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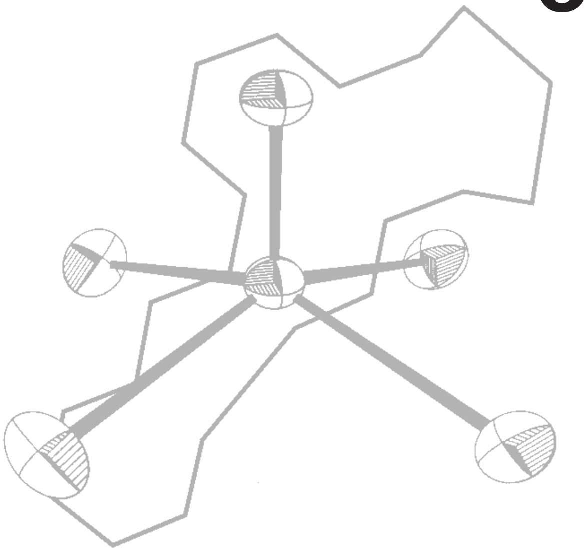

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Solid State Coordination Chemistry of Pyridinedicarboxylic Acid Isomers. I Copper(II) Disodium Bis(pyridine-2,3-dicarboxylate) Octahydrate and Copper(II) Pyridine-3,4-dicarboxylate 3·5 Hydrate

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The crystal structures of $Na_2Cu(2,3\text{-pydc})_2.8H_2O$ (1) and $Cu(3,4\text{-pydc}).3{\cdot}5H_2O$ (2) (pydc = pyridinedicarboxylato) are presented. Compound (1) is monoclinic, space group $C\,2/c$, with a 21·274(1), b 6·114(1), c 17·136(1) Å, β 101·62(1)°, Z 4, D_c 1·776 g cm^{-3}; compound (2) is also monoclinic, space group $P\,2_1/c$, with a 7·272(2), b 11·319(3), c 25·453(9) Å, β 90·58(1)°, Z 4, D_c 1·850 g cm^{-3}. Their stereochemistries are analysed, and compared with other copper(II) pyridine-2,6-dicarboxylates. Ligand constraints are shown to determine the crystal structures and the magnetic properties. Thermal dependence of magnetic susceptibility data and t.g., d.t.g. and d.t.a. measurements are also presented.

Introduction

Copper(II) forms solid carboxylates with a wide variety of coordination stereochemistries. The Jahn–Teller effect together with the ligand's steric requirements and chelate constraints prevent Cu^{II} from adopting regular coordination geometries.[1] Pyridinedicarboxylic acids (H_2pydc) may act as chelating agents for Cu^{II} when the relative positions of the donor atoms are adequate. Several 1 : 1 and 1 : 2 compounds that illustrate the versatility of copper(II) ion coordination and the corresponding variety in magnetic interactions are known. The whole series includes the pyridine-2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dicarboxylic acids, all of which have several donor sites: the oxygen atoms of the two carboxylic groups and the nitrogen atom in the aromatic ring. In the solid state, the five donor atoms may bind to one, two or three Cu^{II} centres, thus leading to molecular solids, as in some dipicolinates, or to chains or three-dimensional structures of diverse complexity, as illustrated in the present work. The possibility of protonating the ligands or introducing a second metal cation, such as Na^+, permits the alteration of both the stoichiometric ratio L : Cu and the coordinative characteristic of the ligand.

A number of metal carboxylates in the series have been the subject of crystallographic, magnetic and/or thermal studies, in particular derivatives of pyridine-2,6-dicarboxylic (or dipicolinic, hereafter $H_2$2,6-pydc) acid (by far the most widely explored), pyridine-2,3-dicarboxylic (or quinolinic, hereafter $H_2$2,3-pydc) acid and pyridine-3,4-dicarboxylic (or cinchomeronic, hereafter $H_2$3,4-pydc) acid. As the most relevant for the forthcoming discussion, we can quote the following works.

(i) X-Ray crystal structure determinations for the 1 : 1 and 1 : 2 copper dipicolinates[2,3] and for 1 : 2 copper bis(hydrogen quinolinate).[4] The thermal behaviour of the copper dipicolinates has also been explored.[3]

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(ii) Crystal structure determinations for Ni(H2,3-pydc)$_2$.2H_2O,[5] Mn(H2,3-pydc)$_2$.2H_2O,[5] Co(H2,3-pydc)$_2$.2H_2O,[6] and Ag(H2,3-pydc)$_2$.2H_2O.[7] The interest on quinolinic acid derivatives may well rely on the neurological activity[8] exhibited by the acid and its behaviour like a neurotoxic tryptophan metabolite.[9] Its content in humans with immunodeficiency virus infection is currently being discussed.[10]

(iii) Magnetic susceptibility and single-crystal electron spin resonance determinations[11] for the two known polymorphic forms of Cu(2,6-pydc).2H_2O, monoclinic and triclinic.

(iv) Thermal stability studies on Cd^{II},[12] and Cu^{II},[13] cinchomeronates and studies on the kinetics of complexation[14] of the Ni^{II} and Co^{II} derivatives in aqueous solution. Though no unambiguous structural data are currently available for the metal cinchomeronates, Cu^{II} coordination on Cu(3,4-pydc).2H_2O has been postulated to be tetrahedral, from the interpretation of its electronic spectrum.[15]

In the present work, and as a part of a general study of metal(II) pyridinedicarboxylates, we present the synthesis, single-crystal X-ray diffraction study, magnetic measurements and thermal behaviour of Na_2Cu(2,3-pydc)$_2$.8H_2O (1) and Cu(3,4-pydc).3·5H_2O (2).

