(4)	115.0(4)	C(8)–C(9)–N(3)	110.5(5)
				N(2)–C(4)–N(1)	128.0(4)	C(8)–C(9)–C(11)	126.5(5)
				N(2)–C(4)–N(4)	116.5(4)	N(3)–C(9)–C(11)	123.0(4)
						N(4)–N(3)–C(9)	105.6(4)

Squarate group

O(1)–C(12)	1.266(5)	C(12)–C(13)	1.438(6)	C(15)–C(12)–C(13)	91.1(3)	C(13)–C(14)–C(15)	90.0(3)
O(2)–C(13)	1.244(6)	C(13)–C(14)	1.462(6)	C(12)–C(13)–C(14)	90.1(3)	C(14)–C(15)–C(12)	88.8(3)
O(3)–C(14)	1.258(5)	C(14)–C(15)	1.469(6)	O(1)–C(12)–C(15)	135.6(4)	O(3)–C(14)–C(13)	136.1(4)
O(4)–C(15)	1.245(6)	C(15)–C(12)	1.464(6)	O(1)–C(12)–C(13)	133.3(4)	O(3)–C(14)–C(15)	133.9(4)
				O(2)–C(13)–C(12)	135.5(4)	O(4)–C(15)–C(14)	136.2(4)
				O(2)–C(13)–C(14)	134.4(4)	O(4)–C(15)–C(12)	135.0(4)

Water molecules, hydrogen bonds and contacts

Ow(1)–H(1)[Ow(1)]	0.95(3)	Ow(1)–H(2)[Ow(1)]	0.95(4)	H(1)[Ow(2)]–Ow(2)–H(2)[Ow(2)]	108(6)
Ow(2)–H(1)[Ow(2)]	0.97(5)	Ow(2)–H(2)[Ow(2)]	0.97(3)	H(1)[Ow(1)]–Ow(1)–H(2)[Ow(1)]	114(4)
H(1)[Ow(1)] ··· O(2)	1.74(3)	H(2)[Ow(1)] ··· O(4)	1.77(3)	Ow(1)–H(1)[Ow(1)] ··· O(2^{I})	152(4)
H(1)[Ow(2)] ··· O(4)	2.50(7)	H(2)[Ow(2)] ··· O(4)	2.43(7)	Ow(1)–H(2)[Ow(1)] ··· O(4)	147(5)
H(2)[Ow(2)] ··· Ow(3)	2.58(9)	Ow(1) ··· O(2^{I})	2.625(5)	Ow(2)–H(1)[Ow(2)] ··· O(4)	101(4)
Ow(1) ··· O(4)	2.621(5)	Ow(2) ··· O(2^{III})	2.878(9)	Ow(2)–H(2)[Ow(2)] ··· O(4)	106(5)
Ow(2) ··· O(4)	2.852(10)			Ow(2)–H(2)[Ow(2)] ··· O(3)	96(5)
Ow(2) ··· Ow(3)	2.847(12)				

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

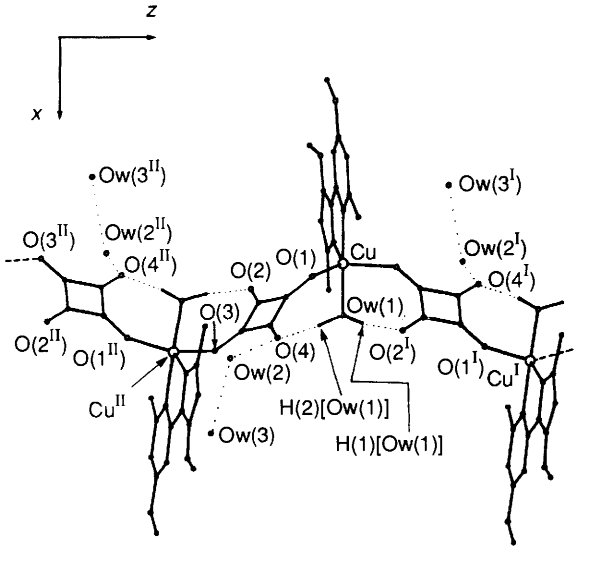

Fig. 2 Chain structure of [Cu(mpym)(H_2O)(C_4O_4)]·$2H_2O$ viewed approximately along the *c* axis. Symmetry operation: II $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$

