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Three one-dimensional systems with end-to-end dicyanamide bridges between copper(II) centres: structural and magnetic properties

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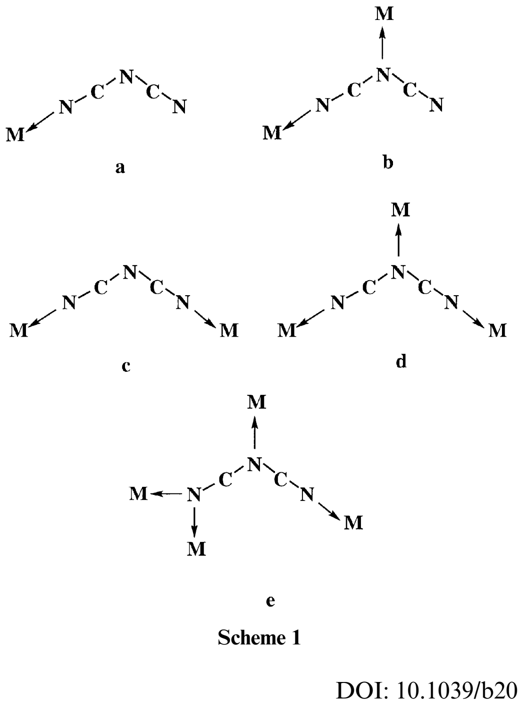
The preparation, crystal structures and magnetic properties of three different copper(II) chains of formula $[Cu(pyim)(H_2O)(dca)]_n(NO_3)_n$ (**1**), $[Cu(dpa)(dca)_2]_n$ (**2**) and $[Cu(bpa)(dca)_2]_n$ (**3**) [pyim = 2-(2-pyridyl)imidazole, dca = dicyanamide anion, dpa = 2,2′-dipyridylamine and bpa = 1,2-bis(4-pyridyl)ethane] are reported. A chain structure with single, symmetrical, end-to-end dca bridges is found in compound **1**. This bridging mode, with two short, equatorially coordinated Cu–N bonds has not been previously observed in the $[Cu(dca)X_n]$ (X = coligand) family of compounds. The copper atom in **1** has a distorted square pyramidal geometry with a bidentate pyim ligand and two nitrile nitrogen atoms from two dca groups in the equatorial positions and a water molecule occupying the axial site. In compound **2**, the single dca bridge is of the asymmetric end-to-end type. The copper environment in **2** is also distorted square pyramidal with a bidentate dpa ligand and two nitrile nitrogen atoms (one from a terminally bound dca and the other from a bridging dca) in the equatorial positions and a nitrile nitrogen atom from another bridging dca occupying the axial site. Compound **3** also features a uniform chain structure. In this case double, asymmetric end-to-end dca bridges and a bis-monodenate bpa bridge in the gauche conformation connect the neighbouring copper atoms. The copper(II) coordination geometry in **3** is elongated octahedral with two *trans* coordinated bpa nitrogen atoms and two dca nitrile nitrogens in the equatorial sites and two nitrile nitrogen atoms from two other dca groups occupying the axial positions. The copper–copper separations across the dca bridges are 7.7011(9) (**1**), 7.689(2) (**2**) and 7.095(3) Å (**3**). Magnetic susceptibility measurements for **1**–**3** in the temperature range 1.9–290 K reveal the occurrence of weak intrachain antiferromagnetic interactions [$J = -0.35$ (**1**), -0.10 (**2**) and -0.22 cm^{-1} (**3**) the Hamiltonian being defined as $\hat{H} = -J\,\Sigma_i \hat{S}_i \cdot \hat{S}_{i+1}$]. The efficiency of the dca bridge to mediate magnetic interactions in copper(II) complexes is analyzed and discussed in the light of the available magneto-structural data.

