Preparation, crystal structures and magnetic properties of a *syn–anti* carboxylate-bridged dinuclear copper(II) complex and its precursor, a hydrogen-bonded polynuclear copper(II) complex

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Abstract

Reaction of the polynuclear zig-zag chain complex [{Cu(L)(H_2O)}$_n$] (H_2L = 5-[(2-carboxyphenyl)azo]-1,3-dimethylbarbituric acid) and pyrazole (Hpz) produces the complex of formula [{Cu(L)(Hpz)(H_2O)}·H_2O] (**1**). By heating **1** at 110 °C and further recrystallization in dry acetone the complex [{Cu(L)(Hpz)}$_2$] (**2**) is isolated. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.011(1)$, $b = 10.399(2)$, $c = 12.815(3)$ Å, $\alpha = 104.15(2)$, $\beta = 107.43(2)$, $\gamma = 105.80(2)$° and $Z = 2$, and complex **2** crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.539(5)$, $b = 20.791(10)$, $c = 8.723(4)$ Å, $\beta = 103.88(1)$° and $Z = 2$. The structure of **1** consists of neutral [{Cu(L)(Hpz)(H_2O)}·H_2O] molecules which are interconnected by hydrogen bonds giving rise to a zig-zag chain of copper(II) ions with two different Cu···Cu distances of 7.862(2) and 7.221(1) Å. The structure of **2** consists of centrosymmetrical dinuclear molecules [{Cu(L)(Hpz)}$_2$], in which copper(II) atoms of the mononuclear fragments are connected by carboxylate groups displaying *syn–anti* conformation, with a Cu···Cu distance of 5.054(2) Å. In both complexes, copper atoms exhibit distorted square-pyramidal environments. In the basal plane, four bonds are formed with the doubly deprotonated L^{2-} ligand and the molecule of pyrazole, while the apical position is occupied either by a molecule of water in **1** or an oxygen atom belonging to the carboxylate group of an adjacent and symmetry-related fragment in **2**. From magnetic susceptibility measurements, complex **1** is found to exhibit a weak intermolecular antiferromagnetic exchange interaction with $J = -0.30$ cm^{-1} whereas a Curie–Weiss law with $C = 0.40$ cm^3 mol^{-1} K and $\theta = 0.45$ K is observed for **2**. Magnetic experimental data are discussed on the basis of the structural results and compared to those of other related complexes.

Key words: Crystal structures; Magnetism; Copper complexes; Dinuclear complexes; Carboxylate complexes

Introduction

Studies on structural and magnetic properties of polynuclear metal complexes in which the electronic exchange coupling is mediated by multiatom-bridging ligands continue to be of interest for inorganic and bio-inorganic chemists [1–3]. Among numerous examples of well structurally and magnetically characterized polynuclear copper(II) complexes those containing either *syn–anti* carboxylate bridges or hydrogen-bonded ones are still scarce [4, 5]. It must be noted that the former bridging mode generally favours the formation of either chain or layer compounds which are characterized by weak ferromagnetic (and in two cases antiferromagnetic) exchange interaction between copper ions [4]. Nevertheless, we have recently shown that the inclusion of the carboxylate group into a polydentate ligand allows the formation of trinuclear and tetranuclear complexes with *syn–anti* carboxylate-bridging groups and weak ferromagnetic exchange interaction between copper ions [6, 7].

As for the polynuclear copper(II) complexes with hydrogen-bonded bridges, those containing triatomic ones of the type Cu–O–H···O–Cu were found to support noticeable antiferromagnetic interactions with $2J$ values varying up to about 100 cm^{-1} [8], whereas much reduced values were observed for complexes with more extended bridges [5, 9]. It must be pointed out that, even though some particular structural features were found to affect the magnitude of the exchange interaction, no general magneto-structural correlation was found for these complexes. In view of this, more examples of hydrogen bond bridged complexes are needed for an understanding of the structural and

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electronic factors affecting the magnitude of the exchange coupling.

As part of our study on multiatom-bridged exchange coupled systems, we report in this paper the structural and magnetic properties of the complexes $[\{Cu(L)(Hpz)(H_2O)\}\cdot H_2O]$ (**1**) and $[\{Cu(L)(Hpz)\}_2]$ (**2**) (L stands for the doubly deprotonated form of 5-[(2′-carboxyphenyl)azo]1,3-dimethylbarbituric acid). Complex **1** was obtained from the reaction of the polynuclear chain complex $[\{Cu(L)(H_2O)\}_n]$ [4] with pyrazole in methanol–water and is a new example of a polynuclear complex with hydrogen-bonded bridges. Complex **2**, which is obtained by heating complex **1** at 110 °C and further recrystallization in dry acetone, is a *syn–anti* carboxylate-bridged dinuclear complex.

Experimental

Preparation of the compounds

The ligand H_2L and the complex $[\{CuL(H_2O)\}_n]$ were prepared as described earlier [4].

