Syntheses, crystal structures and magnetic properties of new oxalato-, croconato- and squarato-containing copper(II) complexes†

José Carranza,[ab] Conor Brennan,[a] Jorunn Sletten,*[c] Brita Vangdal,[c] Paul Rillema,[d] Francesc Lloret[a] and Miguel Julve*[a]

[a] *Departament de Química Inorgànica, Instituto de Ciencia Molecular, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100, Burjassot (València), Spain. E-mail: miguel.julve@uv.es*
[b] *Facultad de Ciencias Químicas, Universidad Autónoma de Zacatecas, Jardín Juárez s/n, 98000, Zacatecas, México*
[c] *Department of Chemistry, University of Bergen, Allégaten 41, N-5007, Bergen, Norway. E-mail: jorunn.sletten@kj.uib.no*
[d] *Department of Chemistry, Wichita State University, Wichita, KS 67260-0051, U.S.A. E-mail: paul.rillema@wichita.edu*

Received (in Montpellier, France) 29th January 2003, Accepted 15th July 2003
First published as an Advance Article on the web 13th October 2003

The preparation and magnetic investigation of five mononuclear copper(II) complexes of formula $[Cu(pyim)(C_2O_4)(H_2O)]\cdot 2H_2O$ (**1**), $[Cu(pyim)(C_4O_4)(H_2O)_2]_n\cdot 2H_2O$ (**2**), $Cu(pyim)(C_5O_5)\cdot 2.5H_2O$ (**3**), $[Cu(H_2bim)(C_2O_4)(H_2O)]\cdot H_2O$ (**4**) and $[Cu(bpz)(C_5O_5)(H_2O)]$ (**5**) [pyim = 2-(2-pyridyl)imidazole, H_2bim = 2,2′-biimidazole, bpz = 2,2′-bipyrazine, $C_2O_4^{2-}$ = dianion of oxalic acid, $C_4O_4^{2-}$ = dianion of squaric acid and $C_5O_5^{2-}$ = dianion of croconic acid] are reported. The crystal structures of **1**, **2**, **4** and **5** have been determined. The copper atom has a distorted square pyramidal geometry in this family of complexes: two nitrogen atoms from the bidentate nitrogen donor [pyim (**1** and **2**), H_2bim (**4**) and bpz (**5**)] and two oxygen atoms either from a chelating oxalate (**1** and **4**)/croconate (**5**) or from a monodentate squarate and a water molecule (**2**) build the basal plane whereas a water molecule fills the apical position (**1**, **2**, **4** and **5**). A semi-coordinated oxalate (**1** and **4**)/croconate (**5**) oxygen atom of a neighbouring molecule occupies the sixth coordination position, leading to centrosymmetric dinuclear units. Magnetic susceptibility measurements for **1**–**5** in the temperature range 2–290 K reveal the occurrence of weak intermolecular ferro- (**1**) and antiferromagnetic (**2**–**5**) interactions. The different strategies to use these neutral complexes as ligands in order to design polynuclear species are analyzed and discussed.

Introduction

Neutral copper(II) chains of formula $[Cu(C_2O_4)\cdot 1/3H_2O]_n$[1] ($C_2O_4^{2-}$ = dianion of oxalic acid), $[Cu(C_4O_4)(H_2O)_2]_n$[2a] and $[Cu(C_4O_4)(H_2O)_4]_n$[2b] [$C_4O_4^{2-}$ = dianion of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione)] and $[Cu(C_5O_5)(H_2O)_3]_n$[3] [$C_5O_5^{2-}$ = dianion of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione)] are formed by reaction of copper(II) with oxalate, squarate and croconate in aqueous solution. Although these dianions act as bridging ligands in these chain compounds, they exhibit different coordination modes: the oxalate exhibits the usual bischelating coordination mode through its four oxygen atoms, croconate binds as bidentate to one copper atom and monodentate towards the adjacent one using only three of its five oxygen atoms and finally, squarate adopts a bismonodentate bridging mode through two oxygen atoms in *trans* positions. The formation of these highly insoluble polymeric compounds is a difficulty that synthetic chemists have to overcome in their attempts to prepare nuclearity tailored mono- and polynuclear species. The use of polydentate ligands to partially block the coordination sites of the metal ion prevents the formation of these chain compounds and affords oxalato-, squarato- and croconato-containing lower nuclearity complexes that can be used as ligands toward other transition metal ions. This preparative methodology is known as the building block strategy and recent examples concerning oxamidato-,[4] cyanide-[5] and oxalato-based[6] precursors have illustrated its potentiality and richness.

As far as the case of copper(II) is concerned, the coordination of bidentate 2,2′-bipyridine (bipy),[7] 1,10-phenantroline (phen)[7b,8] or bisbidentate 2,2′-bipyrimidine (bpym)[9] nitrogen donors precludes chain formation. Restricting ourselves to the case of bpym, the mononuclear complexes of formula $[Cu(bpym)(C_2O_4)]\cdot 5H_2O$,[9a] $[Cu(bpym)(C_4O_4)(H_2O)_3]\cdot 2H_2O$[9c] and $[Cu(bpym)(C_5O_5)(H_2O)_2]\cdot H_2O$[9b] were obtaind in which bpym, oxalate, squarate and croconate are the terminal ligands. These stable mononuclear complexes can act as ligands through the uncoordinated nitrogen (bpym) and oxygen (oxalate, squarate and croconate) donor atoms. In fact, their reaction with copper(II) ions in aqueous solution afforded the honeycomb layered compound $\{[Cu_2(bpym)(C_2O_4)_2]\cdot 5H_2O\}_n$[9a] and the dinuclear complexes $[Cu_2(bpym)(C_4O_4)_2(H_2O)_6]$[9c] and $[Cu_2(bpym)(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$.[9b] Strong antiferromagnetic interactions between the copper(II) ions across bischelating bpym (all three complexes) and oxalato (two-dimensional species) were observed, in agreement with the remarkable ability of bpym[10] and oxalato[11] to transmit magnetic interactions between magnetic centres bridged by them.

---

† Electronic supplementary information (ESI) available: Stereoview of the structure of compound **2** (Fig. S1) and X-ray data as described in the text. See http://www.rsc.org/suppdata/nj/b3/b301212n/

The efficiency of squarate and croconate to mediate magnetic interactions between copper(II) ions when acting as bridging ligands is lower than that of oxalate but it is significant.[12,13]

In our efforts to prepare new mononuclear magnetic compounds to be used as ligands, we have obtained the copper(II) complexes of formula [Cu(pyim)(C_2O_4)(H_2O)]·$2H_2O$ (**1**), [Cu(pyim)(C_4O_4)(H_2O)$_2$]·$2H_2O$ (**2**), Cu(pyim)(C_5O_5)·$2.5H_2O$ (**3**), [Cu(H_2bim)(C_2O_4)(H_2O)]·H_2O (**4**) and [Cu(bpz)(C_5O_5)(H_2O)] (**5**) [pyim = 2-(2-pyridyl)imidazole, H_2bim = 2,2′-biimidazole and bpz = 2,2′-bipyrazine]. The synthesis and magnetic properties of **1**–**5** and the structural characterization of **1**, **2**, **4** and **5** are presented here.

Experimental

Materials

Copper(II) nitrate trihydrate, potassium oxalate monohydrate, squaric acid and lithium hydroxide monohydrate were purchased from commercial sources and used as received. Anhydrous potassium croconate and the organic ligands pyim, H_2bim and 2,2′-bpz were prepared by previously reported procedures.[14–17] Elemental analysis (C, H, N) were carried out by the Microanalytical Service of the Universidad Autónoma de Madrid

Preparation of the complexes

[Cu(pyim)(C_2O_4)(H_2O)]·$2H_2O$ (1). This compound separates as a blue crystalline solid by adding a concentrated aqueous solution of potassium oxalate (0.046 g, 0.25 mmol) to a warm aqueous solution containing copper(II) nitrate (0.060 g, 0.25 mmol) and pyim (0.036 g, 0.25 mmol). The yield is practically quantitative. Single crystals of **1** as blue parallelepipeds were grown by slow diffusion in an H-shaped tube of aqueous solutions containing $K_2C_2O_4·H_2O$ (0.125 mmol) in one arm and [2-(2-pyridyl)imidazole] copper(II) nitrate (0.125 mmol) [mixture of $Cu(NO_3)_2·3H_2O$ and pyim in stoichiometric amounts] in the other. The first crystals appeared after 10 days and the diffusion was complete in one month. The yield is quantitative. Anal. calcd for $C_{10}H_{13}CuN_3O_7$ (**1**): C, 34.25; H, 3.71; N, 11.98; found: C, 34.01; H, 3.62; N, 11.87%.

