Acta Chemica Scandinavica, 1998: 52: 770–777
Printed in UK all rights reserved

ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Synthesis and Crystal Structures of Two Dinuclear Copper(II) Complexes with 2,3-Bis(2-pyridyl)pyrazine as Bridging Ligand

Jorunn Sletten* and Ole Bjørsvik

Department of Chemistry, University of Bergen, N-5007 Bergen, Norway

Sletten, J. and Bjørsvik, O., 1998. Synthesis and Crystal Structures of Two Dinuclear Copper(II) Complexes with 2,3-Bis(2-pyridyl)pyrazine as Bridging Ligand. – Acta Chem. Scand. 52: 770–777. © Acta Chemica Scandinavica 1998.

Two dinuclear copper(II) complexes with 2,3-bis(2-pyridyl)pyrazine (dpp) as bridging ligand, $Cu_2(dpp)(sq)_2(H_2O)_6$ (**1**) and $[Cu_2(dpp)(cr)_2(H_2O)_3]\cdot 2H_2O$ (**2**) [dpp = 2,3-bis(2-pyridyl)pyrazine, sq = $C_4O_4^{2-}$ dianion of squaric acid, cr = $C_5O_5^{2-}$ dianion of croconic acid] have been synthesized and structurally characterized by X-ray diffraction methods. Crystals of **1** are monoclinic, space group $C2/c$, with $a = 13.687(3)$, $b = 8.169(4)$, $c = 21.619(4)$ Å, $\beta = 92.32(3)°$ and $Z = 4$; crystals of **2** are triclinic, space group $P\bar{1}$, with $a = 8.654(1)$, $b = 9.702(1)$, $c = 16.156(1)$ Å, $\alpha = 94.63(1)$, $\beta = 99.75(1)$, $\gamma = 98.93(1)°$ and $Z = 2$. In both compounds dpp exhibits the bis(chelating) coordination mode; in **1** the dpp ligand is situated on a two-fold rotation axis, while in **2** there is no such crystallographic symmetry restriction. Squarate acts as a monodentate, terminal ligand (**1**) while croconate acts as chelating ligand (**2**). Water molecules constitute the remaining ligands in both compounds. In **1** the copper atom is six coordinated and displays a distorted compressed octahedral geometry, the short bonds being formed to a pyridyl nitrogen and a squarate oxygen atom. In **2** the two crystallographically independent copper atoms display significantly different coordination geometries; Cu(1) has a distorted, elongated octahedral environment where the long bonds are formed to the pyrazine nitrogen and a croconate oxygen atom, while Cu(2) is five-coordinated, square pyramidal, with a water molecule in apical position and short equatorial bonds to both pyridyl and pyrazine nitrogen atoms and two croconate oxygen atoms. The intramolecular metal–metal separations are 6.993(2) and 6.913(1) Å in **1** and **2**, respectively. The magnetic behaviour of **1** has been investigated over the temperature range 4.2–100 K. Fitting of the magnetic susceptibility data by a simple Bleany–Bowers expression yields a value for the singlet–triplet energy gap (J) of $-1.2\ cm^{-1}$, corresponding to a very weak antiferromagnetic interaction.

Luminescent and redox-active ruthenium(II) and rhenium(I) complexes of 2,3-bis(2-pyridyl)pyrazine (hereafter shortened dpp) have been extensively studied during the last decade.[1] The X-ray structure determination of two Ru^{II}-dpp species have been reported.[2] Also, a limited number of studies have appeared on complexes between dpp and 3d transition-metal ions, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Cu^{I}.[3–8] These studies mainly describe synthesis, spectroscopic and electrochemical properties. Only two X-ray crystallographic structure determinations have been reported; one chain Cu^{II} compound with dpp as bridging ligand,[6] and one monomeric Cu^{I} complex.[8] In both of these compounds dpp coordinates to the metal through pyridyl and pyrazine nitrogen atoms forming five-membered chelate rings. In other cases complex formation with the two pyridine rings in a *cis*-conformation, giving a seven-membered chelate, has been inferred from spectroscopic evidence.[5,7] A bridging dpp ligand may propagate a magnetic interaction between metal centres. It is well known that the related 2,2′-bipyrimidine ligand very efficiently transmits a strong antiferromagnetic interaction,[9] and that pyrazine to some degree transmits such an interaction.[10]

In the present study we report the synthesis and X-ray structure determinations of two dpp-bridged dinuclear copper(II) complexes with squarate (sq) and croconate (cr), respectively, as terminal ligands. Variable-temperature magnetic susceptibility measurements of the former compound have been performed.

Experimental

Preparation of $Cu_2(dpp)(sq)_2(H_2O)_6$ (**1**). A stock solution, 0.5 mM in $Cu_2(dpp)^{2+}(aq)$, was prepared by dis-

* To whom correspondence should be addressed.

solving $Cu(NO_3)_2 \cdot 3H_2O$ and dpp (molar ratio 2:1) in 50/50 water/propanol. The same solvent was used for preparing a 0.5 mM squarate stock solution, dissolving $H_2C_4O_4$ and $LiOH \cdot H_2O$ in a molar ratio 1:2. 80 ml of the squarate solution were added to 50 ml of the Cu_2dpp solution under stirring. Slow evaporation at room temperature afforded dark brownish-red microcrystals of **1**. Crystals suitable for X-ray diffraction studies were prepared by diffusion in a U-tube through an agar gel.

Preparation of $[Cu_2(dpp)(cr)_2(H_2O)_3] \cdot 2H_2O$ (**2**). $K_2C_5O_5$ was synthesized according to a method described in the literature.[11] Attempts were made to synthesize the dinuclear croconate complex by utilizing a procedure analogous to that outlined above, and varying the dpp:cr ratio. However, a mixed product always resulted, probably due to the high stability and low solubility of the copper(II)–croconate polymer.[12] Dark moss-green, single crystals of **2** were prepared by diffusion in an H-tube utilizing water/propanol solutions.