Introduction

The first report on coordination compounds with the pseudohalide dicyanamide anion [dca, $N(CN)_2^-$] was published by Madelung and Kern in 1922[1] and its coordinating ability towards 3d transition metal ions was explored by Köhler and coworkers in the 1960s and 1980s.[2] However, the homoleptic dca-containing complexes have been subject of intensive research in the last four years due to the capability of dca in designing extended networks with a great diversity of magnetic properties.[3–6] In particular, long-range magnetic ordering was observed in the rutile-like homoleptic M(dca) compounds, where M is a six-coordinated first-row transition metal ion. The versatility of dca as a ligand is well illustrated by its five structurally characterized coordination modes shown in Scheme 1:[3–10] monodentate coordination through a nitrile nitrogen atom (**1a**), bis-monodentate bridging though one nitrile and the amide nitrogen atoms (**1b**), end-to-end bridging through the two nitrile nitrogen atoms (**1c**), tris-monodentate bridging of three metal atoms (**1d**)[10] and the rarer μ_4 coordination where one of the two nitrile nitrogen atoms is coordinated to two metal ions (**1e**).

The structures and magnetic properties of the coordination polymers of dca can be strongly modified by the introduction



Scheme 1

of coligands (L). For simplicity, we will restrict ourselves to the results obtained when pyrazine (pyz) and 2,2′-bipyrimidine (bpm) were use as coligands. In the former case, two neutral phases noted α (structure containing two interpenetrating three-dimensional α-Po related networks)[12] and β (structure made up of interdigitated two-dimensional sheets) of formula $[M(dca)_2(pyz)]$ [M = Mn (α), Fe (α), Co (α, β), Ni (α, β), Cu (α, β) and Zn (α, β)] were isolated and investigated.[9a,9g,11] The pyz molecule acts as a bismonodentate bridging ligand in all these compounds and weak antiferromagnetic interactions between the paramagnetic centres were observed in them. As far as the combined use of dca and bpm is concerned, several one- and two-dimensional homometallic complexes with divalent first row transition metal ions (M = Mn, Fe, Co, Ni, Cu and Zn) were reported whose structures reveal the presence of end-to-end dicyanamide bridges and either chelating[13,14] or bischelating[8,15,16] bpm ligands. The remarkable efficiency of bpm in mediating strong antiferromagnetic interactions when acting as a bridge[8] and the assumed comparatively low efficiency of the end-to-end bridging dca allowed the authors to interpret their magnetic curves through a simple expression for the M(II)-bpm-M(II) dinuclear unit.

The evaluation of the weak exchange coupling through the extended dca bridge is quite complicated due to the lack of theoretical models to analyze the magnetic properties of the resulting high dimensionality compounds it forms with transition metal ions. In this respect, low dimensionality dca-bridged compounds such as the uniform copper(II) chains of formula $[Cu(pyim)(H_2O)(dca)]_n(NO_3)_n$ (**1**), $[Cu(dpa)(dca)_2]_n$ (**2**) and $[Cu(bpa)(dca)_2]_n$ (**3**) [pyim = 2-(2-pyridyl)imidazole, dpa = 2,2′-dipyridylamine and bpa = 1,2-bis(4-pyridyl)ethane] are better candidates to characterize the ability of the dca bridge to mediate magnetic interactions. In the present work, we report their preparation, structural characterization and magnetic investigation.

Experimental

Materials

Copper(II) nitrate trihydrate, sodium dicyanamide, 2,2′-dipyridylamine, and 1,2-bis(4-pyridyl)ethane were purchased from commercial sources and used as received. The ligand 2-(2-pyridyl)imidazole was prepared as previously described.[17]

Preparations

$[Cu(pyim)(H_2O)(dca)]_n(NO_3)_n$ (1). This compound separates as a dark green crystalline solid by adding an aqueous solution of $NaN(CN)_2$ (1 mmol) to another one containing a mixture of $Cu(NO_3)_2\cdot 3H_2O$ (1 mmol) and pyim (1 mmol). The yield is practically quantitative. Single crystals of **1** as dark green parallelepipeds were grown by slow diffusion in an H-shaped tube of aqueous solutions containing of $NaN(CN)_2$ (0.125 mmol) in one arm and [2-(2-pyridyl)imidazole]copper(II) nitrate (0.125 mmol) [mixture of $Cu(NO_3)_2\cdot 3H_2O$ and pyim in stoichiometric amounts] in the other. The diffusion was complete after two months and most of the crystals grow in the arm containing the copper salt. Anal. Found: C, 33.69; H, 2.46; N, 27.52. Calc. for $C_{10}H_9CuN_7O_4$: C, 33.87; H, 2.54; N, 27.63%.

