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FULL PAPER

Syntheses, crystal structures and magnetic properties of copper(II) dicyanamide complexes; dinuclear, chain and ladder compounds

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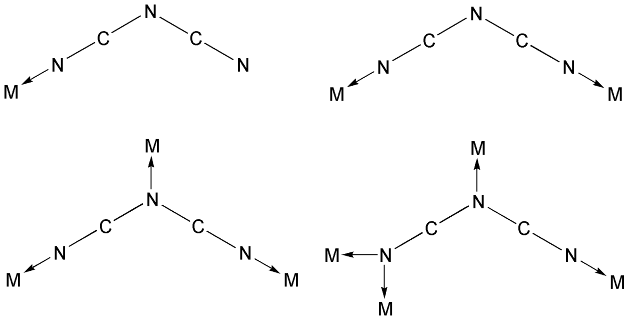
The preparation, crystal structures and magnetic properties of three heteroleptic copper(II) complexes with dicyanamide (dca) bridges, $[Cu(bpca)(H_2O)(dca)]_2$ (**1**) (bpca = bis(2-pyridylcarbonyl)amidate), $[Cu(bpy)(dca)_2]_n$ (**2**) (bpy = 2,2′-bipyridine), $[Cu_2(bpm)(dca)_4]_n$ (**3**) (bpm = 2,2′-bipyrimidine) are reported. In addition, magnetic susceptibility measurements of the sheetlike polymer $[Cu(phen)(dca)_2]$ (**4**) (phen = 1,10-phenanthroline), structurally characterized previously, have been performed. In complex **1** pairs of mononuclear structural building blocks, $[Cu(bpca)(dca)(H_2O)]$, are loosely connected through a 1,3-dca bridge in which nitrile is equatorially bound and the amide is semi-coordinated in axial position to copper. The bis-monodentate 1,3-bridging mode of dca has been postulated, but not previously observed. A chain structure is present in **2**, one of the dca units serving as an end-to-end out-of-plane bridging ligand, while the other dca is terminal, monodentate. The chain structure is very similar to that found in **4**, but while the chains in **4** are connected, forming sheets, this is not so in **2**. Compound **3** forms a ladder-like polynuclear structure in which the rungs are formed by bis-chelating bpm bridges and the uprights by end-to-end bridging dca units. The copper ··· copper separations across the dca bridges are 5.732(2) Å (**1**), 8.1999(8) Å (**2**) and 7.5550(2) Å (**3**), respectively, and 5.5673(4) Å across the bpm bridge (**3**). These values are to be compared with the intrasheet copper ··· copper separations of 7.3002(7) Å (through a single end-to-end dca bridge) and 7.7079(4) Å (through a double end-to-end dca bridge) in **4**. Variable-temperature magnetic susceptibility measurements reveal Curie law behaviour with no detectable magnetic coupling in compounds **1** and **2**, a very weak ferromagnetic interaction across the single end-to-end dca bridge in **4** ($J = +0.2(1)$ cm^{-1}), and a strong antiferromagnetic interaction across the bpm bridge in compound **3** ($J = -211(1)$ cm^{-1}).

Introduction

Dicyanamide (dca), $N(CN)_2^-$, is a versatile ligand which has been shown to coordinate to metal ions in various modes: monodentate bonding through a nitrile nitrogen, end-to-end bridging through the two nitrile nitrogen atoms, tris-monodentate bridging of three metal atoms, as well as an unusual μ_4 coordination where one nitrile nitrogen binds to two metal atoms (Scheme 1).[1–3] The coordination properties thus allow for the preparation of compounds with a large variety of architectures: mononuclear, dinuclear, as well as one-, two- and three-dimensional (*n*D, *n* = 1–3) networks. A series of binary compounds of the general formula $[M^{II}(dca)_2]$, with a 3D rutile type structure, have gained much interest as several of these have been shown to be ferromagnets.[1] Also, superconductors with tetrathiafulvalene cations and dca anions have been synthesized and characterized.[2] Introduction of auxiliary ligands into the M^{II}–dca system has allowed for the syntheses of several ternary systems, $[M^{II}L_x(dca)_y]$ (L = organic ligand, $x = 1$ or 2, $y = 1$ or 2), with a wide variety of topologies.[3,4] In a few cases long range magnetic ordering has been observed at low temperature. Among the copper(II) complexes of this class of compounds only a few have been both structurally and magnetically characterized.[4a,b,d,e] In the present work, we describe the syntheses, crystal structures and magnetic properties of three copper(II) complexes with dca and auxiliary ligands, $[Cu(bpca)(H_2O)(dca)]_2$ (**1**, dinuclear) (bpca = bis(2-pyridylcarbonyl)amidate), $[Cu(bpy)(dca)_2]_n$ (**2**, zig-zag chain) (bpy = 2,2′-bipyridine), $[Cu(bpm)(dca)_2]_n$ (**3**, ladder-like structure) (bpm = 2,2′-bipyrimidine). In addition the magnetic properties of $[Cu(phen)(dca)_2]$ (**4**, sheetlike polymer)[4c] (phen = 1,10-phenanthroline) which has been previously structurally characterized, were investigated.



Scheme 1

Experimental

Materials

$[Cu(bpca)(H_2O)_2]NO_3{\cdot}2H_2O$ and $[Cu_2(bpm)(NO_3)_4]$ were prepared as reported in the literature.[5a,b] All other chemicals were puchased from commercial sources and used as received.

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Preparations

[Cu(bpca)(H_2O)(dca)]$_2$ (1). This compound is obtained as a blue crystalline solid by reaction of aqueous solutions containing stoichiometric amounts of [Cu(bpca)(H_2O)$_2$]NO_3·$2H_2O$ and sodium dicyanamide. The yield is quantitative. Single crystals of **1** as deep blue plates were grown by slow diffusion in an H-shaped tube of aqueous solutions containing 0.125 mmol of [Cu(bpca)(H_2O)$_2$]NO_3·$2H_2O$ in one arm and 0.250 mmol of NaN(CN)$_2$ in the other one. Anal. Found: C, 44.9; H, 2.6; N, 22.4. Calc. for $C_{14}H_{10}CuN_6O_3$: C, 45.0; H, 2.7; N, 22.5%.

[Cu(bpy)(dca)$_2$]$_n$ (2). Single crystals of **2** in the form of dark blue needles were grown by slow diffusion in an H-shaped tube of aqueous solutions containing 0.25 mmol of (2,2′-bipyridyl)-copper(II) nitrate (mixture of Cu(NO_3)$_2$·$3H_2O$ and bpy in stoichiometric amounts) in one arm and 0.50 mmol of NaN(CN)$_2$ in the other one. The yield is practically quantitative after two months. Direct reactions of aqueous solutions containing 0.5 mmol of (2,2′-bipyridyl)copper(II) nitrate and 1.0 mmol of sodium dicyanamide leads to the formation of a blue solid whose elemental analysis is in agreement with the proposed formulation for **2**. Anal. Found: C, 47.7; H, 2.2; N, 31.7. Calc. for $C_{14}H_8CuN_8$: C, 47.8; H, 2.3; N, 31.9%.

[Cu$_2$(bpm)(dca)$_4$]$_n$ (3). This compound is obtained as a green solid when reacting aqueous solutions of [Cu$_2$(bpm)(NO_3)$_4$] and NaN(CN)$_2$ in 1 : 4 molar ratio. Single crystals of **3** as green needles were obtained by slow evaporation of aqueous solutions containing 0.5 mmol of (2,2′-bipyrimidine)copper(II) nitrate (mixture of bpm and Cu(NO_3)$_2$·$3H_2O$ in a 1 : 1 molar ratio) and 1.0 mmol of NaN(CN)$_2$. Anal. Found: C, 34.9; H, 1.0; N, 40.7. Calc. for $C_{16}H_6Cu_2N_{16}$: C, 35.0; H, 1.1; N, 40.8%.