significantly shorter than the Cu–O(sq) distances [mean 2.054(3) Å] despite the electronegativity of the C_4O_4 ligand. The co-ordination polyhedron can be described as a trigonal bipyramid (TBPY) distorted towards a square pyramid (SPY).[10] Such a geometry can be quantitatively characterized using the parameter τ as defined by Addison *et al.*[11] The calculated value $\tau = 0.69$ (relative to 1 for a regular TBPY and 0 for a regular SPY) clearly indicates the predominance of the TBPY form. In the TBPY description of the co-ordination polyhedron the O(1), O(3^{I}) and N(3) atoms occupy the equatorial positions and N(1) and Ow(1) the axial positions [N(1)–Cu–Ow(1) 175.9(1)°]. According to previous studies[12,13] on several monoaqua five-co-ordinated copper(II) complexes, the water molecule would have been expected to occupy an equatorial position or the apex of the SPY. The observed tendency of the water molecule to occupy an axial position of a TBPY is a striking feature of the present compound.

The squarate anion is almost planar, within the limits of error, the largest deviation from the mean plane being 0.007 Å, and it is twisted by an angle of 58.7° with respect to the equatorial plane of the copper(II) polyhedron. The C–C bond lengths [mean 1.458(6) Å] are slightly shorter than those reported for other O^1O^3 bis(monodentate) squarates (means range from 1.460 to 1.473 Å).[6,8] As usual, the C–C–C angles are close to 90° [mean 90.0(3)°], and the O–C–C angles vary between 133.3 and 136.2°. The C–O bond lengths of the co-ordinated oxygen atoms, O(1) and O(3), are *ca.* 0.02 Å longer than the other two remaining C–O bonds involving the O(2) and the O(4) atoms, which are only subject to hydrogen-bond interactions (see below). Notwithstanding, the two C–O (co-ordinated) bonds are not equivalent (Table 1); as expected, the longest C–O distance is associated with the shortest Cu–O.

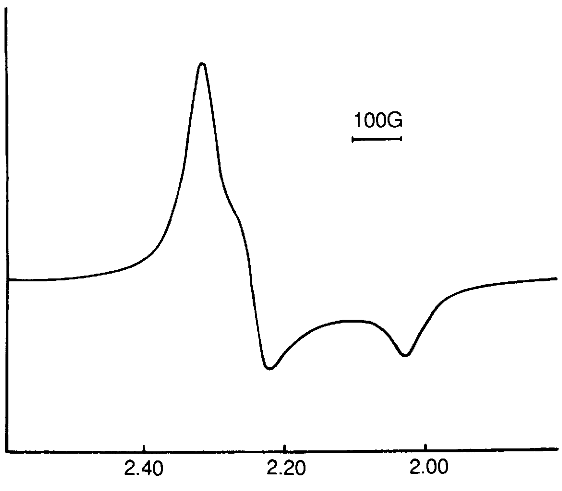

Fig. 3 X-Band powder ESR spectrum (295 K) of [Cu(mpym)(H_2O)(C_4O_4)]·$2H_2O$ (ν = 9.43 GHz)