Physical measurements. Infrared spectra were recorded with a Perkin Elmer 1310 spectrophotometer as KBr pellets in the 2000–600 cm^{-1} region. Magnetic susceptibility measurements of complex **1** were carried out in the range 4.2–100 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer equipped with a TBT continous-flow cryostat and a Bruker BE15 electromagnet operating at 1.8 T. Mercury tetrakis(thiocyanato)-cobaltate(II) was used as a susceptibility standard. A diamagnetic correction for the constituent atoms was estimated from Pascal's constants and found to be -408×10^{-6} cm^3 mol^{-1}.

Crystal structure determinations and refinements. X-Ray diffraction data of compounds **1** and **2** were collected at room temperature with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were determined from least-squares refinement of the setting angles of 25 reflections within 2θ ranges of 25–42° (**1**) and 31–44° (**2**). Totals of 2743 (**1**) and 5985 (**2**) unique reflections were recorded within $2\theta < 55°$ using the $\omega/2\theta$ scan technique. Three reference reflections monitored throughout each data collection showed no intensity loss for **1** and an average decrease of 3% for **2**. The data were corrected for Lorentz-polarization effects, and in the case of **2** for linear decay. Experimental absorption corrections based on ψ-scans of seven reflections were carried out for both compounds, minimum and maximum correction factors in F^2 being 0.7814, 0.9968 (**1**) and 0.9162, 0.9992 (**2**).[13]

The intensity statistics in both cases suggested a centrosymmetric space group, hence $C2/c$ and $P\bar{1}$ were chosen. The structures were solved by direct methods, and refined by full-matrix least-squares methods based on F^2 and including all reflections. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in difference Fourier maps and refined isotropically. The refinements converged at conventional R-values of 0.0319 (**1**) and 0.0283 (**2**), in both cases the values refer to reflections with $I > 2\sigma(I)$. A summary of the crystal data is given in Table 1; coordinates and bond distances and angles of non-hydrogen atoms are listed in Tables 2–5.

The programs utilized for structure solutions and refinements are SHELXS-86, SHELXL-94 and XPL.[14] Supplementary material contains a complete list of atom coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen-bond parameters, least-squares planes, torsional angles, and structure factor tables, and is available from the authors (J. S.) on request.

Results and discussion

Infrared spectra. The IR spectra of **1** and **2** are dominated by broad and strong bands centered around 1490 cm^{-1}, which are characteristic of salts of the $C_nO_n^{2-}$ ($n = 4$–6) ions and are attributed to vibrational modes representing mixtures of C–O and C–C stretching motions.[15] These strong features more or less obscure the bands in the 1390–1620 cm^{-1} region characteristic of pyridyl and

Table 1. Summary of crystal data and structure refinement parameters for $[Cu_2(dpp)(sq)_2(H_2O)_6]$ (**1**) and $[Cu_2(dpp)(cr)_2(H_2O)_3] \cdot 2H_2O$ (**2**).

Compound	**1**	**2**
Empirical formula	$C_{22}H_{22}Cu_2N_4O_{14}$	$C_{24}H_{20}Cu_2N_4O_{15}$
Formula weight	693.52	731.52
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	13.687(3)	8.654(1)
b/Å	8.169(2)	9.702(1)
c/Å	21.619(4)	16.156(1)
α/°	90.00	94.63(1)
β/°	92.32(3)	99.75(1)
γ/°	90.00	98.93(1)
Volume/Å^3	2415.2(9)	1312.7(2)
Z	4	2
ρ(calc)/g cm^{-3}	1.907	1.851
μ/mm^{-1}	1.85	1.71
F(000)	1408	740
Crystal size/mm	$0.55 \times 0.41 \times 0.21$	$0.52 \times 0.16 \times 0.10$
Max. 2θ/°	55	55
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan width/°	$1.00 + 0.35 \tan\theta$	$1.00 + 0.35 \tan\theta$
Refl. collected	3116	6600
Independent refl.	2743	5985
Refl. with $I > 2\sigma(I)$	2147	4482
$R1$ [$I > 2\sigma(I)$]	0.0319	0.0283
$wR2$ [$I > 2\sigma(I)$]	0.0825	0.0748
$R1$ (all data)	0.0568	0.0598
$wR2$ (all data)	0.0930	0.0823
Residual electron density/e Å^{-3}	0.498, −0.560	0.435, −0.458

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where a is 0.0329 (**1**) and 0.0463 (**2**), b is 8.30 (**1**) and 0.25 (**2**), $P = 0.3333 \times$ [(maximum of 0 or F_o^2) + $2F_c^2$].

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non-hydrogen atoms for $[Cu_2(dpp)(sq)_2(H_2O)_6]$ (**1**).

	X/a	*Y/b*	*Z/c*	*U*(eq)[a]
Cu	1675(1)	96(1)	6321(1)	24(1)
O(30)	2175(2)	2218(2)	6592(1)	36(1)
O(31)	3515(2)	2622(3)	5393(1)	35(1)
O(32)	3779(2)	6528(3)	5758(1)	45(1)
O(33)	2588(2)	5844(2)	6995(1)	38(1)
O(50)	2666(2)	−425(4)	5585(1)	43(1)
O(60)	2770(2)	−884(3)	6967(1)	38(1)
O(70)	756(2)	1116(4)	5625(2)	59(1)
N(1)	958(2)	−2055(3)	6303(1)	24(1)
N(2)	569(2)	404(3)	7004(1)	26(1)
C(1)	1037(2)	−3133(4)	5845(1)	29(1)
C(2)	542(2)	−4612(4)	5832(2)	31(1)
C(3)	−91(2)	−4929(4)	6289(2)	31(1)
C(4)	−204(2)	−3801(3)	6762(1)	26(1)
C(5)	349(2)	−2384(3)	6764(1)	22(1)
C(6)	234(2)	−1033(3)	7215(1)	22(1)
C(7)	334(2)	1804(3)	7271(2)	31(1)
C(30)	2657(2)	3342(3)	6348(1)	24(1)
C(31)	3243(2)	3557(3)	5809(1)	26(1)
C(32)	3381(2)	5308(3)	5981(2)	28(1)
C(33)	2826(2)	5020(3)	6539(1)	26(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

pyrazine ring vibrations.[16,17] It is therefore not possible to see whether these bands are shifted to higher wavenumbers upon complex formation. Weaker bands around 800 cm^{-1} and in the region 1200–1000 cm^{-1} are consistent with bands found in the free ligand.[16,17]