[Cu(phen)(dca)$_2$] (4). Direct reaction of aqueous solutions of 0.5 mmol of (1,10-phenanthroline)copper(II) nitrate (mixture of stoichiometric amounts of copper(II) nitrate and phen) and 1.0 mmol of sodium dicyanamide causes the precipitation of **4** as a blue solid. Single crystals of **4** as blue blocks were grown by slow diffusion of aqueous solutions in an H-shaped tube containing 1/8 mmol of (1,10-phenanthroline)copper(II) nitrate and 2/8 mmol of NaN(CN)$_2$. The cell parameters of these crystals are identical to those previously reported for this compound.[4c]

Physical techniques

Infrared spectra were recorded with a Nicolet 800 FTIR spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. The magnetic susceptibility measurements of polycrystalline samples of the complexes were performed in the temperature range 1.9–290 K with a Quantum Design SQUID susceptometer and using applied magnetic fields of 1000 G for **1**–**4** (over the whole temperature range) and of 50 G for **4** (for $T < 50$ K). The complex $(NH_4)_2Mn(SO_4)_2·6H_2O$ was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants and found to be -166×10^{-6} cm^3 mol^{-1} (**1**), -170×10^{-6} (**2**), -226×10^{-6} (**3**) and -193×10^{-6} (**4**) cm^3 mol^{-1} K (per copper atom in **1**, **2** and **4** and per two copper atoms in **3**).[6] A value of 60×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of the copper(II) ion.

Crystallography

Diffraction data 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.[7] 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 were included in the model at idealized positions, those bound to oxygen (water) were located in Fourier difference maps and all hydrogen atoms were refined according to the riding model. For compound **1** refinement in both $P1$ and $P\bar{1}$ were tested, the centrosymmetric choice proved to be the correct one. Structure **2** could only be solved in space group Cc, and the refinement showed that higher symmetry is not present.

Data collection and data reduction were done with the SMART and SAINT programs.[8] All other calculations were performed with the SHELXS-86, SHELXL-93 and XP programs.[9] Selected bond distances and angles are listed in Tables 2–4.

CCDC reference numbers 174338–174340.

See http://www.rsc.org/suppdata/dt/b1/b105981p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structures

[Cu(bpca)(H_2O)(dca)]$_2$ 1. The structural building block is the neutral [Cu(bpca)(dca)(H_2O)] complex in which the three bpca nitrogen atoms and a terminal dca nitrogen bind to copper in equatorial positions (Cu–N 1.9491(14)–2.034(2) Å), and a water molecule resides in an apical position (Cu–O = 2.3638(15) Å). Considering only these bonds the copper coordination geometry may be described as distorted square pyramidal, the trigonality parameter τ being 0.15.[10a] The amide dca nitrogen atom of a centrosymmetrically related unit is semi-coordinated[10b] to copper (Cu(1)–N(5a) = 2.799(2) Å, where N(5a) is at $1 - x$, $1 - y$, $1 - z$), resulting in a dinuclear entity (Fig. 1).

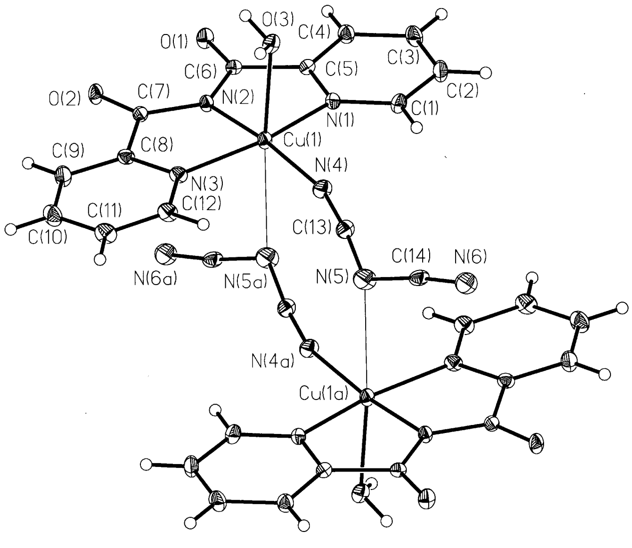

Fig. 1 The dinuclear entity in **1**, [Cu(bpca)(dca)(H_2O)]$_2$. Thermal ellipsoids are plotted at the 30% probability level. Symmetry code a: $-x + 1$, $-y + 1$, $-z + 1$.

The copper equatorial plane is essentially planar (maximum atomic deviation 0.024 Å), the copper atom is displaced by 0.120 Å from the plane towards the apical water. The dihedral angles between the equatorial plane and the plane of the bpca and dca groups are 2.0° and 40.1°, respectively. The bpca group acts as a tridentate ligand through its three nitrogen atoms, the copper to amido-nitrogen bond being significantly shorter than the two copper to pyridine-nitrogen ones, as observed in other copper(II)–bpca complexes.[11a] The average C–C, C–N and C–O bond lengths in the bpca ligand are in agreement with those reported previously.[11a] The pyridyl rings of bpca are planar and the dihedral angle between these rings is 4.8°.

Table 1 Crystal data and structure refinement for $[Cu(bpca)(dca)(H_2O)]_2$ (**1**), $[Cu(bpy)(dca)_2]_n$ (**2**) and $[Cu_2(bpm)dca)_4]_n$ (**3**)

	1	**2**	**3**
Empirical formula	$C_{28}H_{20}Cu_2N_{12}O_6$	$C_{14}H_8CuN_8$	$C_{16}H_6Cu_2N_{16}$
Formula weight	747.64	351.82	549.45
Temperature/K	153(2)	153	153
λ/Å	0.71073	0.71073	0.71073
Space group	$P\bar{1}$	Cc	$P2_1/c$
Crystal symmetry	Triclinic	Monoclinic	Monoclinic
a/Å	7.2838(15)	8.6391(10)	7.5550(2)
b/Å	10.357(2)	17.165(5)	11.3017(5)
c/Å	11.003(2)	10.4638(13)	11.8904(4)
α/°	115.50(3)		
β/°	97.85(3)	114.307(2)	107.142(2)
γ/°	96.98(3)		
V/Å^3	726.9(3)	1414.1(3)	970.15(6)
Z	1	4	2
ρ/Mg m^{-3}	1.708	1.653	1.881
μ/mm^{-1}	1.530	1.557	2.239
Max 2θ/°	60.9	62	61
Refl. collected	6562	6199	8482
Independent refl.	4304 [R(int) = 0.0206]	3434[R(int) = 0.0175]	2938 [R(int) = 0.0200]
Refl. with $I > 2\sigma(I)$	3477	3173	2570
Data/restraints/parameters	4301/0/217	3434/2/208	2937/0/154
Flack x-parameter		0.011(8)	
Goodness-of-fit, S, on F^2	1.028	1.014	1.086
$R\,[I > 2\sigma(I)]$	0.0333	0.0220	0.0224
$R_w[I > 2\sigma(I)]$	0.0807	0.0545	0.0608

The copper ··· copper separation within the dinuclear unit is 5.732(2) Å, and the shortest inter-dimer copper ··· copper distance is 6.783(2) Å. The water molecule forms hydrogen bonds to bpca oxygen atoms in two neighbouring units, one of these being a bifurcated bond (see Table 2).

The bis-monodentate 1,3-bridging mode of dca has been postulated for the β-isomer of $[Cu(N(CN)_2)_2](iz)_2$ (iz = imidazole),[4l] but until now this bridging mode has not been confirmed by crystallography. In the present compound, however, one nitrile nitrogen and the amide nitrogen are metal bound, although the latter interaction is weak and of the semi-coordination type.