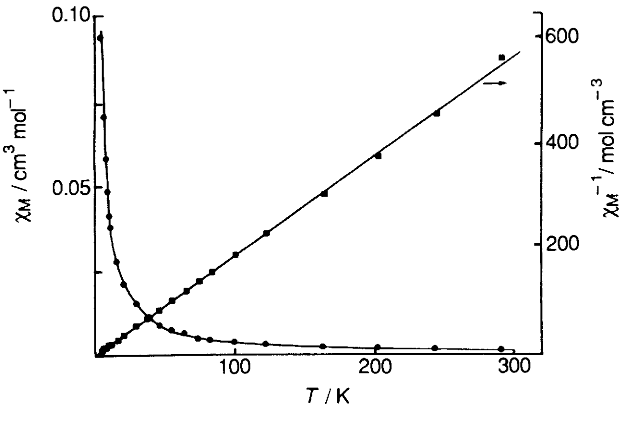

Fig. 4 Temperature dependence of the molar magnetic susceptibility χ_M and the inverse susceptibility of [Cu(mpym)(H_2O)(C_4O_4)]·$2H_2O$. The solid lines were obtained by Curie–Weiss fitting (see text)

The geometry of the mepirizole molecule (interatomic distances and angles) is similar to that previously found in several mepirizole-containing copper(II) systems.[2,3] The dihedral angle between the pyrazole and the pyrimidine ring is 0.2°. So, the planarity of the mepirizole ligand as well as its rigidity [the bite value, 1.28 Å, compares well with the mean of 1.29 ± 0.2 Å found in related copper(II) mepirizole oxalates] is once again confirmed. Finally, it must be stressed that the mepirizole molecule as a whole is located in a plane nearly orthogonal (dihedral angle 90.4°) to the equatorial Cu–O(1)–O(3^I)–N(3) plane.

The co-ordinated water molecule Ow(1) is involved in two intramolecular hydrogen bonds each involving one hydrogen atom. They bind the water molecule to the O(4) and O(2) oxygen atoms of the closest squarato groups (Fig. 2). The mean H[Ow(1)] ··· O(sq) distance of 1.76 Å is indicative of a quite strong interaction. In addition the asymmetric unit contains two non-co-ordinated water molecules Ow(2) and Ow(3). Both are quite diffuse [the hydrogen atoms of Ow(3) have not been located]. However, on the basis of the O ··· O distances (Table 1) both appear to be involved in hydrogen bonds. It should be noted that the Ow(2) ··· O(2^{III}) hydrogen bond (if present) is the only interchain interaction besides the van der Waals contacts.

Infrared and Electronic Spectra.—The IR spectrum of the present compound shows a broad band centred at *ca.* 3480 cm^{-1} besides a sharper one at 3130 cm^{-1}, both assignable to the O–H stretching vibrations. The latter may be tentatively attributed to the O–H groups from Ow(1) water molecules, which are involved, as discussed before, in quite strong hydrogen-bond interactions. This assignment is in agreement with the observed relationship between the ν(OH) frequency and the O ··· O distance of the hydrogen bridge.[14–16] With regard to the bands originating from the C_4O_4 groups, the spectrum exhibits a strong absorption at 1465 cm^{-1}, assigned to ν(C–C) + ν(C–O) vibrations. In addition a strong band observed in the same region (1610 cm^{-1}) is assignable to ν(C=N) vibrations from the mepirizole molecule.[3]

In the visible region the electronic spectrum exhibits a very broad structure centred on 12 200 cm^{-1}; the position of the maximum of the band intensity is in agreement with a roughly TBPY geometry of the environment of the copper(II) ion.[17] Due to the unequivalence of bond lengths and angles, the CuN_2O_2O' chromophore does not possess any element of symmetry. However, if these deviations are neglected, there is an approximate plane of symmetry containing the Cu–N(1) and Cu–N(3) directions, the point-group symmetry of the copper(II) ions being thus close to C_s. Taking these considerations into account, it may be assumed that the unresolved d–d band arises from the overlap of the $A''(d_{yz}, d_{xz}) \longrightarrow A'(d_{z^2})$ and $A'(d_{x^2-y^2}, d_{xy}) \longrightarrow A'(d_{z^2})$ transitions.[18] In addition to the d–d band, the spectrum displays two more intense bands centred at 21 500 and *ca.* 30 000 cm^{-1}. The former is assignable to a metal–ligand ($e_g \longrightarrow \pi^*$) transition[4,8] and the latter to both squarate and mepirizole internal bands.