$[Cu(dpa)(dca)_2]_n$ (2). Single crystals of **2** in the form of olive green needles were grown by slow diffusion in an H-shaped tube of aqueous solutions containing (2,2′-dipyridylamine)copper(II) nitrate (0.125 mmol) [mixture of $Cu(NO_3)_2\cdot 3H_2O$ and dpa in stoichiometric amounts] in one arm and $NaN(CN)_2$ (0.250 mmol) in the other one. The diffusion was complete after one month and most of the crystals grow in the tube connecting the two arms. The yield is practically quantitative. Anal. Found: C, 45.74; H, 3.38; N, 34.10. Calc. for $C_{14}H_9CuN_9$: C, 45.85; H, 2.45; N, 34.36%.

$[Cu(bpa)(dca)_2]_n$ (3). Single crystals of **3** in the form of sky blue needles were grown by slow diffusion in an H-shaped tube of aqueous solutions containing [1,2-bis(4-pyridyl)ethane]-copper(II) nitrate (0.125 mmol) [a mixture of $Cu(NO_3)_2\cdot 3H_2O$ and bpa in stoichiometric amounts] in one arm and $NaN(CN)_2$ (0.250 mmol) in the other. The diffusion was complete after one month and crystals of **3**, which grow in the tube containing the dca ligand, were obtained in low yield (*ca.* 20%). Cubic apple green crystals growing in the other arm and also in the horizontal connection are the main product. Although their IR spectrum reveals the presence of water, dca and bpa, they were not further investigated because they were not single crystals when tested on the diffractometer. Anal. Found: C, 50.48; H, 3.05; N, 29.39. Calc. for $C_{16}H_{12}CuN_8$: C, 50.61; H, 3.16; N, 29.50%.

Physical techniques

Infrared spectra were recorded with a Bruker IF S55 spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. The magnetic susceptibilities of polycrystalline samples of the complexes were performed in the temperature range 1.9–290 K with a Quantum Design SQUID susceptometer, using an applied magnetic field of 1000 G. The complex $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$ was used as a susceptibility standard. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants[18] and found to be -153×10^{-6}, -180×10^{-6} and -183×10^{-6} cm^3 mol^{-1} (per copper atom) for **1**, **2** and **3**, respectively. 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.[19] The structures were solved by direct methods and refined by full-matrix least-squares based on F^2, including all reflections. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms bound to carbon 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** rather broad reflection profiles were observed. Several crystals were tested on the diffractometer, and the crystal quality was approximately the same in all cases. The refinement revealed a probable disorder in the nitrate counter ion, but a reasonable model for the disorder could not be fitted. The larger of the residual electron density peaks are in the region of the nitrate, outside this region peaks higher than 0.4 e $Å^{-3}$ are not encountered. For compound **2** broad and irregular reflection profiles were encountered. The internal agreement factors between symmetry related reflections clearly favoured the monoclinic system, with a β angle of close to 90°. Intensity statistics indicated that the crystal might be twinned. The structure was solved in the space group $P2_1/n$ and initially refined to an R value of 0.15. After twinning was accounted for (twin law 1 0 0, 0 −1 0, 0 0 −1) the R value dropped to 0.05. Solution and refinement in the possible non-centrosymmetric monoclinic space groups as well as in the orthorhombic space groups $Pmn2_1$ and $P2_12_12$ were also attempted in the process, but did not result in satisfactory models.

Data collection and data reduction were done with the SMART and SAINT programs.[20] All other calculations were performed with the SHELX-97, SHELXL/PC and XP programs.[21] Selected bond distances and angles of complexes **1**, **2** and **3** are listed in Tables 2, 3 and 4, respectively.

Table 1 Crystal data and structure refinement for [Cu(pyim)(H$_2$O)(dca)]$_n$(NO$_3$)$_n$ (**1**), [Cu(dpa)(dca)$_2$]$_n$ (**2**) and [Cu(bpa)(dca)$_2$]$_n$ (**3**)