$[Cu(bpy)(dca)_2]_n$ 2. A chain structure is present in this compound, one of the dca units serving as an end-to-end 1,5-bridging ligand, while the other dca is terminal, monodentate. The chain extends along the *c*-glide plane in a zig-zag fashion (Fig. 2). The copper atom is distorted square pyramidal (trigonality parameter τ = 0.30),[10a] the equatorial positions being occupied by four nitrogen atoms, two from bpy (Cu(1)–N(1) 2.003(2) Å and Cu(1)–N(2) 2.0213(14) Å), one from a monodentate and one from a bridging dca (Cu(1)–N(3) 1.963(3) Å and Cu(1)–N(6) 1.996(2) Å), the apical position being occupied by the other nitrile nitrogen of the neighbouring dca (Cu(1)–N(8a) = 2.167(2) Å where N(8a) is at $x,-y,-0.5+z$). The copper equatorial plane has a significant tetrahedral distortion (maximum atomic deviation of 0.167 Å) with copper displaced by 0.279 Å from this plane in the direction towards the apical ligand atom. The dihedral angle between the equatorial plane and the bpy plane is 15.7°, and that between the equatorial planes of two consecutive copper atoms in the chain is 23.7°. The Cu ··· Cu distance across the dca bridge is 8.1999(8) Å and the Cu ··· Cu ··· Cu angle 79.29(1)°. Each pyridyl group of the bpy ligand is planar, the dihedral angle between the two rings being 5.0(1)°. Average C–C and C–N bond lengths are in good agreement with those reported previously in other bpy-containing copper(II) complexes.[11b]

In the crystal of **2** neighbouring chains pack such that the non-bridging dca of one chain protrudes into the region of the other chain between bpy units (Fig. 3, Table 3), the distances from the dca atoms to the nearest bpy plane being from 3.17 to 3.59 Å, and the dihedral angle between bpy and dca planes being 16.5°. The shortest *inter* chain metal ··· metal distance is 5.707(1) Å.

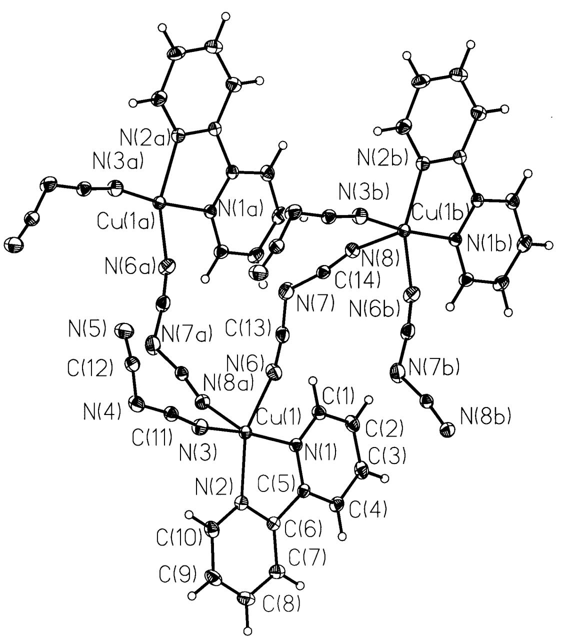

Fig. 2 Section of the $[Cu(bpy)(dca)_2]_n$ chain (**2**). Thermal ellipsoids are plotted at the 30% probability level. Symmetry codes a: x, $-y$, $-0.5+z$; b: x, $-y$, $0.5+z$.

The chain feature of **2** with a single dca-bridge is similar to that found in compound **4**,[4c] the two major differences between the two structures being that the apical Cu–N(dca) bond in **4** is appreciably longer than in **2** (2.286(3) *vs.* 2.167(2) Å) and that the packing pattern in **4** allows for semi-coordination, Cu ··· N(nitrile dca) of 2.821(3) Å, between neighbouring chains, leading to a weak double end-to-end bridge and a connection into a sheetlike polymer. The other characterized copper(II)–dca chain compound, $[Cu(ampym)_2(dca)_2]_n$ (ampym = 2-aminopyrimidine), features a double end-to-end dca bridge.[4d]

Table 2 Selected bond lengths [Å] and angles [°] for [Cu(bpca)(dca)(H_2O)]$_2$ (**1**)[a]

Copper coordination sphere			
Cu(1)–N(2)	1.9491(14)	Cu(1)–N(3)	2.034(2)
Cu(1)–N(4)	1.962(2)	Cu(1)–O(3)	2.3638(15)
Cu(1)–N(1)	2.023(2)	Cu(1)–N(5a)	2.799(2)
N(2)–Cu(1)–N(4)	171.57(6)	N(1)–Cu(1)–O(3)	89.70(6)
N(2)–Cu(1)–N(1)	81.51(6)	N(3)–Cu(1)–O(3)	96.70(6)
N(4)–Cu(1)–N(1)	98.86(7)	N(2)–Cu(1)–N(5a)	88.48(6)
N(2)–Cu(1)–N(3)	81.64(6)	N(4)–Cu(1)–N(5a)	83.10(7)
N(4)–Cu(1)–N(3)	97.15(7)	N(1)–Cu(1)–N(5a)	89.68(7)
N(1)–Cu(1)–N(3)	162.57(6)	N(3)–Cu(1)–N(5a)	85.44(7)
N(2)–Cu(1)–O(3)	96.76(6)	O(3)–Cu(1)–N(5a)	174.57(5)
N(4)–Cu(1)–O(3)	91.67(6)		
dca ligand			
N(4)–C(13)	1.163(3)	N(5)–C(14)	1.326(3)
N(5)–C(13)	1.305(3)	N(6)–C(14)	1.151(3)
C(13)–N(4)–Cu(1)	163.9(2)	N(4)–C(13)–N(5)	171.9(2)
C(13)–N(5)–C(14)	121.5(2)	N(6)–C(14)–N(5)	172.9(2)
Hydrogen bonds[b]			
A ··· H–D	A ··· D (Å)	A ··· H–D (°)	
O(1b) ··· H(31)–O(1)	2.829(2)	152	
O(2c) ··· H(32)–O(1)	2.847(2)	148	
O(1c) ··· H(32)–O(1)	3.100(2)	134	

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

Table 3 Selected bond lengths [Å] and angles [°] for [Cu(bpy)(dca)$_2$]$_n$ (**2**)

Copper coordination sphere			
Cu(1)–N(3)	1.963(3)	Cu(1)–N(2)	2.0213(14)
Cu(1)–N(6)	1.996(2)	Cu(1)–N(8a)	2.167(2)
Cu(1)–N(1)	2.003(2)		
N(3)–Cu(1)–N(6)	90.41(8)	N(1)–Cu(1)–N(2)	80.56(6)
N(3)–Cu(1)–N(1)	172.03(10)	N(3)–Cu(1)–N(8a)	95.48(9)
N(6)–Cu(1)–N(1)	92.06(7)	N(6)–Cu(1)–N(8a)	94.64(7)
N(3)–Cu(1)–N(2)	93.96(7)	N(1)–Cu(1)–N(8a)	91.88(8)
N(6)–Cu(1)–N(2)	154.04(7)	N(2)–Cu(1)–N(8a)	110.34(7)
bpy ligand			
N(1)–C(1)	1.327(3)	C(4)–C(5)	1.384(2)
N(1)–C(5)	1.359(2)	C(5)–C(6)	1.481(2)
N(2)–C(10)	1.337(2)	C(6)–C(7)	1.392(2)
N(2)–C(6)	1.353(2)	C(7)–C(8)	1.393(3)
C(1)–C(2)	1.390(3)	C(8)–C(9)	1.365(3)
C(2)–C(3)	1.384(3)	C(9)–C(10)	1.399(3)
C(3–C(4)	1.388(3)		
C(1)–N(1)–C(5)	119.5(2)	N(1)–C(5)–C(4)	121.5(2)
C(1)–N(1)–Cu(1)	124.76(14)	N(1)–C(5)–C(6)	114.2(2)
C(5)–N(1)–Cu(1)	115.61(14)	C(4)–C(5)–C(6)	124.3(2)
C(10)–N(2)–C(6)	119.4(2)	N(2)–C(6)–C(7)	121.8(2)
C(10)–N(2)–Cu(1)	125.65(13)	N(2)–C(6)–C(5)	114.64(14)
C(6)–N(2)–Cu(1)	114.89(11)	C(7)–C(6)–C(5)	123.6(2)
N(1)–C(1)–C(2)	122.0(2)	C(6)–C(7)–C(8)	118.2(2)
C(3)–C(2)–C(1)	118.9(2)	C(9)–C(8)–C(7)	119.9(2)
C(2)–C(3)–C(4)	119.3(2)	C(8)–C(9)–C(10)	119.2(2)
C(5)–C(4)–C(3)	118.8(2)	N(2)–C(10)–C(9)	121.5(2)
dca ligand			
N(3)–C(11)	1.159(4)	N(6)–C(13)	1.142(3)
N(4)–C(11)	1.293(3)	N(7)–C(13)	1.295(3)
N(4)–C(12)	1.311(3)	N(7)–C(14)	1.303(3)
N(5)–C(12)	1.152(3)	N(8)–C(14)	1.139(2)
C(11)–N(3)–Cu(1)	163.6(2)	N(3)–C(11)–N(4)	173.2(2)
C(11)–N(4)–C(12)	123.2(2)	N(5)–C(12)–N(4)	172.4(2)
C(13)–N(6)–Cu(1)	167.7(2)	N(6)–C(13)–N(7)	172.6(2)
C(13)–N(7)–C(14)	124.5(2)	N(8)–C(14)–N(7)	171.2(2)
C(14)–N(8)–Cu(1b)	155.90(15)		

Symmetry transformations used to generate equivalent atoms: a: $x, -y, z-1/2$; b: $x, -y, z + 1/2$.