Electron Spin Resonance and Magnetic Behaviour.—The room-temperature polycrystalline X-band ESR spectrum shows an orthorhombic signal with $g_1 = 2.025$, $g_2 = 2.217$ and $g_3 = 2.285$ (which remain practically constant from room temperature to 110 K) but no copper hyperfine splitting (Fig. 3), the high-field signal being at $g \leqslant 2.04$ indicative of an essentially d_{z^2} ground state for the copper(II) ion.[10,17] A co-ordinate system with z and x axes close to the quasi-orthogonal Cu–N(1) and Cu–O(3^I) directions [N(1)–Cu–O(3^I) 89.4(1)°] can be set up for the CuN_2O_2O' chromophore. The highest-energy orbital in a ligand-field formalism can be described as $(\cos\alpha)|z^2\rangle + (\sin\alpha|x^2 - y^2\rangle$, with $\alpha = 0°$ for a regular TBPY geometry and $\alpha = 30°$ for a regular SPY geometry ($d_{x^2-y^2}$ ground state) and where the contribution to the ground state of the d_{xy} orbital as well as the d–s and d–p mixing has been neglected.[19] The α value may be estimated by fitting of the g factors by suitable expressions for a symmetry close to C_s.[17,20] For this purpose g_1, g_2 and g_3 were identified with g_z, g_y and g_x respectively. The absence of significant interactions between the copper(II) ions (see below), as well as the approximately parallel/antiparallel orientation of the Cu–N(1) directions in the unit cell ('canting' angle of *ca.* 11°), supports this approximation.[20,21] The obtained value of $\alpha = 14°$ results in a $d_{x^2-y^2}$ contribution to the copper(II) ground-state wavefunction of about 6%; this is in excellent agreement with the topology of the copper(II) co-ordination polyhedron (predominancy of the TBPY geometry) deduced from the X-ray data.

The μ_{eff} values stay practically constant (1.89 μ_B) from 290 to 4.2 K, and the magnetic susceptibility exhibits a Curie–Weiss dependence (Fig. 4); the whole data set can be fitted by the expression $\chi = (T + 0.4)/0.454$. The small absolute value of the Weiss correction might suggest a very weak antiferromagnetic coupling ($|J| < 0.5$ cm^{-1}) which would be detected only at temperatures below 4.2 K. From the Curie constant $C = N\beta^2g^2S(S + 1)/3k$ with $S = \frac{1}{2}$ a g value of 2.20 can be obtained, which compares well with that obtained from the ESR spectrum ($g_0 = 2.18$). This result indicates that the copper(II) ions in a chain may be viewed as essentially magnetically non-coupled.

This behaviour may be understood in terms of the nature of the orbitals involved in the exchange interactions together with structural considerations on the bridging network. The extent of

Table 2 Fractional atomic coordinates with e.s.d.s in parentheses for $[Cu(mpym)(H_2O)(C_4O_4)]\cdot 2H_2O$