	1	**2**	**3**
Empirical formula	$C_{10}H_9CuN_7O_4$	$C_{14}H_9CuN_9$	$C_{16}H_{12}CuN_8$
Formula weight	354.78	366.84	379.88
Temperature/K	153(2)	153	153
λ/Å	0.71073	0.71073	0.71073
Space group	$P2_1/n$	$P2/n$	$I2/a$
a/Å	8.1036(11)	7.689(2)	13.106(3)
b/Å	10.7607(14)	16.975(5)	9.140(2)
c/Å	15.554(2)	11.689(3)	14.190(6)
β/°	102.276(3)	90.208(7)	98.862(4)
V/Å^3	1325.3(3)	1525.7(8)	1679.5(9)
Z	4	4	4
ρ/Mg m^{-3}	1.778	1.597	1.502
μ/mm^{-1}	1.681	1.448	1.317
Max 2θ/°	56.0	50.5	52.8
Refl. collected	9581	9149	5630
Independent refl.	3200 [R(int) = 0.0283]	2739 [R(int) = 0.0548]	1725 [R(int) = 0.0406]
Refl. with $I > 2\sigma(I)$	2659	2279	1315
Data/restraints/parameters	3200/0/199	2739/0/218	1725/0/115
Goodness-of-fit, S, on F^2	1.120	1.110	1.029
R [$I > 2\sigma(I)$]	0.0587	0.0494	0.0342
R_w [$I > 2\sigma(I)$]	0.1533	0.1002	0.0742

Table 2 Selected bond lengths [Å] and angles [°] for [Cu(pyim)(H$_2$O)(dca)]$_n$(NO$_3$)$_n$ (**1**)[a]

Copper coordination sphere

Cu–N(4)	1.964(4)	Cu–N(1)	2.040(4)
Cu–N(6a)	1.979(4)	Cu–O(1)	2.231(4)
Cu–N(2)	1.979(4)		
N(4)–Cu–N(6a)	91.16(16)	N(2)–Cu–N(1)	81.10(14)
N(4)–Cu–N(2)	165.39(16)	N(4)–Cu–O(1)	97.15(15)
N(6a)–Cu–N(2)	92.24(15)	N(6a)–Cu–O(1)	93.73(16)
N(4)–Cu–N(1)	92.78(15)	N(2)–Cu–O(1)	96.80(15)
N(6a)–Cu–N(1)	167.53(15)	N(1)–Cu–O(1)	97.51(14)

Bridging dca ligand

N(4)–C(9)	1.147(6)	N(6)–C(10)	1.142(6)
N(5)–C(9)	1.304(6)	N(6)–Cub	1.979(4)
N(5)–C(10)	1.306(6)		
C(9)–N(4)–Cu	167.8(4)	N(4)–C(9)–N(5)	173.4(5)
C(9)–N(5)–C(10)	119.9(4)	N(6)–C(10)–N(5)	174.6(5)
C(10)–N(6)–Cub	174.4(4)		

Bidentate pyim ligand

N(1)–C(1)	1.343(6)	N(1)–C(5)	1.355(3)
C(1)–C(2)	1.385(6)	C(2)–C(3)	1.368(7)
C(3)–C(4)	1.382(7)	C(4)–C(5)	1.400(6)
C(5)–C(6)	1.459(6)	C(6)–N(2)	1.328(5)
C(6)–N(3)	1.341(6)	N(2)–C(7)	1.384(6)
N(3)–C(8)	1.385(6)	C(7)–C(8)	1.365(6)
C(1)–N(1)–C(5)	118.5(4)	C(1)–N(1)–Cu	127.3(3)
C(5)–N(1)–Cu	114.1(3)	N(1)–C(1)–C(2)	121.8(4)
C(1)–C(2)–C(3)	119.8(4)	C(2)–C(3)–C(4)	119.6(4)
C(3)–C(4)–C(5)	118.2(4)	C(4)–C(5)–N(1)	122.1(4)
C(4)–C(5)–C(6)	125.5(4)	N(1)–C(5)–C(6)	112.4(4)
C(5)–C(6)–N(2)	118.6(4)	C(5)–C(6)–N(3)	129.9(4)
N(2)–C(6)–N(3)	111.4(4)	C(6)–N(2)–C(7)	106.2(4)
C(6)–N(2)–Cu	113.7(3)	C(7)–N(2)–Cu	140.1(3)
N(2)–C(7)–C(8)	108.7(4)	C(7)–C(8)–N(3)	106.6(4)
C(8)–N(3)–C(6)	107.0(4)		

Hydrogen bonds[b]

A	D	H	A · · · D/Å	A · · · H/Å	A · · · H–D/°
O(3)	O(1)	H(11)	2.650(7)	1.47	171
O(4c)	O(1)	H(12)	2.899(7)	2.12	145
O(4d)	N(3)	H(31)	2.825(6)	1.95	174

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x + 3/2, y + 1/2, -z + 1/2$; (b) $-x + 3/2, y - 1/2, -z + 1/2$; (c) $-x + 1/2, y - 1/2, -z + 1/2$; (d) $x - 1/2, -y + 3/2, z - 1/2$. [b] A = acceptor and D = donor.