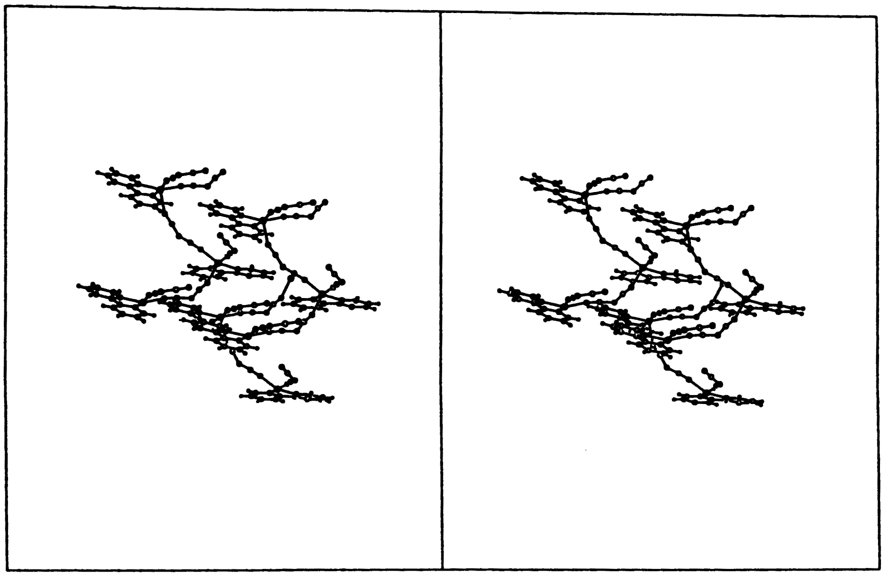

Fig. 3 Stereoview showing the interaction between neighbouring chains in $[Cu(bpy)(dca)_2]_n$ (**2**).

$[Cu_2(bpm)(dca)_4]_n$ 3.‡ The compound forms a ladder-like polynuclear structure in which the rungs are formed by centrosymmetric, bis-chelating bpm bridges and the uprights by end-to-end bridging dca units (Fig. 4, Table 4). The copper atom is best described as distorted square pyramidal (trigonality parameter $\tau = 0.09$),[10a] the equatorial positions being occupied by four nitrogen atoms, two from bpm (Cu(1)–N(2a) 2.0543(12) Å (a referring to symmetry operation $1 - x, -y, 1 - z$) and Cu(1)–N(1) 2.0934(12) Å), one from a monodentate and one from a bridging dca (Cu(1)–N(3) 1.9661(14) Å and Cu(1)–(6) 1.9672(13) Å), and the apical position being occupied by a nitrogen atom of another bridging dca (Cu(1)–N(8b) = 2.1444(13) Å, where N(8b) is at position $1 + x, y, z$). The copper equatorial plane has a small tetrahedral distortion (maximum atomic deviation of 0.067 Å) with copper displaced by 0.287 Å from this plane in the direction towards the apical ligand atom. The dihedral angle between the equatorial plane and the bpm plane is 12.7°. The Cu ··· Cu distances across the bpm and dca bridges are 5.5673(4) Å and 7.5550(2) Å, respectively.

Ladders related by the glide operation are arranged such that the N(5) end of the terminal dca protrudes into the cavities of the neighbouring ladder (Fig. 5) forming a weak interaction with copper (Cu(1) ··· N(5f) = 3.220(2) Å; where N(5f) is at $x, 0.5 + y, 0.5 + z$). Through this very weak connection the ladders are loosely linked into a three-dimensional network.

The combination of bpm and dca ligands have also been utilized together with metal ions other than copper (Co^{II}, Mn^{II} and Fe^{II}), and it is of interest to look at the structural differences that result.[3e] In the case of cobalt(II) two products were obtained in the same synthesis, one of these being $[Co_2(bpm)(dca)_4]_n{\cdot}nH_2O$. In this structure a ladder-like arrangement similar to that found in **3** is discernible, but the ladders are connected by double end-to-end dca bridges into a two-dimensional sheet structure. The other product is $[Co(bpm)(H_2O)(dca)_2]_n$ which has a zig-zag form one-dimensional chain structure where the metal ions are bridged by single end-to-end dca bridges and bpm serves as a terminal ligand. This latter cobalt complex and the corresponding manganese and iron complexes are isomorphic.[3e]

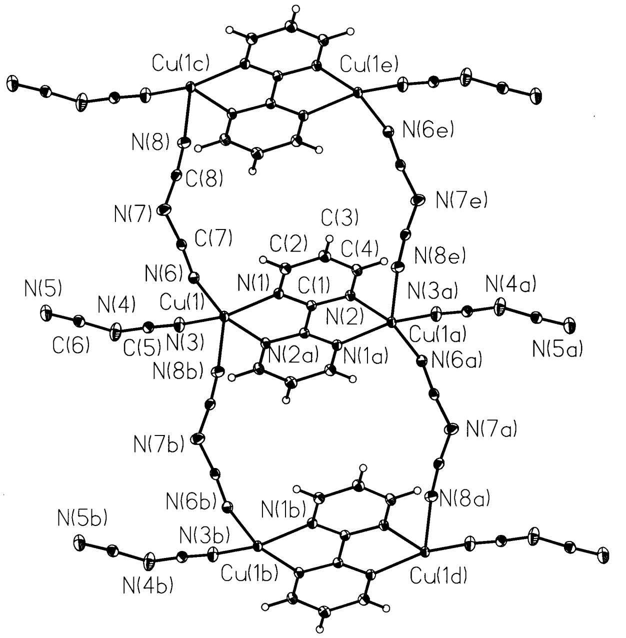

Fig. 4 Ladder structure of **3**, $[Cu_2(bpm)(dca)_4]_n$. Thermal ellipsoids are plotted at the 30% probability level. Symmetry codes a: $-x + 1, -y, -z + 1$; b: $x + 1, y, z$; c: $x - 1, y, z$; d: $2 - x, -y, 1 - z$; e: $-x, -y, 1 - z$.

Through several investigations it has been demonstrated that the $[Cu_2(bpm)_4]^{4+}$ unit is capable of forming a great variety of structural patterns through combination with different anions. Propagation in one dimension has been observed in the single alternating chain compound $[Cu_2(bpm)(NO_3)_4]_n$,[5b] as well as in the ladder arrangement of **3**. Two dimensional propagation is present in the complexes created with chloro- and bromo-bridges ($[Cu_2(bpm)X_4]_n$, X = Cl, Br),[12a] and in the honeycomb

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‡ *Note added at proof:* After submission of this paper, the room temperature crystal structure of compound **3** was reported, as well as magnetic susceptibility studies of this compound. (S. Martín, M. Gotzone Barandika, J. Ignacio Ruiz de Larramendi, R. Cortés, M. Font-Bardia, L. Lezama, Z. E. Serne, X. Solans and T. Rojo, *Inorg. Chem.*, 2001, **40**, 3687). The structural parameters of the two investigations agree very well, considering standard deviations and the difference in temperature. While the authors of the present paper have chosen to describe the structure as a ladder structure in which weak Cu ··· N interactions (3.22 Å) loosely link the ladders into a three-dimensional network, Martín *et al.* have chosen to emphasize more strongly the 3D feature of the structure. However, the results of the magnetic susceptibility studies differ markedly. Martín *et al.* derive a *J*-value of -76 cm^{-1} ($R = 2.1 \times 10^{-3}$) in contrast to our value of $-211(1)$ cm^{-1} ($R = 1.5 \times 10^{-6}$). The position of the maximum in the χ_m *vs.* T curve published by Martín *et al.* suggests that the *J*-value given is too low. Considering the exchange parameters observed in other bipyrimidine bridged copper(II) complexes with similar bridging geometries (Table 5), our result seems very reasonable.