Experimental

The ligands pyridine-2,3- and -3,4-dicarboxylic acids (Sigma Chemical Company) as well as all the other reagents (analytical-grade purity) were used as provided. Water was purified by a Millipore Milli-Q system yielding 18 MΩ cm. Elemental analyses (C, H, N) were performed in a Carlo Erba EA 1108 microanalyser at Instituto de Química Física de los Materiales, Medio Ambiente y Energía. The metal contents of the solids were obtained at the Departamento de Química Inorgánica, Universidad de Buenos Aires, with a Varian Techtrom A-A5R atomic absorption spectrometer. Thermogravimetric data were obtained in a Mettler Recording Thermoanalyzer 1 with powdered samples of about 30 mg under an inert (N_2) atmosphere (temperature range 298–693 K) at a heating rate of 6 K s^{-1}. Water content was calculated from t.g. determinations. Variable-temperature magnetic susceptibility studies were performed on powdered samples in the range 5–70 K by using a SQUID SHE 905 magnetometer on a QUANTUM Design Model MPMS, with the field set at 0·5 T. Experimental susceptibilities were corrected for diamagnetic contributions according to Pascal's constants[16] and correction for temperature-independent paramagnetism was estimated to be 60×10^{-6} cm^3 mol^{-1}. Electronic spectra were recorded in the range 250–800 nm in a Shimadzu u.v.-3101 PC scanning spectrophotometer equipped with an integrating sphere attachment.

Synthesis of the Solids

Na_2Cu(2,3-pydc)$_2$.8H_2O (1). A $CuSO_4$ solution (1·2 ml, 0·1 M) was added to an aqueous solution (200 ml) containing pyridine-2,3-dicarboxylic acid (0·133 g, 0·8 mmol) and NaOH (0·064 g, 1·6 mmol). The mixture was stirred for 30 min at 80°C.

Cu(3,4-pydc).3·5H_2O (2). To a hot solution of pyridine-3,4-dicarboxylic acid (0·50 g, 3 mmol) and NaOH (0·12 g, 3 mmol) in water (200 ml) was added, with stirring, $CuSO_4$.5H_2O (0·37 g, 1·5 mmol).

In both cases, the *solids* were obtained by slow evaporation of the solutions at 298 K; the blue crystals formed were collected by filtration and washed with bidistilled water (Found for (1): C, 28·7; H, 3·7; Cu, 11·2; N, 4·9; Na, 7·9; H_2O, 25·8. $Na_2Cu(C_{14}H_6N_2O_8)$.8H_2O requires C, 28·8; H, 3·7; Cu, 10·9; N, 4·7; Na, 7·8; H_2O, 24·7%. Found for (2): C, 28·8; H, 3·3; Cu, 21·8; N, 4·8; H_2O, 20·4. $Cu(C_7H_3NO_4)$.3·5H_2O requires C, 28·8; H, 3·4; Cu, 21·8; N, 4·8; H_2O, 21·6%).

X-Ray Structural Solution and Refinement

(1), $C_{14}H_{22}CuN_2Na_2O_{16}$, *M* 583·33. Monoclinic, space group $C2/c$ (C^6_{2h}, No. 15), *a* 21·274(1), *b* 6·114(1), *c* 17·136(1) Å, *β* 101·62(1)°, *V* 2183·3(4) Å^3. $D_c(Z = 4)$ 1·776 g cm^{-3}; *F*(000) 1196. μ_{Mo} 11·26 cm^{-1}; specimen 0·30 by 0·20 by 0·20 mm. N_{tot} 3283, N_{ind} 3180, N_{obs} 1783. $-29 < h < 29$, $0 < k < 8$, $-24 < l < 0$; $2\theta_{max}$ 59·92°, R_1 0·0547, wR_2 0·1199 for 164 parameters. Largest difference peak and hole 0·677 and −0·664 e Å^{-3}.

(2), $C_{14}H_{20}Cu_2N_2O_{15}$, *M* 583·40. Monoclinic, space group $P2_1/c$ (C^5_{2h}, No. 14), *a* 7·272(2), *b* 11·319(3), *c* 25·453(9) Å, *β* 90·58(1)°, *V* 2095·0(11) Å^3. $D_c(Z = 4)$ 1·850 g cm^{-3}; *F*(000) 1184. μ_{Mo} 21·12 cm^{-1}; specimen 0·30 by 0·10 by 0·05 mm. N_{tot} 4008, N_{ind} 3767, N_{obs} 1910. $-8 < h < 8$, $0 < k < 13$, $0 < l < 30$; $2\theta_{max}$ 50·30°, R_1 0·0513, wR_2 0·0888 for 338 parameters. Largest difference peak and hole 0·471 and −0·406 e Å^{-3}.

Details in common. Diffractometer: Siemens R3m; radiation used was Mo Kα, λ 0·71074 Å; scan mode $\omega/2\theta$; temp. 293 K; refinement method used was full-matrix least-squares on F^2; programs used were SHELXS,[17] SHELXL,[18] and PARST.[19] H atoms attached to C atoms were placed at their idealized positions and allowed to ride. Those bonded to O atoms were located in a difference Fourier synthesis, and subsequently refined with restrained O–H and H···H distances. In all cases isotropic thermal parameters were used for H atoms, 1·3 times larger than the equivalent isotropic displacement factors of the host atom. Non-hydrogen atoms were refined anisotropically. Material deposited comprises hydrogen coordinates, structure factors, bond lengths and angles, torsion angles and anisotropic displacement parameters.*

Results and Discussion

Table 1 shows the fractional atomic positions and equivalent isotropic displacement factors for compound (1) while Table 2 presents a selection of relevant bond lengths and angles. The displacement ellipsoids plot in Fig. 1 shows the numbering scheme used.

The crystal structure can be described as being formed by chains running along the crystallographic *b* axis, their elemental units being centrosymmetric Cu_2(pydc)$_2$ dimers centred at crystallographic sites *d* and joined together through the sharing of the common copper centres at sites *c* (Fig. 2). The double-link chain thus formed is transversally connected along *a* through double bridges, –Na–(H_2O)$_2$–Na–, to end up with a two-dimensional network parallel to (0 0 1).