Structure of $[Cu_2(dpp)(sq)_2(H_2O)_6]$ (**1**). The molecular unit is shown in Fig. 1, and bond distances and angles are listed in Table 4. The bridging dpp ligand is situated on a two-fold axis. The copper atom is six-coordinated with a distorted compressed octahedral geometry, suggesting the presence of an inverse pseudo-Jahn–Teller distortion. The short, axial bonds are found between copper and the pyridyl nitrogen and a squarate oxygen [Cu–N(1) = 2.012(2) Å, Cu–O(30) = 1.945(2) Å], while the longer equatorial bonds are formed between copper and the pyrazine nitrogen and the three coordinated water molecules [Cu–N(2) = 2.173(3) Å and Cu–O 2.095(3)–2.175(3) Å]. The equatorial plane has a very slight tetrahedral distortion, and the copper atom is displaced from the plane by 0.033 Å towards O(30). Squarate occurs as a monodentate ligand, but forms in addition an intramolecular hydrogen bond to one of the coordinated water molecules, O(50). The squarate moiety is approximately planar, the mean squarate plane making a dihedral angle of 17.1° with the N(1),N(2),O(30),O(50) plane. The pyridyl rings of the dpp ligand are approximately planar and are rotated and bent around the C(5)–C(6) bond to form dihedral angles of 26.6° with the pyrazine mean plane and 53.1° with each other. The N(1)–C(5)–C(6)–N(2) and C(5)–C(6)–C(6a)–C(5a) torsional angles are 15.1 and 31.0°, respectively. The pyrazine ring is appreciably puckered, the maximum individual atomic deviation from the mean plane being 0.097 Å. The copper atom deviates by 0.371 Å from the mean pyrazine plane. The dihedral angle between the mean pyrazine plane and the equatorial plane of copper is 66.3°. The Cu···Cu distance across the dpp bridge is 6.993(2) Å.

The molecules are laced together by hydrogen bonds, the three water molecules form five intermolecular hydrogen bonds to uncoordinated squarate oxygen atoms. The shortest intermolecular Cu···Cu distance is 6.843(1) Å

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non-hydrogen atoms for $[Cu_2(dpp)(cr)_2(H_2O)_3] \cdot 2H_2O$ (**2**).

	X/a	*Y/b*	*Z/c*	*U*(eq)[a]
Cu(1)	71(1)	3200(1)	1145(1)	23(1)
Cu(2)	6474(1)	1711(1)	3902(1)	24(1)
O(20)	−1149(2)	1439(2)	474(1)	33(1)
O(21)	−1725(2)	4162(2)	170(1)	33(1)
O(22)	−4695(3)	3902(2)	−1104(2)	61(1)
O(23)	−5849(3)	915(3)	−1605(2)	64(1)
O(24)	−3651(3)	−657(2)	−592(2)	56(1)
O(30)	5618(2)	−239(2)	4069(1)	29(1)
O(31)	8188(2)	1652(2)	4861(1)	26(1)
O(32)	10041(2)	373(2)	6275(1)	31(1)
O(33)	8604(2)	−2615(2)	6066(1)	36(1)
O(34)	5468(2)	−2909(2)	4938(1)	44(1)
O(50)	−1564(2)	3216(2)	1890(1)	35(1)
O(60)	1685(2)	3313(2)	401(1)	32(1)
O(70)	7833(2)	1040(2)	2846(1)	31(1)
O(80)	−4600(2)	3284(3)	1232(1)	44(1)
O(90)	1195(3)	1331(2)	−1006(2)	46(1)
N(1)	1257(2)	4955(2)	1877(1)	23(1)
N(2)	1828(2)	2363(2)	2116(1)	23(1)
N(3)	4569(2)	1862(2)	3054(1)	22(1)
N(4)	6975(2)	3726(2)	3788(1)	24(1)
C(1)	689(3)	6158(2)	1852(2)	29(1)
C(2)	1200(3)	7255(3)	2484(2)	33(1)
C(3)	2281(3)	7088(3)	3180(2)	33(1)
C(4)	2867(3)	5850(3)	3225(2)	28(1)
C(5)	2367(2)	4814(2)	2546(1)	21(1)
C(6)	2908(3)	3431(2)	2536(1)	20(1)
C(7)	2103(3)	1054(2)	2163(2)	27(1)
C(8)	3432(3)	795(2)	2678(2)	27(1)
C(9)	4391(2)	3195(2)	2946(1)	20(1)
C(10)	5870(2)	4235(2)	3261(1)	21(1)
C(11)	6201(3)	5548(2)	2994(2)	27(1)
C(12)	7644(3)	6397(3)	3334(2)	32(1)
C(13)	8731(3)	5907(3)	3905(2)	36(1)
C(14)	8378(3)	4555(3)	4099(2)	32(1)
C(20)	−2324(3)	1679(2)	−54(2)	28(1)
C(21)	−2611(3)	3067(2)	−201(2)	28(1)
C(22)	−4069(3)	2947(3)	−830(2)	36(1)
C(23)	−4641(3)	1416(3)	−1078(2)	39(1)
C(24)	−3556(3)	626(3)	−580(2)	36(1)
C(30)	6596(3)	−583(2)	4667(1)	23(1)
C(31)	7947(3)	404(2)	5080(1)	21(1)
C(32)	8866(3)	−206(2)	5743(1)	22(1)
C(33)	8096(3)	−1716(2)	5675(1)	24(1)
C(34)	6547(3)	−1901(2)	5051(1)	26(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond lengths (in Å) and angles (in °) for $[Cu_2(dpp)(sq)_2(H_2O)_6]$ (**1**).

