Syntheses, Crystal Structures and Electronic Properties of $[Cu(bipym)(C_5O_5)(H_2O)_2]\cdot H_2O$ and $[Cu_2(bipym)(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (bipym = 2,2′-bipyrimidine)†

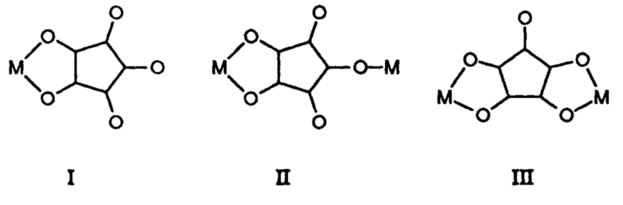
Isabel Castro,[a] Jorunn Sletten,[b] Lisbeth K. Glærum,[b] Francesc Lloret,[a] Juan Faus[a] and Miguel Julve*,[a]

[a] *Departament de Química Inorgànica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100 Burjassot (València), Spain*

[b] *Kjemisk Institutt, Universitetet i Bergen, 5007 Bergen, Norway*

Two new complexes $[Cu(bipym)(C_5O_5)(H_2O)_2]\cdot H_2O$ **1** and $[Cu_2(bipym)(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ **2** [bipym = 2,2′-bipyrimidine and $C_5O_5^{2-}$ = dianion of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione)] have been synthesised and characterized by spectroscopic and X-ray diffraction methods. Crystals of **1** and **2** are triclinic, space group $P\bar{1}$, with $a = 6.604(1)$, $b = 9.491(1)$, $c = 12.019(1)$ Å, $\alpha = 88.37(1)$, $\beta = 79.77(1)$, $\gamma = 86.08(1)°$ and $Z = 2$ for **1**, and $a = 6.638(1)$, $b = 8.765(2)$, $c = 10.093(2)$ Å, $\alpha = 95.96(2)$, $\beta = 93.11(2)$, $\gamma = 91.73(2)°$ and $Z = 1$ for **2**. Compound **1** consists of mononuclear $[Cu(bipym)(C_5O_5)(H_2O)_2]$ units in which the copper atom shows a slightly distorted elongated octahedral co-ordination with two bipym nitrogens and two croconate oxygens forming the equatorial plane, and two water molecules in the axial positions. The structure of compound **2** is made up of centrosymmetric bipym-bridged dinuclear $[Cu_2(bipym)(C_5O_5)_2(H_2O)_2]$ units in which the copper atom exhibits a slightly distorted square-pyramidal co-ordination, with two bipym nitrogens and two croconate oxygens defining the equatorial plane whereas a water molecule occupies the axial position. In addition, the second axial position is occupied by a water molecule at a distance of close to 3 Å. The intradimer metal–metal separation is 5.384 Å. The croconate group acts as a bidentate ligand in both complexes whereas bipym adopts the chelating and bis(chelating) co-ordination modes in **1** and **2**, respectively. The temperature dependence of the magnetic susceptibility of **2** reveals the occurrence of a relatively strong intramolecular antiferromagnetic coupling, J (singlet–triplet energy gap) = -160 cm^{-1}. This value is compared with those of related compounds on the basis of structural data and theoretical calculations.

4,5-Dihydroxycyclopent-4-ene-1,2,3-trione, $H_2C_5O_5$, commonly referred to as croconic acid, and its deprotonated form as a potassium salt were first isolated in 1825.[1] However, the exploration of the co-ordination chemistry of croconate was only initiated thirty years ago when a rational synthetic procedure for croconate was developed.[2] Potassium croconate is obtained in good yield by oxidation of rhodizonate (5,6-dihydroxycyclohex-5-ene-1,2,3,4-tetronate) with manganese dioxide. A more direct and less tedious method uses H_2O_2 instead of MnO_2 as the oxidising agent.[3] The crystal structure of diammonium croconate[4] showed that the anion adopts a symmetry close to D_{5h} and although sandwich complexes with ring-bonding from croconate to transition-metal ions were predicted in the light of this structure, such π complexes have not been found. Available structural data dealing with croconate-containing transition-metal complexes show that this multi-atom ligand can act as either a terminal[5–10] (**I**, Scheme 1) or a bridging[11–14] (**II** and **III**, Scheme 1) ligand. Only the bis(chelating) co-ordination mode has been shown to mediate a significant exchange coupling between the paramagnetic centres.[14] Chelating, bis(chelating), monodentate and bis(monodentate) co-ordination modes for croconate have been observed in its rare-earth metal complexes.[15,16]



Scheme 1

The good co-ordinating properties and the versatility as ligands of croconate and 2,2′-bipyrimidine (bipym)[17,18] make them suitable for preparing the corresponding mixed-ligand complexes which could subsequently be used as 'complex ligands' to obtain both homo- and hetero-polymetallic species. Our first attempts in this regard led us to synthesize the heteroleptic species $[Cu(bipym)(C_5O_5)(H_2O)_2]\cdot H_2O$ **1** and $[Cu_2(bipym)(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ **2** whose crystal structures and electronic properties are presented herein.