The copper atom lies on a symmetry centre, and it is bonded to four symmetry-related quinolinate groups: two of them coordinate equatorially in a bidentate fashion through their nitrogen atom and

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one oxygen, O(3), from the 2-carboxylate group. The axial sites are provided by the other two quinolinates, through the oxygen atoms O(2) from the remaining 3-carboxylate group. Each pydc group thus binds to two different copper centres (Fig. 2). As typical in Jahn–Teller deformed octahedra, apical bonds are elongated (2·660(4) Å) and equatorial ones, from the two symmetry-related bidentate bites, are shorter (mean value 1·949(3) Å). Due to strong hydrogen-bonding interactions the apical bond Cu–O(2) is bent *c.* 14° out of the normal plane, in the most conspicuous deformation shown by the coordination polyhedron.

The 2-carboxylate group is coplanar with the pyridine ring (O(3)–C(8)–C(2)–N 0·8(6)°) whilst the one at position 3 is twisted out (O(1)–C(7)–C(3)–C(2) −83·6(6)°), allowing O(2) to coordinate apically to a vicinal Cu. Both carboxylates differ in their interatomic distances: while the latter shows the same C–O bond lengths (1·242(6) Å) the former presents a marked difference (C(8)–O(3) 1·279(5) and C(8)–O(4) 1·228(5) Å) attributable to the pronounced double-bond character of the C=O group bound to Na.

The Na ions appear in pairs of centrosymmetrically-related octahedral polyhedra (defined by one carboxylate O atom (O(4)) and five hydration water molecules), and are linked through the sharing of a common edge bisected by a symmetry centre. Similar configurations have been found in the literature.[20] $Na_2(H_2O)_8$ dimers bind neighboring copper chains through the carboxylato oxygen atom. Distances in the Na octahedron reveal that the interaction to O(4) (Na–O(4) 2·333(4) Å) is stronger than those to the water groups (mean Na–O_{water} 2·48(1) Å).

Table 1. Atomic coordinates and equivalent isotropic displacement parameters for compound (1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq} (Å^2)
Cu	0·2500	0·2500	0·0000	0·033(1)
N	0·2670(2)	0·0116(6)	0·0769(2)	0·027(1)
C(2)	0·2180(2)	−0·1308(7)	0·0698(3)	0·024(1)
C(3)	0·2172(2)	−0·3005(7)	0·1232(3)	0·028(1)
C(4)	0·2702(2)	−0·3223(8)	0·1842(3)	0·033(1)
C(5)	0·3205(2)	−0·1789(8)	0·1917(3)	0·033(1)
C(6)	0·3173(2)	−0·0118(8)	0·1372(3)	0·033(1)
C(7)	0·1616(2)	−0·4565(7)	0·1190(3)	0·031(1)
O(1)	0·1172(2)	−0·3916(6)	0·1504(2)	0·041(1)
O(2)	0·1670(2)	−0·6408(6)	0·0905(2)	0·043(1)
C(8)	0·1655(2)	−0·0878(7)	−0·0023(3)	0·025(1)
O(3)	0·1755(2)	0·0732(5)	−0·0458(2)	0·032(1)
O(4)	0·1185(2)	−0·2089(6)	−0·0155(2)	0·038(1)
Na	0·0173(1)	−0·1220(4)	−0·0902(1)	0·050(1)
O(1w)	−0·0894(2)	−0·0406(6)	−0·1594(2)	0·039(1)
O(2w)	0·0354(2)	0·2512(8)	−0·0127(3)	0·058(1)
O(3w)	0·0017(2)	−0·4688(8)	−0·1585(3)	0·070(2)
O(4w)	0·0679(2)	0·0795(7)	−0·1807(2)	0·053(1)

Table 2. Selected bond lengths (Å) and angles (deg) for compound (1)

Symmetry transformations used to generate equivalent atoms: [a] x, y+1, z; [b] $-x$, $-y$, $-z$

	Bond distances		
Cu–O(3)	1·948(3)	Na–O(3w)	2·413(6)
Cu–N	1·950(4)	Na–O(4w)	2·400(5)
Cu–O(2)^a	2·660(4)	Na–O(2w)^b	2·405(5)
Na–O(4)	2·333(4)	O(2w)–Na^b	2·405(5)
Na–O(1w)	2·392(4)	Na···Na^b	3·638(5)
Na–O(2w)	2·629(5)		
	Bond angles		
O(3)–Cu–N	83·28(14)	O(3)–Cu–O(2)^a	78·01(13)
O(3)^b–Cu–N	96·72(14)	N–Cu–O(2)^a	81·27(14)

All water molecules are involved in a fairly complex hydrogen-bonding scheme stabilizing the structure through a four-step cascade process starting at O(2w), and which involves five different quinolinate groups interacting via non-ketonic atoms. Details of the hydrogen-bonding geometry are presented in Table 3.

The structural details found in (1) are not unusual in compounds containing pydc: a similar double-link chain structure has been observed in Cu(H2,3-pydc)$_2$,[4] and the coordination around Cu^{II} is analogous to that shown by Ag^{II}, also a d^9 ion, in the related complex Ag(2,3-pydc)$_2$.2H_2O.[7] However, it may be contrasted with the structures of Cu(2,6-pydc)($H_2$2,6-pydc).H_2O[3] and Cu(2,6-pydc)($H_2$2,6-pydc).3H_2O,[2,3] where a dianion and a diprotonated acid ligand coexist.