[Cu(pyim)(C_4O_4)(H_2O)$_2$]·$2H_2O$ (2). Single crystals of **2** as green parallelepipeds were grown by slow diffusion in an H-shaped tube of aqueous solutions containing lithium squarate (0.25 mmol) [mixture of $H_2C_4O_4$ (0.028 g, 0.25 mmol) and $LiOH·H_2O$ (0.021 g, 0.5 mmol)] in one arm and [2-(2-pyridyl)-imidazole] copper(II) nitrate (0.25 mmol) [mixture of $Cu(NO_3)_2·3H_2O$ (0.060 g, 0.25 mmol) and pyim (0.036 g, 0.25 mmol)] in the other. Well-shaped crystals appeared after 15 days and the diffusion was complete in one month and a half. The yield is quantitative. Anal. calcd for $C_{12}H_{15}CuN_3O_8$ (**2**): C, 36.70; H, 3.82; N, 10.70; found: C, 36.61; H, 3.73; N, 10.59%.

Cu(pyim)(C_5O_5)·$2.5H_2O$ (3). Compound **3** was obtained as plate-like dark green crystals by slow diffusion in an H-shaped tube of aqueous solutions containing $K_2C_5O_5$ (0.055 g, 0.25 mmol) in one arm and [Cu(pyim)](NO_3)$_2$ [mixture of $Cu(NO_3)_2·3H_2O$ (0.060 g, 0.25 mmol) and pyim (0.036 g, 0.25 mmol)] in the other. The yield is practically quantitative. These crystals diffract poorly and all our attempts to get suitable crystals for X-ray diffraction (change of solvent, temperature) were unsuccessful. Anal. calcd for $C_{13}H_{12}CuN_3O_{7.5}$ (**3**): C, 39.66; H, 3.05; N, 10.67; found: C, 39.48; H, 2.90; N, 10.55%.

[Cu(H_2bim)(C_2O_4)(H_2O)]·H_2O (4). Single crystals of **4** as green parallelepipeds were grown by slow diffusion in an H-shaped tube of aqueous solutions containing $K_2C_2O_4·H_2O$ (0.046 g, 0.25 mmol) in one arm and a mixture of $Cu(NO_3)_2·3H_2O$ (0.060 g, 0.25 mmol) and H_2bim (0.017 g, 0.125 mmol) in the other. The yield based on the H_2bim ligand is above 90%. Anal. calcd for $C_8H_{10}CuN_4O_6$ (**4**): C, 29.87; H, 3.11; N, 14.41; found: C, 29.75; H, 3.06; N, 14.25%.

[Cu(bpz)(C_5O_5) (H_2O)] (5). Green parallelepipeds of **5** suitable for X-ray diffraction were obtained by slow diffusion in an H-shaped tube of aqueous solutions containing $K_2C_5O_5$ (0.055 g, 0.25 mmol) in one arm and [Cu(bpz)](NO_3)$_2$ (0.25 mmol) [mixture of $Cu(NO_3)_2·3H_2O$ (0.060 g, 0.25 mmol) and bpz (0.040 g, 0.25 mmol)] in the other. The yield is about 70%. Anal. calcd for $C_{13}H_8CuN_4O_6$ (**4**): C, 41.12; H, 2.11; N, 14.75; found: C, 39.98; H, 2.05; N, 14.61%.

Physical techniques

IR spectra (4000–400 cm^{-1}) were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. Variable temperature (2–290 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID susceptometer using an applied magnetic field of 1000 G over the whole temperature range. The complex $(NH_4)_2Mn(SO_4)_2·6H_2O$ was used as a susceptibility standard. Diamagnetic corrections for the constituent atoms were estimated from Pascal's constants[18] as -158×10^{-6} (**1**), -189×10^{-6} (**2**), -181×10^{-6} (**3**), -129×10^{-6} (**4**) and -177×10^{-6} (**5**) $cm^3\ mol^{-1}$. A value of $-60 \times 10^{-6}\ cm^3\ mol^{-1}$ was used for the temperature-independent paramagnetism of the copper(II) ion

X-Ray data collection and structure refinement

Diffraction data for complexes **1**, **2**, **4** and **5** were collected at 153 K with a Bruker-AXS SMART 2K CCD area detector diffractometer equipped with an Oxford Cryostream N_2 cooling device. Crystal parameters and refinement results are summarized in Table 1. Empirical absorption corrections were carried out using SADABS.[19] The structures were solved by direct methods and refined by full-matrix least-squares based on F^2, including all reflections. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms bound to carbon and nitrogen were included in the model at idealized positions; those bound to oxygen (water) were located on Fourier difference maps and all hydrogen atoms were refined according to the riding model. Data collection and data reduction were done with the SMART and SAINT programs.[20] All other calculations were performed with the SHELXS-97, SHELXL/PC and XP programs.[21] Selected bond distances and angles are listed in Tables 2–5 for **1**, **2**, **4** and **5**, respectively.[‡]

Results and discussion

Description of the structures

[Cu(pyim)(C_2O_4)(H_2O)]·$2H_2O$ (1). The structure of **1** is built of mononuclear [Cu(pyim)(C_2O_4)(H_2O)] units and water of hydration. Centrosymmetrically related molecules are pairwise connected through weak Cu···O(oxalate) interactions of 3.1072(15) Å (Fig. 1). In the crystal structure the complex units are arranged in parallel layers (Fig. 2). The layers are pairwise connected through the Cu···O(oxalate) interactions mentioned above. These pairs of layers are connected to the

---

[†] CCDC reference numbers 200154-200157 for **1**, **2**, **4** and **5**. See http://www.rsc.org/suppdata/nj/b3/b301212n/ for crystallographic data in .cif or other electronic format.

Table 1 Crystal data and structure refinement for [Cu(pyim)(C_2O_4)(H_2O)]·$2H_2O$ (**1**), [Cu(pyim)(C_4O_4)(H_2O)$_2$]·$2H_2O$ (**2**), [Cu(H_2bim)(C_2O_4)(H_2O)]·H_2O (**4**) and [Cu(bpz)(C_5O_5)(H_2O)] (**5**)

	1	**2**	**4**	**5**
Empirical formula	$C_{10}H_{13}CuN_3O_7$	$C_{12}H_{15}CuN_3O_8$	$C_8H_{10}CuN_4O_6$	$C_{13}H_8CuN_4O_6$
Formula weight	350.77	392.81	321.74	379.77
T/K	153(2)	153(2)	153(2)	153(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	7.0936(6)	8.4848(4)	6.9893(4)	6.7113(4)
b/Å	9.8281(6)	21.1731(12)	9.2227(5)	9.2977(5)
c/Å	10.1197(8)	9.3035(5)	9.8112(5)	11.8250(6)
α/°	80.231(2)		102.266(1)	106.316(1)
β/°	81.306(3)	111.533(2)	106.779(1)	97.995(1)
γ/°	71.641(3)		103.5270(1)	107.840(1)
U/Å^3	656.28(9)	1554.72(8)	561.45(5)	653.31(6)
Z	2	4	2	2
μ/mm^{-1}	1.703	1.453	1.978	1.717
Total reflect.	5501	13 985	4689	6057
Indep. reflect.	3501	4716	2979	4055
R_{int}	0.0182	0.0198	0.0176	0.0182
Obs. reflect. [$I > 2\sigma(I)$]	2939	4093	2556	3684
R [$I > 2\sigma(I)$]	0.0305	0.0263	0.0304	0.0296
R_w [$I > 2\sigma(I)$]	0.0688	0.0748	0.0686	0.0796
R (all data)	0.0431	0.0339	0.0395	0.0335
R_w (all data)	0.0716	0.0845	0.0709	0.0813

neighbouring layers through coordinated water···oxalate and coordinated water···crystal water···oxalate hydrogen bonds. Thus, the interlayer interactions are of two different types and alternate between layers. Within the layers there are oxalate···H–N(imidazole) as well as oxalate···crystal water···H–C hydrogen bonds/contacts (a complete list of hydrogen bonds is given at the end of Table 2). The two shortest Cu···Cu distances occur across the semi-coordinated oxalate [5.3550(5) Å] and across a hydrogen bond involving the coordinated water and oxalate in a neighbouring unit [5.3956(6) Å].