Table 4 Selected bond lengths [Å] and angles [°] for $[Cu_2(bpm)(dca)_4]_n$ (**3**)

Copper coordination sphere			
Cu(1)–N(3)	1.9661(14)	Cu(1)–N(1)	2.0934(12)
Cu(1)–N(6)	1.9672(13)	Cu(1)–N(8b)	2.1444(13)
Cu(1)–N(2a)	2.0543(12)		
N(3)–Cu(1)–N(6)	94.49(6)	N(2a)–Cu(1)–N(1)	79.86(5)
N(3)–Cu(1)–N(2a)	91.97(5)	N(3)–Cu(1)–N(8b)	99.44(6)
N(6)–Cu(1)–N(2a)	164.46(5)	N(6)–Cu(1)–N(8b)	100.34(5)
N(3)–Cu(1)–N(1)	159.17(6)	N(2)#1–Cu(1)–N(8b)	92.51(5)
N(6)–Cu(1)–N(1)	89.24(5)	N(1)–Cu(1)–N(8b)	100.04(5)
bpm ligand			
N(1)–C(1)	1.331(2)	C(1)–C(1a)	1.467(3)
N(1)–C(2)	1.353(2)	C(2)–C(3)	1.388(2)
N(2)–C(1)	1.339(2)	C(3)–C(4)	1.393(2)
N(2)–C(4)	1.343(2)		
C(1)–N(1)–C(2)	116.65(12)	N(1)–C(1)–N(2)	126.81(12)
C(1)–N(1)–Cu(1)	112.75(9)	N(1)–C(1)–C(1a)	116.98(15)
C(2)–N(1)–Cu(1)	130.60(10)	N(2)–C(1)–C(1a)	116.21(15)
C(1)–N(2)–C(4)	116.69(12)	N(1)–C(2)–C(3)	120.50(13)
C(1)–N(2)–Cu(1a)	114.17(9)	C(2)–C(3)–C(4)	118.62(13)
C(4)–N(2)–Cu(1a)	129.14(10)	N(2)–C(4)–C(3)	120.69(13)
dca ligands			
N(3)–C(5)	1.147(2)	N(6)–C(7)	1.157(2)
N(4)–C(5)	1.301(2)	N(7)–C(7)	1.290(2)
N(4)–C(6)	1.319(2)	N(7)–C(8)	1.307(2)
N(5)–C(6)	1.154(2)	N(8)–C(8)	1.151(2)
C(5)–N(3)–Cu(1)	166.33(13)	N(3)–C(5)–N(4)	173.0(2)
C(5)–N(4)–C(6)	121.78(15)	N(5)–C(6)–N(4)	173.2(2)
C(7)–N(6)–Cu(1)	145.41(12)	N(6)–C(7)–N(7)	172.0(2)
C(7)–N(7)–C(8)	123.07(14)	N(8)–C(8)–N(7)	172.4(2)
C(8)–N(8)–Cu(1c)	165.89(13)		

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

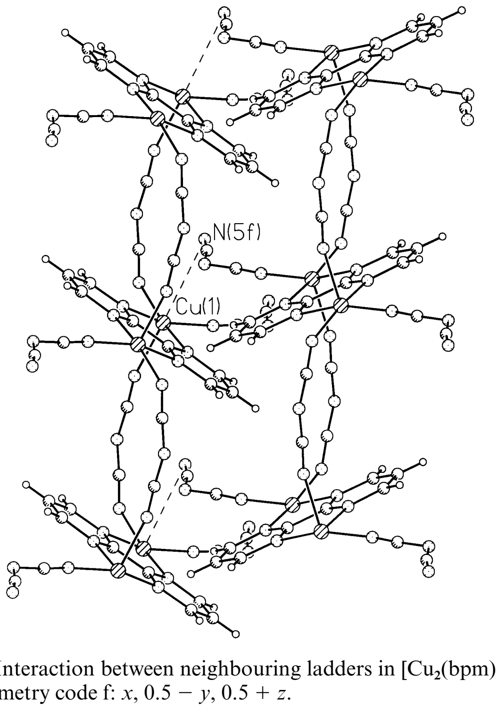

Fig. 5 Interaction between neighbouring ladders in $[Cu_2(bpm)(dca)_4]_n$ (**3**). Symmetry code f: $x, 0.5 - y, 0.5 + z$.

structure with alternating bpm and oxalate bridges ($[Cu_2(bpm)(ox)_2]_n \cdot 5nH_2O$),[12b] while thiocyanate as anion leads to a three-dimensional arrangement ($[Cu_2(bpm)(NCS)_4]_n$).[12c] On the other hand in combination with *e.g.* the dianions squarate and croconate isolation of dinuclear species has been possible ($[Cu_2(bpm)(H_2O)_6(C_4O_4)_2]$ and $[Cu_2(bpm)(H_2O)_2(C_5O_5)_2] \cdot 4H_2O$).[12d,e]

Infrared spectra

The dca anion in $NaN(CN)_2$ shows three sharp and strong characteristic stretch frequencies in the 2290 to 2170 cm^{-1} region attributed to ν_{as} + ν_s(C≡N) combination modes (2286 cm^{-1}), ν_{as}(C≡N) (2232 cm^{-1}) and ν_s(C≡N) (2179 cm^{-1}), respectively.[13a] Monodentate coordination has been reported to have but minor effect on these features.[13b] In compound **1** the three bands occur at 2293, 2239, 2177 cm^{-1}, with an additional satellite medium/weak band at 2365 cm^{-1}. These features might be indicative of monodentate bonding, and are consistent with the X-ray structure where dca is found to coordinate to copper through one of its cyano nitrogen atoms and in addition is semi-coordinated through the amide nitrogen. The spectra for compounds **2** and **3** resemble each other in the 2150 to 2400 cm^{-1} region, but are distinctly different from that of compound **1**. A splitting into several maxima is found; for compound **2**: 2398(w), 2323(s), 2293(s) cm^{-1} (ν_{as} + ν_s(C≡N)), 2258(s), 2225(s) cm^{-1} (ν_{as}(C≡N)) and 2202(s), 2164(s) cm^{-1} (ν_s(C≡N)); for compound **3**: 2340(m, with shoulder on the high frequency side), 2288(s) cm^{-1} (ν_{as} + ν_s(C≡N)), 2256(m/s), 2232(m/s) cm^{-1} (ν_{as}(C≡N)) and 2164(s, broad with shoulder on the high frequency side) cm^{-1} (ν_s(C≡N)). The bridging modes of dca cause a displacement of the bands towards higher frequencies, the effect increasing as one goes from bidentate to tridentate bonding.[13,4a,d,k,l,n,o,3m] The splitting of the bands and the displacements observed are consistent with the presence of both bridging (bidentate) and terminal (monodentate) dca in these compounds, as revealed by the X-ray structure determinations. Bands corresponding to the ν_{as}(C–N) stretching frequencies (1400–1300 cm^{-1} region), and the ν_s(C–N) stretch (950–900 cm^{-1} region), are also found in all spectra.