Comparison of the Cu^{II} environments for Cu(2,6-pydc)($H_2$2,6-pydc).H_2O and compound (1) proves to be illuminating: while the coordination polyhedron in (1) is rather regular, with interatomic angles differing from expected values by less than 10% (Table 3),

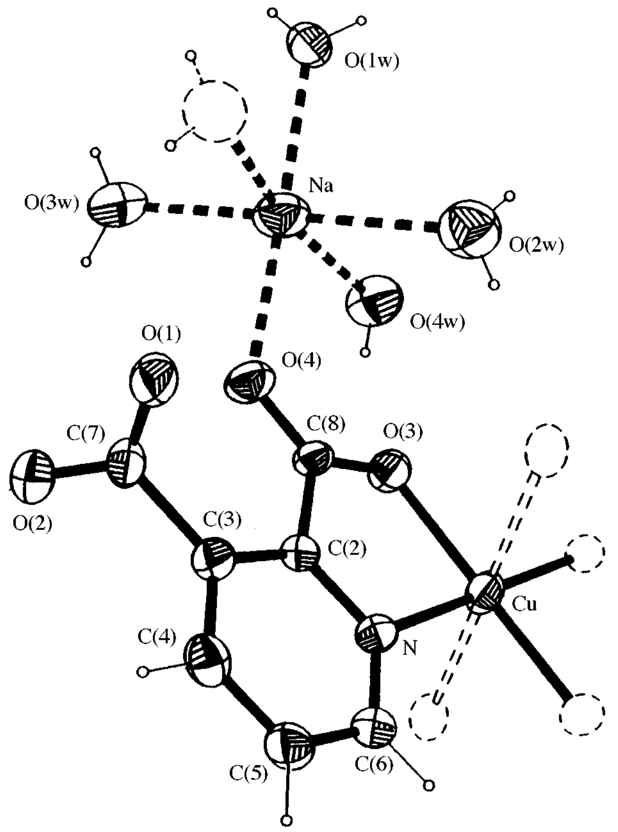

Fig. 1. Cu^{II} and Na coordination polyhedra in Na_2Cu(2,3-pydc)$_2$.8H_2O (1). Displacement ellipsoids are shown at a 50% level.

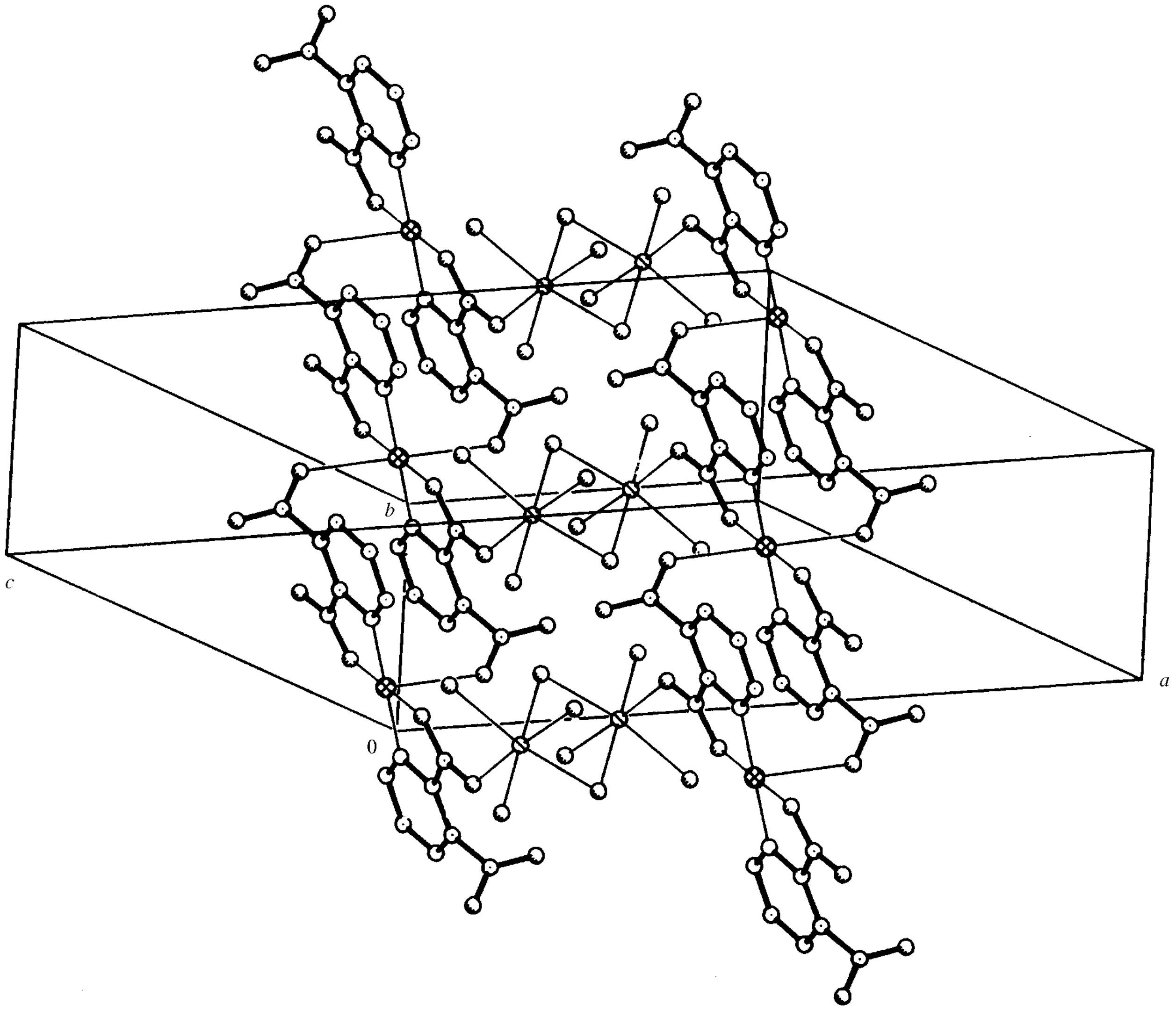

Fig. 2. Packing view of (1) showing interlinked chains.