Table 2 Selected bond lengths (Å) and angles (°) for [Cu(pyim)(C_2O_4)(H_2O)]·$2H_2O$ (**1**)[a]

Copper coordination sphere			
Cu(1)–O(1)	1.9666(13)	Cu(1)–N(1)	2.0186(16)
Cu(1)–O(4)	1.9666(13)	Cu(1)–O(5)	2.2896(14)
Cu(1)–N(2)	1.9789(15)	Cu(1)–O(2a)	3.1072(15)
O(1)–Cu(1)–O(4)	84.19(5)	N(2)–Cu(1)–O(5)	94.12(6)
O(1)–Cu(1)–N()	172.56(6)	N(1)–Cu(1)–O(5)	97.51(6)
O(4)–Cu(1)–N(2)	97.98(6)	O(1)–Cu(1)–O(2a)	80.35(5)
O(1)–Cu(1)–N(1)	94.64(6)	O(4)–Cu(1)–O(2a)	87.46(5)
O(4)–Cu(1)–N(1)	170.57(6)	N(2)–Cu(1)–O(2a)	92.61(5)
N(2)–Cu(1)–N(1)	82.04(6)	N(1)–Cu(1)–O(2a)	83.12(5)
O(1)–Cu(1)–O(5)	92.92(5)	O(5)–Cu(1)–O(2a)	173.27(4)
O(4)–Cu(1)–O(5)	91.90(5)		
Oxalate group			
O(1)–C(9)	1.287(2)	O(4)–C(10)	1.285(2)
O(2)–C(9)	1.234(2)	C(9)–C(10)	1.547(3)
O(3)–C(10)	1.229(2)		
C(9)–O(1)–Cu(1)	112.62(12)	O(1)–C(9)–C(10)	115.44(15)
C(10)–O(4)–Cu(1)	112.99(12)	O(3)–C(10)–O(4)	126.53(18)
O(2)–C(9)–O(1)	124.44(18)	O(3)–C(10)–C(9)	118.95(16)
O(2)–C(9)–C(10)	112.12(16)	O(4)–C(10)–C(9)	114.52(15)

Hydrogen bonds[b]

D–H···A	D···A/Å	H···A/Å	D–H···A/°
N(3)–H31···O(2b)	2.793(2)	1.93	166
O(5)–H(51)···O(1c)	2.888(2)	2.08	157
O(5)–H(52)···O(6d)	2.709(2)	1.84	170
O(6)–H(61)···O(7e)	2.755(2)	1.94	169
O(6)–H(62)···O(3)	2.796(2)	1.94	167
O(7)–H(71)···O(5d)	2.934(2)	2.10	170
O(7)–H(72)···O(4)	2.795(2)	1.96	177

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x+1, -y+1, -z+1$; (b) $x, y, z-1$; (c) $-x, 1-y, 1-z$; (d) $1-x, -y, 1-z$; (e) $2-x, -y, 1-z$. [b] A = acceptor, D = donor.

The copper atom has a distorted square pyramidal coordination geometry with two pyim nitrogen [Cu(1)–N(1) = 2.0186(16) Å, Cu(1)–N(2) = 1.9789(15) Å] and two oxalate oxygen [Cu(1)–O(1) = 1.9618(13) Å, Cu(1)–O(4) = 1.9666(13) Å] atoms in the equatorial positions and a water molecule [Cu(1)–O(5) = 2.2896(14) Å] in the apical position. In the sixth coordination position resides, as mentioned above, a semi-coordinated oxalate oxygen of a neighbouring molecule. The presence of the water molecule in the apical position in **1** precludes chain formation through out-of-plane oxalato-to-copper interactions, which is observed in the complexes $M_2[Cu(C_2O_4)_2 \cdot 2H_2O$ (M = Na, K and NH_4^+),[22,23a] (Hpy)$_2$-[Cu(C_2O_4)$_2$][23b] and H_2pda[Cu(C_2O_4)$_2$][24] (Hpy and H_2pda are pyridinium and propylenediammonium cations, respectively). The atoms defining the equatorial plane of copper are approximately coplanar (maximum atomic deviation being 0.023 Å) and the metal is displaced by 0.141 Å from this plane towards the apical oxygen. The values of the bite angle subtended by the bidentate oxalato and pyim ligands are 84.19(5)° and 82.04(6)°, respectively. The oxalate group is essentially planar (maximum atomic deviation 0.028 Å) and nearly coplanar with the equatorial plane (dihedral angle 1.9°). The value of the C(9)–C(10) bond distance is 1.547(3) Å, in agreement with its carbon-carbon single bond character. O(2) and O(3) oxygens are closer to the respective oxalato carbon atoms C(9) and C(10) [O(2)–C(9) = 1.234(2) Å and O(3)–C(10) = 1.229(2) Å] than are the O(1) and O(4) atoms involved in copper coordination [O(1)–C(9) = 1.287(2) Å and O(4)–C(10) = 1.285(2) Å]. The O(2)–C(9) and O(3)–C(10) distances are also shorter than those occurring in the free ligand (ave. value 1.258 Å).[25] The two rings of the pyim group form a dihedral angle of 4.4°. This small deviation from planarity of the pyim molecule is in agreement with the significant double bond character of the inter-ring C(5)–C(6) bond [1.459(3) Å]. Bond distances and angles within the pyridyl

Table 3 Selected bond lengths (Å) and angles (°) for $[Cu(pyim)(C_4O_4)(H_2O)_2]\cdot 2H_2O$ (**2**)[a]

Copper coordination sphere

Cu(1)–O(1)	1.9612(10)	Cu(1)–N(1)	2.0489(11)
Cu(1)–O(5)	1.9758(10)	Cu(1)–O(6)	2.2057(11)
Cu(1)–N(2)	1.9932(12)		
O(1)–Cu(1)–O(5)	97.37(4)	N(2)–Cu(1)–N(1)	81.40(5)
O(1)–Cu(1)–N(2)	164.76(5)	O(1)–Cu(1)–O(6)	94.70(4)
O(5)–Cu(1)–N(2)	91.97(5)	O(5)–Cu(1)–O(6)	94.89(4)
O(1)–Cu(1)–N(1)	87.70(4)	N(2)–Cu(1)–O(6)	96.47(5)
O(5)–Cu(1)–N(1)	170.22(5)	N(1)–Cu(1)–O(6)	93.01(4)

Squarate group

O(1)–C(9)	1.2645(16)	C(9)–C(10)	1.4626(18)
O(2)–C(10)	1.2600(17)	C(9)–C(12)	1.4654(18)
O(3)–C(11)	1.2524(17)	C(10)–C(11)	1.4687(19)
O(4)–C(12)	1.2553(17)	C(11)–C(12)	1.472(2)
O(1)–C(9)–C(10)	137.39(12)	O(3)–C(11)–C(10)	135.67(14)
O(1)–C(9)–C(12)	132.19(12)	O(3)–C(11)–C(12)	134.39(13)
C(10)–C(9)–C(12)	90.41(10)	C(10)–C(11)–C(12)	89.93(10)
O(2)–C(10)–C(9)	134.42(12)	O(4)–C(12)–C(9)	135.05(13)
O(2)–C(10)–C(11)	135.66(13)	O(4)–C(12)–C(11)	135.26(12)
C(9)–C(10)–C(11)	89.92(11)	C(9)–C(12)–C(11)	89.69(11)

Hydrogen bonds[b]

D–H···A	D···A/Å	H···A/Å	D–H···A/°
N(3)–H(31)···O(4b)	2.7682(15)	1.90	169
O(5)–H(51)···O(2)	2.6374(14)	1.89	173
O(5)–H(52)···O(7)	2.6644(16)	1.80	178
O(6)–H(61)···O(4c)	2.7420(15)	1.93	176
O(6)–H(62)···O(8d)	2.7398(15)	1.93	166
O(7)–H(71)···O(8e)	2.8601(17)	2.19	147
O(7)–H(72)···O(3e)	2.7260(17)	1.92	170
O(8)–H(81)···O(3f)	2.7929(16)	2.04	176
O(8)–H(82)···O(2)	2.7333(15)	1.91	168

[a] Symmetry transformations used to generate equivalent atoms: (b) $1-x$, $1.5-y$, $-0.5+z$; (c) x, $1.5-y$, $-0.5+z$; (d) $-x$, $1-y$, $-z$; (e) $1+x$, y, z; (f) $-x$, $1-y$, $1-z$. [b] A = acceptor, D = donor.