Experimental

Materials.—2,2′-Bipyrimidine and copper(II) nitrate trihydrate were purchased from Merck and used as received. Anhydrous potassium croconate was prepared according to the literature.[3]

Preparations.—$[Cu(bipym)(C_5O_5)(H_2O)_2]\cdot H_2O$ **1**. The salt $K_2(C_5O_5)$ (0.055 g, 0.25 mmol) dissolved in water (20 cm^3) was added with continuous stirring to a warm aqueous solution (80 cm^3) containing $Cu(NO_3)_2\cdot 3H_2O$ (0.121 g, 0.5 mmol) and bipym (0.079 g, 0.5 mmol). Elongated prisms of **1** were obtained from the resulting greenish yellow solution by slow evaporation at room temperature. They were collected by vacuum filtration, washed with water, ethanol and diethyl ether and stored over calcium chloride. Yield: practically quantitative (Found: C,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: emu = SI × $10^6/4\pi$, G = 10^{-4} T.

37.55; H, 2.80; N, 12.90. Calc. for $C_{13}H_{12}CuN_4O_8$: C, 37.55; H, 2.90; N, 13.45%).

$[Cu_2(bipym)(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ **2**. A blue solution was obtained by adding bipym (0.079 g, 0.5 mmol) to a warm aqueous solution (100 cm^3) of $Cu(NO_3)_2\cdot 3H_2O$ (0.241 g, 1 mmol). It turned greenish yellow by dropwise addition of an aqueous solution (25 cm^3) of $K_2(C_5O_5)$ (0.055 g, 0.25 mmol) and a dark green microcrystalline precipitate appeared at the end of the addition. The solid was filtered off, washed with water, ethanol and diethyl ether and stored over calcium chloride. Analytical data (C, H, N) revealed slight contamination of the chain compound $Cu(C_5O_5)\cdot 3H_2O$. It is insoluble in common solvents (methanol, ethanol, acetone, acetonitrile, nitromethane and trichloromethane), slightly soluble in water and soluble in dimethyl sulfoxide (dmso) and dimethylformamide. Single crystals of **2** were obtained by slow diffusion using an H-double-tube glass vessel. The starting solutions were aqueous solutions of $[Cu_2(bipym)(NO_3)_4]$ in one arm and $K_2(C_5O_5)$ in the other. Well formed plate-like crystals of **2** were grown after a few weeks (Found: C, 32.65; H, 2.00; N, 8.30. Calc. for $C_{18}H_{18}Cu_2N_4O_{16}$: C, 32.10; H, 2.70; N, 8.30%).

Physical Techniques.—Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–225 cm^{-1} region and electronic spectra on Perkin-Elmer Lambda 9 (as Nujol mulls) and Varian Cary 1 (dmso and water as solvents) spectrophotometers. Variable-temperature X-band ESR spectra were recorded on polycrystalline samples with a Brüker ER 200D spectrometer equipped with a nitrogen cryostat. Magnetic susceptibility measurements of complex **2** were carried out in the range 4–300 K with a fully automated AZTEC DSM5 pendulum-type susceptometer equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. The apparatus was calibrated with $Hg[Co(NCS)_4]$. Corrections for the diamagnetism were estimated from Pascal's constants as -230×10^{-6} emu mol^{-1}.

Crystal Structure Determination and Refinement.—Diffraction data for complexes **1** and **2** were collected at 294 K with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Crystal parameters and refinement results are listed in Table 1. Three reference reflections monitored throughout the data collection showed no significant decay. The usual corrections for Lorentz and polarization effects were carried out. Correction for absorption in complex **1** was achieved by the Gaussian integration method.[19]

The structures of complexes **1** and **2** were solved by direct methods and refined by the full-matrix least squares in space group $P\bar{1}$. Attempts were made to solve the structure of compound **2** in the space group $P1$, since the intensity statistics were not unambiguous, but it did not refine satisfactorily in this space group. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in Fourier-difference maps and refined isotropically. The final full-matrix least-squares refinement, minimizing $\Sigma[w(F_o - F_c)^2]$, including 3160 (**1**) and 2460 (**2**) reflections with $I \geqslant 2\sigma(I)$, converged at R and R' indices of 0.023 and 0.031 for **1** and 0.034 and 0.046 for **2**. The number of reflections/number of variable parameters was 11.1 and 11.3 for **1** and **2**, respectively. In the final difference map the residual maxima and minima were 0.33 and −0.15 e Å^{-3} for **1** and 0.98 and −0.91 e Å^{-3} for **2**. All calculations were carried out on a MICRO-VAX II computer with the Enraf-Nonius Structure Determination Programs.[20] The scattering curves, with anomalous scattering terms included, where those of Cromer and Waber.[21] The final atomic coordinates for non-hydrogen atoms and selected bond lengths and angles for compounds **1** and **2** are given in Tables 2–5.