$[\{Cu(L)(Hpz)(H_2O)\}\cdot H_2O]$ (1)

This complex was prepared by adding 0.2 g (3 mmol) of pyrazole to a stirred solution of $[\{CuL(H_2O)\}_n]$ (1.15 g, 3 mmol) in methanol/water (50 cm^3, 4:1) at room temperature. After 10 min, a dark green homogeneous solution resulted, from which, by slow evaporation in the refrigerator for two days at 4 °C, dark green crystals of **1** were obtained. These were filtered off, washed with methanol and air-dried. Yield 85%. *Anal.* Found: C, 40.8; H, 4.0; N, 17.5; Cu, 13.4. Calc. for $C_{16}H_{18}N_6O_7Cu$: C, 40.9; H, 3.8; N, 17.9; Cu, 13.5%. IR (KBr, cm^{-1}): 3548 [$\nu_{asym}(OH)$], 3453 [$\nu_{sym}(OH)$], 3283 [$\nu(NH)$], 1705 [$\nu(C(2){=}O)$], 1650 [$\nu(C(6){=}O)$], 1580 [$\nu_{asym}(CO_2)$], 1401 [$\nu_{sym}(CO_2)$] and 1380 [$\nu(N{=}N)$].

$[\{Cu(L)(Hpz)\}_2]$ (2)

This complex was obtained by heating compound **1** at 110 °C in a thermobalance using a flow of air and a scan rate of 5 °C min^{-1}. The resulting brown powder was recrystallized in dry acetone. After two days, black crystals of **2** were obtained by slow evaporation at 4 °C. Yield 80%. *Anal.* Found: C, 44.4; H, 3.2; N, 19.2; Cu, 14.7. Calc. for $C_{32}H_{28}N_{12}O_{10}Cu_2$: C, 44.3; H, 3.2; N, 19.4; Cu, 14.6%. IR (KBr, cm^{-1}): 3359 [$\nu(NH)$], 1709 [$\nu(C(2){=}O)$], 1660 [$\nu(C(6){=}O)$], 1623 [$\nu_{asym}(CO_2)$], 1390 [$\nu_{sym}(CO_2)$] and 1374 [$\nu(N{=}N)$].

Physical measurements

Microanalyses of C, H and N were performed with a Perkin-Elmer 240C analyzer. Copper was determined thermogravimetrically as CuO using a Mettler TG-50 thermobalance. IR spectra were recorded in the 4000–180 cm^{-1} range on a Perkin-Elmer 983G spectrophotometer using KBr and polyethylene pellets. Magnetic susceptibility data were collected on powdered samples of the title compound with use of a Squid-based sample magnetometer on a Quantum Design model MPMS instrument. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants and TIP. EPR spectra were recorded at X-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz. Electronic reflectance spectra were obtained with a Shimadzu MPC3100 spectrometer using $BaSO_4$ as reference.

X-ray data collection and structure determination

Single-crystal data collections were performed at 293 K with a Nicolet P3 diffractometer using graphite monochromatized Mo Kα ($\lambda = 0.71069$ Å) for **1** and with a Siemens R3m/v diffractometer using graphite monochromatized Cu Kα ($\lambda = 1.5418$ Å) for **2**. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 8.011(1)$, $b = 10.399(2)$, $c = 12.815(3)$ Å, $\alpha = 104.15(2)$, $\beta = 107.43(2)$, $\gamma = 105.80(2)°$, $U = 916(1)$ Å^3, $Z = 2$, $D_c = 1.70$ g cm^{-3}, $F(000) = 482$ and μ(Mo Kα) = 1.25 mm^{-1}. Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 9.539(5)$, $b = 20.791(10)$, $c = 8.723(4)$ Å, $\beta = 103.88(1)°$, $U = 1679(2)$ Å^3, $Z = 2$, $D_c = 1.72$ g cm^{-3}, $F(000) = 884$ and μ(Cu Kα) = 2.20 mm^{-1}.

The unit-cell parameters were calculated by least-squares refinement of 25 high angle independent reflections. The data were collected by ω–2θ scan mode (4526 reflections within $3 < 2\theta < 55°$ for **1** and 2565 reflections within $3 < 2\theta < 115°$ for **2**). Intensities of three check reflections measured periodically during data collection showed only statistical variation. A total of 3689 and 1968 reflections was considered as observed with $F > 3.0\sigma(F_o)$ and $F > 6.0\sigma(F_o)$, for **1** and **2**, respectively. The data were corrected for Lorentz and polarization effects, but not for absorption.

The direct methods of the SHELXS program [10] were used to find the positions of heavy atoms. Subsequent Fourier synthesis and least-squares refinement using XTAL program [11] allowed the location of all atoms. In the final cycles the non-hydrogen atoms were refined with anisotropic and the hydrogen atoms with isotropic temperature parameters, except the hydrogen atoms connected to the methyl groups of **2**. These hydrogen atoms were included with fixed isotropic temperature factors $U = 0.060$ restrained to a distance of 0.95 Å from the respective carbon and not refined. Neutral atomic scattering and dispersion factors were those included in the program package.