Table 3. Hydrogen-bonding geometry for compound (1)

Symmetry codes: [a] $-x,\ -y-1,\ -z$; [b] $-x,\ -y,\ -z$; [c] $-x,\ y,\ -z-1/2$; [d] $x,\ y+1,\ z$; [e] $x,\ y-1,\ z$

D–H···A	D–H (Å)	D···A (Å)	H···A (Å)	D–H···A (deg)
O(1w)–H(1wA)···O(2)[a]	0·744(4)	2·950(5)	2·209(4)	174·2(2)
O(1w)–H(1wB)···O(1)[b]	0·750(3)	2·720(5)	1·985(3)	166·6(3)
O(2w)–H(2wA)···O(2)[d]	0·759(4)	3·066(5)	2·329(3)	163·9(3)
O(2w)–H(2wB)···O(3w)[d]	0·750(4)	2·996(6)	2·379(5)	140·5(3)
O(3w)–H(3wA)···O(1)[a]	0·743(4)	2·701(6)	2·019(4)	152·6(3)
O(3w)–H(3wB)···O(4w)[e]	0·900(5)	3·158(6)	2·421(4)	139·2(3)
O(4w)–H(4wA)···O(1w)[c]	0·747(4)	2·959(5)	2·243(4)	160·7(3)
O(4w)–H(4wB)···O(3)	0·749(4)	2·907(4)	2·243(3)	148·3(3)

the one in Cu(2,6-pydc)($H_2$2,6-pydc).H_2O appears as more distorted[3] from the ideal D_{4h} symmetry, and with a smaller axial ratio. This diversity in geometry may be explained through the ligand characteristics: in dipicolinic ligands, carboxylate groups are located in positions 2 and 6 determining a flat or planar ligand that strongly coordinates the metal ion in three short equatorial bonds.[2,3] Octahedral coordination is completed with a neutral dipicolinic acid molecule that perpendicularly chelates the copper(II) ion. Longer axial Cu–O distances, as required by the Jahn–Teller effect, are thus associated with a higher basicity of axial carboxylic groups, at longer distances from the metal centre. Ligand constraints and Jahn–Teller requirements determine a final highly distorted octahedral coordination; protonation of the ligands is thus defined by the coordination chemistry of copper(II). Quinolinate ligands, instead, present carboxylates in the 2- and 3-positions that do not permit a tridentate chelation to the same metal centre. Thus, a bidentate chelate forms a strong planar bond in the equatorial plane and the twisted, out-of-the-plane, carboxylate

Table 4. Atomic coordinates and equivalent isotropic displacement parameters for compound (2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U_{eq} (Å^2)
Cu(1)	0·0000	0·0000	0·0000	0·018(1)
Cu(2)	−0·7587(1)	−0·2620(1)	0·2482(1)	0·022(1)
Cu(3)	−0·5000	−0·5000	0·0000	0·032(1)
O(1)	−0·0758(6)	0·1988(5)	0·1933(2)	0·028(1)
O(2)	0·1805(6)	0·2980(5)	0·2163(2)	0·041(2)
O(3)	0·5545(6)	0·1792(4)	0·2095(2)	0·021(1)
O(4)	0·5652(7)	0·3478(5)	0·1646(2)	0·036(1)
N(1)	0·1523(7)	0·0902(5)	0·0541(2)	0·016(1)
C(1)	0·0811(8)	0·1364(6)	0·0975(3)	0·019(2)
C(2)	0·1834(8)	0·1872(6)	0·1383(2)	0·014(2)
C(3)	0·3731(9)	0·1921(6)	0·1320(2)	0·015(2)
C(4)	0·4478(9)	0·1464(6)	0·0869(2)	0·022(2)
C(5)	0·3378(9)	0·0961(7)	0·0491(2)	0·023(2)
C(6)	0·0909(9)	0·2329(6)	0·1862(2)	0·018(2)
C(7)	0·5059(9)	0·2460(7)	0·1728(2)	0·020(2)
O(5)	−0·5113(7)	−0·3768(5)	0·0524(2)	0·035(1)
O(6)	−0·2229(7)	−0·3085(5)	0·0466(2)	0·036(1)
O(7)	0·0233(6)	−0·1403(5)	0·1091(2)	0·030(1)
O(8)	−0·1725(6)	−0·0493(5)	0·0537(2)	0·020(1)
N(2)	−0·5801(7)	−0·2079(5)	0·1939(2)	0·016(1)
C(8)	−0·5484(9)	−0·2669(7)	0·1496(2)	0·023(2)
C(9)	−0·4098(8)	−0·2401(6)	0·1154(2)	0·016(2)
C(10)	−0·2969(8)	−0·1456(6)	0·1271(2)	0·014(2)
C(11)	−0·3334(9)	−0·0783(6)	0·1714(4)	0·017(2)
C(12)	−0·4745(9)	−0·1144(7)	0·2034(2)	0·020(2)
C(13)	−0·3774(10)	−0·3134(7)	0·0677(3)	0·024(2)
C(14)	−0·1342(9)	−0·1106(6)	0·0935(2)	0·019(2)
O(1w)	0·0399(9)	0·5404(6)	0·0935(2)	0·055(2)
O(2w)	−0·7289(9)	−0·3847(7)	−0·0593(2)	0·053(2)
O(3w)	−0·6950(7)	−0·5776(5)	0·0397(2)	0·037(2)
O(4w)	−0·9514(8)	−0·1876(10)	0·2091(2)	0·096(3)
O(5w)	−0·8477(10)	−0·4472(6)	0·2046(3)	0·066(2)
O(6w)	0·2151(10)	−0·1706(5)	0·0117(2)	0·051(2)
O(7w)	−1·2351(10)	−0·4531(8)	0·2108(3)	0·105(3)

at position 3 makes a longer bond to one Cu$^{\mathrm{II}}$ from an adjacent link. Again, metal configuration (d^9) and ligand hindrance determine the crystal characteristics.

Final atomic parameters for compound (2) and a selection of bond lengths and angles involving copper can be found in Tables 4 and 5, respectively. A molecular plot is shown in Fig. 3, with the atom numbering and displacement ellipsoids at a 50% level.