Table 1 Crystallographic data[a] for $[Cu(bipym)(C_5O_5)(H_2O)_2]\cdot H_2O$ **1** and $[Cu_2(bipym)(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ **2**

Compound	**1**	**2**
Formula	$C_{13}H_{12}CuN_4O_8$	$C_{18}H_{18}Cu_2N_4O_{16}$
M	415.80	673.44
a/Å	6.604(1)	6.638(1)
b/Å	9.491(1)	8.765(2)
c/Å	12.019(1)	10.093(2)
α/°	88.37(1)	95.96(2)
β/°	79.77(1)	93.11(2)
γ/°	86.08(1)	91.73(2)
U/Å^3	739.5(2)	582.8(4)
Z	2	1
D_c/kg m^{-3}	1.867	1.919
Crystal size/mm	0.44 × 0.30 × 0.20	0.57 × 0.32 × 0.08
μ(Mo-Kα)/mm^{-1}	1.533	1.918
Max., min. transmission factors[b]	0.757, 0.655	
Scan range/°	0.80 + 0.347 tan θ	0.70 + 0.347 tan θ
No. of unique reflections	3403	2655
No. of independent reflections,[c] N_o	3160	2460
No. of refined parameters, N_p	284	218
$R\ \{=[\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert]\}$	0.023	0.034
$R'\ \{=[\Sigma w(\lvert\lvert F_o - \lvert F_c\rvert\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}\}$	0.031	0.046
$S\ \{=[\Sigma w(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/(N_o - N_p)]^{\frac{1}{2}}\}$	2.26	1.92
k[d]	0.02	0.04

[a] Details in common: triclinic, space group $P\bar{1}$, 2θ range 2–55°, scan type ω, scan speed 2.67° min^{-1}. [b] Absorption correction by the Gaussian integration method for compound **1**, no correction for compound **2**. [c] $I \geqslant 2\sigma(I)$. [d] $w = 4F_o^2/[\sigma_c^2 + (kF_o^2)^2]$, where σ_c is the standard deviation on F^2 based on counting statistics alone.

Table 2 Final atomic coordinates for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Cu	0.458 69(3)	0.365 50(2)	0.306 97(1)
O(1)	0.291 1(2)	0.414 1(1)	0.456 60(9)
O(2)	0.409 4(2)	0.165 7(1)	0.349 08(8)
O(3)	0.246 9(2)	−0.078 6(1)	0.497 2(1)
O(4)	0.054 6(2)	0.048 3(1)	0.716 3(1)
O(5)	0.057 8(2)	0.356 0(1)	0.691 6(1)
O(6)	0.157 2(2)	0.370 3(1)	0.204 3(1)
O(7)	0.783 7(2)	0.344 0(1)	0.382 3(1)
O(8)	0.246 3(2)	0.090 1(1)	0.121 6(1)
N(1)	0.635 9(2)	0.319 1(1)	0.160 3(1)
N(2)	0.501 9(2)	0.562 1(1)	0.247 3(1)
N(3)	0.789 0(2)	0.422 6(1)	−0.013 3(1)
N(4)	0.646 9(2)	0.685 1(1)	0.080 1(1)
C(1)	0.242 2(2)	0.296 5(2)	0.505 1(1)
C(2)	0.303 9(2)	0.166 3(2)	0.448 2(1)
C(3)	0.229 5(2)	0.048 3(2)	0.520 3(1)
C(4)	0.126 3(2)	0.112 5(2)	0.630 1(1)
C(5)	0.131 0(2)	0.269 7(2)	0.618 2(1)
C(6)	0.607 2(2)	0.569 5(1)	0.141 2(1)
C(7)	0.574 9(3)	0.807 1(2)	0.132 0(1)
C(8)	0.468 5(3)	0.812 1(2)	0.240 8(1)
C(9)	0.432 2(2)	0.685 7(2)	0.297 1(1)
C(10)	0.683 3(2)	0.428 9(1)	0.091 1(1)
C(11)	0.855 2(2)	0.291 7(2)	−0.049 8(1)
C(12)	0.818 7(3)	0.173 2(2)	0.016 6(1)
C(13)	0.706 2(3)	0.189 4(2)	0.123 5(1)