Atom	X/a	Y/b	Z/c
Cu	0.323 89(3)	0.161 31(4)	0.394 03(4)
Ow(1)	0.220 1(2)	0.161 8(2)	0.404 9(2)
H(1)[Ow(1)]	0.206(3)	0.133(3)	0.464(2)
H(2)[Ow(1)]	0.198(3)	0.137(4)	0.349(2)
N(1)	0.432 0(2)	0.151 2(2)	0.384 0(2)
C(1)	0.481 7(2)	0.219 7(3)	0.379 2(3)
C(2)	0.552 1(3)	0.199 9(3)	0.368 5(3)
C(3)	0.572 4(2)	0.108 3(3)	0.364 9(3)
N(2)	0.525 6(2)	0.041 5(3)	0.372 9(3)
C(4)	0.457 8(2)	0.067 4(3)	0.381 9(3)
C(5)	0.456 4(3)	0.316 7(3)	0.384 4(4)
O(5)	0.641 7(2)	0.089 1(3)	0.352 7(3)
C(6)	0.663 4(3)	−0.005 6(4)	0.350 0(4)
N(3)	0.335 7(2)	0.024 2(3)	0.399 4(3)
N(4)	0.406 8(2)	−0.001 4(2)	0.389 9(3)
C(7)	0.411 6(3)	−0.094 9(3)	0.389 8(3)
C(8)	0.343 7(3)	−0.127 2(4)	0.398 2(4)
C(9)	0.298 2(3)	−0.053 5(3)	0.404 5(3)
O(6)	0.476 0(2)	−0.133 5(2)	0.382 7(3)
C(10)	0.474 7(4)	−0.231 7(3)	0.376 9(4)
C(11)	0.219 9(3)	−0.056 3(4)	0.417 0(5)
O(1)	0.318 5(2)	0.252 4(2)	0.286 5(2)
O(2)	0.315 8(2)	0.363 9(3)	0.087 3(2)
O(3)	0.164 2(2)	0.270 8(2)	0.028 0(2)
O(4)	0.167 8(2)	0.154 8(3)	0.228 1(3)
C(12)	0.274 9(2)	0.257 4(3)	0.215 9(3)
C(13)	0.274 6(2)	0.308 5(3)	0.126 8(3)
C(14)	0.206 4(2)	0.266 3(3)	0.099 3(3)
C(15)	0.207 4(2)	0.212 6(3)	0.189 3(3)
Ow(2)	0.089 3(4)	0.010 4(6)	0.139 7(8)
H(1)[Ow(2)]	0.108(5)	0.004(4)	0.205(2)
H(2)[Ow(2)]	0.081(5)	0.075(1)	0.128(5)
Ow(3)	−0.055 6(5)	0.058 6(5)	0.097 2(8)

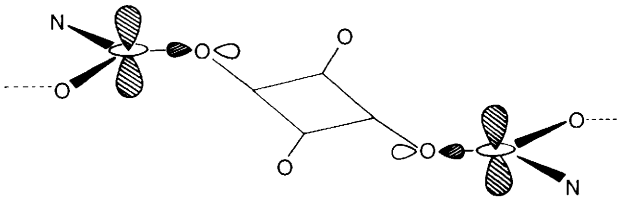

Fig. 5 Schematic view of the overlap of the magnetic orbitals through the squarato bridging groups

the antiferromagnetic interactions depends on the overlap of magnetic orbitals. This, in turn, arises basically from the overlap among the spin-carrying orbitals of the metals and the suitable orbitals of the bridging group. As discussed above, in the present compound the unpaired electron of the copper(II) ion is essentially described by a magnetic orbital built from the d_{z^2} metallic orbital [pointing toward the Ow(1) and N(1) atoms] with some admixture of the $d_{x^2-y^2}$ orbital. So, the squarate ion molecular orbitals will be able to overlap basically only with the copper(II) d_{z^2} orbital through the equatorial lobe (Fig. 5) and consequently a significant exchange coupling cannot be achieved. This fact together with the usually poor support of exchange provided by the squarato groups (related to the stabilization of the ligand orbitals by π-delocalization in the C_4O_4 ring)[22,23] may explain the lack of magnetic interactions observed above 4.2 K for $[Cu(mpym)(H_2O)(C_4O_4)]\cdot 2H_2O$.

Experimental

Preparation of the complex.—The mepirizole ligand (Daiichi Seiyaku Co. Japan) was purified by crystallization from methanol. All other reagents were used as received. The 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, solutions of $Cu(NO_3)_2\cdot 3H_2O$ (0.4 mmol) in water (10 cm^3), mepirizole (0.4 mmol) in ethanol (10 cm^3) and $Na_2C_4O_4$ (0.2 mmol) in water (10 cm^3) were mixed in sequence with stirring. Brown single crystals were grown by slow evaporation at room temperature after several days, separated by filtration and washed with a water–ethanol mixture (Found: C, 39.0; H, 4.20; Cu, 13.60; N, 12.2. $C_{15}H_{20}CuN_4O_9$ requires C, 38.85; H, 4.30; Cu, 13.70; N, 12.10%).