The function minimized was $\Sigma w(\Delta F)^2[1/w = \sigma(F_o)]$, resulting in final $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ values of 0.051 and 0.039 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ values of 0.052

and 0.047 for **1** and **2**, respectively. Atomic coordinates for the non-hydrogen atoms for complexes **1** and **2** are listed in Table 1. See also 'Supplementary material'.

Results and discussion

Description of the structures

Crystal structure of 1

The structure consists of neutral [{Cu(L)(Hpz)(H_2O)}·H_2O] molecules which are involved in an extended network of hydrogen bonds. A perspective view of the molecule with the numbering scheme is shown in Fig. 1. Selected intramolecular bond distances and angles are listed in Table 2.

The copper(II) ion displays a (4+1) coordination environment. Four short bonds of *c.* 2.0 Å are formed by two oxygen atoms, O(4) and O(16), and one nitrogen atom, N(8), of the doubly deprotonated ligand L^{2-}, and the nitrogen atom, N(18), belonging to the neutral pyrazole, while a water molecule, O(23), is coordinated in the axial position at a longer distance (2.339(4) Å). Bond lengths in the coordination polyhedron have normal values [4–7].

The (4+1) coordination mode is compatible with two idealized geometries: square pyramidal and trigonal bipyramidal. According to the procedure described by Addison *et al.* [12], the magnitude of the square-based pyramidal distortion can be measured by the τ value (τ is 1.0 for the regular trigonal bipyramid and 0.0 for the square based pyramid). As the calculated τ value is 0.08, the coordination polyhedron can be described as a square-based pyramid with a small trigonal bipyramidal distortion. In this square pyramidal geometry, the basal plane is defined by O(4), O(16), N(8) and N(18) whereas the apical position is occupied by O(23), in accordance with the longer Cu–O(23) distance. Deviations from planarity less than 0.03 Å are observed for the equatorial donor atoms. As usual, the copper atom is lifted by 0.154(2) Å from the mean basal plane toward the axial donor.

The tridentate behaviour of the ligand results in the formation of two six-membered rings having the Cu–N(8) bond in common. Both rings are nearly planar, since the maximum deviations are *c.* 0.18 Å. The dihedral angle between the two related mean planes is 5.01(8)°. These deviations are more important for the O(16)C(15)C(10)C(9)N(8)Cu ring (with maximum values of 0.182(4) Å for O(16) and 0.137(5) Å for C(15)) than for the N(8)N(7)C(5)C(4)O(4)Cu ring (with maximum values of 0.017(3) Å for O(4)). A greater planarity characterizes the barbituric, phenyl and pyrazole rings for which the maximum deviations are *c.* 0.006(5), 0.014(5) and 0.005(6) Å, respectively. The pyrazole ring is nearly coplanar with the basal plane of the square pyramidal polyhedron, with a dihedral angle value of

TABLE 1. Fractional atomic coordinates, with e.s.d.s in parentheses, and equivalent isotropic parameters for **1** and **2**