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

Table 3 Final atomic coordinates for complex **2** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.552 56(4)	0.658 70(3)	0.243 15(2)
O(1)	0.598 8(2)	0.879 2(2)	0.298 1(1)
O(2)	0.681 2(3)	0.622 7(2)	0.416 9(2)
O(3)	0.844 7(3)	0.711 6(2)	0.701 1(2)
O(4)	0.896 5(3)	1.047 6(2)	0.730 3(2)
O(5)	0.751 8(2)	1.161 2(2)	0.478 5(2)
O(6)	0.928 2(4)	0.622 7(3)	0.101 2(3)
O(7)	0.232 1(3)	0.609 5(2)	0.306 9(2)
O(8)	0.863 8(3)	0.875 2(2)	−0.026 4(2)
N(1)	0.574 2(3)	0.441 0(2)	0.158 8(2)
N(3)	0.549 2(3)	0.306 6(2)	−0.057 5(2)
C(1)	0.684 4(3)	0.889 6(2)	0.414 7(2)
C(2)	0.723 6(3)	0.755 0(2)	0.478 3(2)
C(3)	0.804 8(3)	0.796 8(2)	0.613 8(2)
C(4)	0.827 8(3)	0.968 6(2)	0.630 4(2)
C(5)	0.753 5(3)	1.025 8(2)	0.502 4(2)
C(10)	0.533 6(3)	0.430 2(2)	0.028 2(2)
C(11)	0.618 0(3)	0.180 8(2)	−0.006 5(2)
C(12)	0.666 6(3)	0.181 4(2)	0.127 9(2)
C(13)	0.641 0(3)	0.315 0(2)	0.210 0(2)

Table 4 Selected interatomic distances (Å) and angles (°) for complex **1** with e.s.d.s in parentheses

Copper environment

Cu–O(1)	1.986(1)	Cu–O(7)	2.467(1)
Cu–O(2)	1.982(1)	Cu–N(1)	1.978(1)
Cu–O(6)	2.520(1)	Cu–N(2)	2.000(1)
O(1)–Cu–O(2)	86.58(4)	O(2)–Cu–N(2)	173.55(5)
O(1)–Cu–O(6)	95.37(4)	O(6)–Cu–O(7)	171.51(4)
O(1)–Cu–O(7)	92.93(4)	O(6)–Cu–N(1)	86.92(5)
O(1)–Cu–N(1)	177.62(5)	O(6)–Cu–N(2)	86.89(5)
O(1)–Cu–N(2)	98.08(4)	O(7)–Cu–N(1)	84.81(5)
O(2)–Cu–O(6)	88.24(4)	O(7)–Cu–N(2)	93.75(5)
O(2)–Cu–O(7)	90.44(4)	N(1)–Cu–N(2)	81.36(5)
O(2)–Cu–N(1)	94.17(4)		

Croconate ligand

O(1)–C(1)	1.279(2)	C(1)–C(2)	1.429(2)
O(2)–C(2)	1.269(2)	C(1)–C(5)	1.450(2)
O(3)–C(3)	1.237(2)	C(2)–C(3)	1.455(2)
O(4)–C(4)	1.224(2)	C(3)–C(4)	1.499(2)
O(5)–C(5)	1.232(2)	C(4)–C(5)	1.497(2)
Cu–O(1)–C(1)	105.96(8)	O(3)–C(3)–C(4)	126.7(1)
Cu–O(2)–C(2)	106.46(9)	C(2)–C(3)–C(4)	105.5(1)
O(1)–C(1)–C(2)	120.5(1)	O(4)–C(4)–C(3)	126.3(1)
O(1)–C(1)–C(5)	129.3(1)	O(4)–C(4)–C(5)	125.2(1)
C(2)–C(1)–C(5)	110.2(1)	C(3)–C(4)–C(5)	108.4(1)
O(2)–C(2)–C(1)	120.5(1)	O(5)–C(5)–C(1)	128.3(1)
O(2)–C(2)–C(3)	129.4(1)	O(5)–C(5)–C(4)	126.0(1)
C(1)–C(2)–C(3)	110.1(1)	C(1)–C(5)–C(4)	105.7(1)
O(3)–C(3)–C(2)	127.9(1)		

Table 5 Selected interatomic distances (Å) and angles (°) for complex **2** with e.s.d.s in parentheses *