Three independent copper centres are found in the structure, each one presenting a different coordination: Cu(1) is situated in an inversion centre; the octahedral environment is generated by the equatorial

Table 5. Selected bond lengths (Å) and angles (deg) for compound (2)

Symmetry transformations used to generate equivalent atoms: ^{c} $-x,\ y-1/2,\ -z+1/2$; ^{d} $-x-1,\ y-1/2,\ -z+1/2$

	Bond distances		
Cu(1)–O(8)	1·947(4)	Cu(2)–N(2)	2·002(5)
Cu(1)–N(1)	2·033(5)	Cu(2)–O(5w)	2·456(7)
Cu(1)–O(6w)	2·501(6)	Cu(3)–O(5)	1·932(5)
Cu(2)–O(4w)	1·907(6)	Cu(3)–O(3w)	1·958(6)
Cu(2)–O(3)^{c}	1·944(4)	Cu(3)–O(2w)	2·590(7)
Cu(2)–O(1)^{d}	1·974(4)		
	Bond angles		
O(8)–Cu(1)–N(1)	91·1(2)	O(1)^{d}–Cu(2)–O(5w)	89·4(2)
O(8)–Cu(1)–O(6w)	95·8(2)	O(3)^{c}–Cu(2)–O(1)^{d}	88·5(2)
N(1)–Cu(1)–O(6w)	88·4(2)	O(3)^{c}–Cu(2)–N(2)	89·4(2)
O(4w)–Cu(2)–O(1)^{d}	92·5(2)	O(3)^{c}–Cu(2)–O(5w)	98·9(2)
O(4w)–Cu(2)–N(2)	89·0(2)	N(2)–Cu(2)–O(5w)	96·8(2)
O(4w)–Cu(2)–O(5w)	87·2(4)	O(5)–Cu(3)–O(3w)	86·0(2)
O(4w)–Cu(2)–O(3)^{c}	173·8(4)	O(5)–Cu(3)–O(2w)	90·4(2)
O(1)^{d}–Cu(2)–N(2)	173·7(2)	O(3w)–Cu(3)–O(2w)	93·6(2)

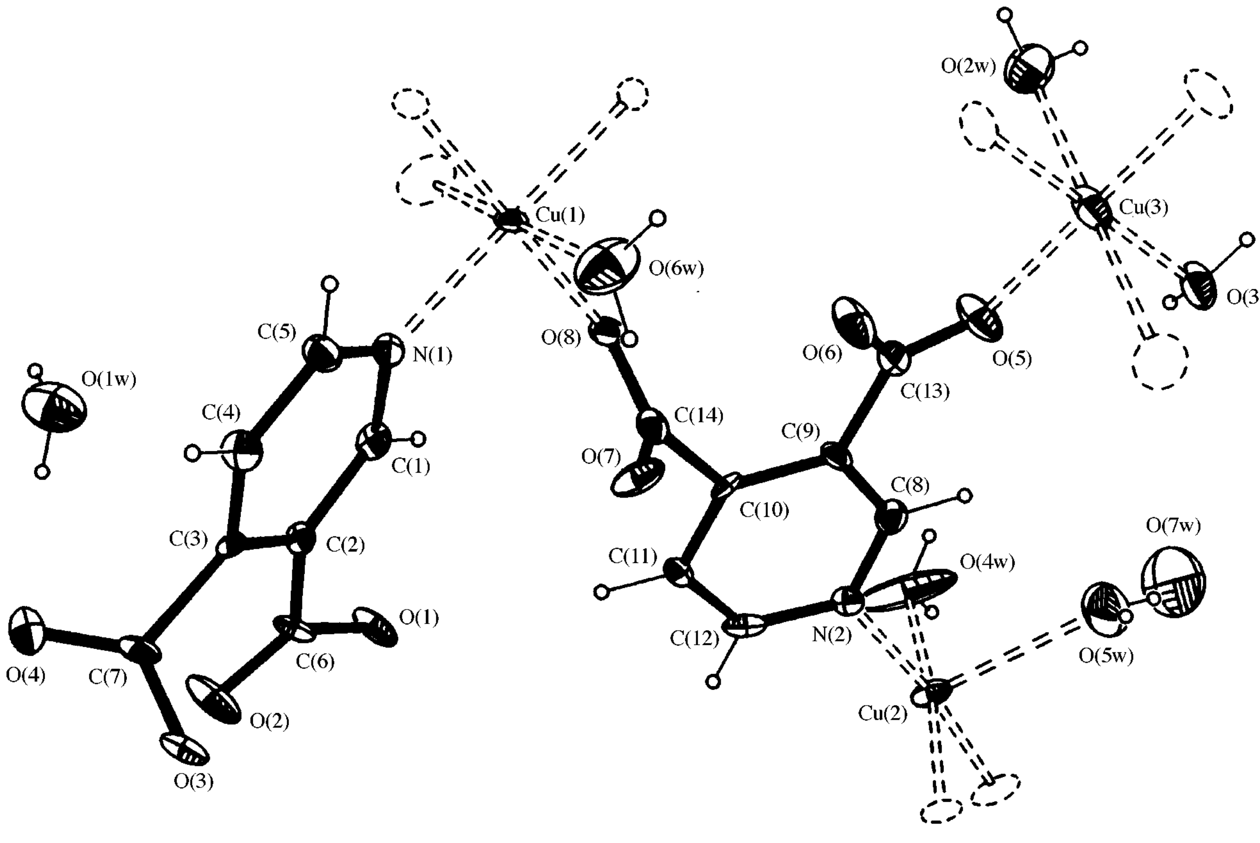

Fig. 3. Molecular structure of Cu(3,4-pydc).3·5H_2O (2). Displacement ellipsoids are shown at a 50% level.