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
1				
Cu(1)	0.43453(7)	0.98846(5)	0.18089(4)	0.0281(1)
O(2)	0.0972(4)	0.5062(3)	−0.3228(2)	0.054(1)
O(4)	0.3729(3)	0.8224(2)	0.0474(2)	0.045(1)
O(6)	0.0006(3)	0.9232(3)	−0.2632(2)	0.048(1)
O(16)	0.5491(4)	1.1562(3)	0.3152(2)	0.063(1)
O(17)	0.5332(4)	1.3281(3)	0.4450(2)	0.070(1)
N(1)	0.0519(4)	0.7167(3)	−0.2934(2)	0.041(1)
N(3)	0.2394(4)	0.6682(3)	−0.1381(2)	0.038(1)
N(7)	0.2109(4)	1.0196(3)	−0.0305(2)	0.037(1)
N(8)	0.3013(4)	1.0757(3)	0.0818(2)	0.037(1)
N(18)	0.5974(4)	0.9092(3)	0.2753(2)	0.045(1)
N(19)	0.6783(4)	0.9673(3)	0.3942(2)	0.049(1)
C(1)	−0.0625(6)	0.6709(4)	−0.4190(3)	0.056(2)
C(2)	0.1271(5)	0.6237(4)	−0.2567(3)	0.040(1)
C(3)	0.3147(6)	0.5658(4)	−0.1000(3)	0.051(2)
C(4)	0.2749(5)	0.7975(3)	−0.0571(3)	0.036(1)
C(5)	0.1951(5)	0.8919(3)	−0.0969(3)	0.035(1)
C(6)	0.0766(5)	0.8502(4)	−0.2211(3)	0.039(1)
C(9)	0.2904(5)	1.2139(3)	0.1272(3)	0.037(1)
C(10)	0.3815(5)	1.2988(3)	0.2469(3)	0.038(1)
C(11)	0.3699(6)	1.4331(4)	0.2844(3)	0.048(2)
C(12)	0.2668(6)	1.4823(4)	0.2073(3)	0.051(2)
C(13)	0.1713(5)	1.3960(4)	0.0896(3)	0.048(2)
C(14)	0.1831(5)	1.2638(4)	0.0499(3)	0.044(1)
C(15)	0.4938(5)	1.2591(4)	0.3427(3)	0.044(1)
C(20)	0.7649(6)	0.8891(4)	0.4400(3)	0.056(2)
C(21)	0.7426(6)	0.7760(4)	0.3492(3)	0.061(2)
C(22)	0.6391(6)	0.7932(4)	0.2490(3)	0.054(2)
O(23)	0.1790(4)	0.8803(3)	0.2235(2)	0.064(1)
O(24)	0.2380(4)	0.7659(3)	0.4098(2)	0.062(1)
2				
Cu(1)	0.03623(6)	0.50786(3)	0.72298(3)	0.0341(3)
O(2)	0.4014(4)	0.7033(2)	0.4186(4)	0.053(1)
O(4)	0.1488(3)	0.5459(1)	0.5876(4)	0.040(2)
O(6)	0.0487(4)	0.7657(2)	0.6519(5)	0.059(1)
O(16)	−0.0766(3)	0.4591(1)	0.8355(4)	0.040(1)
O(17)	−0.1876(3)	0.4501(1)	1.0298(4)	0.041(1)
N(1)	0.2260(4)	0.7348(2)	0.5369(4)	0.037(1)
N(3)	0.2712(4)	0.6249(2)	0.5016(4)	0.036(1)
N(7)	−0.0335(4)	0.6431(2)	0.6879(4)	0.034(1)
N(8)	−0.0740(3)	0.5869(2)	0.7198(4)	0.032(1)
N(18)	0.1470(4)	0.4272(2)	0.7158(4)	0.035(1)
N(19)	0.1123(4)	0.3710(2)	0.7729(5)	0.044(2)
C(1)	0.2623(6)	0.8015(2)	0.5208(6)	0.052(2)
C(2)	0.3046(5)	0.6890(2)	0.4818(5)	0.040(2)
C(3)	0.3642(5)	0.5755(2)	0.4534(6)	0.049(2)
C(4)	0.1653(4)	0.6052(2)	0.5747(5)	0.032(2)
C(5)	0.0809(4)	0.6531(2)	0.6240(5)	0.033(2)
C(6)	0.1114(5)	0.7209(2)	0.6085(6)	0.041(2)
C(9)	−0.2052(4)	0.5908(2)	0.7761(5)	0.033(2)
C(10)	−0.2437(4)	0.5413(2)	0.8665(5)	0.034(2)
C(11)	−0.3702(5)	0.5486(2)	0.9213(6)	0.046(2)
C(12)	−0.4551(5)	0.6038(3)	0.8857(6)	0.050(2)
C(13)	−0.4155(5)	0.6516(2)	0.7986(6)	0.048(2)
C(14)	−0.2923(5)	0.6453(2)	0.7415(6)	0.040(2)
C(15)	−0.1637(4)	0.4799(2)	0.9166(5)	0.033(2)
C(20)	0.2013(6)	0.3241(2)	0.7554(7)	0.057(2)
C(21)	0.3026(6)	0.3500(3)	0.6869(7)	0.056(2)
C(22)	0.2653(5)	0.4137(2)	0.6640(6)	0.047(2)

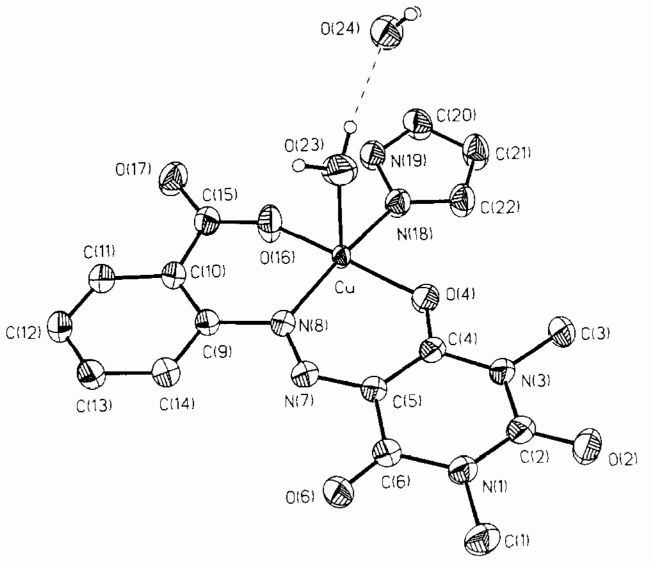

Fig. 1. Molecular structure of [{Cu(L)(Hpz)(H_2O)}·H_2O] (**1**).

10.9(1)°. On the other hand, bond lengths and angles in the ligand do not differ significantly from those found in other complexes with the same ligand [4, 7].

[{Cu(L)(Hpz)(H_2O)}·H_2O] units are held together in pairs by hydrogen bonds, which involve the two water molecules, the O(17)^i oxygen atom of the carboxylate group and the N(19)^i nitrogen atom of the pyrazole molecule belonging to one neighbouring unit and one symmetry-related unit ($i=1-x$, $2-y$, $1-z$) giving rise to a Cu···Cu^i distance of 7.862(2) Å. An additional hydrogen bond is formed between the axial water molecule and the O(6)^{ii} oxygen atom of a neighbouring unit ($ii=-x, 2-y, -z$), resulting in a Cu···Cu^{ii} distance of 7.221(1) Å. Owing to these hydrogen bond interactions, the compound may be considered as a zig-zag chain of Cu(II) ions with two different Cu···Cu distances, 7.862(2) and 7.221(1) Å. A view of the hydrogen-bonded zig-zag chain of **1** is given in Fig. 2.