Table 4 Selected bond lengths (Å) and angles (°) for $[Cu(H_2bim)(C_2O_4)(H_2O)]\cdot H_2O$ (**4**)[a]

Copper coordination sphere

Cu(1)–O(1)	1.9521(14)	Cu(1)–N(1)	2.0127(17)
Cu(1)–O(2)	1.9651(13)	Cu(1)–O(5)	2.2378(15)
Cu(1)–N(2)	1.9836(16)	Cu(1)–O(3a)	3.3583(17)
O(1)–Cu(1)–O(2)	84.36(6)	N(2)–Cu(1)–O(5)	92.81(6)
O(1)–Cu(1)–N(2)	93.34(6)	N(1)–Cu(1)–O(5)	100.70(6)
O(2)–Cu(1)–N(2)	176.14(7)	O(1)–Cu(1)–O(3a)	85.00(5)
O(1)–Cu(1)–N(1)	160.90(7)	O(2)–Cu(1)–O(3a)	71.80(5)
O(2)–Cu(1)–N(1)	98.64(6)	N(2)–Cu(1)–O(3a)	104.95(6)
N(2)–Cu(1)–N(1)	82.54(7)	N(1)–Cu(1)–O(3a)	78.14(6)
O(1)–Cu(1)–O(5)	98.11(6)	O(5)–Cu(1)–O(3a)	161.80(4)
O(2)–Cu(1)–O(5)	90.58(6)		

Oxalate group

O(1)–C(1)	1.281(2)	O(4)–C(1)	1.229(2)
O(2)–C(2)	1.278(2)	C(1)–C(2)	1.562(3)
O(3)–C(2)	1.228(2)		
C(1)–O(1)–Cu(1)	112.74(13)	O(1)–C(1)–C(2)	114.77(16)
C(2)–O(2)–Cu(1)	112.40(12)	O(3)–C(2)–O(2)	126.51(19)
O(4)–C(1)–O(1)	125.78(19)	O(3)–C(2)–C(1)	118.90(18)
O(4)–C(1)–C(2)	119.45(17)	O(2)–C(2)–C(1)	114.59(16)

Hydrogen bonds[b]

D–H···A	D···A/Å	H···A/Å	D–H···A/°
N(3)–H(31)···O(3d)	2.8582(24)	2.11	146
N(3)–H(31)···O(4d)	2.8661(22)	2.23	131
N(4)–H(41)···O(3d)	2.8179(22)	2.05	148
O(5)–H(51)···O(2b)	2.7877(20)	1.99	170
O(5)–H(52)···O(6)	2.7582(21)	1.88	171
O(6)–H(61)···O(1e)	2.8817(22)	2.09	159
O(6)–H(62)···O(4c)	2.8702(22)	2.04	165

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x,-y,-z$; (b) $1-x$, $-y$, $-z$; (c) $1-x$, $1-y$, $-z$; (d) x, y, $z-1$; (e) $1+x$, y, z. [b] A = acceptor, D = donor.

and imidazole rings are in agreement with those observed for this ligand in the chain complex $[Cu(pyim)(H_2O)(dca)]_n$[26] (dca = dicyanamide anion).

$[Cu(pyim)(C_4O_4)(H_2O)_2]\cdot 2H_2O$ (2). The structure of **2** is built of mononuclear $[Cu(pyim)(C_4O_4)(H_2O)_2]$ units and water of hydration (Fig. 3). In the crystal, molecules related by a *c*-glide and unit translations along the *a* axis form bands of stacked molecules. Centrosymmetrically related bands alternate along the *b* axis as shown in Fig. S1 (Electronic supplementary information). An extensive network of hydrogen bonds is present (see end of Table 3). Stacked molecules are connected through coordinated water···squarate and coordinated water···crystal water···squarate hydrogen bonds. The bands are linked by hydrogen bonds through crystal water. Relatively strong hydrogen bonds between squarate oxygen and imidazole N–H occur within each layer of a band. The molecular geometry is furthermore stabilized through a strong hydrogen bond between the equatorially coordinated water and a squarate oxygen [O(5)–O(6) = 2.637 Å] The shortest intermolecular Cu···Cu distance is 6.1011(3) Å and it occurs between stacked molecules related by the *c*-glide translation.

The copper atom has a distorted square pyramidal coordination geometry with two pyim nitrogen atoms [Cu(1)–N(1) = 2.0489(11) Å and Cu(1)–N(2) = 1.9932(12) Å], a squarate oxygen atom [Cu(1)–O(1) = 1.9612(10) Å] and a water molecule [Cu(1)–O(5) = 1.9758(10) Å] in the equatorial positions, and a water molecule [Cu(1)–O(6) = 2.2057(11) Å] in the apical position. The sixth coordination position is screened by a piym group of a neighbouring molecule, the shortest Cu···C distance being 3.69 Å. The value of the angle subtended at the copper atom by the bidentate pyim is 81.40(5)°. The atoms defining the equatorial plane of the copper atom are close to coplanar (maximum atomic deviation being 0.031 Å) and the metal is displaced by 0.166 Å from this plane towards the apical oxygen. The dihedral angle between the equatorial plane and the squarate group is only 3.3°, possibly as a consequence of the strong intramolecular hydrogen bond [O(5)···O(2)] of 2.6374(14) Å. The piym group is essentially planar, the dihedral angle between the five- and six-membered rings being 1.0°. The value of the inter-ring C(5)–C(6) bond length of pyim [1.4601(19) Å], as well as those within the pyridyl and imidazole fragments, agree with those observed for this ligand in**1**. Bond lengths and angles of the monodentate squarate in**1** are in agreement with those observed for this group in previous mononuclear compounds of copper(II) with squarate and bidentate 2,2′-bipyridine,[7b] 1,10-phenanthroline[7b] or 2,2′-bipyrimidine[9c] nitrogen donors.

$[Cu(H_2bim)(C_2O_4)(H_2O)]\cdot H_2O$ (4). The structure is built of mononuclear $[Cu(H_2bim)(C_2O_4)(H_2O)]$ units and water of hydration. Centrosymmetrically related molecules are pairwise connected through very weak Cu···O(oxalate) interactions of 3.3583(17) Å (Fig. 4). In the crystal structure the complex units are arranged in parallel layers (Fig. 5). The layers are alternatively connected through weak Cu···O(oxalate) interactions, such as those mentioned above, and through coordinated water···oxalate and coordinated water···crystal water···oxalate hydrogen bonds (see end of Table 4). Within the layers, oxalate and H_2bim of neighbouring units form two

Table 5 Selected bond lengths (Å) and angles (°) for [Cu(bpz)-(C_5O_5)(H_2O)] (**5**)[a]

Copper coordination sphere			
Cu(1)–O(1)	1.9705(11)	Cu(1)–N(1)	1.9891(13)
Cu(1)–O(2)	1.9805(11)	Cu(1)–O(6)	2.2192(13)
Cu(1)–N(2)	1.9858(13)	Cu(1)–O(3a)	2.9568(13)
O(1)–Cu(1)–O(2)	86.71(4)	N(2)–Cu(1)–O(6)	91.10(5)
O(1)–Cu(1)–N(2)	173.43(5)	N(1)–Cu(1)–O(6)	92.90(5)
O(2)–Cu(1)–N(2)	94.04(5)	O(1)–Cu(1)–O(3a)	97.80(4)
O(1)–Cu(1)–N(1)	96.10(5)	O(2)–Cu(1)–O(3a)	87.98(4)
O(2)–Cu(1)–N(1)	166.99(5)	N(2)–Cu(1)–O(3a)	75.72(4)
N(2)–Cu(1)–N(1)	81.73(5)	N(1)–Cu(1)–O(3a)	79.06(4)
O(1)–Cu(1)–O(6)	95.21(5)	O(6)–Cu(1)–O(3a)	165.34(4)
O(2)–Cu(1)–O(6)	99.51(5)		
Croconate ligand			
O(1)–C(9)	1.2692(19)	C(9)–C(10)	1.426(2)
O(2)–C(10)	1.2825(18)	C(9)–C(13)	1.471(2)
O(3)–C(11)	1.2425(19)	C(10)–C(11)	1.448(2)
O(4)–C(12)	1.2276(19)	C(11)–C(12)	1.497(2)
O(5)–C(13)	1.223(2)	C(12)–C(13)	1.510(2)
C(9)–O(1)–Cu(1)	106.75(10)	O(3)–C(11)–C(12)	126.37(14)
C(10)–O(2)–Cu(1)	105.89(9)	C(10)–C(11)–C(12)	106.00(13)
O(1)–C(9)–C(10)	120.17(13)	O(4)–C(12)–C(11)	125.66(15)
O(1)–C(9)–C(13)	129.71(14)	O(4)–C(12)–C(13)	126.01(15)
C(10)–C(9)–C(13)	110.12(13)	C(11)–C(12)–C(13)	108.32(12)
O(2)–C(10)–C(9)	120.36(13)	O(5)–C(13)–C(9)	128.72(15)
O(2)–C(10)–C(11)	129.29(14)	O(5)–C(13)–C(12)	126.42(15)
C(9)–C(10)–C(11)	110.33(13)	C(9)–C(13)–C(12)	104.85(13)
O(3)–C(11)–C(10)	127.62(14)		

Hydrogen bonds[b]

D–H···A	D···A/Å	H···A/Å	D–H···A/°
O(6)–H(61)···N(4c)	3.0088(18)	2.17	155
O(6)–H(62)···O(3d)	2.7018(17)	1.91	166

[a] Symmetry transformations used to generate equivalent atoms: (a) = $-x, -y, -z$; (c) = $1-x, 1-y, 1-z$; (d) = $1-x, -y, -z$. [b] A = acceptor; D = donor.