Physical Measurements.—Infrared spectra was obtained on KBr pellets in the 4000–400 cm^{-1} region using a Philips Analytical SP 2000 spectrophotometer, diffuse-reflectance electronic spectra on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer and ESR spectra on a Bruker ER 200D spectrometer equipped with a nitrogen cryostat. Variable-temperature (4.2–290 K) magnetic susceptibility data were obtained on a polycrystalline sample with a Faraday-type magnetometer equipped with a continuous-flow Oxford Instruments cryostat, $Co[Hg(SCN)_4]$ was used as the susceptibility standard. Experimental susceptibilities were corrected for the diamagnetic corrections [χ(squarate) = -31×10^{-6} cm^3 mol^{-1} [24] and χ(mepirizole) = -88×10^{-6} cm^3 mol^{-1} [25]] and for the temperature-independent paramagnetism, estimated to be 60×10^{-6} cm^3 mol^{-1} per Cu^{II}.

X-Ray Structure Determination of $[Cu(mpym)(H_2O)(C_4O_4)]\cdot 2H_2O$.—*Crystal data.* $C_{15}H_{20}CuN_4O_9$, $M = 463.9$, orthorhombic, space group *Pbcn* (no. 60), $a = 18.592(3)$, $b = 14.723(2)$, $c = 13.755(3)$ Å, $U = 3765(2)$ Å^3, D_m (flotation) = 1.61 g cm^{-3}, $Z = 8$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1912$, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, $\mu = 12.2$ cm^{-1}, $T = 293$ K.

Data collection and processing. A brown prismatic crystal (0.35 × 0.25 × 0.20 mm) was selected and mounted on a Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The unit-cell dimensions were determined from the setting angles of 25 reflections in the range $12 < \theta < 14.7°$. A data set of 6049 reflections ($1.5 < \theta < 30°$, h,k,l) was recorded as described previously[26] by the θ–2θ scan technique (scan width $0.90 + 0.35 \tan\theta$, speed 1.0–8.2° min^{-1}). The intensities of three standard reflections monitored every 2 h showed no significant variation during data collection. Data reflections were corrected for Lorentz and polarization effects[27] and for absorption.[28] 2697 Reflections with $F_o^2 > 3\sigma(F_o^2)$ were considered 'observed' and used for the structure solution and least-squares refinement.

Structure determination. The structure was solved by the heavy-atom method. After location of the Cu atom on a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps using SHELX[29] enabled all the non-hydrogen atoms in the structure to be located; they were refined anisotropically. All hydrogen atoms, except those bonded to the Ow(3) water molecule, were located on a Fourier difference map. Water molecule [Ow(1) and Ow(2)] hydrogen atoms were refined isotropically with thermal parameters first allowed to vary, then kept fixed at 0.05 and 0.11 Å^2 respectively. All other hydrogen atoms were introduced in calculations in constrained geometry (C–H 0.97 Å) with fixed isotropic thermal parameters (0.065 Å^2 for methyls, 0.05 Å^2 for others). Neutral-atom scattering factors were used, those for non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[30] The following weighting scheme was used: $w = [\sigma^2(F_o) + 0.0015\,F_o^2]^{-1}$. In the last full-matrix least-squares refinement cycle the mean parameter shift was 0.04 times the estimated standard deviation (maximum value: 2σ on an hydrogen parameter) and the final R value was 0.053 ($R' = 0.070$); $S = [\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{\frac{1}{2}} = 1.5$ with $n = 2697$ observations and $m = 274$ variables. A final Fourier difference map showed a residual electron density of 0.7 e Å^{-3} close to the Cu atom. All calculations were performed on a VAX-11/730 DEC computer. Atomic coordinates are listed in Table 2.