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

Copper coordination sphere

Cu–N(1)	1.971(4)	Cu–N(7)	2.016(4)
Cu–N(9)	2.000(3)	Cu–N(6a)	2.175(7)
Cu–N(4)	2.012(6)		
N(1)–Cu–N(9)	173.9(3)	N(2)–Cu–N(7)	151.3(2)
N(1)–Cu–N(4)	89.6(2)	N(1)–Cu–N(6a)	93.7(2)
N(9)–Cu–N(4)	88.8(2)	N(9)–Cu–N(6a)	92.4(2)
N(1)–Cu–N(7)	90.61(17)	N(4)–Cu–N(6a)	104.8(2)
N(9)–Cu–N(7)	87.91(16)	N(7)–Cu–N(6a)	103.9(2)

Terminal and bridging dca ligands

N(1)–C(1)	1.155(6)	N(4)–C(3)	1.154(8)
N(2)–C(1)	1.308(6)	N(5)–C(3)	1.285(11)
N(2)–C(2)	1.314(7)	N(5)–C(4)	1.289(10)
N(3)–C(2)	1.146(7)	N(6)–C(4)	1.146(9)
C(1)–N(1)–Cu	176.9(6)	C(3)–N(4)–Cu	157.2(5)
C(1)–N(2)–C(2)	121.5(4)	C(3)–N(5)–C(4)	122.4.(5)
C(2)–N(3)–Cuc	91.3(4)	C(4)–N(6)–Cub	168.1(5)
N(1)–C(1)–N(2)	171.6(5)	N(4)–C(3)–N(5)	173.3(6)
N(3)–C(2)–N(2)	172.5(5)	N(6)–C(4)–N(5)	172.5(7)

Hydrogen bonds[b]

A	D	H	A · · · D/Å	A · · · H/Å	A · · · H–D/°
N(3d)	N(8)	H(81)	2.951(6)	2.17	151

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

CCDC reference numbers 182810–182812 for **1**–**3**.

See http://www.rsc.org/suppdata/dt/b2/b203085n/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structures

[Cu(pyim)(H$_2$O)(dca)]$_n$(NO$_3$)$_n$ (1). The structure of **1** consists cationic [Cu(pyim)(H$_2$O)(dca)]$_n^{n+}$ chains (Fig. 1) and nitrate counterions linked by electrostatic forces, Van der Waals interactions and hydrogen bonds (see end of Table 2). Each chain extends along the two-fold screw-axis, and features a single, symmetric end-to-end dca bridge in which both of the terminal nitrogen atoms form short, equatorial bonds to copper. To our knowledge, this bridging mode of dca has not previously been

Table 4 Selected bond lengths [Å] and angles [°] for $[Cu(bpe)dca)_2]_n$ (**3**)[a]

Copper coordination sphere			
Cu–N(1)	2.001(2)	Cu–N(3b)	2.467(2)
Cu–N(4)	2.026(2)		
N(1)–Cu–N(1a)	180.000(1)	N(4)–Cu–N(4a)	180.000(1)
N(1)–Cu–N(4a)	89.78(9)	N(4a)–Cu–N(3b)	88.98(8)
N(1)–Cu–N(4)	90.22(9)	N(4)–Cu–N(3b)	91.02(8)
N(1)–Cu–N(3b)	89.08(8)	N(1)–Cu–N(3c)	90.92(8)
N(1a)–Cu–N(3b)	90.92(8)	N(3b)–Cu–N(3c)	180.00(10)
Bridging dca ligand			
N(1)–C(1)	1.145(3)	N(3)–C(2)	1.148(3)
N(2)–C(1)	1.300(3)	N(3)–Cuc	2.467(2)
N(2)–C(2)	1.307(4)		
C(1)–N(1)–Cu	168.2(2)	N(1)–C(1)–N(2)	173.1(3)
C(1)–N(2)–C(2)	122.3(2)	N(3)–C(2)–N(2)	174.0(3)
C(2)–N(3)–Cuc	129.53(19)		

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x + 3/2, -y + 1/2, -z + 1/2$; (b) $x, -y + 1/2, z - 1/2$; (c) $-x + 3/2, y, -z + 1$.