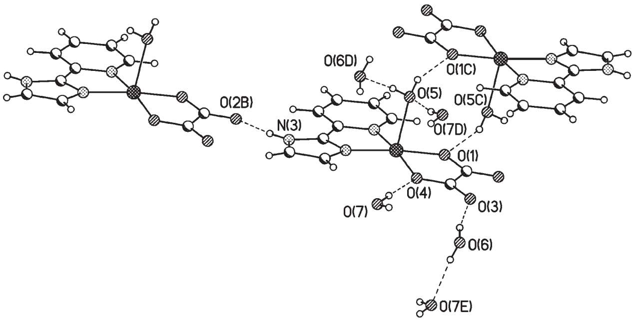


Fig. 2 A view showing the layer structure of **1** through hydrogen bonds (broken lines).

hydrogen bonds (one of these being bifurcated). Centrosymmetrically related oxalate groups and H_2bim groups in neighbouring layers partially overlap, the interplanar spacings being 3.05 (oxalate) and 3.28 (H_2bim) Å. The two shortest Cu···Cu distances occur across the hydrogen bond involving the coordinated water and oxalate in a neighbouring layer [5.0928(6) Å] and across the semi-coordinated oxalate [5.6862(5) Å]. The crystal packing of compound **4** is similar to that in compound **1**, but not identical. There is a difference in the number of crystal water molecules present and this evidently allows for a somewhat shorter distance in **4** between the layers connected through coordinated water···oxalate hydrogen bonds, but at the same time the Cu···O(oxalate) interactions are longer.

The copper atom has a distorted square pyramidal coordination geometry with two H_2bim nitrogen [Cu(1)–N(1) = 2.0127(17) Å, Cu(1)–N(2) = 1.9836(16) Å] and two oxalate oxygen [Cu(1)–O(1) = 1.9521(14) Å, Cu(1)–O(2) = 1.9651(13) Å] atoms in the equatorial positions and a water molecule [Cu(1)–O(5) = 2.2378(15) Å] in the apical position. The sixth coordination position is, as mentioned above, screened by the proximity of a neighbouring molecule and a weak semi-coordination to an oxalate oxygen may be inferred (Table 4). The values of the bite angle subtended at the copper atom by the bidentate oxalate and H_2bim ligands are 82.54(7)° and 84.36(6)°, respectively. The atoms defining the equatorial plane of copper have a significant tetrahedral distortion (maximum atomic deviation being 0.136 Å) and the metal is displaced by 0.191 Å from this plane towards the apical water. The oxalate group is essentially planar (maximum atomic deviation 0.020 Å) and makes a dihedral angle of 6.8° with the equatorial plane. The O–C bond lengths of oxalate occur in two sets [1.228(2) and 1.229(2) Å for O(3)–C(2) and O(4)–C(1), and 1.281(2) and 1.278(2) Å for O(1)–C(1) and O(2)–C(2)] as a result of its bidentate coordination to copper. The two rings of the H_2bim group form a dihedral angle of 2.8°. This value compares well with that observed in the free H_2bim molecule (1.2°)[27] and in the mononuclear nickel(II) complex *trans*-[Ni(H_2bim)$_2$(H_2O)$_2$](NO_3)$_2$ (1.18°)[28] but it is smaller than that reported for the mononuclear oxovanadium(IV) species [VOCl(H_2bim)$_2$]Cl [9.90(9) and 9.2(1)°].[29] The value of the inter-ring C(5)–C(6) bond distance of the H_2bim in **4** [1.447(3) Å] is similar to those found for the free [1.423(8) Å] and coordinated biimidazole [*ca.* 1.441(3) Å in

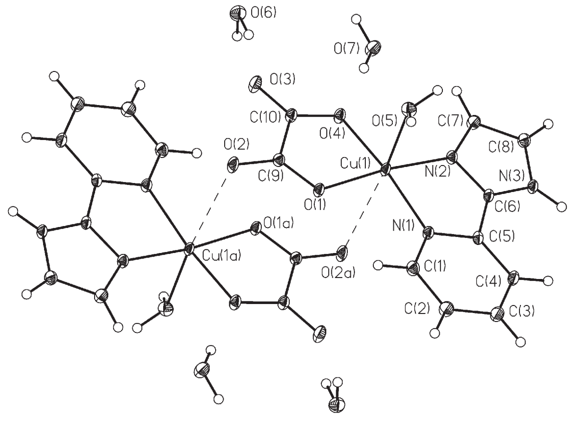


Fig. 1 Two asymmetric units in [Cu(pyim)(C_2O_4)(H_2O)]·2 H_2O (**1**), showing the atomic numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. Symmetry code: (a) $-x+1, -y+1, -z+1$.

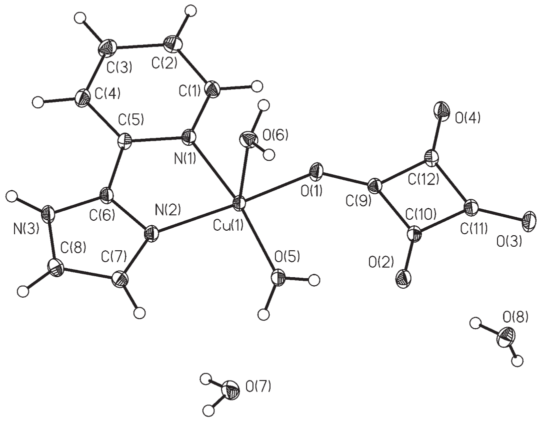


Fig. 3 The asymmetric unit in [Cu(pyim)(C_4O_4)(H_2O)$_2$]·2H_2O (**2**). Thermal ellipsoids are plotted at the 30% probability level.

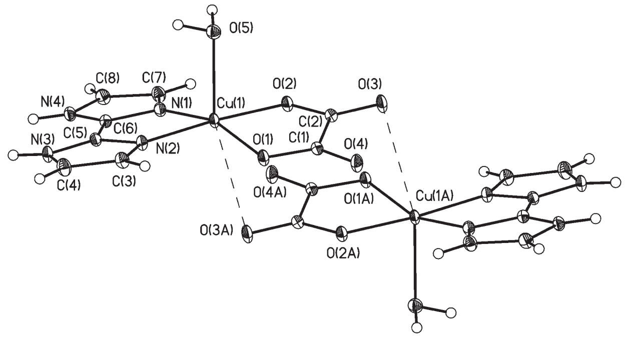


Fig. 4 Two asymmetric units in $[Cu(H_2bim)(C_2O_4)(H_2O)]\cdot H_2O$ (**4**) showing the atomic numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. Symmetry code: (a) $-x$, $-y$, $-z$.

the nickel(II) and oxovanadium(IV) complexes]. The short single C–C bond that connects the two imidazole rings, together with their near coplanarity, reveal the importance of resonance in the bonding description of this molecule.

$[Cu(bpz)(C_5O_5)(H_2O)]$ (5). The structure of **5** is built of neutral mononuclear $[Cu(bpz)(C_5O_5)(H_2O)]$ units. Centrosymmetrically related complex units are pairwise connected through weak Cu···O(croconate) interactions of 2.9568(13) Å (Fig. 6). The molecular units in the crystal are arranged in parallel layers (Fig. 7). The coordinated water molecule participates in hydrogen bonding to croconate oxygen and to pyrazine nitrogen of molecules in neighbouring layers, and thus stabilizes the layer structure (end of Table 5). Neighbouring layers are alternatingly connected through the hydrogen bonds mentioned above and through Cu···O(croconate) interactions. A pirazine ring in one layer overlaps C(12)–O(4) of a croconate group in the neighbouring level, the distances from the pyrazine plane to O and C being 3.12 and 3.17 Å, respectively. The pyrazine ring also overlaps a centrosymmetrically related pyrazine ring in the neighbouring level on the other side, the average distance between the planes of the two groups being 3.26 Å. The Cu···Cu distance across the semi-coordinated croconate is 5.7722(4) Å. The Cu···Cu distances across the coordinated water···croconate and coordinated water···pyrazine hydrogen bonds are both appreciably longer, above 7.5 Å. The shortest intermolecular metal–metal distance is 5.4768(4) Å [Cu(1)···Cu(1b), (b) $1-x$, $1-y$, $-z$] and occurs between molecules that are not directly linked through hydrogen bonds.

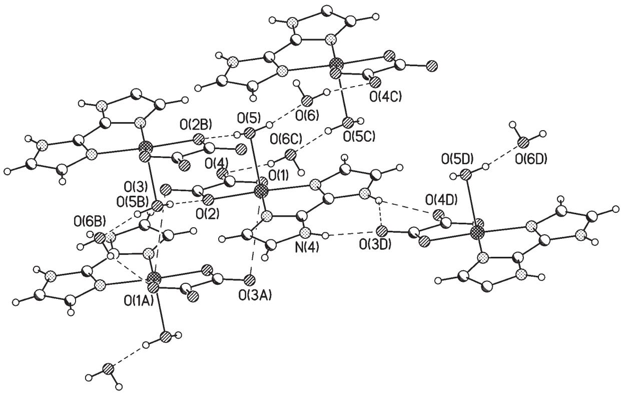


Fig. 5 A view of the layered structure of **4** through hydrogen bonding (broken lines).