Copper environment

Cu–O(1)	1.965(1)	Cu–O(7)	2.297(2)
Cu–O(2)	1.968(2)	Cu–N(1a)	2.019(2)
Cu–O(6)	2.951(3)	Cu–N(3)	2.013(2)
O(1)–Cu–O(2)	87.18(6)	O(2)–Cu–N(3)	173.81(7)
O(1)–Cu–O(6)	95.23(7)	O(6)–Cu–O(7)	160.08(6)
O(1)–Cu–O(7)	103.47(6)	O(6)–Cu–N(1a)	68.97(7)
O(1)–Cu–N(1a)	164.10(7)	O(6)–Cu–N(3)	79.74(7)
O(1)–Cu–N(3)	93.08(6)	O(7)–Cu–N(1a)	92.04(6)
O(2)–Cu–O(6)	94.08(7)	O(7)–Cu–N(3)	92.30(6)
O(2)–Cu–O(7)	93.65(6)	N(1a)–Cu–N(3)	82.69(6)
O(2)–Cu–N(1a)	95.40(6)		

Croconate ligand

O(1)–C(1)	1.273(2)	C(1)–C(2)	1.425(3)
O(2)–C(2)	1.273(2)	C(1)–C(5)	1.456(2)
O(3)–C(3)	1.236(3)	C(2)–C(3)	1.448(3)
O(4)–C(4)	1.220(2)	C(3)–C(4)	1.500(3)
O(5)–C(5)	1.236(2)	C(4)–C(5)	1.498(3)
Cu–O(1)–C(1)	106.1(1)	O(3)–C(3)–C(4)	125.6(2)
Cu–O(2)–C(2)	106.0(1)	C(2)–C(3)–C(4)	106.0(2)
O(1)–C(1)–C(2)	120.4(2)	O(4)–C(4)–C(3)	126.0(2)
O(1)–C(1)–C(5)	129.5(2)	O(4)–C(4)–C(5)	126.1(2)
C(2)–C(1)–C(5)	110.1(2)	C(3)–C(4)–C(5)	107.9(2)
O(2)–C(2)–C(1)	120.3(2)	O(5)–C(5)–C(1)	128.1(2)
O(2)–C(2)–C(3)	129.6(2)	O(5)–C(5)–C(4)	126.2(2)
C(1)–C(2)–C(3)	110.1(2)	C(1)–C(5)–C(4)	105.7(2)
O(3)–C(3)–C(2)	128.4(2)		

* Symmetry code: (a) $1 - x, 1 - y, -z$.

Results and Discussion

Structures of Complexes **1** *and* **2**.—The structure of complex **1** is made up of neutral mononuclear [Cu(bipym)(C_5O_5)(H_2O)$_2$] units (Fig. 1) and water of crystallization linked by an extensive network of hydrogen bonds. The copper atom has a six-co-ordinate CuN_2O_4 chromophore with a slightly distorted, elongated octahedral co-ordination. It is bound to two nitrogen atoms [1.978(1) and 2.000(1) Å] and two oxygen atoms [1.986(1) and 1.982(1) Å] of the chelating bipym and croconate ligands in the equatorial positions. The axial positions are occupied by two weakly bound water molecules [2.467(1) and 2.520(1) Å for Cu–O(7) and Cu–O(6), respectively]. The copper atom is displaced only 0.020 Å out of the least-squares plane defined by the equatorial ligand atoms, toward the axial O(7) oxygen atom.

The structure of complex **2** consists of neutral bipym-bridged [Cu_2(bipym)(C_5O_5)$_2$(H_2O)$_2$] dinuclear units, with a crystallographically imposed inversion centre located at the midpoint of the bipym inter-ring carbon–carbon bond (Fig. 2), and water of crystallization. Each copper atom has a five-co-ordinate CuN_2O_3 chromophore with a slightly distorted square-pyramidal co-ordination. It is bonded to two bipym nitrogen atoms [2.019(2) and 2.013(2) Å] and two croconato oxygen atoms [1.965(1) and 1.968(2) Å] in the basal plane and a water molecule in the apical position [2.297(2) Å for Cu–O(7)]. In addition the sixth position is occupied by a water molecule [O(6)] at a distance of 2.951(3) Å. Although this is long even for semi-co-ordination, this water molecule has been assigned to the copper co-ordination sphere in Fig. 2 to emphasize the similarity in co-ordination in **1** and **2**. The copper atom is displaced by 0.187 Å from the least-squares plane defined by the equatorial ligand atoms, toward the axial O(7) oxygen atom. The dihedral angle between the mean equatorial plane of copper and the mean plane of the bridging bipym ligand is 14.4°. The average Cu$^{\rm II}$–N(bipym) bond distance [2.016(2) Å] is shorter than those reported for bipym-bridged dinuclear iron(II) (2.22 Å),[18a] cobalt(II) (2.16 Å)[18b,22] and nickel(II) complexes (2.11 Å)[23] in agreement with the decreasing ionic radii in the series Fe$^{\rm II}$ > Co$^{\rm II}$ > Ni$^{\rm II}$ > Cu$^{\rm II}$. The intramolecular metal–metal separation is 5.384(1) Å, and is thus among the shortest observed for bipym-bridged copper(II) complexes. Intermolecular metal–metal separations shorter than 7 Å are: Cu$\cdots$Cu$^{\rm I}$ ($\rm I = 1 - x, 1 - y, 1 - z$) 6.195(1) Å and Cu$\cdots$Cu$^{\rm VI}$ ($\rm VI = 1 + x, y, z$) 6.683(1) Å.