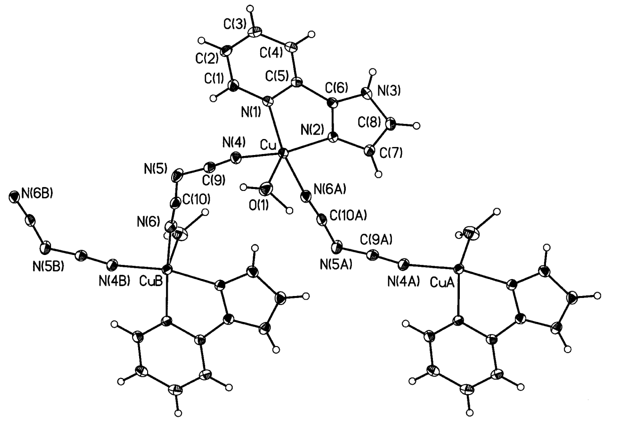


Fig. 1 Section of the $[Cu(pyim)(H_2O)(dca)]_n^{n+}$ chain (**1**). Thermal ellipsoids are plotted at the 30% probability level. Symmetry codes: (a) = $-x + 3/2, y + 1/2, -z + 1/2$; (b) = $-x + 3/2, y - 1/2, -z + 1/2$.

observed in the $[Cu(dca)_nL_n]$ (n = 1 or 2) family of compounds. The copper atom has a square pyramidal coordination geometry with two pyim nitrogen atoms [Cu–N(1) = 2.040(4) Å, Cu–N(2) = 1.979(4) Å] and two terminal dca nitrogen atoms [Cu–N(4) = 1.964(4) Å, Cu–N(6a) = 1.979(4) Å; (a) = $1.5 - x$, $0.5 + y$, $0.5 - z$] in the equatorial positions and a water molecule [Cu–O(1) = 2.231(4) Å] in the apical one. The sixth coordination position is screened by the proximity to the pyridyl ring of the pyim ligand from a neighbouring chain [Cu ··· N(3e) = 3.454(4) Å; (e) = $1 - x$, $1 - y$, $-z$]. The atoms defining the equatorial plane of copper are approximately coplanar (maximum atomic deviation being 0.021 Å) and the metal is displaced by 0.217 Å from this plane towards the apical oxygen. The atoms of the dca bridge are approximately coplanar (maximum atomic deviation 0.043 Å) and it forms angles of 8.5 and 8.2° with the equatorial planes of the two copper atoms to which it is bonded. The dihedral angle between the equatorial planes of neighbouring copper atoms in the chain is 5.9°. The Cu ··· Cu distance across the dca bridge is 7.7011(9) Å.

To our knowledge no crystallographic structure determination of pyim has been reported. A comparison of our results with some recent, low temperature studies where 2,2′-bipyridyl[22b,c] and imidazole[23] occur as ligands, as well as the early structure determination of 2,2′-bipyridyl itself,[22a] shows that bond distances and angles are as expected for these ring systems. The inter-ring C(5)–C(6) bond of 1.459(6) Å has a considerable amount of double bond character in agreement with the fact that the dihedral angle between the two individual planar pyridyl and imidazole rings (maximum atomic deviation from mean planes 0.07 and 0.06 Å, respectively) is only 4.1°. The nitrate counter ion forms hydrogen bonds to coordinated water in two different chains, and in addition to the NH of the imidazole ring of the pyim ligand in a third chain, thus providing relatively strong links between chains. The connection to the latter chain is furthermore strengthened by the stacking of centrosymmetrically related pyim molecules at an average distance of 3.42 Å. The shortest interchain metal–metal distance also occurs between the latter two chains [Cu ··· Cu(e) = 4.9785(11) Å].