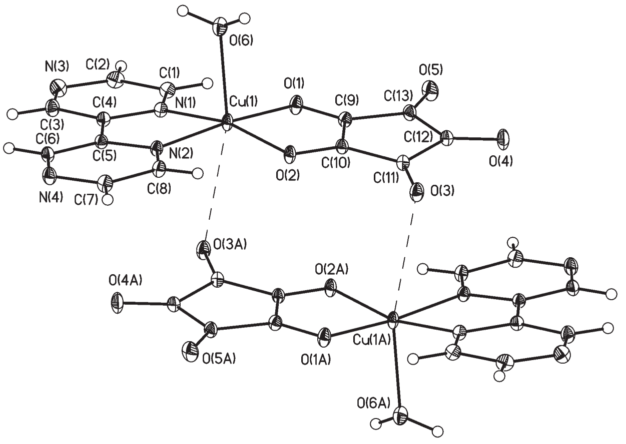


Fig. 6 Two asymmetric $[Cu(bpz)(C_5O_5)(H_2O)]$ units in **5**, showing the atomic numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. Symmetry code: (a) $-x$, $-y$, $-z$.

The copper atom has a distorted square pyramidal coordination geometry with two bpz nitrogen [Cu(1)–N(1) = 1.9891(13) Å, Cu(1)–N(2) = 1.9858(13) Å] and two croconate oxygen [Cu(1)–O(1) = 1.9705(11) Å, Cu(1)–O(2) = 1.9805(11) Å] atoms in the equatorial positions and a water molecule [Cu(1)–O(6) = 2.2192(13) Å] in the apical position. In the sixth coordination position resides, as mentioned above, a semi-coordinated croconate oxygen of a neighbouring molecule. The values of the bite angle subtended at the copper atom by the bidentate bpz and croconato ligands are 81.73(5)° and 86.71(4)°, respectively. The atoms defining the equatorial plane of copper show a small tetrahedral distortion (maximum atomic deviation being 0.055 Å) and the metal is displaced by 0.164 Å from this plane towards the apical oxygen. The croconate group is significantly puckered (maximum atomic deviation 0.126 Å), probably as a result of hydrogen bonding. The average C–C and C–O bond distances of the croconato ligand in **5** are close to the corresponding average values found in the ionic salts $(NH_4)_2C_5O_5$[30] and $K_2C_5O_5$.[31] However, a lengthening of the C–O bond distances is observed for the croconate oxygens coordinated to copper in **1** [1.2692(19) and 1.2825(18) Å for O(1)–C(9) and O(2)–C(10), respectively] with respect to the C–O bond distances in the ammonium (ave. value 1.21 Å) and potassium (mean value 1.246 Å) salts. These features, together with the shortening of the C(9)–C(10) bond [1.426(2) Å] of the croconato in **1** compared to the other C–C distances [1.471(2)–1.510(2) Å], support an enediol form for this quasi symmetrical bidentate ligand.[7c,9b] To our knowledge, complex **5** is the first structurally characterized example of a bpz complex with copper(II). Previous structural reports of metal complexes with bpz concern Ag(I),[32] Co(II),[33] Ru(II),[34] Pd(II)[35] and Pt(II).[35a–d] The bpz ligand in **5** is quasi-planar, its two pyrazine rings forming a dihedral angle of 2.9°. The bond distances and angles within each pyrazine ring compare well with those reported for the free pyrazine[36] and bpz[32b] molecules. Finally, the value of the inter-ring C(4)–C(5) bond length of bpz in **5** [1.481(2) Å] is identical to that observed in the uncoordinated bpz [1.484(3) Å][32b] and it is as expected for a single C–C bond.

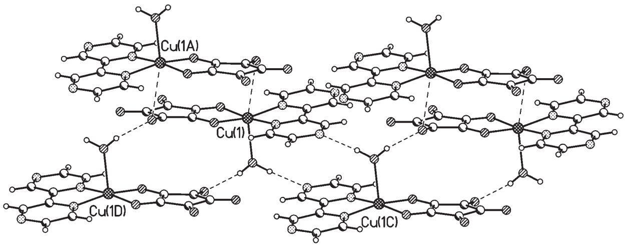


Fig. 7 A view of the layer structure of **5**.

IR characterization

The infrared spectra of **1**–**5** have in common the occurrence of a strong and broad absorption centred at *ca.* 3400 cm^{-1}, which is attributed to the OH stretching of both coordinated and crystallization water molecules involved in hydrogen bonds. Additional peaks in this high frequency region attributed to the N–H stretching of pyim [3130 cm^{-1} (**1**–**3**)] and H$_2$bim [3120 cm^{-1} (**4**)] and to the C–H stretching of pyim [multiplet between 3080 and 2650 cm^{-1}], H$_2$bim [heptuplet between 3100 and 2700 cm^{-1}] and bpz [quadruplet centred at 3035 cm^{-1}] ligands are also observed. It deserves to be noted that the N–H and C–H stretching vibrations of the free pyim and H$_2$bim molecules appear as multiplets in the region 3200–2500 cm^{-1} whereas the C–H stretching modes of the uncoordinated bpz molecules appear as a triplet at 3075, 3050 and 3015 cm^{-1}. The absorption peaks at 1710 (**1** and **4**), 1685 (**1**) and 1670 (**4**) [ν_{as}(CO)], 1425 (**1** and **4**), 1278 (**1**) and 1282 (**4**) [ν_s(CO)] and 795 (**1** and **4**) [δ(OCO)] cm^{-1} are characteristic of bidentate oxalato.[8,37–39] A very weak band at 1790 cm^{-1} and a strong absorption at 1485 cm^{-1} in the infrared spectrum of **2** are assigned to stretching vibrations of uncoordinated C=O bonds[40] and mixtures of C–C and C–O vibrations[41] of squarato. Their position and intensity agree with those observed in structurally characterized copper(II) complexes containing monodentate squarato.[7b,9c] According to the analysis of West and Niu,[42] the peaks at 1740, 1720 and 1710 cm^{-1} in the infrared spectrum of **5** are assigned to the uncoordinated carbonyl groups of the croconate ligand. The coordinated carbonyl groups of croconate in the IR spectrum of this complex are characterized by medium absorptions at 1670, 1640 and 1598 cm^{-1} whereas the vibrational modes representing mixtures of C–C and C–O stretching motions appear as a strong intensity doublet at 1510 and 1465 cm^{-1}. This set of peaks for croconate in **5** agrees with that reported for bidentate croconato in structurally characterized croconato-containing copper(II) complexes.[7c,9b] Finally, bidentate croconato is most likely present in **3** given that the absoption peaks of croconate in the IT spectrum of this complex [1740, 1720, 1715, 1670, 1640, 1598, 1505, 1470 and 1450 cm^{-1}] are very close to those observed for this ligand in complex **5**.

Magnetic properties

The thermal dependence of the $\chi_M T$ product [χ_M is the magnetic susceptibility per mol of copper(II) ions] is shown in Fig. 8. At room temperature, $\chi_M T$ for **1**–**5** is close to 0.41 cm^3 mol^{-1} K, a value that is as expected for a magnetically isolated spin doublet. Upon cooling, a Curie law behaviour is observed down to 40 K. In the lower temperature range, $\chi_M T$ smoothly increases (**1**) or decreases (**2**–**5**) to reach values of 0.427 (**1**), 0.388 (**2**), 0.371 (**3**), 0.387 (**4**) and 0.343 (**5**) cm^3 mol^{-1} K at 2.0 K. These features indicates the occurrence of weak intermolecular ferro- (**1**) and antiferromagnetic (**2**–**5**) interactions. In agreement with their crystal structures, the magnetic susceptibility data of **1**–**5** were analyzed through the simple Curie–Weiss expression [eqn. (1)]:

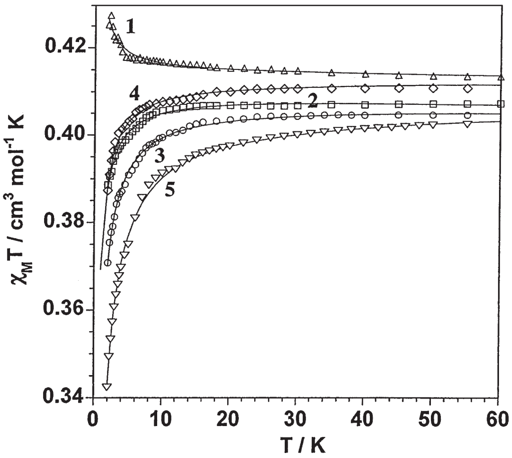


Fig. 8 Temperature dependence of the $\chi_M T$ product for **1**–**5**. Solid lines are best-fit curves through eqn. (1) (see text).

$$\chi_M = N\beta g^2/4k(T-\theta) \qquad (1)$$

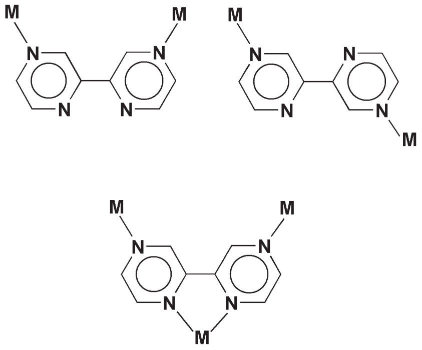
where N, β, g and T have their usual meaning and θ accounts for the intermolecular interactions. Best-fit parameters for **1**–**5** through eqn. (1) are: $g = 2.10$ (**1** and **4**), 2.09 (**2** and **3**) and 2.08 (**5**) and $\theta = +0.06$ (**1**), -0.13 (**2**), -0.20 (**3**), -0.12 (**4**) and -0.36 K (**5**) with R varying in the range $(1–3) \times 10^{-5}$ where R is the agreement factor defined as $\frac{\sum_i [(\chi_M T)_{obs(i)} - (\chi_M T)_{calc(i)}]^2}{\sum_i [(\chi_M T)_{obs(i)}]^2}$.