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

Acknowledgements

We thank the Spanish Ministerio de Educación y Ciencia (DGICYT) and the French Ministère de la Recherche et de la Technologie for financial support (Acción Integrada 181/90 F – Action Intégrée 95).

References

1 *Magneto-structural Correlations in Exchange Coupled Systems*, eds. R. D. Willet, D. Gatteschi and O. Khan, NATO ASI Series, Reidel, Dordrecht, 1985.

2 L. Soto, J. Garcia, E. Escrivá, J.-P. Legros, J.-P. Tuchagues, F. Dahan and A. Fuertes, *Inorg. Chem.*, 1989, **28**, 3378.

3 J. García, M. Mollá and J. Borrás, *Polyhedron*, 1984, **4**, 757; M. Mollá, J. García, J. Borrás, C. Foces, F. H. Cano and M. Martinez, *Transition Met. Chem.*, 1985, **10**, 460; L. Soto, J.-P. Legros., M. C. Mollá and J. García, *Acta Crystallogr. Sect. C*, 1987, **43**, 834; J. Suarez-Varela, L. Soto, J.-P. Legros, C. Esteve and J. García, *Polyhedron*, 1988, **7**, 229.

4 M. Habenschuss and B. C. Gerstein, *J. Chem. Phys.*, 1974, **61**, 852.

5 J. A. C. van Ooijen, J. Reedijk and A. L. Spek, *Inorg. Chem.*, 1979, **18**, 1184.

6 R. Soules, F. Dahan, J.-P. Laurent and P. Castan, *J. Chem. Soc., Dalton Trans.*, 1988, 587; R. Soules, G. Bernardinelli, D. Dequenon and P. Castan, *Can. J. Chem.*, 1989, **67**, 1158.

7 X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 784.

8 J. T. Wrobleski and D. B. Brown, *Inorg. Chem.*, 1978, **10**, 2959.

9 A. Weiss, E. Riegler, I. Alt, H. Boehme and C. Robl, *Z. Naturforsch., Teil B*, 1986, **41**, 18; A. Weiss, E. Riegler and C. Robl, *Z. Naturforsch., Teil B*, pp. 1329, 1333; C. Robl and A. Weiss, *Z. Naturforsch., Teil B*, p. 1341.

10 B. J. Hathaway, *Struct. Bonding (Berlin)* 1984, **57**, 55 and refs. therein.

11 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.

12 *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1985, vol. 5, p. 606.

13 D. Harrison and B. J. Hathaway, *Acta Crystallogr., Sect. B*, 1979, **35**, 2910.

14 M. Falk and O. Knop, in *Water: a Comprehensive Treatise*, ed. F. Franks, Plenum, New York, 1973, vol. 2, p. 71.

15 K. Nakamoto, M. Marghoses and R. E. Rundle, *J. Am. Chem. Soc.*, 1955, **77**, 6480.

16 L. J. Bellamy and A. J. Owen, *Spectrochim. Acta, Part A*, 1969, **25**, 329.

17 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.

18 D. Reinen and M. Atanasov, *Chem. Phys.*, 1989, **136**, 527.

19 A. Bencini, I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem.*, 1978, **17**, 11.

20 D. Reinen and C. Friebel, *Inorg. Chem.*, 1978, **10**, 2959.

21 J. R. Wasson, D. M. Klassen, H. W. Richardson and W. E. Hatfield, *Inorg. Chem.*, 1977, **16**, 1096.

22 P. J. Hay, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1975, **97**, 489.

23 G. C. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 3470.

24 R. West and H. Y. Niu, *J. Am. Chem. Soc.*, 1963, **85**, 2589.

25 M. C. Mollá, *D. Thesis*, Universitat de València, 1985.

26 A. Mosset, J.-J. Bonnet and J. Galy, *Acta Crystallogr., Sect. B*, 1977, **33**, 2639.

27 B. A. Frenz, SDP Structure Determination Package, Enraf-Nonius, Delft, 1982.

28 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

29 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

30 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

Received 25*th June* 1990; *Paper* 0/02851G