Finally, the non-coordinated water molecule forms a hydrogen bonding with the oxygen atom O(2)^{iii} ($iii=-x, 1-y, -z$) of the barbituric ring of an adjacent unit. In this case the Cu···Cu^{iii} distance is 9.607(2) Å. It must be noted that the shortest Cu···Cu^{iv} ($iv=1-x$, $2-y$, $-z$) distance of 5.096(1) Å occurs between non-hydrogen-bonded molecules. Relevant hydrogen bonding distances are also given in Table 2.

Crystal structure of 2

The structure of **2** consists of dinuclear [{Cu(L)(Hpz)}$_2$] molecules with C_i symmetry, in which copper(II) atoms of the mononuclear fragments are connected by carboxylate groups displaying a *syn–anti* conformation. A perspective view of the dinuclear unit with the atom numbering scheme is given in Fig. 3, while selected intramolecular bond distances and angles are given in Table 2.

As in **1**, the copper atom adopts a (4+1) coordination mode, with four short bonds of *c.* 2.0 Å formed with

TABLE 2. Selected interatomic distances (Å) and bond angles (°), with e.s.d.s in parentheses, for **1** and **2**

	1	**2**		**1**	**2**
Cu(1)–O(4)	1934(2)	1.945(4)	O(4)–Cu(1)–O(16)	167.6(1)	171.2(1)
Cu(1)–O(16)	1.887(2)	1.912(3)	O(4)–Cu(1)–N(8)	92.1(1)	91.3(1)
Cu(1)–N(8)	1.964(3)	1 948(4)	O(4)–Cu(1)–N(18)	86.6(1)	87.1(1)
Cu(1)–N(18)	1.993(4)	1.991(4)	O(16)–Cu(1)–N(8)	93.8(1)	95.0(1)
Cu(1)–X^a	2.339(4)	2.451(3)	O(16)–Cu(1)–N(18)	86.2(1)	86.4(1)
O(2)–C(2)	1.217(4)	1.220(7)	N(8)–Cu(1)–N(18)	172 5(1)	177 5(1)
O(4)–C(4)	1.252(4)	1 251(5)	O(4)–Cu(1)–X^a	93.8(1)	95.4(1)
O(6)–C(6)	1.221(5)	1.215(6)	O(16)–Cu(1)–X^a	96.5(1)	91.3(1)
O(16)–C(15)	1.278(5)	1.288(6)	N(8)–Cu(1)–X^a	95.3(1)	85.0(1)
O(17)–C(15)	1.225(4)	1.232(6)	N(18)–Cu(1)–X^a	92 1(1)	97.1(1)
N(7)–N(8)	1.293(3)	1.282(5)	Cu(1)–O(4)–C(4)	126.7(3)	123.7(3)
N(7)–C(5)	1.340(4)	1.355(6)	Cu(1)–O(16)–C(15)	129.7(2)	128.3(2)
N(8)–C(9)	1.449(5)	1 452(6)	Cu(1)–N(8)–N(7)	125.8(2)	125.6(3)
C(10)–C(15)	1.508(6)	1.498(6)	Cu(1)–N(8)–C(9)	123.4(2)	123.3(3)
C(9)–C(10)	1.408(4)	1.398(6)	O(16)–C(15)–O(17)	121.6(4)	122.6(4)
C(9)–C(14)	1.406(6)	1.395(6)	O(16)–C(15)–C(10)	119.1(3)	118.5(4)
			O(17)–C(15)–C(10)	119.2(4)	118.9(4)

Relevant hydrogen bond distances (Å) for **1**^{b}

O(23)··O(24)	2.891(4)
N(19)···O(24)^i	3.004(4)
O(24)···O(17)^i	2.758(5)
O(23)·· O(6)^{ii}	2.835(5)
O(24)···O(2)^{iii}	2.996(6)

[a] X is O(23) for **1** and O(17)^v for **2**. [b] Symmetry codes: $i=1-x$, $2-y$, $1-z$; $ii=-x$, $2-y$, $-z$; $iii=-x$, $1-y$, $-z$.