The weak magnetic coupling between the copper(II) ions in **1**–**5** is as expected when taking into account their mononuclear nature. The unpaired electron on each copper(II) ion in this series is defined by a $d_{x^2-y^2}$ type magnetic orbital (the x and y axes being roughly defined by copper to nitrogen bonds), which is mainly centred on the metal atom. The shortest intermolecular exchange pathway involves axially coordinated oxygen atoms on which the spin density must be very weak. Consequently, the overlap between the magnetic orbitals of adjacent copper(II) ions is predicted to be very small and a very weak antiferromagnetic coupling is expected[11] as observed in **2**–**4**. The weak ferromagnetic coupling observed in **1** is most likely due to an accidental orthogonality between the magnetic orbitals through the out-of-plane exchange pathway mentioned above. In this respect, it deserves to be noted that in a previous magnetostructural study dealing with oximato-bridged dinuclear copper(II) complexes for which the out-of-plane exchange pathway is involved, the intramolecular magnetic coupling is always weak and it is ferro- or antiferromagnetic, depending on structural parameters such as the values of the axial copper to oximato oxygen bond distance and the angle at the apical oximato oxygen.[43] Finally, either weak ferro- or antiferromagnetic interactions were reported for the copper(II) compounds of formula $M_2[Cu(C_2O_4)_2{\cdot}2H_2O$ O (M = K and NH$_4^+$)[44] and $(H_2pda)[Cu(C_2O_4)_2]$[24] in which the oxalate exhibits the same coordination mode observed in complexes **1** and **4** (bidentate in equatorial positions to one copper atom and monodentate through a very weak axial bond to a another copper atom).

Complexes 1–5 as precursors of polynuclear species

Compounds **1**–**5** have in common the presence of peripheral groups that can act as ligands (Lewis bases) towards metal ions (Lewis acids). So, free oxalate (**1** and **4**), squarate (**2**) and croconate (**3** and **5**) oxygen atoms are basic centres that can bind metal ions, affording a plethora of oxalato-, squarato- and croconato-bridged homo- and heterometallic species. The variety of structurally characterized bridging modes of these oxygen donors, together with their ability to transmit relatively large magnetic interactions between the metal ions that they bridge,[6,11–13,45–47] make this strategy very promising and interesting.

Additional coordination modes of complexes **1**–**5** are possible by using the free pyrazine nitrogen atoms of bpz (**5**) and imidazole nitrogen atoms (after deprotonation) of the H–N groups of the pym (**1**–**3**) and H$_2$bim (**4**) ligands. Previous work has illustrated the capacity of H$_2$bim in its various stages of deprotonation to create many different type of metal assemblies,[48] whereas this possibility remains unexplored for pyim. The fact that significant antiferromagnetic interactions



Scheme 1

through bischelating biimidazolate were observed in bim-bridged copper(II) and nickel(II) dinuclear compounds[49] enhances the interest in the deprotonated forms of **4** as a ligand (and also in the parent pyim) to build extended magnetic compounds. As far as the possibility of the coordinated bpz of complex **5** to act as a bridging ligand, recent work with some diamagnetic transition metal ions has provided nice examples of extended arrays of metal ions for which the bridging modes shown in Scheme 1 are observed.[32,35] As significant magnetic interactions were observed between copper(II) ions bridged by the parent planar aromatic nitrogen-containing heterocycles pyrazino[2,3-*f*][4,7]phenanthroline[50] and 1,4,5,8,9,12-hexaazatriphenylene,[51] it is expected that the use of complex **5** as a ligand towards paramagnetic metal ions would provide examples of homo- and heterometallic bpz-bridged compounds with interesting magnetic properties.

Conclusions

Five new mononuclear copper(II) complexes (**1**–**5**) were prepared and structurally characterized in 4 cases (**1**, **2**, **4** and **5**). Intermolecular interactions (in particular extensive hydrogen bonds) among these neutral units lead to three-dimensional networks in all cases. Their magnetic properties, which were investigated as a function of the temperature, reveal the occurrence of very weak intermolecular magnetic interactions, the exchange pathways through the intermolecular interactions/contacts having a very low efficiency to mediate electronic effects. A brief analysis of their potential use as ligands using the so-called building block strategy points out their possibilitites in designing extended magnetic arrays in the near future.

Acknowledgements

Thanks are due to the NFR (Research Council of Norway) and the University of Bergen for grants allowing the purchase of X-ray equipment. Financial support of the European Union through the Training and Mobility Research Program (TMR Contract ERBFMRCT-980181) and the Spanish Ministry of Science and Technology (Project BQU2001-2928) is acknowledged. One of us (C. B.) thanks the European Union for a postdoctoral grant in the foregoing TMR contract.

References

1 (*a*) L. Dubicki, C. M. Harris, E. Kokot and R. L. Martin, *Inorg. Chem.*, 1996, **5**, 93; (*b*) A. Michalowicz, J. J. Girerd and J. Goulon, *Inorg. Chem.*, 1979, **18**, 3004.
2 (*a*) C. Robl and A. Weiss, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1986, **41**, 1341; (*b*) G. M. Frankenbach, M. A. Beno, A. M. Kini, J. M. Williams, U. Welp, J. E. Thompson and M. H. Whangbo, *Inorg. Chim. Acta*, 1992, **192**, 195
3 (*a*) M. D. Glick, G. L. Downs and L. F. Dahl, *Inorg. Chem.*, 1964, **3**, 1712; (*b*) A. Cornia, A. C. Fabretti, A. Giusti, F. Ferraro and D. Gatteschi, *Inorg. Chim. Acta*, 1993, **212**, 87.
4 R. Ruiz, J. Faus, F. Lloret, M. Julve and Y. Journaux, *Coord. Chem. Rev.*, 1999, **193–195**, 1069.
5 M. Ohba and H. Okawa, *Coord. Chem. Rev.*, 2000, **198**, 313.
6 S. Decurtins, S. Ferlay, P. Pellaux, M. Gross and H. Schmalle, in *Supramolecular Engineering of Synthetic Metallic Materials*, eds., J. Veciana, C. Rovira and D. B. Amabilino, NATO ASI Ser. C, Kluwer, Dordrecht, 1999, vol. 518, p. 175 and references therein.
7 (*a*) 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; (*b*) X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775; (*c*) I. Castro, J. Sletten, J. Faus and M. Julve, *J. Chem. Soc., Dalton Trans.*, 1992, 2271.
8 A. C. Fabretti, G. Franchini, P. Zanini and M. Divaira, *Inorg. Chim. Acta*, 1985, **105**, 187.
9 (*a*) G. De Munno, M. Julve, F. Nicolò, F. Lloret, J. Faus, R. Ruiz and E. Sinn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 613; (*b*) I. Castro, J. Sletten, L. K. Glærum, F. Lloret, J. Faus and M. Julve, *J. Chem. Soc., Dalton Trans.*, 1994, 2777; (*c*) I. Castro, J. Sletten, L. K. Glærum, J. Cano, F. Lloret, J. Faus and M. Julve, *J. Chem. Soc., Dalton Trans.*, 1995, 3207.
10 G. De Munno and M. Julve, in *Metal Ligand Interactions. Structure and Reactivity*, eds. N. Russo and D. R. Salahub, Kluwer, Dordrecht, 1996, vol. 474, p. 139 and references therein.
11 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993.
12 L. A. Hall and D. J. Williams, *Adv. Inorg. Chem.*, 2001, **52**, 249 and references therein.
13 I. Castro, M. L. Calatayud, F. Lloret, J. Sletten and M. Julve, *J. Chem. Soc., Dalton Trans.*, 2002, 2397.
14 L. M. Schwartz, R. I. Gelb and J. O. Yardley, *J. Phys. Chem.*, 1975, **79**, 2246.
15 K. A. Reeder, E. V. Dose and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1071.
16 B. F. Fieselmann, D. N. Hendrickson and G. D. Stucky, *Inorg. Chem.*, 1978, **17**, 2078.
17 R. J. Crutchley and A. B. P. Lever, *Inorg. Chem.*, 1982, **21**, 2276.
18 A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London and New York, 1968.
19 *SADABS*, v. 2.03, Bruker AXS Inc., Madison, WI, USA, 2000.
20 (*a*) *SMART Data Collection Software*, v. 5.054, Bruker AXS Inc., Madison, WI, USA, 1999; (*b*) *SAINT Data Integration Software*, v. 6.02a, Bruker AXS Inc., Madison, WI, USA, 2001.
21 (*a*) SHELXS97: G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) G. M. Sheldrick, *SHELXTL/PC*, v. 6.12, Bruker AXS Inc., Madison, WI, USA, 1998; (*c*) G. M. Sheldrick, *XP*, v. 5.1, Bruker AXS Inc., Madison, WI, USA, 1998.
22 (*a*) M. A. Viswamitra, *J. Chem. Phys.*, 1962, **37**, 1408; (*b*) M. A. Viswamitra, *Z. Kristallogr., Kristallgeom., Kristallphys. Kristallchem.*, 1962, **117**, 437.
23 (*a*) A. Gleizes, F. Maury and J. Galy, *Inorg. Chem.*, 1980, **19**, 2074; (*b*) U. Geiser, B. L. Ramakrishna, R. D. Willett, F. B. Hulsbergen and J. Reedijk, *Inorg. Chem.*, 1987, **26**, 3750.
24 D. R. Bloomquist, J. J. Hansen, C. P. Landee, R. D. Willett and R. Buder, *Inorg. Chem.*, 1981, **20**, 3308.
25 F. S. Stephens, *J. Chem. Soc. A*, 1969, 2493.
26 J. Carranza, C. Brennan, J. Sletten, F. Lloret and M. Julve, *J. Chem. Soc., Dalton Trans.*, 2002, 3164.
27 D. T. Cromer, R. R. Ryan and C. B. Storm, *Acta Crystallogr., Sect. C*, 1987, **43**, 1435.
28 A. D. Mighell, C. W. Reimann and F. A. Mauer, *Acta Crystallogr., Sect. B*, 1969, **25**, 60.
29 J. Cancela, M. J. González-Garmendia and M. Quirós, *Inorg. Chim. Acta*, 2001, **313**, 156.
30 N. C. Baenziger and J. J. Hegenbarth, *J. Am. Chem. Soc.*, 1964, **86**, 3250.
31 J. D. Dunitz, P. Seiler and W. Czechtizky, *Angew. Chem., Int. Ed.*, 2001, **40**, 1779.
32 (*a*) A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 665; (*b*) A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson and C. Wilson, *J. Chem. Soc., Dalton Trans.*, 2000, 3811.
33 (*a*) D. M. Adams, A. Dei, A. L. Reinhold and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 880; (*b*) D. M. Adams, A. Dei, A. L. Reinhold and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 8221.