Copper coordination sphere			
Cu–O(30)	1.945(2)	Cu–O(70)	2.095(3)
Cu–O(50)	2.175(3)	Cu–N(1)	2.012(2)
Cu–O(60)	2.160(3)	Cu–N(2)	2.173(3)
O(30)–Cu–O(50)	99.97(10)	O(50)–Cu–N(2)	173.18(10)
O(30)–Cu–O(60)	84.78(10)	O(60)–Cu–O(70)	172.96(11)
O(30)–Cu–O(70)	93.20(13)	O(60)–Cu–N(1)	90.81(10)
O(30)–Cu–N(1)	161.69(10)	O(60)–Cu–N(2)	95.03(10)
O(30)–Cu–N(2)	86.45(9)	O(70)–Cu–N(1)	93.15(12)
O(50)–Cu–O(60)	87.92(11)	O(70)–Cu–N(2)	91.57(11)
O(50)–Cu–O(70)	85.79(12)	N(1)–Cu–N(2)	76.22(9)
O(50)–Cu–N(1)	97.62(10)		
Squarate group			
O(30)–C(30)	1.259(3)	C(30)–C(33)	1.447(4)
O(31)–C(31)	1.247(4)	C(30)–C(31)	1.453(4)
O(32)–C(32)	1.242(4)	C(31)–C(32)	1.489(4)
O(33)–C(33)	1.249(4)	C(32)–C(33)	1.470(4)
C(30)-O(30)–Cu	135.0(2)	O(32)–C(32)–C(33)	134.2(3)
O(30)–C(30)–C(33)	130.7(3)	O(32)–C(32)–C(31)	136.6(3)
O(30)–C(30)–C(31)	137.8(3)	C(33)–C(32)–C(31)	89.3(2)
C(33)–C(30)–C(31)	91.5(2)	O(33)–C(33)–C(30)	133.8(3)
O(31)–C(31)–C(30)	134.0(3)	O(33)–C(33)–C(32)	136.2(3)
O(31)–C(31)–C(32)	136.9(3)	C(30)–C(33)–C(32)	90.0(2)
C(30)–C(31)–C(32)	89.0(2)		
Bridging 2,3-bis(2-pyridyl)pyrazine			
N(1)–C(1)	1.332(4)	C(4)–C(3)	1.390(4)
N(1)–C(5)	1.352(4)	C(5)–C(4)	1.382(4)
N(2)–C(6)	1.347(3)	C(6)–C(5)	1.487(4)
N(2)–C(7)	1.326(4)	C(6)–C(6a)	1.410(5)
C(2)–C(1)	1.385(4)	C(7)–C(7a)	1.374(7)
C(3)–C(2)	1.365(5)		
C(1)–N(1)–Cu	122.5(2)	C(5)–C(4)–C(3)	118.7(3)
C(1)–N(1)–C(5)	119.1(2)	N(1)–C(5)–C(4)	121.3(3)
C(5)–N(1)–Cu	118.3(2)	N(1)–C(5)–C(6)	114.9(2)
C(6)–N(2)–Cu	112.7(2)	C(4)–C(5)–C(6)	123.4(3)
C(7)–N(2)–C(6)	120.8(3)	N(2)–C(6)–C(6a)	117.9(2)
C(7)–N(2)–Cu	125.7(2)	N(2)–C(6)–C(5)	112.2(2)
N(1)–C(1)–C(2)	122.6(3)	C(6a)–C(6)–C(5)	129.6(2)
C(3)–C(2)–C(1)	118.3(3)	N(2)–C(7)–C(7a)	119.6(2)
C(2)–C(3)–C(4)	120.0(3)		

Symmetry transformations used to generate equivalent atoms: (a) $-x, y, -z+3/2$.

and occurs between molecules related by a screw axis translation. The crystalline packing is illustrated in Fig. 2.

Structure of $[Cu_2(dpp)(cr)_2(H_2O)_3]\cdot 2H_2O$ (**2**). The neutral, dinuclear dpp-bridged complex unit is shown in Fig. 3, bond distances and angles are listed in Table 5. The two copper atoms are crystallographically independent and have significantly different coordination geometries. Cu(1) is six-coordinated with a distorted, elongated octahedral geometry. The longer, axial bonds occur between copper and the pyrazine nitrogen and a croconate oxygen [Cu(1)–N(2) = 2.283(2) Å, Cu(1)–O(21) = 2.372(2) Å], while the short, equatorial bonds are formed between copper and the pyridyl nitrogen, a croconate oxygen, and two coordinated water molecules [Cu(1)–N(1) = 2.017(2) Å and Cu(1)–O 1.989(2)–2.007(2) Å]. The equatorial plane has a very slight tetrahedral distortion, and the copper atom is displaced from the plane by 0.012 Å towards N(2). Cu(2) is five-coordinated, elongated square pyramidal, with two croconate oxygen atoms, one pyridyl and one pyrazine nitrogen atom in the equatorial positions [Cu(2)–O 1.967(2)–1.979(2) Å, Cu(2)–N 1.966(2)–1.989(2) Å], and with a water in apical position [Cu(2)–O(70) = 2.336(2) Å]. The sixth position is screened by the proximity of the croconate group of a centrosymmetrically related molecule [Cu(2)–O(34)($1-x, -y, 1-z$) = 3.002(2) Å]. The equatorial ligand atoms are practically coplanar, and the copper atom is displaced by 0.146 Å towards the apical water molecule. The dihedral angle between the equatorial planes of the two copper atoms is 86.2°. Both of the croconate ions coordinate in the bidentate, chelating mode, but while the one bonded to Cu(2) is symmetric-

Table 5. Bond lengths (in Å) and angles (in °) for $[Cu_2(dpp)(cr)_2(H_2O)_3]\cdot 2H_2O$ (**2**).