$[Cu(dpa)(dca)_2]_n$ (2). A uniform chain extending along the *a*-axis is found, one of the dca units serving as an asymmetric end-to-end 1,5-bridging ligand, while the other dca is terminal, monodentate (Fig. 2, Table 3). The copper atom is distorted square pyramidal (trigonality parameter $t = 0.38$),[24] the equatorial positions being occupied by four nitrogen atoms, two from dpa [Cu–N(7) 2.016(4) Å and Cu–N(9) 2.000(3) Å], one from a monodentate and one from a bridging dca [Cu–N(1) 1.971(4) Å and Cu–N(4) 2.012(6) Å], the apical position being occupied by the other nitrile nitrogen of the neighbouring dca-bridge [Cu–N(6a) = 2.175(7) where N(6a) is at $x - 1, y, z$]. The copper equatorial plane has a significant tetrahedral distortion (maximum atomic deviation of 0.198 Å) with copper displaced by 0.302 Å from this plane in the direction towards the apical ligand atom. The intrachain copper–copper distance across the dca bridge is 7.689(2) Å. Each pyridyl ring of dpa is essentially planar, the dihedral angle between the two rings being 27.2°. This value is very close to that of the free dpa (23°)[25] and the twist serves to relieve the steric hindrance within the ligand. The bond lengths and angles about chemically equivalent atoms in the two pyridine rings are practically identical [1.380(6) and 1.376(6) Å for N(8)–C(9) and N(8)–C(10), respectively].

In the crystal of **2** neighbouring chains related by a two-fold axis pack such that the terminal end of the non-bridging dca of one chain forms a close contact to copper in the other chain, N(3) ··· Cu(c) = 3.482(6) Å [c denoting symmetry operation $-x + 0.5$, y, $-z + 0.5$] and N(3)–Cu(c)–N(6a) = 175.3(2)° (Fig. 3). In addition N(3) participates in a hydrogen bond to the dpa amine group in the chain displaced by a unit cell translation along *c* [N(3) ··· N(8)($x, y, z - 1$) = 2.951(6) Å]. These two sets of contacts link the chains into layers (Fig. 3). The shortest interchain copper–copper distances occur between chains symmetry related by a two-fold axis [Cu ··· Cu($-x + 0.5$, y, $-z + 0.5$) = 6.301(2) Å and Cu ··· Cu($-x - 0.5$, y, $-z + 0.5$) = 6.211(2) Å].

$[Cu(bpa)(dca)_2]_n$ (3). The structure consists of neutral, uniform chains where neighbouring copper atoms are connected through one bpa and two asymmetric end-to-end dca bridges (Fig. 4, Table 4). Each copper atom is situated at a centre of symmetry and a two-fold axis runs through the midpoints of the bpa exocyclic C–C bond and the Cu ··· Cu intrachain line. The copper atom has an elongated octahedral coordination geometry with short equatorial bonds to two bpa and two dca nitrogen atoms [Cu–N(4) = 2.026(2) Å and Cu–N(1) = 2.001(2) Å], and long axial bonds to the other terminal nitrogen atoms of the dca bridges [Cu–N(3b) = 2.467(2) Å; b referring to symmetry operation $-x + 1.5$, y, $-z + 1$]. The dihedral angle between the equatorial planes of neighbouring copper atoms is 30.1°. The bridging bpa ligand in **3** exhibits the *gauche* (angular) conformation[26] and the dihedral angle between the two pyridyl mean planes is 59.5°. The C–C and C–N bond distances within the bpa molecule are in agreement with those reported for this ligand in its metal complexes.[26,27]

The chains extends along the the crystallographic *c*-axis. Parallel chains stack in the *b*-direction such that the convex bpa

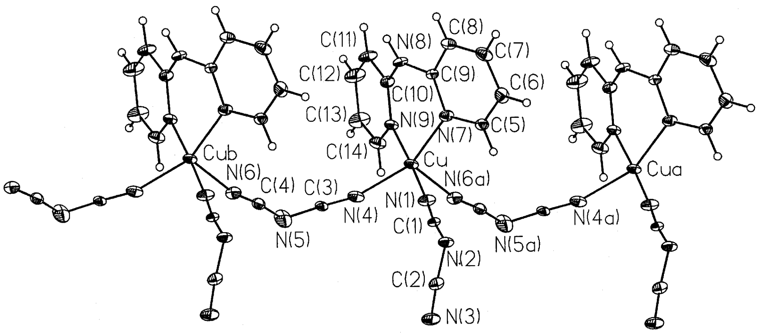


Fig. 2 Section of the chain in [Cu(dpa)(dca)$_2$]$_n$ (**2**). Thermal ellipsoids are plotted at the 30% probability level. Symmetry codes. (a) = $-1 + x, y, z$; (b) = $1 + x, y, z$.