34 (*a*) H. Lai, D. S. Jones, D. C. Schwind and P. D. Rillema, *J. Crystallogr. Spectrosc. Res.*, 1990, **20**, 321; (*b*) A. Gerli, J. Reedijk, M. T. Lakin and A. L. Spek, *Inorg. Chem.*, 1995, **34**, 1836; (*c*) P. A. Anderson, R. F. Anderson, M. Furue, P. C. Funk, F. R. Keene, B. T. Patterson and B. D. Yeomans, *Inorg. Chem.*, 2000, **39**, 2721.

35 (*a*) R. D. Scnebeck, L. Randaccio, E. Zangrando and B. Lippert, *Angew. Chem., Int. Ed.*, 1998, **37**, 119; (*b*) R. D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem., Int. Ed.*, 1999, **38**, 168; (*c*) R. D. Schnebeck, E. Freisinger and B. Lippert, *Chem Commun.*, 1999, 675; (*d*) R. D. Schnebeck, E. Freisinger, F. Glahé and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381; (*e*) R. D. Schnebeck, E. Freisinger and B. Lippert, *Eur. J. Inorg. Chem.*, 2000, 1193.

36 P. J. Wheatley, *Acta Crystallogr.*, 1957, **10**, 182.

37 J. Fujita, A. E. Martell and K. Nakamoto, *J. Chem. Phys.*, 1962, **36**, 324.

38 I. Castro, J. Faus, M. Julve, M. C. Muñoz, W. Díaz and X. Solans, *Inorg. Chim. Acta*, 1991, **179**, 59.

39 A. Gleizes, M. Julve, M. Verdaguer, J. A. Real, J. Faus and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1992, 3209.

40 (*a*) C. G. Pierpont, L. C. Francesconi and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 3470; (*b*) F. G. Baglin and C. B. Rose, *Spectrochim. Acta, Part A*, 1970, **26**, 2293; (*c*) J. T. Reinprecht, J. G. Miller, G. C. Vogel, M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, 1980, **19**, 927.

41 M. Ito and R. West, *J. Am. Chem. Soc.*, 1963, **85**, 2580.

42 R. West and Y. H. Niu, *J. Am. Chem. Soc.*, 1963, **85**, 2586.

43 B. Cervera, R. Ruiz, F. Lloret, M. Julve, J. Cano, J. Faus, C. Bois and J. Mrozinski, *J. Chem. Soc., Dalton Trans.*, 1997, 395.

44 D. Y. Jeter and W. E. Hatfield, *Inorg. Chim. Acta*, 1972, **6**, 523.

45 (*a*) K. V. Krishnamurthy and G. M. Harris, *Chem. Rev.*, 1961, **61**, 213; (*b*) M. Julve, M. Verdaguer, O. Kahn, A. Gleizes and M. Philoche-Levisalles, *Inorg. Chem.*, 1984, **23**, 3808; (*c*) P. Román, C. Guzmán-Miralles, A. Luque, J. I. Beitia, J. Cano, F. Lloret, M. Julve, S. Alvarez, *Inorg. Chem.*, 1996, **35**, 3741; (*d*) S. Decurtins, H. W. Schmalle, R. Pelleaux, P. Fisher and A. Hauser, *Mol. Cryst. Liq. Cryst.*, 1997, **305**, 227; (*e*) J. Cano, P. Alemany, S. Alvarez, M. Verdaguer and E. Ruiz, *Chem.-Eur. J.*, 1998, **4**, 476; (*f*) R. Andrés, M. Brissard, M. Gruselle, C. Train, J. Vaissermann, B. Malézieux, J. P. Jamet and M. Verdaguer, *Inorg. Chem.*, 2001, **40**, 4633; (*g*) D. Armentano, G. de Munno, F. Lloret, M. Julve, J. Curély, A. M. Babb and J. Y. Lu, *New J. Chem.*, 2003, **27**, 161; (*h*) R. Chiozzone, R. González, C. Kremer, G. De Munno, D. Armentano, F. Lloret, M. Julve and J. Faus, *Inorg. Chem.*, 2003, **42**, 1064.

46 (*a*) X. Solans, M. Aguiló, A. Gleizes, J. Faus, M. Julve and M. Verdaguer, *Inorg. Chem.*, 1990, **29**, 775; (*b*) C. E. Xanthopoulos, M. P. Sigalas, G. A. Katsoulos, C. A. Tsipis, C. C. Hadjikostas, A. Terzis and M. Mentzafos, *Inorg. Chem.*, 1993, **32**, 3743; (*c*) I. Castro, J. Lloret, M. L. Calatayud, M. Julve, J. Cano, F. Lloret and A. Caneschi, *Inorg. Chem.*, 1995, **34**, 4903; (*d*) I. Castro, M. L. Calatayud, J. Sletten, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 1999, **287**, 173.

47 (*a*) I. Castro, J. Sletten, J. Faus, M. Julve, Y. Journaux, F. Lloret and S. Alvarez, *Inorg. Chem.*, 1992, **31**, 1889; (*b*) I. Castro, M. L. Calatayud, J. Sletten, M. Julve and F. Lloret, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2001, **4**, 235; (*c*) I. Castro, M. L. Calatayud, F. Lloret, J. Sletten and M. Julve, *J. Chem. Soc., Dalton Trans.*, 2002, 2307.

48 (*a*) M. Tadokoro and K. Nakasuji, *Coord. Chem. Rev.*, 2000, **198**, 205 and references therein; (*b*) L. Öhrström, K. Larsson, S. Borg and S. T. Norberg, *Chem. Eur. J.*, 2001, **7**, 4805; (*c*) M. tadokoro, T. Shiomi, K. Isobe and K. Nakasuji, *Inorg. Chem.*, 2001, **40**, 5476

49 M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 2622.

50 H. Grove, J. Sletten, M. Julve, F. Lloret and J. Cano, *J. Chem. Soc., Dalton Trans.*, 2001, 259.

51 H. Grove, J. Sletten, M. Julve and F. Lloret, *J. Chem. Soc., Dalton Trans.*, 2001, 1029.