Copper coordination spheres			
Cu(1)–O(20)	1.991(2)	Cu(2)–O(30)	1.979(2)
Cu(1)–O(21)	2.372(2)	Cu(2)–O(31)	1.967(2)
Cu(1)–O(50)	2.007(2)	Cu(2)–O(70)	2.336(2)
Cu(1)–O(60)	1.989(2)	Cu(2)–N(3)	1.989(2)
Cu(1)–N(1)	2.017(2)	Cu(2)–N(4)	1.966(2)
Cu(1)–N(2)	2.283(2)		
O(60)–Cu(1)–O(20)	91.21(8)	N(1)–Cu(1)–O(21)	100.80(7)
O(60)–Cu(1)–O(50)	176.35(8)	N(2)–Cu(1)–O(21)	177.67(6)
O(20)–Cu(1)–O(50)	91.26(8)	N(4)–Cu(2)–O(31)	97.60(7)
O(60)–Cu(1)–N(1)	91.49(8)	N(4)–Cu(2)–O(30)	169.94(8)
O(20)–Cu(1)–N(1)	177.03(8)	O(31)–Cu(2)–O(30)	86.71(6)
O(50)–Cu(1)–N(1)	86.10(8)	N(4)–Cu(2)–N(3)	81.45(8)
O(60)–Cu(1)–N(2)	88.14(7)	O(31)–Cu(2)–N(3)	171.83(7)
O(20)–Cu(1)–N(2)	101.95(7)	O(30)–Cu(2)–N(3)	92.99(7)
O(50)–Cu(1)–N(2)	93.98(8)	N(4)–Cu(2)–O(70)	94.27(8)
N(1)–Cu(1)–N(2)	76.90(7)	O(31)–Cu(2)–O(70)	96.37(7)
O(60)–Cu(1)–O(21)	92.30(7)	O(30)–Cu(2)–O(70)	94.28(7)
O(20)–Cu(1)–O(21)	80.33(6)	N(3)–Cu(2)–O(70)	91.80(8)
O(50)–Cu(1)–O(21)	85.47(8)		
Croconate groups			
O(20)–C(20)	1.275(3)	C(20)–C(21)	1.438(3)
O(21)–C(21)	1.250(3)	C(20)–C(24)	1.455(3)
O(22)–C(22)	1.220(3)	C(21)–C(22)	1.462(3)
O(23)–C(23)	1.236(3)	C(22)–C(23)	1.490(4)
O(24)–C(24)	1.232(3)	C(23)–C(24)	1.478(4)
O(30)–C(30)	1.274(3)	C(30)–C(31)	1.419(3)
O(31)–C(31)	1.284(3)	C(30)–C(34)	1.464(3)
O(32)–C(32)	1.240(3)	C(31)–C(32)	1.447(3)
O(33)–C(33)	1.212(3)	C(32)–C(33)	1.499(3)
O(34)–C(34)	1.222(3)	C(33)–C(34)	1.511(3)
C(20)–O(20)–Cu(1)	111.52(14)	O(24)–C(24)–C(23)	128.1(3)
C(21)–O(21)–Cu(1)	100.6(2)	C(20)–C(24)–C(23)	105.8(2)
C(30)–O(30)–Cu(2)	106.44(14)	O(30)–C(30)–C(31)	120.0(2)
C(31)–O(31)–Cu(2)	106.15(13)	O(30)–C(30)–C(34)	129.7(2)
O(20)–C(20)–C(21)	123.5(2)	C(31)–C(30)–C(34)	110.3(2)
O(20)–C(20)–C(24)	126.1(2)	O(31)–C(31)–C(30)	120.5(2)
C(21)–C(20)–C(24)	110.4(2)	O(31)–C(31)–C(32)	129.1(2)
O(21)–C(21)–C(20)	123.4(2)	C(30)–C(31)–C(32)	110.3(2)
O(21)–C(21)–C(22)	128.0(2)	O(32)–C(32)–C(31)	128.3(2)
C(20)–C(21)–C(22)	108.7(2)	O(32)–C(32)–C(33)	125.7(2)
O(22)–C(22)–C(21)	127.3(3)	C(31)–C(32)–C(33)	105.9(2)
O(22)–C(22)–C(23)	126.5(3)	O(33)–C(33)–C(32)	126.1(2)
C(21)–C(22)–C(23)	106.2(2)	O(33)–C(33)–C(34)	126.2(2)
O(23)–C(23)–C(24)	126.7(3)	C(32)–C(33)–C(34)	107.6(2)
O(23)–C(23)–C(22)	124.4(3)	O(34)–C(34)–C(30)	128.5(2)
C(24)–C(23)–C(22)	108.8(2)	O(34)–C(34)–C(33)	126.5(2)
O(24)–C(24)–C(20)	126.0(3)	C(30)–C(34)–C(33)	104.9(2)

Continued

ally coordinated in two equatorial positions, the one bonded to Cu(1) is asymmetrically coordinated forming one short and one long Cu–O bond. The croconate moiety bonded to Cu(1) is approximately planar, while the group bonded to Cu(2) is significantly puckered, probably as a result of its weak interaction with Cu(2) of a centrosymmetrically related molecule. The dihedral angle between the Cu(1)-bonded croconate and the N(1),N(2),O(20),O(21) plane is 8.8°, and the angle between the Cu(2)-bonded croconate and the equatorial plane of Cu(2) is 1.7°. The pyridyl rings of the dpp ligand form dihedral angles of 30.6° and 22.1°, respectively, with the pyrazine plane and 46.9° with each other. The torsional angles N(1)–C(5)–C(6)–N(2) and N(4)–C(10)–C(9)–N(3) are 27.9 and 16.5°, respectively, and the C(5)–C(6)–C(9)–C(10) angle is 18.4°. The pyrazine ring is somewhat puckered, the maximum individual atomic deviation from the mean plane being 0.070 Å. The copper atoms deviate by 0.561 and 0.315 Å to opposite sides of the mean pyrazine plane. Dihedral angles between the equatorial planes of the two copper atoms and the pyrazine group are 75.0 and 20.2°, respectively. The intramolecular Cu(1)···Cu(2) distance is 6.913(1) Å.

Table 5. (Continued).