The spectrum of compound **1** also features an intense band at 1701 cm^{-1}, characteristic of the ν_{as}(C≡O) vibration of the uncoordinated imide group of bpca.[14] Furthermore a broad and intense band from 3600 to 3300 cm^{-1}, with maxima at 3503 and 3436 cm^{-1} may be attributed to the OH stretching of coordinated water.[15] The characteristic ring stretching modes and H-bend of uncoordinated bpy occur at 1579(s), 1553(m), 1448(s) and 1410(s) cm^{-1}. In the spectrum of complex **2** the corresponding bands are found at 1605(s), as a quasi-symmetric doublet with maxima at 1575(m) and 1567(m), 1500(m), 1476(s) and 1446(s) cm^{-1}; the displacement towards higher frequencies in the complex being consistent with metal coordination.[16] The spectrum of **3** shows a very asymmetric doublet at 1590(s/m) and 1562 (m/w) cm^{-1}, characteristic of bis-chelating bpm and due to the ring stretching modes. When monochelating this band occurs as a quasi-symmetric doublet at identical frequencies.[12c] Additional evidence for bis-chelation is provided by the single sharp, weak band found at 1228 cm^{-1} in the spectrum of **3**; for monochelation two sharp, weak peaks are observed at around 1220 and 1250 cm^{-1}.[12d,e]

Magnetic properties

The magnetic properties of the complexes **1**, **2** and **4** in the form of χ_mT *versus* T plots (χ_m is the magnetic susceptibility per copper(II) ion) are shown in Fig. 6. The values of χ_mT at 290 K are 0.42 cm^3 mol^{-1} K, which are as expected for a magnetically isolated spin doublet. These values remain practically constant upon cooling, and this feature holds for the two former compounds throughout the temperature region studied, while in the case of complex **4** the value starts increasing at 40 K, attaining a value of 0.475 cm^3 mol^{-1} K at 1.9 K. The described features are characteristic of Curie law behaviour (complex **1** and **2**) and weak ferromagnetic interaction (complex **4**), respectively. For complex **3** the χ_m *versus* T plot is shown in Fig. 7 with χ_mT *versus* T as an insert. The value of χ_mT at 290 K is 0.55 cm^3 mol^{-1} K per two copper(II) ions. The χ_mT value decreases gradually on cooling, attaining a value of 0.0 at 60 K (insert of Fig. 7), the χ_m *versus* T plot having a rounded maximum at 190 K. These features are characteristic of a strong antiferromagnetic interaction between a pair of copper(II) ions.

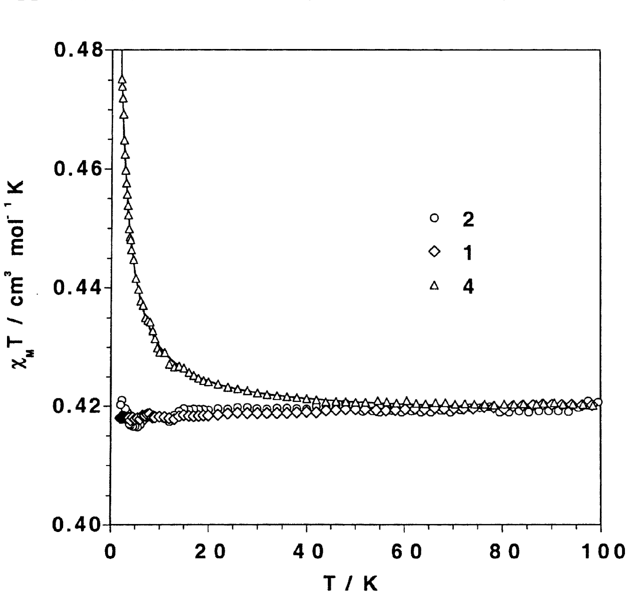

Fig. 6 χ_mT *vs.* T plot for complexes **1**, **2** and **4**. The solid line is the best fit (see text).

In compound **1** the X-ray structure (Fig. 1) reveals that the mononuclear building blocks are pairwise loosely connected through 1,3-dca bridges binding equatorially to copper through a nitrile nitrogen and being semi-coordinated to the neighbouring copper in an axial position through its amide nitrogen. The magnetic susceptibility data show, as expected, that this weak, out-of-plane $\mu_{1,3}$-dca bridge is not efficient in propagating magnetic interaction. In compound **2** dca is bridging end-to-end in an out-of-plane fashion. The magnetic orbital on the copper ion is roughly defined by the short copper to nitrogen bonds (that is it lies in the equatorial plane). Given that the spin density in the apical position is very weak, the overlap between the two parallel magnetic orbitals is very small. Under these conditions the exchange coupling is expected to be very weak or zero. Two compounds with end-to-end out-of-plane bridges between copper(II) of elongated octahedral geometry have previously been investigated, and no significant magnetic interactions were detected in these cases either.[4a,e]

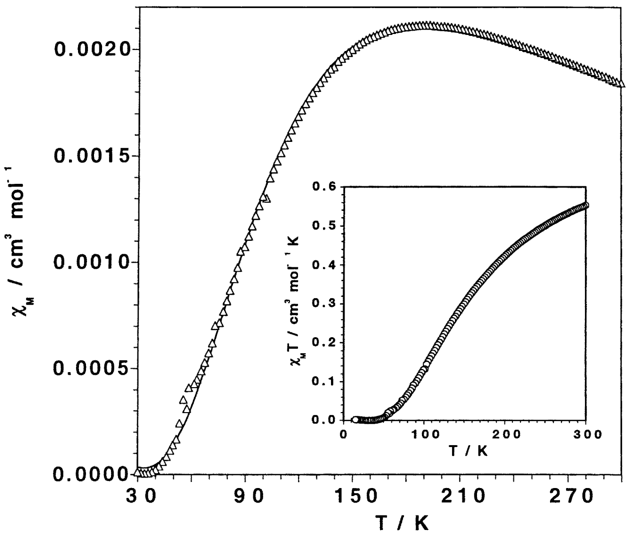

Fig. 7 χ_m *vs.* T plot for complex **3** (the insert shows the temperature dependence of the χ_mT product). The solid line is the best fit (see text).

Complex **4**, which has been structurally characterized previously,[4c] may, as complex **2**, be described as a chain compound with a single end-to-end out-of-plane dca bridge between the copper(II) centres. There are additional weak connections between the chains through double 1,5-dca bridges in which one end is equatorially bound and the other end is semi-coordinated to the copper ions. In the study of compound **1**, we found that no magnetic interaction was detectable even through a semi-coordinated 1,3-bridging dca; it is thus reasonable to ignore this latter interaction as a possible magnetic pathway. We have accordingly analyzed the magnetic data through the numerical expression proposed by Baker and Rushbrooke[17a] for a ferromagnetically coupled uniform chain of spin doublets: $\chi = Ng^2\beta^2/4kT\,[(1+Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5)/(1 + A'x + B'x^2 + C'x^3 + D'x^4)]^{2/3}$ where $x = |J|/kT$ and $A = 5.7979916$, $B = 16.902653$, $C = 29.376885$, $D = 29.832959$, $E = 14.036918$, $A' = 2.7979916$, $B' = 7.0086780$, $C' = 8.6538644$, $D' = 4.5743114$.