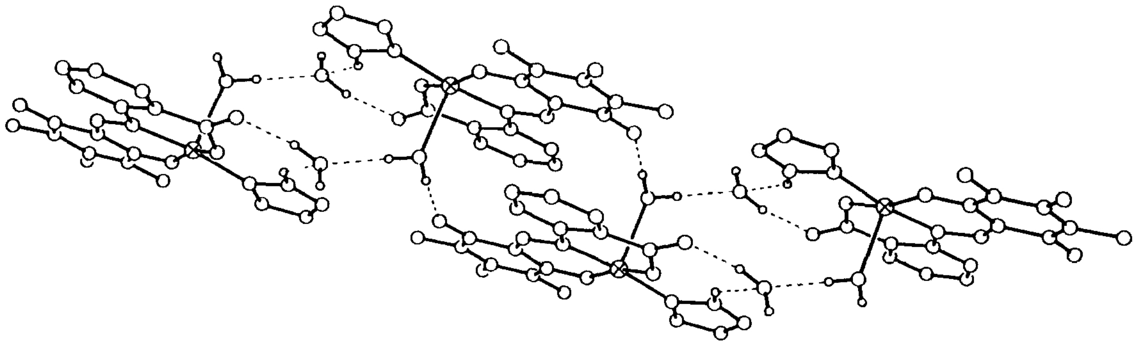

Fig. 2. A perspective view of the hydrogen bonded zig-zag chain of **1**.

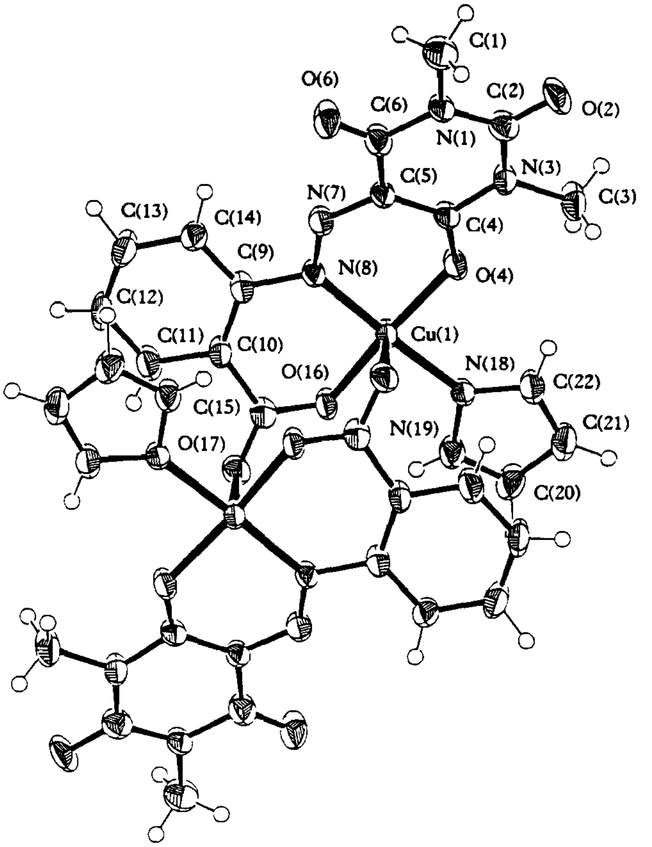

Fig. 3. A perspective view of [{Cu(L)(Hpz)}$_2$] (**2**).

O(4), O(16) and N(8) from the doubly deprotonated ligand and N(18) of a neutral pyrazole molecule. The O(17)^{v} atom belonging to the carboxylate group of an adjacent and symmetry-related fragment ($v=-x$, $1-y$, $2-z$) is coordinated at a longer distance of 2.451(3) Å. The calculated τ value is 0.11, so that the geometry of the copper ion is very close to square pyramidal, in which the basal plane is defined by O(4), O(16), N(8) and N(18) whereas the apical position is occupied by O(17)^{v}.

Each *syn–anti* carboxylate group bridges two copper(II) ions through the O(16) and O(17) oxygen atoms involving equatorial and axial positions on the copper(II) coordination polyhedra, respectively. This coordination behaviour causes non-planarity of the Cu–O–C–O–Cu^{v} fragment and gives rise to the formation of a chair like eight-membered ring Cu–O(16)–C(15)–O(17)–Cu^{v}–O(16)^{v}–C(15)^{v}–O(17)^{v}–Cu with a Cu···Cu^{v} distance of 5.054(2) Å. Nevertheless, it should be noted that the shortest Cu···Cu^{vi} ($vi=-x$, $1-y$, $1-z$) distance is 3.798(2) Å.

A similar conformation of the dinuclear fragment has been observed for two complexes, [{Cu$_2$(OAc)-A}$_n$(ClO$_4$)$_{2n}$] (where A is the macrocycle 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane) [13] and [Cu-(IDA)(Him)$_2$] (where IDA is iminodiacetato and Him, imidazol) [14]. The first complex, unlike [{CuL-(Hpz)}$_2$], is not a genuine example of a dinuclear compound, because the macrocyclic ligand A bridges the dinuclear units to form infinite chains. In the second complex, [Cu(IDA)(Him)$_2$], the oxygen atom belonging to the carboxylate group of an adjacent and symmetry-related fragment is located at 2.873(7) Å from the copper(II), a distance that is even long for semi-coordination. Therefore, in view of the above discussion, complex **2** would represent the first genuine example reported so far of a structurally and magnetically studied *syn–anti* carboxylate-bridged dinuclear copper(II) complex.