Bridging 2,3-bis(2-pyridyl)pyrazine group			
N(1)–C(1)	1.336(3)	C(3)–C(4)	1.377(4)
N(1)–C(5)	1.350(3)	C(4)–C(5)	1.388(3)
N(2)–C(7)	1.333(3)	C(5)–C(6)	1.488(3)
N(2)–C(6)	1.334(3)	C(6)–C(9)	1.402(3)
N(3)–C(8)	1.338(3)	C(7)–C(8)	1.370(3)
N(3)–C(9)	1.347(3)	C(9)–C(10)	1.487(3)
N(4)–C(14)	1.341(3)	C(10)–C(11)	1.382(3)
N(4)–C(10)	1.349(3)	C(11)–C(12)	1.384(3)
C(1)–C(2)	1.377(4)	C(12)–C(13)	1.371(4)
C(2)–C(3)	1.374(4)	C(13)–C(14)	1.374(4)
C(1)–N(1)–C(5)	118.7(2)	N(1)–C(5)–C(6)	115.3(2)
C(1)–N(1)–Cu(1)	120.7(2)	C(4)–C(5)–C(6)	122.5(2)
C(5)–N(1)–Cu(1)	118.13(14)	N(2)–C(6)–C(9)	120.3(2)
C(7)–N(2)–C(6)	119.4(2)	N(2)–C(6)–C(5)	114.4(2)
C(7)–N(2)–Cu(1)	129.2(2)	C(9)–C(6)–C(5)	125.3(2)
C(6)–N(2)–Cu(1)	109.32(14)	N(2)–C(7)–C(8)	120.6(2)
C(8)–N(3)–C(9)	120.1(2)	N(3)–C(8)–C(7)	120.0(2)
C(8)–N(3)–Cu(2)	125.7(2)	N(3)–C(9)–C(6)	118.1(2)
C(9)–N(3)–Cu(2)	113.72(14)	N(3)–C(9)–C(10)	113.5(2)
C(14)–N(4)–C(10)	118.9(2)	C(6)–C(9)–C(10)	128.4(2)
C(14)–N(4)–Cu(2)	125.1(2)	N(4)–C(10)–C(11)	121.2(2)
C(10)–N(4)–Cu(2)	115.40(14)	N(4)–C(10)–C(9)	113.2(2)
N(1)–C(1)–C(2)	122.2(2)	C(11)–C(10)–C(9)	125.2(2)
C(3)–C(2)–C(1)	119.0(2)	C(10)–C(11)–C(12)	118.9(2)
C(2)–C(3)–C(4)	119.8(2)	C(13)–C(12)–C(11)	119.6(2)
C(3)–C(4)–C(5)	118.2(2)	C(12)–C(13)–C(14)	118.7(2)
N(1)–C(5)–C(4)	121.9(2)	N(4)–C(14)–C(13)	122.4(2)

Hydrogen bonds between water molecules and between water and croconate connect the molecular units. The croconate group bonded to Cu(1) participates in six hydrogen bonds, while the one bonded to Cu(2) only participates in one such bond. This difference is related to the fact that there is a weak interaction between the latter croconate ion and a centrosymmetrically related Cu(2). The shortest intermolecular metal–metal distances are $Cu(1)\cdots Cu(1)(-x, 1-y, -z)=5.289(1)$ Å, $Cu(2)\cdots Cu(2)(1-x, -y, 1-z)=5.698(1)$ Å, $Cu(1)\cdots Cu(2)(x-1, y, z)=5.995(1)$ Å. The crystal packing is illustrated in Fig. 4.

Comparison of selected related structures. To our knowledge only one other copper(II)-dpp complex has been fully structurally characterized, the chain compound $[Cu(dpp)(H_2O)]_x$[6] It is worthwhile to notice that an inverse pseudo-Jahn–Teller distortion, with short, axial bonds to pyridyl nitrogen atoms and long Cu–N(pyrazine) bonds was observed in this structure, just as in the present compound **1**. Although Cu(1) in compound **2** displays the much more common elongated octhedral environment, also in this case the copper–N(pyrazine) bonds are the long ones. In view of the fact that the pyrazine group has a weaker σ-donor strength than the pyridine group,[18] this result may not be surprising. However, the occurrence of short Cu–N bonds both to pyridyl and pyrazine around Cu(2) in compound **2** shows that this coordination mode is also possible for the dpp ligand. Copper(II) complexes of the parent

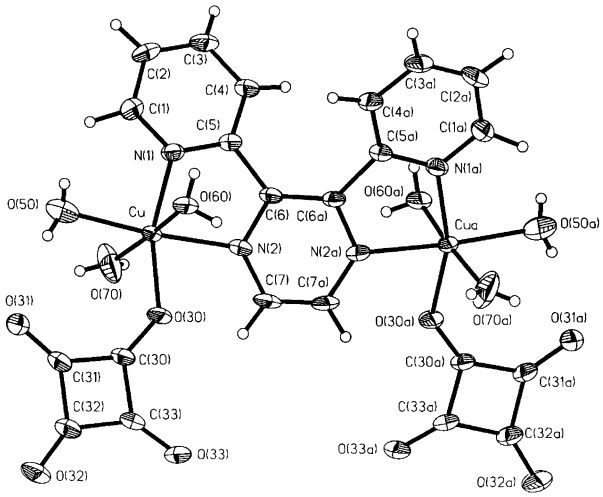

Fig. 1. Molecular unit of $[Cu_2(dpp)(sq)_2(H_2O)_6]$ (**1**). Thermal ellipsoids are plotted at the 50% probability level.

pyrazine ligand also show a wide variation of Cu–N bond lengths, from 1.98–2.53 Å.[10a,b] In a mononuclear copper(I)–dpp complex, with a distorted tetrahedral metal environment, the Cu–N(pyrazine) bond is the longer one, although in this case the difference in bond lengths is much smaller.[8] A dinuclear copper(I) complex with the related 2,3-bis(2-pyridyl)quinoxaline as bridging ligand displays Cu–N(pyridyl) and Cu–N(pyrazine) bonds of comparable lengths, within the limit of error.[19]