The best-fit parameters obtained through this procedure are: $J = +0.2(1)$ cm^{-1}, $g = 2.11(1)$ and $R = 1.2 \times 10^{-5}$ (R is the agreement factor defined as $\Sigma_i[(\chi_mT)_{\mathrm{obs}(i)} - (\chi_mT)_{\mathrm{calc}(i)}]^2/\Sigma_i[(\chi_mT)_{\mathrm{obs}(i)}]^2$). As shown above, no sign of magnetic interaction through the similar chain in complex **2** was found. The ferromagnetic interaction detected in the present case is very weak and it corresponds to a case of accidental orthogonality analogous to that previously observed in other cases where the out-of-plane exchange pathway is operative, either through monoatomic (μ-chloro and di-μ-chloro)[18a–c] or polyatomic (μ-oxalato and μ-oximato) bridges.[11a,18d] This accidental orthogonality between the magnetic orbitals is strongly dependent on structural features and even slight structural modifications can destroy it. This is nicely illustrated by the Curie law behaviour observed in **2** *versus* the ferro-coupling found in **4**. The larger distortion of the square pyramidal environment of the copper atom in **2** (trigonality parameter of 0.13 in **4** *versus* 0.30 in **2**) destroys the accidental orthogonality

Table 5 Selected magneto-structural data for bpm-bridged copper(II) complexes

Compound	Donor set[a]	$-J$/cm^{-1}	Cu–N(bpm)/Å[b]	Cu–X(eq)/Å[b]	Cu–Y(ax)/Å[c]	Cu ⋯ Cu/Å	γ/°[d]	h_M/Å[e]	Ref.
$[Cu_2(bpm)(H_2O)_6(C_4O_4)_2]$	$N_2O_2O_2$	139	2.07	1.96	2.26/2.43	5.54	11.4	0.096	12*d*
$[Cu_2(bpm)(H_2O)_2(mal)_2]\cdot4H_2O$[f]	$N_2O_2O_2$	149	2.04	1.90	2.40	5.45	6.5	0.118	19*a*
$[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot3H_2O$	$N_2O_2O_2$	159	2.04	1.97	2.23/2.50 2.31/2.45	5.46	5.1	0.075	19*b*
$[Cu_2(bpm)(H_2O)_2(C_5O_5)_2]\cdot4H_2O$	$N_2O_2O_2$	160	2.02	1.97	2.30/2.95	5.38	14.4	0.187	12*e*
$[Cu_2(bpm)(N_3)_4]$	$N_2N_2N_2$	178	2.06	1.96	2.48/2.74	5.52	2.6	0.104	19*c*
$[Cu_2(bpm)(NO_3)_4]$	$N_2O_2O_2$	191	2.01	1.96	2.30/2.55	5.37	3.5	0.021	12*a*,5*a*
$[Cu_2(bpm)(NCO)_4]$	N_2N_2NO	199	2.06	1.94	2.46/2.72	5.52	8.7	0.089	12*c*
$[Cu_2(bpm)(dca)_4]$	$N_2N_2N_2$	211	2.07	1.97	2.14/3.22	5.57	12.7	0.287	This work
$[Cu_2(bpm)Cl_4]$	$N_2Cl_2Cl_2$	225	2.06	2.25	2.87	5.53	2.7	0.000	12*a*
$[Cu_2(bpm)(NCS)_4]$	$N_2N_2S_2$	230	2.06	1.92	2.94	5.49	0.7	0.000	12*c*
$[Cu_2(bpm)Br_4]$	$N_2Br_2Br_2$	236	2.07	2.39	3.02	5.55	2.0	0.000	12*a*

[a] The first two atoms are those of bpm, the next two the other atoms (X) in the basal plane, and the last two the axial atoms (Y). [b] Average bond distances are given for each structure. [c] Individual bond distances are given. [d] The height of the metal atom above the basal plane. [e] Metal–metal separation across bpm. [f] mal = dianion of malonic acid.

between the magnetic orbitals, and the ferromagnetic coupling vanishes leading to a Curie law behaviour in **2**.

In the ladder-like structure of compound **3** we again find end-to-end out-of-plane dca bridges, which based on the evidence listed above, must be assumed to give a negligible magnetic interaction between the copper centres. bpm, on the other hand, has been shown to propagate very efficiently magnetic exchange between copper(II) centres.[12*a*,*c*–*e*,19] Hence, we have analyzed the magnetic data through a simple Bleaney–Bowers expression for a copper(II) dimer,[17*b*] derived through the isotropic Hamiltonian $\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$ where J is the exchange coupling parameter and $S_1 = S_2 = 1/2$ (interacting local spins). Least-squares fitting leads to the following parameters: $J = -211(1)$ cm^{-1}, $g = 2.10(1)$, and $R = 1.5 \times 10^{-6}$ (R is the agreement factor defined as $\Sigma_i[\chi_{m,obs(i)} - \chi_{m,calc(i)}]^2/\Sigma_i\,[\chi_{m,obs(i)}]^2$). The J-value lies within the region typically found in bpm-bridged complexes in which bpm binds in all equatorial positions to copper(II) in a square pyramidal or elongated octahedral environment. In Table 5 magneto-structural data for such complexes are collected and sorted after increasing $-J$ values. It has previously been pointed out that the electronegativity of the donor atoms of the peripheral ligands appears to be a very important factor in determining the variation in the strength of the magnetic interaction across a given bridge.[20] Inspection of Table 5 shows that this is the case also in the family of bpm-bridged copper(II) complexes. Although some irregularities are found, a general trend of increasing magnetic interaction with decreasing electronegativity of the peripheral atoms is observed.

Conclusions

The use of di- (bpy and phen) and tri-dentate (bpca) chelating nitrogen donors as terminal ligands and bis-chelating bridges (bpm) allowed us to prepare dca-containing copper(II) complexes where the dimensionality is sequentially increased from zero (compound **1**, dinuclear), to one (compounds **2** and **3**, zigzag and ladder-like chains, respectively) and to two (compound **4**, sheetlike polymer). A new coordination mode of dca is observed in **1**. Finally, a weak ferromagnetic coupling through a single end-to-end dicyanamide bridge is observed in **4** whereas a strong antiferromagnetic coupling through bridging bpm occurs in **3**.

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References

1 (*a*) C. R. Kmety, Q. Huang, J. W. Lynn, R. W. Erwin, J. L. Manson, S. McCall, J. E. Crow, K. L. Stevenson, J. S. Miller and A. J. Epstein, *Phys. Rev. B*, 2000, **62**, 5576; (*b*) J. L. Manson, C. R. Kmety, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, 1999, **38**, 2552; (*c*) P. Jensen, S. R. Batten, G. D. Fallon, B. Moubaraki, K. S. Murray and D. J. Price, *Chem. Commun.*, 1999, 177; (*d*) J. L. Manson, C. R. Kmety, Q. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheingold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 1998, **10**, 2552; (*e*) M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515; (*f*) S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 1998, 439.

2 (*a*) H. Yamochi, T. Komatsu, N. Matsukawa, G. Saito, T. Mori, M. Kusunoki and K. Sagaguchi, *J. Am. Chem. Soc.*, 1993, **115**, 11319; (*b*) H. Yamochi, T. Nakamura, T. Komatsu, N. Matsukawa, T. Inoue, G. Saito, T. Mori, M. Kusunoki and K. Sakaguchi, *Solid State. Commun.*, 1992, **82**, 101; (*c*) U. Geiser, A. M. Kini, H. H. Wang, M. A. Beno and J. M. Williams, *Acta Crystallogr., Sect. C*, 1991, **47**, 190; (*d*) A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. Stupka, D. Jung and M-H. Wangbo, *Inorg. Chem.*, 1990, **29**, 2555.

3 (*a*) J. L. Manson, Q. Huang, J. W. Lynn, H-J. Koo, M-H. Whangbo, R. Bateman, T. Otsuka, N. Wada, D. N. Argyriou and J. S. Miller, *J. Am. Chem. Soc.*, 2001, **123**, 162; (*b*) I. Dasna, S. Golhen, L. Ouahab, O. Peña, N. Daro and J-P. Sutter, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2001, **4**, 125; (*c*) B-W. Sun, S. Gao, B-Q. Ma and Z-M. Wang, *Inorg. Chem. Commun.*, 2001, **4**, 72; (*d*) B-W. Sun, S. Gao, B-Q. Ma, D-Z. Niu and Z-M. Wang, *J. Chem. Soc., Dalton Trans.*, 2000, 4187; (*e*) S. R. Marshall, C. D. Incarvito, J. L. Manson, A. L. Rheingold and J. Miller, *Inorg. Chem.*, 2000, **39**, 1969; (*f*) A. Escuer, F. A. Mautner, N. Sanz and R. Vicente, *Inorg. Chem.*, 2000, **39**, 1668; (*g*) B-W. Sun, S. Gao, B-Q. Ma and Z-M. Wang, *New J. Chem.*, 2000, **24**, 953; (*h*) I. Dasna, S. Golhen, L. Ouahab, O. Peña, J. Guillevic and M. Fettouhi, *J. Chem. Soc., Dalton Trans.*, 2000, 129; (*i*) S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D. J. Price, *J. Chem. Soc., Dalton Trans.*, 1999, 2987; (*j*) J. L. Manson, A. M. Arif and J. S. Miller, *J. Mater. Chem.*, 1999, **9**, 979; (*k*) J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold and J. S. Miller, *J. Solid State Chem.*, 1999, **145**, 369; (*l*) J. L. Manson, C. D. Incarvito, A. Rheingold and J. S. Miller, *J. Chem. Soc., Dalton Trans.*, 1998, 3705; (*m*) M. Hvastijová, J. Kožíšek, J. Kohout, L. Jäger and H. Fuess, *Transition Met. Chem.*, 1995, **20**, 276; (*n*) H. Köhler, H. Wusterhauser, M. Jeschke and A. Kolbe, *Z. Anorg. Allg. Chem.*, 1987, **547**, 69.