The bis(chelating) bipym ligand in complex **2** has a bite distance of 2.664(2) Å, compared to values of 2.71 and 2.70 Å found for the unco-ordinated molecule in the crystal structures of bipym and bipym·2H_2O.[24] In compound **1** the bipym ligand

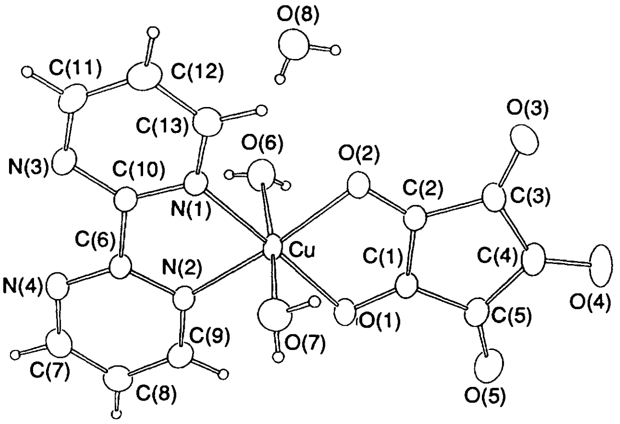

Fig. 1 Molecular structure of complex **1** showing the atom labelling; thermal ellipsoids are drawn at the 50% probability level

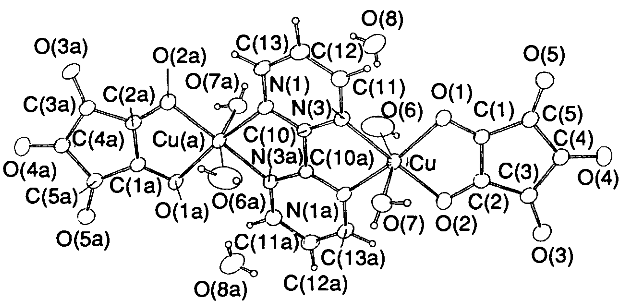

Fig. 2 Molecular structure of complex **2** showing the atom labelling; thermal ellipsoids are drawn at the 50% probability level

is clearly distorted due to its co-ordination to copper(II); the N(1) ··· N(2) bite distance [2.593(2) Å] is significantly reduced compared to the related N(3) ··· N(4) distance [2.796(2) Å]. This asymmetry is also reflected in the bond distances and angles at C(6) and C(10). The bipym ligands are quasi planar in both compounds, the larger deviation from planarity being found in **1** where the maximum atomic displacement is 0.041 Å and the dihedral angle between the two pyramidyl rings is 2.7(5)°. The carbon–carbon inter-ring bond length in **1** [1.497(2) Å] is the same as that found in free bipym in the solid state,[24] but slightly longer than that observed in the dinuclear compound **2** [1.474(3) Å].

The croconato groups, co-ordinated in a symmetrically bidentate fashion in complexes **1** and **2**, display approximately two-fold symmetry around Cu ··· C(4). The lengthening of the C(1)–O(1) and C(2)–O(2) bonds [average values 1.274 in **1** and 1.273 Å in **2**] *versus* the mean of the three remaining C–O(croconate) bond distances (1.231 Å in both **1** and **2**) results in a concurrent shortening of the C(1)–C(2) bond length [1.429(2) in **1** and 1.425(3) Å in **2**] compared to the other C–C(croconate) distances (1.448–1.500 Å). These structural features support an enediol form for the symmetrical bidentate croconate as observed in [Cu(bipy)(C_5O_5)(H_2O)] (bipy = 2,2′-bipyridine).[10] The O(1) ··· O(2) bite distance (2.721 Å in **1** and 2.712 in **2**) is significantly reduced compared to the corresponding distances outside the bite (average value 2.984 Å in both **1** and **2**).