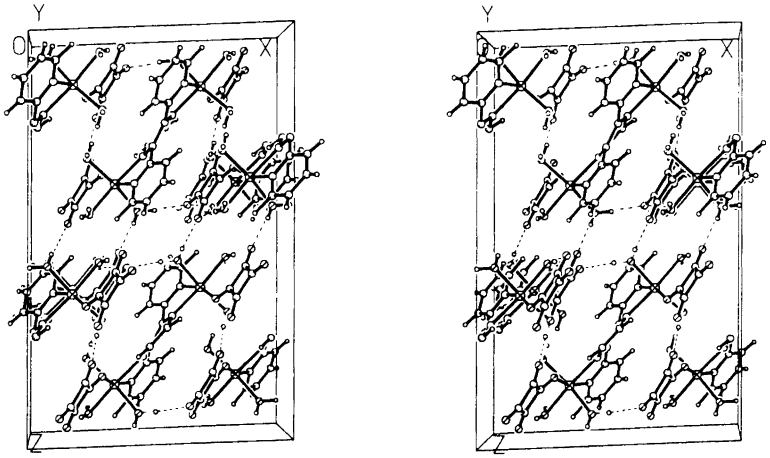

Fig. 2. Crystal packing of $[Cu_2(dpp)(sq)_2(H_2O)_6]$ (**1**).

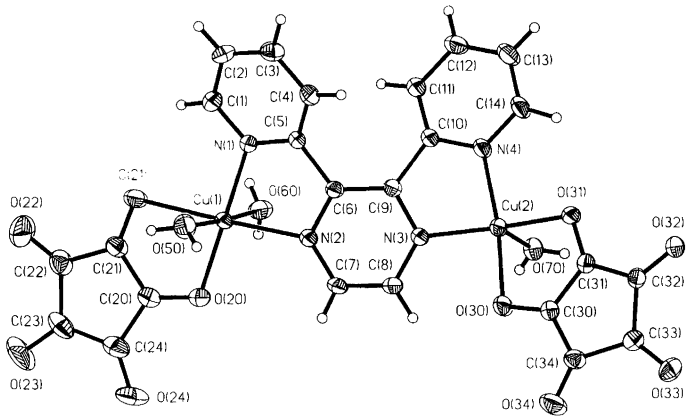

Fig. 3. Molecular unit of $[Cu_2(dpp)(cr)_2(H_2O)_3]\cdot 2H_2O$ (**2**). Thermal ellipsoids are plotted at the 50% probability level.

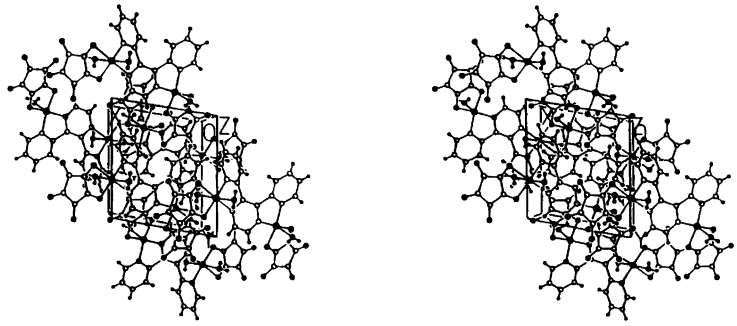

Fig. 4. Crystal packing of $[Cu_2(dpp)(cr)_2(H_2O)_3]\cdot 2H_2O$ (**2**).

The dpp ligands in both of the present complexes are appreciably distorted, as reflected in the torsional and dihedral angles listed above. On the contrary, the free ligand shows a surprisingly small distortion, the pyrazine ring being planar within 0.007 Å and the torsional angle corresponding to C(5)–C(6)–C(9)–C(10) being only 5.4°.[20] It is to be noted that in the solid state free ligand the pyridine nitrogen atoms are rotated towards the centre, while in the complexes both of the pyridine rings have been rotated to accomodate formation of five-membered chelate rings. In case of the related ligands, 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline and 2,3-bis(2-pyridyl)quinoxaline, it has been demonstrated that complex formation to copper(II) may also take place with the two pyridine rings in a *cis*-conformation giving a seven-membered ring.[7,21] For the latter of these ligands seven- and five-membered chelate rings are present in the same complex. The seven-membered chelate ring has also been inferred from spectroscopic evidence in the $Cu(dpp)(hfacac)_2$ complex [hfacac = hexafluoro-acetylacetonate ion][7] and in the corresponding Ni^{II} complex,[5] but presently there are no crystallographic data

available which demonstrate the formation of a seven-membered chelate ring for dpp.

The terminal squarate and croconate ligands in **1** and **2** have bond lengths and angles in good agreement with those found in the analogous bipyrimidine bridged complexes.[9b,22] C–O bonds to the oxygen atoms involved in coordination are significantly longer than the other bonds, this elongation being most pronounced for croconate. In the case of the asymmetrically coordinated croconate the difference in Cu–O bond strength is also reflected in the corresponding C–O bond lengths.

Magnetic properties of **1**. The thermal dependence of $\chi_M T$ (χ_M being the molar magnetic susceptibility) in the temperature range 4.2–100 K has been investigated. The value of $\chi_M T$ at 100 K, 0.83 $cm^3\ mol^{-1}\ K$, corresponds approximately to what is expected for two non-interacting copper(II) centres. The value starts dropping at 20 K and at 4.2 K it is down to 0.75 $cm^3\ mol^{-1}\ K$. Fitting the experimental data to the simple Bleany–Bowers expression for a dinuclear copper(II) complex,[23] $\chi_T = (2N\beta^2g^2)(kT)^{-1}\ [3+\exp(-J/kT)]^{-1}$, where J expresses the intramolecular exchange interaction, $H=-JS_1S_2$, and N, g, and T have their usual meaning, leads to a J value of $-1.2\ cm^{-1}$ ($g=2.10$, $R'=4.6\times10^{-5}$, where R' is defined as $\Sigma_i[(\chi_M)_{obs}T(i)-(\chi_M)_{calc}T(i)]^2/\Sigma_i[(\chi_M)_{obs}T(i)]^2$), indicating a weak antiferromagnetic coupling. Taking into account the unfavourable orientation of the magnetic orbital of copper, this result is not surprising. In the $[Cu(pyrazine)(NO_3)_2]_n$ complex a J-value of $-7.4\ cm^{-1}$ has been observed.[10a] In this case the Cu–N(pyrazine) bond length is short (1.98 Å), and although the relative orientation of the magnetic orbital and the pyrazine plane is not optimal, this allows for an appreciably larger interaction than in our compound **1**. The relative orientation of the magnetic orbitals on the two independent copper atoms in **2** is such that no significant interaction is to be expected. However, the fact that the orientaton of the magnetic orbital, $d(x^2-y^2)$, on Cu(2) in compound **2** is favourably oriented and that a short Cu–N(pyrazine) bond is present, suggests that it may be possible to obtain a dinuclear copper complex of dpp where the geometric conditions for more pronounced magnetic interaction are fulfilled.