4 (*a*) I. Riggio, G. A. van Albade, D. D. Ellis, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta*, 2001, **313**, 120; (*b*) P. Jensen, D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem. Eur. J.*, 2000, **6**, 3186; (*c*) Z.-M. Wang, J. Luo, B.-W. Sun, C.-H. Yan, S. Gao and C.-S. Liao, *Acta Crystallogr., Sect. C*, 2000, **56**, 786; (*d*) G. A. van Albada, M. E. Quiroz-Castro, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta*, 2000, **298**, 221; (*e*) P. Jensen, S. R. Batten, G. D. Fallon, D. C. R. Hockless, B. Moubaraki, K. S. Murray and R. Robson, *J. Solid State Chemistry*, 1999,

145, 387; (*f*) J. Mrozinski, J. Kohout and M. Hvastijová, *Pol. J. Chem.*, 1997, **71**, 883; (*g*) M. Hvastijová, J. Kožíšek, J. Kohout, J. Mrozinski, L. Jäger and I. Svoboda, *Polyhedron*, 1997, **16**, 463; (*h*) M. Dunaj-Jurčo, D. Mikloš, I. Potočňák and L. Jäger, *Acta Crystallogr., Sect. C*, 1996, **52**, 2409; (*i*) I. Potočňák, M. Dunaj-Jurčo, D. Mikloš and L. Jäger, *Acta Crystallogr., Sect. C*, 1996, **52**, 1653; (*j*) I. Potočňák, M. Dunaj-Jurčo, D. Mikloš and M. Kabešová, *Acta Crystallogr., Sect. C*, 1995, **51**, 600; (*k*) M. Hvastijová, J. Kohout, M. Okruhlica, J. Mroziński and L. Jäger, *Transition Met. Chem.*, 1993, **18**, 579; (*l*) J. Mrozinski, M. Hvastijová and J. Kohout, *Polyhedron*, 1992, **11**, 2867; (*m*) J. Mrozinski, J. Kohout and H. Köhler, *Monatsh. Chem.*, 1992, **123**, 493; (*n*) J. Mroziński, J. Kohout and M. Hvastijová, *Polyhedron*, 1989, **8**, 157; (*o*) M. Hvastijová, J. Kohout, H. Köhler and G. Ondrejovic, *Z. Anorg. Allg. Chem.*, 1988, **566**, 111; (*p*) J. Mroziński, J. Kohout, M. Hvastijová and H. Köhler, *Transition Met. Chem.*, 1986, **11**, 481; (*q*) M. Hvastijová, J. Kohout, H. Wusterhausen and H. Köhler, *Z. Anorg. Allg. Chem.*, 1984, **510**, 37.

5 (*a*) I. Castro, J. Faus, M. Julve, J. M. Amigó, J. Sletten and T. Debaerdemaeker, *J. Chem. Soc., Dalton Trans.*, 1990, 891; (*b*) G. De Munno and G. Bruno, *Acta Crystallogr., Sect. C*, 1984, **40**, 2030.

6 A. Earnshaw, in *Introduction to Magnetochemistry*, Academic Press, London, 1968.

7 G. M. Sheldrick, SADABS, Version 2.01, University of Göttingen, Germany, 1996.

8 (*a*) SMART, Version 5.054, Data Collection Software, Bruker AXS, Inc., Madison, Wisconsin, USA, 1999; (*b*) SAINT, Version 5.00, Data Integration Software, Bruker AXS, Inc., Madison, Wisconsin, USA, 1999.

9 (*a*) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (*b*) G. M. Sheldrick, SHELXL-93, University of Göttingen, Germany, 1993; (*c*) XP, Version 4.3, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1992.

10 (*a*) A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349; (*b*) I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc., Dalton Trans.*, 1968, 1678.

11 (*a*) M. L. Calatayud, I. Castro, J. Sletten, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 2000, **300–302**, 846 and references therein; (*b*) I. Castro, M. L. Calatayud, J. Sletten, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 1999, **287**, 173 and references therein.

12 (*a*) M. Julve, G. De Munno, G. Bruno and M. Verdaguer, *Inorg. Chem.*, 1988, **27**, 3160; (*b*) G. De Munno, M. Julve, F. Nicolo, F. Lloret, J. Faus, R. Ruiz and E. Sinn, *Angew. Chem.*, 1993, **32**, 613; (*c*) M. Julve, M. Verdaguer, G. De Munno, J. A. Real and G. Bruno, *Inorg. Chem.*, 1993, **32**, 795; (*d*) I. Castro, J. Sletten, L. K. Glærum, J. Cano, F. Lloret, J. Faus and M. Julve, *J. Chem. Soc., Dalton Trans.*, 1995, 3207; (*e*) I. Castro, J. Sletten, L. K. Glærum, F. Lloret, J. Faus and M. Julve, *J. Chem. Soc., Dalton Trans.*, 1994, 2777.

13 (*a*) H. Köhler, A. Kolbe and G. Lux, *Z. Anorg. Allg. Chem.*, 1977, **428**, 103; (*b*) A. M. Golub, H. Köhler, V. V. Skopenko, *Chemistry of Pseudohalogenides,* Elsevier, Amsterdam, 1986.

14 (*a*) E. I. Lerner and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 5397; (*b*) I. Castro, J. Faus, M. Julve, M. Mollar, A. Monge and E. Gutierrez-Puebla, *Inorg. Chim. Acta*, 1989, **161**, 97; (*c*) I. Castro, J. Sletten, J. Faus, M. Julve, Y. Journaux, F. Lloret and S. Alvarez, *Inorg. Chem.*, 1992, **31**, 1889.

15 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 3rd edn., 1978, 227.

16 (*a*) J. S. Strukl and J. L. Walter, *Spectrochim. Acta, Part A*, 1971, **27**, 223; (*b*) A. R. Katritzky, *Q. Rev. Chem. Soc.*, 1959, **13**, 353.

17 (*a*) G. A. Baker and G. S. Rushbrooke, *Phys. Rev.*, 1964, **135**, 1272; (*b*) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

18 (*a*) M. Hernández-Molina, J. González-Platas, C. Ruiz-Pérez, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 1999, **284**, 258; (*b*) H. Grove, J. Sletten, M. Julve and F. Lloret, *J. Chem. Soc., Dalton Trans.*, 2001, 1029; (*c*) H. Grove, J. Sletten, M. Julve and F. Lloret, *J. Chem. Soc., Dalton Trans.*, 2001, 2487; (*d*) B. Cervera, R. Ruiz, F. Lloret, M. Julve, J. Cano, J. Faus, C. Bois and J. Mrozinski, *J. Chem. Soc., Dalton Trans.*, 1997, 395.

19 (*a*) Y. Rodríguez-Martín, J. Sanchiz, C. Ruiz-Pérez, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 2001, **326**, 20; (*b*) G. De Munno, M. Julve, F. Lloret, J. Cano and A. Caneschi, *Inorg. Chem.*, 1995, **34**, 2048; (*c*) G. De Munno, J. A. Real, M. Julve and M. C. Muñoz, *Inorg. Chim. Acta*, 1993, **211**, 227.

20 P. Román, C. Guzmán-Miralles, A. Luque, J. I. Beitia, J. Cano, F. Lloret, M. Julve and S. Alvarez, *Inorg. Chem.*, 1996, **35**, 3741.