Table 6. Hydrogen-bonding geometry for compound (2)

Symmetry codes: ^{b} $-x, -y, -z$; ^{d} $x, y+1, z$; ^{f} $x+1, y, z$; ^{g} $x-1, y, z$; ^{h} $x+1, y+1, z$; ^{i} $-x-1, -y, -z$; ^{j} $-x-1, -y-1, -z$; ^{k} $x-1, y-1, z$; ^{l} $-x-1, y-1/2, -z+1/2$

D–H···A	D–H (Å)	D···A (Å)	H···A (Å)	D–H···A (deg)
O(1w)–H(1wA)···O(6)^{d}	0·78(9)	2·82(1)	2·06(8)	170(8)
O(1w)–H(1wB)···O(5w)^{h}	0·78(4)	2·94(1)	2·18(5)	167(4)
O(2w)–H(2wA)···O(1w)^{i}	0·80(7)	2·99(1)	2·20(7)	173(6)
O(2w)–H(2wB)···O(4)^{b}	0·80(6)	2·97(1)	2·20(6)	165(5)
O(3w)–H(3wA)···O(1w)^{k}	0·80(6)	2·73(1)	1·94(6)	166(6)
O(3w)–H(3wB)···O(6)^{j}	0·80(6)	2·61(1)	1·86(6)	159(6)
O(4w)–H(4wA)···O(2)^{l}	0·79(7)	2·55(1)	1·84(8)	150(7)
O(4w)–H(4wB)···O(7)^{g}	0·79(6)	2·60(1)	1·97(7)	138(5)
O(5w)–H(5wB)···O(7w)	0·78(6)	2·82(1)	2·19(5)	139(5)
O(6w)–H(6wA)···O(2w)^{f}	0·80(6)	3·06(1)	2·28(6)	166(6)

bonds of a nitrogen atom and a 4-carboxylate oxygen atom, and the axial coordination of a water molecule. The angular geometry of the elongated octahedron is almost undistorted (maximum O–Cu–O 95·8(2)°). Cu(2) is pentacoordinated in a slightly distorted square pyramidal structure; the basal plane is formed by two oxygen atoms from carboxylates in positions 3 and 4 belonging to different pydc molecules, a nitrogen and a water ligand; the apical position is occupied by a second water ligand. Finally, Cu(3) is at an inversion centre, its octahedral environment being defined by the equatorial bonds to a 3-carboxylate and a water molecule, and an apical one to a second water oxygen. Distortions from a regular symmetry are also small.

Water molecules O(2w)–O(6w) are involved in coordination to copper centres, and are accordingly very well defined with rather small displacement factors. The same can be said about O(1w), which, in spite of its hydration character, is strongly anchored to the structure through four different hydrogen bonds. Only O(7w) is weakly bonded to the rest, as evidenced from its large displacement factor and the fact that no hydrogen atom could be confidently found in the difference Fourier. As in (1), hydrogen bonding plays a fundamental role in the crystal stabilization of (2). Details of these interactions can be found in Table 6.

This compound also illustrates the versatility of Cu^{II} coordination capability. The metal ion is found in two different octahedral and one pyramidal environments, all of them slightly distorted; the postulated tetrahedral coordination[15] is not confirmed in this case. The diffuse reflectance spectra of the compound show a broad peak centred at 20449 cm^{-1}. The broadness of the band precludes any attempt to distinguish between the three different coordinative environments of the Cu^{II} ions. The Jahn–Teller effect is reflected in the axial occupation by non-sterically constrained water molecules. The organic ligand behaves as tridentate, but in contrast with Cu(2,6-pydc).$2H_2O$ (monoclinic and triclinic phases) and Cu(2,6-pydc).$3H_2O$,[2,3] where the copper ion is trichelated by the 2,3-pydc^{2-} ligand, coordination is established to three different copper centres; bidentate and tridentate chelation is precluded by the relative position of N and $CO_2{}^-$ donors. Accordingly, a highly interconnected and complex three-dimensional structure results that may be attributed to constrained twisted carboxylates (dihedral angles O(1)–C(6)–C(2)–C(1) 16(1), O(3)–C(7)–C(3)–C(2) 85(1), O(5)–C(13)–C(9)–C(8) 20(1) and O(8)–C(14)–C(10)–C(9) 82(1)°).

Thermal Properties

Fig. 4 shows the thermograms obtained for (1) and (2). The one for compound (1) displays two dehydration steps: the first one at 368 K (weight loss 18·53%) accounts for six water molecules, the second at 436 K is attributable to two other H_2O groups. Decomposition of the aromatic moiety together with redox phenomena involving the metal centre are detected in one endothermic and one exothermic process (d.t.a. peaks at 525 and 535 K). At 693 K the final products are C, Cu^0 and small quantities of Na_2CO_3, the last two being characterized by X-ray diffraction.

T.g., d.t.g. and d.t.a. measurements for compound (2) reveal only one peak at 411 K corresponding to dehydration (weight loss 20·35%); decomposition is accomplished through two exothermic peaks at 520 and 526 K. The final residue at 693 K comprises C and Cu^0.

The thermal behaviour is typical of Cu^{II} carboxylates,[21] the decomposition of which is triggered by internal electron transfer (O–Cu homolytic bond breakage) followed by CO_2 release and subsequent decomposition of the organic radicals.

Magnetic Susceptibility

Magnetic susceptibility data for compound (1) collected in the range 5–70 K were found to fit the Curie–Weiss law. When the temperature is lowered the product χ_T decreases steadily from an initial value of 0·438 emu mol^{-1} to a value of 0·417 emu mol^{-1} at 5 K. This behaviour is described by a Curie constant of 0·440 and a θ value of $-0{\cdot}281(0{\cdot}007)$ K ($g = 2{\cdot}167(1)$). The results indicate a very weak antiferromagnetic coupling between copper centres connected by ligands placed in the equatorial plane of one copper polyhedron and in an axial position of a neighbouring copper atom.