On the other hand, bond lengths and angles in the tetradentate doubly deprotonated ligand do not significantly differ from those found in **1**. Within the dinuclear molecules, the barbituric ring of one fragment is over the pyrazole ring of the other fragment and the pyrazole ring over the barbituric ring. The shortest distance between these rings is 3.579(9) Å.

Finally, dinuclear molecules are interconnected by a hydrogen bond involving the N(19) atom of one molecule and the O(6)^{vii} atom ($vii=-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) of a neighbouring one, with a donor–acceptor distance of 2.840(6) Å.

As indicated elsewhere, complex **2** can be obtained by thermal treatment of **1**. In view of the X-ray crystal structures of **1** and **2**, the thermal process occurring in the solid state must be as follows. By heating **1** at 110 °C, the non-coordinated and coordinated molecules of water are eliminated giving rise simultaneously to a rearrangement of two dehydrated molecules each, in which the O(17) atom of the carboxylate group of each molecule is bonded to the copper(II) ion of a neighbouring one. This leads ultimately to the formation of **2**.

Because the results from the structural determination of **1** and **2** clearly indicate that in both complexes there are bridging groups through which an exchange interaction may be mediated, we have performed a magnetic study of them.

Spectroscopic and magnetic properties

The IR spectra of **1** and **2** exhibit features characteristic of the coordination modes of L^{2-} and pyrazole. The electronic reflectance spectra of **1** and **2** are quite similar, exhibiting an absorption maximum at 16 200 and 16 000 cm^{-1}, respectively. By reference to the assignment of electronic spectra of copper(II) complexes with trigonal bipyramidal and square pyramidal geometries reported by Hathaway and co-workers [15], that band can be assigned to the d_{xy}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition for a square pyramidal system.

Magnetic susceptibility data for **1** and **2** were collected on powdered samples in the range 2–250 K and are displayed in Fig. 4 as μ_{eff} versus T in the range 50–2 K. For **1**, where the temperature is lowered, μ_{eff} decreases steadily from a value of 1.86 BM at 250 K to a value of 1.70 BM at 2 K. This suggests the existence of a weak intermolecular antiferromagnetic exchange interaction between copper(II) ions, as does the temperature dependence of χ^{-1}, which is well represented by the Curie–Weiss law with $\theta = -0.66$ K and $C = 0.44$ $cm^3\ mol^{-1}$ K ($g = 2.17$). From the expression defining θ in terms of the molecular-field exchange parameter [16], a value for zJ' of 0.9 cm^{-1} can be obtained, where z is the number of nearest neighbours. In keeping with the structure of **1**, the experimental susceptibilities corrected for the diamagnetism of the ligands were fitted to the empirical expression of the magnetic susceptibility for an antiferromagnetic 1D Heisenberg $S = 1/2$ chain [17] to yield $g = 2.17$, $J = -0.30$ cm^{-1} and $R = \Sigma_i[(\chi_i^{obs} - \chi_i^{calc})^2 / \Sigma(\chi_i^{obs})^2] = 2.5 \times 10^{-4}$. As expected this J value is of the same order as that obtained from θ.

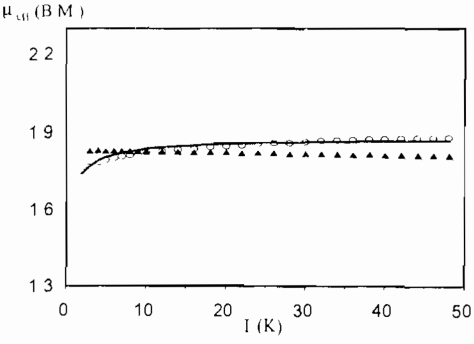

Fig. 4. Temperature dependences of the effective magnetic moment per copper ion for **1** (○) and **2** (▲). The solid line for **1** was calculated from the best theoretical fit (see text).

The J value for **1** is much smaller than those obtained for the majority of the dinuclear copper(II) complexes of amino- or imino-alcohols containing triatomic O–H···O bridges [8] ($2J$ varying up to *c.* 100 cm^{-1}) but slightly higher than those for the complexes $[Cu_2(tren)X]^{2+}$ (where X = NCS or NCO) with extended bridges of the type Cu–X···H–N–Cu [9]. In view of this, for **1**, where very extended pathways involving the hydrogen bonding exist, the observed value is not unexpected. In addition to this, the structure of the complex displays that the Cu–O(16)–C(15)–O(17)···H–O(24)^{i} ···H–O(23)^{i}–Cu^{i} (or alternatively through N(19)–H belonging to the pyrazole) and Cu–O(23)H··· O(6)^{ii}–barbituric ring–Cu^{ii} pathways involve an axial position on the copper(II) ion where the spin density of the unpaired electron is very weak (in a distorted square-based pyramidal geometry the unpaired electron is predominantly in a $d_{x^2-y^2}$ or d_{xy} type orbital). This feature is also unfavourable to the propagation of strong interactions. It may be noted that **1**, compared with the closely related hydrogen-bonded dinuclear complex $[\{Cu(L')(Py)\}_2 \cdot 0.5H_2O]$ [5] (where L′ represents the doubly deprotonated form of 1,3-dimethyl-6-amino-5(2-carboxyphenyl)azouracil) shows a much lower J value. The main reason for this discrepancy must obviously be that in the former the exchange pathways are more extended than in the latter.