Acknowledgement. Thanks are due to Professor Francesc Lloret, Department of Inorganic Chemistry, University of Valencia for performing the temperature-dependent magnetic susceptibility measurements.

References

1. (a) Roffia, S., Marcaccio, M., Paradisi, C., Paolucci, F., Balzani, V., Denti, G., Serroni, S. and Campagna, S. *Inorg. Chem. 32* (1993) 3003; (b) Yoblinski, B. J., Stathis, M. and Guarr, T. F. *Inorg. Chem. 31* (1992) 5; (c) Baiano, J. A. and Murphy, W. R. *Inorg. Chem. 30* (1991) 4594, and references therein.
2. Yam, V. W-W., Lee, V. W-M. and Cheung, K-K. *J. Chem. Soc., Chem. Commun.* (1994) 2075.
3. Brewer, K. J., Murphy, R. and Petersen, J. D. *Inorg. Chem. 26* (1987) 3376.
4. Escuer, A., Vicente, R., Comas, T., Ribas, J., Gomez, M. Solans, X., Gatteschi, D. and Zanchini, C. *Inorg. Chim. Acta 181* (1991) 51.
5. Escuer, A., Vicente, R., Comas, T., Ribas, J., Gomez, M. and Solans, X. *Inorg. Chim. Acta 177* (1990) 161.
6. Morgan, L. W., Goodwin, K. V., Pennington, W. T. and Petersen, J. D. *Inorg. Chem. 31* (1992) 1103.
7. Escuer, A., Comas, T., Ribas, J., Vicente, R. Solans, X., Zanchini, C. and Gatteschi, D. *Inorg. Chim. Acta 162* (1989) 97.
8. Brooks, K. T., Finnen, D. C., Kirchhoff, J. R. and Pinkerton, A. A. *Acta Crystallogr., Sect. C 50* (1994) 1696.
9. (a) De Munno, G. and Julve, M. in Russo, N. and Salahub, D. R., eds. *Metal–Ligand Interactions, Structure and Reactivity*, NATO-ASI Series, Vol. 474, Kluwer, Dordrecht, 1996, p. 139; (b) Castro, I., Sletten, J., Glærum, L. K., Cano, J., Lloret, F., Faus, J. and Julve, M. *J. Chem. Soc., Dalton Trans.* (1995) 3207.
10. (a) Richardson, H. W. and Hatfield, W. E. *J. Am. Chem. Soc. 98* (1976) 835; (b) Richardson, H. W., Wasson, J. R. and Hatfield, W. E. *Inorg. Chem. 16* (1977) 484; (c) Blake, A. B. and Hatfield, W. E. *J. Chem. Soc., Dalton Trans.* (1978) 869.
11. Schwartz, L. M., Gelb, R. I. and Yardley, J. O. *J. Phys. Chem. 79* (1975) 2246.
12. (a) Glick, M. D., Downs, G. L. and Dahl, L. F. *Inorg. Chem. 3* (1964) 1712; (b) West, R. and Niu, H. Y. *J. Am. Chem. Soc. 85* (1963) 2586.
13. (a) North, A. C. T., Phillips, D. C. and Mathews, F. S. *Acta Crystallogr., Sect. A 24* (1968) 351; (b) Kopfman, G. and Huber, R. *Acta Crystallogr., Sect. A 24* (1968) 348.
14. (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A 46* (1990) 467; (b) Sheldrick, G. M. *SHELXL-93*, University of Göttingen 1993; (c) Sheldrick, G. M. *SHELXTL-PLUS Version 4.21*, Siemens Analytical X-Ray Instruments, Inc., Madison, WI 1990.
15. Ito, M. and West, R. *J. Am. Chem. Soc. 85* (1963) 2580.
16. Allan, J. R. and Paton, A. D. *Thermochem. Acta 214* (1993) 227.
17. Du Preez, J. G. H., Gerber, T. I. A. and Jacobs, R. *J. Coord. Chem. 33* (1994) 147.
18. Rillema, D. P., Taghdiri, D. G., Jones, D. S., Kelle, C. D., Worl, L. A., Meyer, T. J. and Levy, H. A. *Inorg. Chem. 26* (1987) 578.
19. Gordon, K. C., Al-Obaidi, A. H. R., Jayaweera, P. M., McGarvey, J. J., Malone, J. F. and Bell, S. E. J. *J. Chem. Soc., Dalton Trans.* (1996) 1591.
20. Huang, N., Pennington, W. T. and Petersen, J. D. *Acta Crystallogr., Sect. C 47* (1991) 2011.
21. Goodwin, K. V., Pennington, W. T. and Petersen, J. D. *Acta Crystallogr., Sect. C 46* (1990) 898.
22. Castro, I., Sletten, J., Glærum, L. K., Lloret, F., Faus, J. and Julve, M. *J. Chem. Soc., Dalton Trans.* (1994) 2777.
23. Bleaney, B. and Bowers, K. D. *Proc. R. Soc. London, Ser. A 214* (1952) 451.

Received October 22, 1997.