Infrared, Electronic and ESR Spectra of Complexes **1** *and* **2**.—The most relevant IR features are those associated with the presence of chelating croconate (**1** and **2**) and chelating (**1**) and bis(chelating) (**2**) bipym. In agreement with the analysis of West and Niu,[25] the peaks at 1775 (**1**), 1740 (**1** and **2**), 1720 (**2**) and 1710 cm^{-1} (**1**) are assigned to the non-co-ordinated carbonyls of the croconate entity. The co-ordinated carbonyl groups are characterized by medium absorptions at 1665 (**2**), 1660 (**1**), 1590 (**2**) and 1580 cm^{-1} (**1**). A very strong and broad peak centred at 1540 cm^{-1}, which is characteristic of salts of the $C_nO_n^{2-}$ (n = 4–6) ion,[26] is attributed to vibrational modes representing mixtures of C–O and C–C stretching motions. This strong feature obscures the ring stretching modes of bipym, and precludes the use of this region for spectroscopic prediction of chelating or bis(chelating) bipym.[17d] Nevertheless, a careful comparison between the IR spectra of compounds **1** and **2** reveals a clear difference in the 1250–1200 cm^{-1} region: two peaks at 1240w and 1220m cm^{-1} for **1** and a sharp single peak at 1225m cm^{-1} for **2**. The same patterns are found when reviewing the IR spectra of a group of previously investigated bipym-containing copper(II) complexes.[17,27,28] These features are consistent with the occurrence of chelating and bis(chelating) bipym, respectively. Consequently, a simple study of this lower frequency region in bipym-containing metal complexes provides reliable information on the co-ordination mode of bipym.

The absorption spectra of complexes **1** and **2** in dmso display a broad maximum centred at 690 (ε 70) (**1**) and 730 nm (139 dm^{-3} mol^{-1} cm^{-1}) (**2**), due to d–d ligand-field absorptions, a shoulder at 450 nm (**1** and **2**) and an intense absorption at 370 nm [ε 7.5×10^4 (**1**) and 1.6×10^5 dm^{-3} mol^{-1} cm^{-1} (**2**)] with a shoulder at 330 nm (**1** and **2**) due to ligand-to-metal charge-transfer and intraligand (croconate) transitions. The characteristic bipym $\pi^* \longleftarrow \pi$ transition appears in the ultraviolet region at wavelengths below 250 nm. The absorption spectra of aqueous solutions of **1** and **2** are similar to those in dmso, the only difference being the lack of the shoulder at 450 nm. The reflectance spectra for **1** and **2** at wavelengths above 500 nm display two maxima which are centred at 950 and 670 nm for **1** and at 1025 and 700 nm for **2**. The distortion from an elongated octahedral geometry in **1**, towards a co-ordination closer to square pyramidal in **2** accounts for the shift toward lower energies of the d–d transitions in **2**.[29]

The X-band ESR spectrum of compound **1** at room temperature presents an axial doublet with $g_{\parallel}$ and $g_{\perp}$ values of 2.28 and 2.08, respectively. No half-field forbidden transition is observed at room temperature. The observed pattern $g_{\parallel} > g_{\perp} > 2.0$, is indicative of a copper(II) $d_{x^2-y^2}$ orbital ground state in agreement with the tetragonally distorted octahedral environment surrounding the metal ion. This spectrum remains practically unchanged on cooling to liquid nitrogen temperature, the only modification being the appearance of a weak $\Delta M_s = 2$ forbidden transition which could be due to intermolecular interaction between the mononuclear copper(II) units, as observed in structurally characterized monomeric copper(II) species.[30] The X-band ESR spectrum of compound **2** at room temperature consists of an asymmetric feature centred at 3188 G (g = 2.12) whose intensity vanishes upon cooling, as expected for an excited triplet (see later). A weak $\Delta M_s = 2$ forbidden transition associated with the triplet was detected at *ca.* 1590 G only at low temperatures.

Magnetic Properties of Complex **2**.—The thermal dependence of the molar magnetic susceptibility, χ_M, of compound **2** is shown in Fig. 3. The curve exhibits a behaviour which is characteristic of antiferromagnetically coupled copper(II) ions with a smooth maximum of the susceptibility at about 130 K. The experimental data were fitted by a modified Bleaney–Bowers expression for a dinuclear copper(II) complex [equation (1)] where J is the singlet–triplet energy gap defined by the Hamiltonian (2); J expresses the intramolecular exchange

$$\chi_M = \frac{2N\beta^2 g^2}{kT}\left[\frac{(1-\rho)}{3+\exp(-J/kT)}\right] + \left(\frac{N\beta^2 g^2}{2kT}\right)\rho + 2N\alpha \qquad (1)$$

$$\hat{H} = -J\hat{S}_1\cdot\hat{S}_2 \qquad (2)$$

Table 6 Selected magnetostructural data for a series of bipym-bridged copper(II) complexes