Compound (2) is also paramagnetic and follows a Curie behaviour in the range 16–70 K ($C = 0{\cdot}470$ emu K mol^{-1} and $g = 2{\cdot}238(2)$). When the temperature is lowered from 16 to 5 K, the product χ_T increases

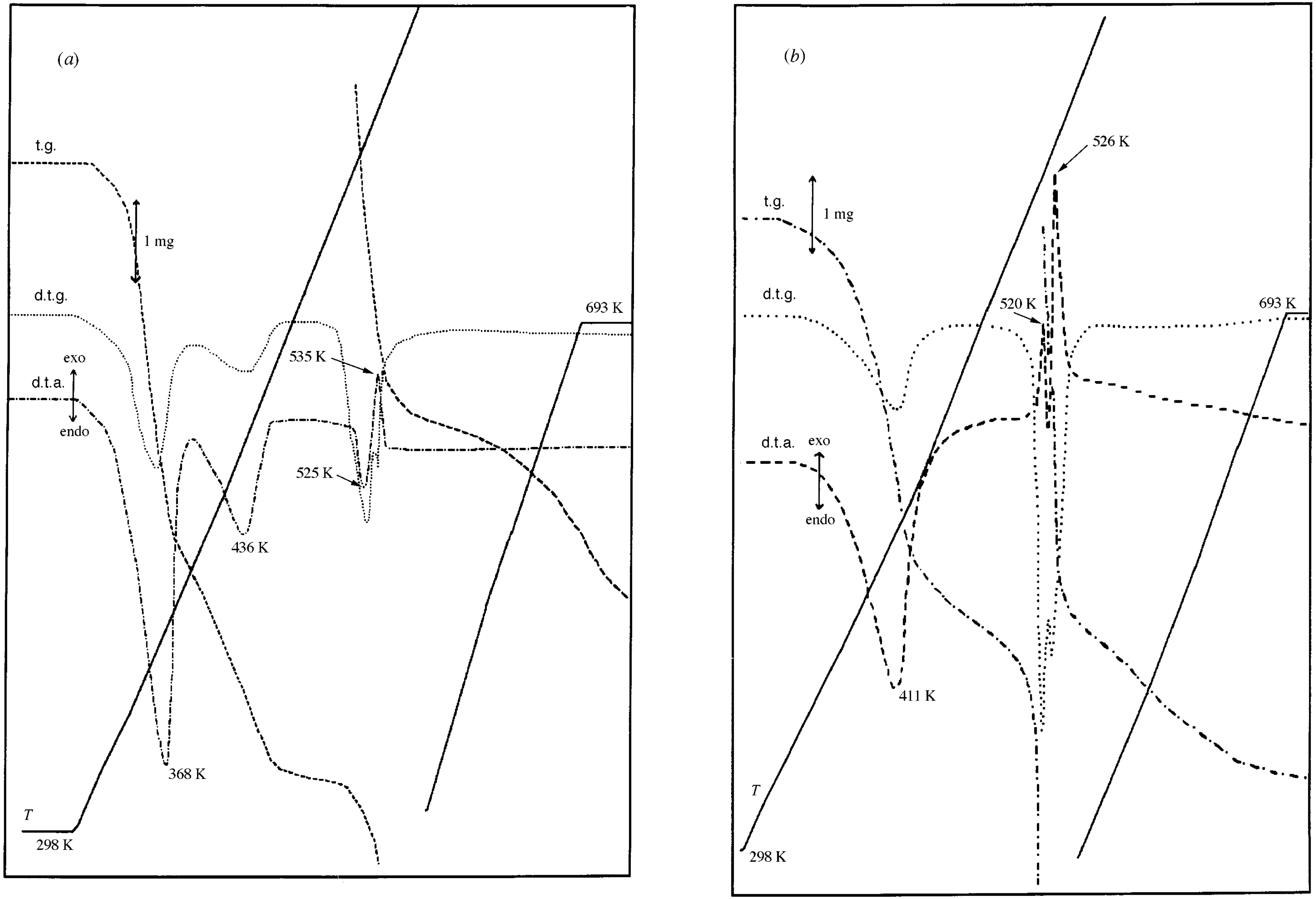

Fig. 4. T.g., d.t.g. and d.t.a. traces of: (*a*) (1); (*b*) (2).

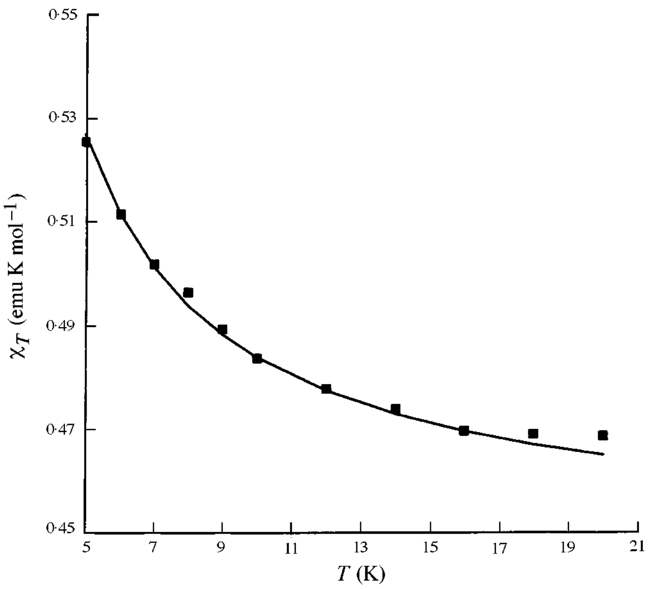

Fig. 5. χ_T against T plot between 5 and 20 K for (2). Solid line shows calculated values for the molecular field approximation.

steadily from a value of 0·468 emu K mol^{-1} to a value of 0·525 emu K mol^{-1}. Fig. 5 shows these features together with calculated values obtained from the molecular field treatment of the Curie equation:

$$\chi = \frac{Ng^2\mu_B{}^2S(S+1)}{3k_BT - 2S(S+1)zJ}$$

where J is the exchange constant and z is the number of interacting nearest neighbors ($S = 1/2$). The best fit parameters are $g = 2{\cdot}184$ and $zJ/k = 1{\cdot}496$. These values and the appearance of the χ_T against T curve are indicative of a weak ferromagnetic coupling between non-equivalent copper ions.

In spite of the variety of coordination geometries of the different Cu–pydc complexes, the coupling between metal centres is weak in all cases studied until now (including Cu(2,3-pydc).2H_2O, monoclinic and triclinic phases).[11] In future work, the magnetic properties of copper pyrazinedicarboxylates shall be studied and compared with those of the Cu–pydc complexes reported here.

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