Although for **2**, there appears to be a slight increase of μ_{eff} when the temperature is lowered, the variation is not large and $|J|$ must be considered as less than ≈ 0.5 cm^{-1}. The data obey the Curie–Weiss law with $C = 0.40$ $cm^3\ mol^{-1}$ K and $\theta = 0.45$ K. The positive value of θ may suggest that the complex displays a very weak overall ferromagnetic behaviour. The absence of an appreciable exchange interaction between the two copper atoms is not unexpected in the light of the following electronic and structural features of **2**: (i) the *syn–anti* conformation of the carboxylate group, (ii) the non-planarity of the Cu–O–C–O–Cu′ fragment, (iii) each carboxylate bridge involves an axial position on a copper(II) ion where the spin density of the unpaired electron is very small, (iv) the relatively long Cu–O(17)^{v} distance. All these factors are expected to give rise to an overlap integral close to zero and a magnetically-dilute system.

It should be noted that polynuclear copper(II) complexes of the same and related ligands also containing *syn–anti* carboxylate-bridging groups between copper atoms, such as $[\{Cu_4(L^1)_3(HL^1)(NO_3)(H_2O)\cdot 2H_2O\}_n]$ [6] (where H_2L^1 = 6-amino-5-[(2-carboxyphenyl)azo]-1,3-dimethyluracil), $[\{Cu(H_2O)_4\}\{Cu(L^2)(H_2O)(ClO_4)\}_2](ClO_4)_2\cdot 2H_2O$ [7] (HL^2 = 6-methylamino-5-[(2-carboxyphenyl)azo]-1,3-dimethyluracil) and $[\{Cu(L)(H_2O)\}_n]$ [4], exhibit weak but definitive ferromagnetic exchange interaction with J values of 6.8, 2.7 and 3.3 cm^{-1}, respectively. An examination of the structural data strongly suggests that the origin of the quite different magnitude of the exchange interaction may be found in two facts: (i) in contrast to **2**, for which the carboxylate bridges pairs of copper ions from a basal position to an axial one, in the tetranuclear and polynuclear chain complexes, both having square pyramidal copper(II) ions, as well as in the trinuclear complex, with copper(II) atoms in octahedral and square pyramidal geometries, each bridge links two equatorial positions; (ii) the longer Cu–O(17) distance in **2** compared with that found in the other complexes, which are in the range 1.95–1.97 Å.

The room temperature X-band polycrystalline EPR spectra of **1** and **2** exhibit signals attributable to an axial doublet spectrum ($g_{\parallel}=2.17$ and $g_{\perp}=2.03$ for **1**, $g_{\parallel}=2.14$ and $g_{\perp}=2.09$ for **2**) as expected for copper(II) ions with either $d_{x^2-y^2}$ or d_{xy} ground state. For **1**, lowering the temperature to 90 K produces no effect on the shape and positions of the signals but, at high gain the half-field signal $\Delta M_s=2$ is detected at $g=4.2$. For **2**, the half-field signal can be observed at $g=4.07$ even at room temperature, clearly pointing out the presence of a populated triplet which is not made evident by magnetic susceptibility data. The overall appearance of the spectrum does not vary in the range 250–4 K, but increases slightly in intensity. It must be pointed out that in dimethyl sulfoxide (dmso) solution at 90 K, complexes **1** and **2** exhibit essentially superimposable EPR spectra, with signals attributable to an axial doublet spectrum, in which the hyperfine structure on the $g_{\parallel}$ component is not clearly resolved ($g_{\parallel}\approx 2.20$ and $g_{\perp}=2.06$) and a well resolved feature of medium intensity at $g=1.92$, which would be attributable to a component of a pair of zero-field split transitions. In addition, the half-field signal transition appears as a seven-line hyperfine pattern at $g=4.22$ with an average hyperfine spacing of 74×10^{-4} cm^{-1}. The appearance of this pattern proves the presence of a dinuclear complex in solution. The observed spectral features seem to indicate that **1** and **2** dissolved in dmso give rise to a $[Cu(L)(Hpz)(H_2O)] \leftrightharpoons [\{Cu(L)(Hpz)\}_2]$ monomer–dimer equilibrium in solution. A similar equilibrium was also observed by EPR spectroscopy for the complexes $[Cu(L)(Py)_2]$ and $[\{Cu(L)(Py)\cdot 3H_2O\}_n]$ in dmso and pyridine solutions [18].

The formation of **2** from two molecules of **1** in dmso solution might occur by a process similar to that suggested to occur in the solid state by heating **1** at 110 °C. Further evidence supporting this was the isolation of crystals of **2** from slow evaporation of a dmso solution of **1**.

Supplementary material

Hydrogen atom coordinates, equivalent isotropic parameters (S1), anisotropic thermal displacement parameters (S2), remaining bond distances and angles (S3) and structure factors, for both complexes **1** and **2** are available from the authors on request.

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