Compound	Donor set^a	γ^b/°	$h_M{}^c$/Å	$d_{Cu-Cu}{}^d$/Å	$-J$/cm^{-1}	Ref.
$[Cu_2(bipym)Br_4]$	$N_2Br_2Br_2$	2.0	0.000	5.545(1)	236	17(*e*)
$[Cu_2(bipym)(NCS)_4]$	$N_2N_2S_2$	0.8	0.000	5.492(2)	230	17(*d*)
		0.6	0.000	5.506(3)		
$[Cu_2(bipym)Cl_4]$	$N_2Cl_2Cl_2$	2.7	0.000	5.528(2)	225	17(*e*)
$[Cu_2(bipym)(NCO)_4]$	N_2N_3O	8.7	0.089	5.520(1)	199	17(*d*)
$[Cu_2(bipym)(NO_3)_4]$	N_2O_4	3.5	0.021	5.371(1)	191	17(*f*)
$[Cu_2(bipym)(N_3)_4]$	N_2N_4	2.6	0.104	5.520(1)	178	28
2	N_2O_2OO'	14.4(1)	0.187	5.384(1)	160	This work

[a] The first two atoms are those of bipym and the first four form the basal plane. [b] Dihedral angle between the mean equatorial plane around the metal ion and the bipym plane. [c] The height of the metal atom above the basal plane. [d] Metal–metal separation across bipym.

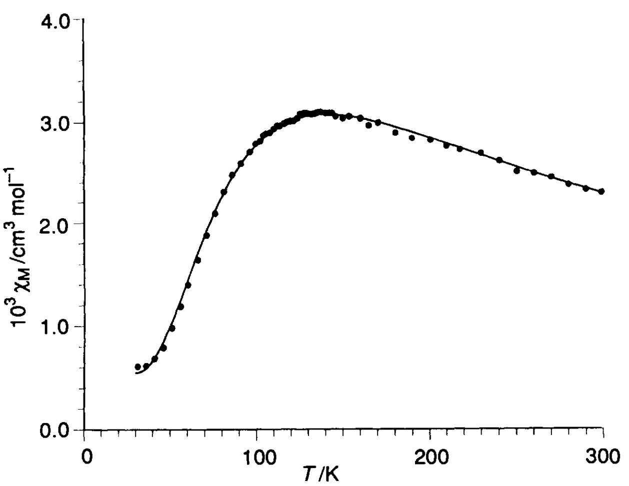

Fig. 3 Thermal dependence of the molar magnetic susceptibility of complex **2**. The solid line corresponds to the best theoretical fit

interaction, $\hat{S}_1$ and $\hat{S}_2$ are quantum spin operators ($S_1 = S_2 = \frac{1}{2}$), N, g, β and T have their usual meaning, $N\alpha$ is the temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1}) and ρ is the mass portion of uncoupled impurity, assumed to follow the Curie law and to have a molecular weight identical to that of the dimer. A least-squares fit of the data through equation (1) by a Simplex method leads to values of -160 cm^{-1}, 2.10, 0.01 and 1.3×10^{-4} for J, g, ρ and R, respectively, where R is the agreement factor defined as $\Sigma[(\chi_M)^{obs} - (\chi_M)^{calc}]^2/\Sigma(\chi_M)^{obs}]^2$.

The value of J reveals that a strong antiferromagnetic coupling between copper(II) ions separated by 5.384(1) Å occurs in complex **2**. This large coupling arises from the overlap between the $d_{x^2-y^2}$ magnetic orbitals centred on each metal ion [the x and y axes being defined roughly by the Cu–N(1) and Cu–N(3) bonds, respectively] through the N(bipym) atoms. Since the axial distances around copper(II) are longer than the equatorial ones, the admixture of the d_{z^2} orbital in the $d_{x^2-y^2}$ ground state is assumed to be weak. It is well known that the bipym bridge has a remarkable ability to mediate strong antiferromagnetic interactions [$-J$ values up to 236 cm^{-1} in bipym-bridged copper(II) complexes][17d,e] when the σ in-plane exchange pathway is involved. However, an inspection of the values of J which are listed in Table 6 shows that the magnitude of the coupling in compound **2**, even if strong, is the smallest in the series. In general, the values of h, γ and d_{Cu-Cu} all influence the exchange coupling. Although the intramolecular metal–metal separation in **2** is one of the shortest, the significant displacement of the metal atom from the equatorial plane and the large angle between the bipym and equatorial planes in this compound (the largest values of h and γ in Table 6) would account for the significant reduction in the antiferromagnetic coupling. The relevance of these structural factors as far as the magnetic properties are concerned was previously analysed in the related oxalato-bridged dinuclear copper(II) species.[31]

A mixed-ligand complex such as **1** can be used as a ligand towards metal ions due to the potential bis(chelating) capability of the bipym and/or croconato groups. Complex **1** can act as either a nitrogen donor through bipym and/or an oxygen donor through croconate. In this regard, complex **2** could be viewed as an example showing polymerisation through bipym. In fact, complex **1** should be a good candidate to obtain homo- and hetero-polymetallic compounds through the well known strategy of using 'complexes as ligands'.

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