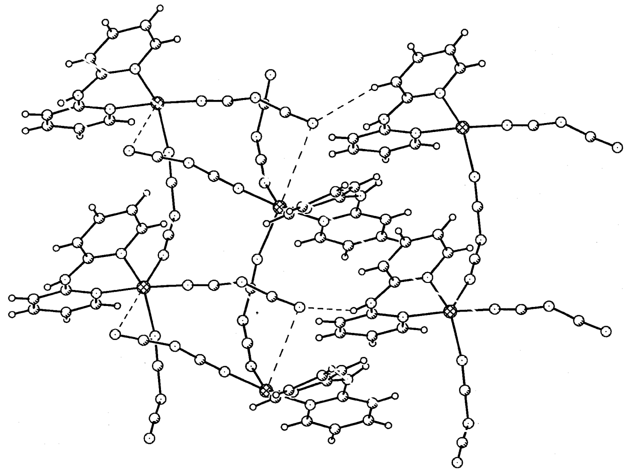


Fig. 3 Interaction between neighbouring chains in [Cu(dpa)(dca)$_2$]$_n$ (**2**) creating a layer structure.

bow of one chain extends into the concave section of the neighbouring chain. Between chains related by the *I*-centring, weak N(6) ··· H–C(6)′ interactions (N ··· H = 2.45 Å) stabilize the structure. The intrachain copper–copper separation is 7.095(3) Å, whereas that of the shortest interchain metal–metal distance is 7.989(3) Å.

Infrared spectra

Table 5 IR absorptions and tentative assignment for the dicyanamide ligand in **1**–**3**[a]

Compound	ν_{as}(C≡N) + ν_s(C≡N)	ν_{as}(C≡N)	ν_s(C≡N)
Na[N(CN)$_2$]	2286s	2232s	2179vs
1	2341s	2284s	2221vs, 2197vs
2	2305s	2249s	2174vs
3	2300s	2240s	2173vs

[a] Values in cm^{-1}.

The infrared spectra of the three compounds exhibit strong absorptions in the 2345–2170 cm^{-1} region corresponding to ν(C≡N) of the dicyanamide ligand.[2d] They are listed in Table 5 together with those of the sodium dicyanamide salt for comparison. The shift towards higher frequencies of these peaks in **1**–**3** as compared to those of the free dca is due to the bridging coordination modes of dca in the three compounds. Although dca adopts the same end-to-end bridging mode in **1**–**3**, it links two equatorial positions of the neighbouring copper atoms in **1** and one equatorial with one axial positions in **2** and **3**. This analogy between the dca bridge in **2** and **3** accounts for their practically identical frequency values in Table 5. The somewhat higher wavenumbers for the peaks of dca in **1** may be attributed to its stronger coordination as a bridge. Bands concerning 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 observed in all spectra. The absorptions at 3450br (O–H stretching of water) and at 3160w, 3090w and 2920w cm^{-1} (N–H and C–H stretching vibrations) in the spectrum of **1** are due to the presence of coordinated water molecule and the pyim ligand. The bands of the ionic nitrate[28] for this compound are located at 2430w, 1384s and 830 cm^{-1}. The N–H stretching vibration of the coordinated dpa in **2** is found at 3300w cm^{-1} (to be compared with the medium intensity peak at 3250 cm^{-1} in the spectrum of free dpa). Finally, H–C, C=N and C=C stretching vibrations of coordinated bpa in **3** appear at 3077w, 1619m and 1560w cm^{-1}, respectively.

Magnetic properties

The magnetic properties of the complexes **1**–**3** in the form of $\chi_M T$ *versus* T plots [χ_M is the magnetic susceptibility per copper(II) ion] are shown in Fig. 5. The values of $\chi_M T$ at 290 K for **1**–**3** are practically identical and equal to *ca.* 0.42 cm^3 mol^{-1} K, a value which is as expected for a magnetically isolated spin doublet. Upon cooling, a Curie law behaviour is observed and a

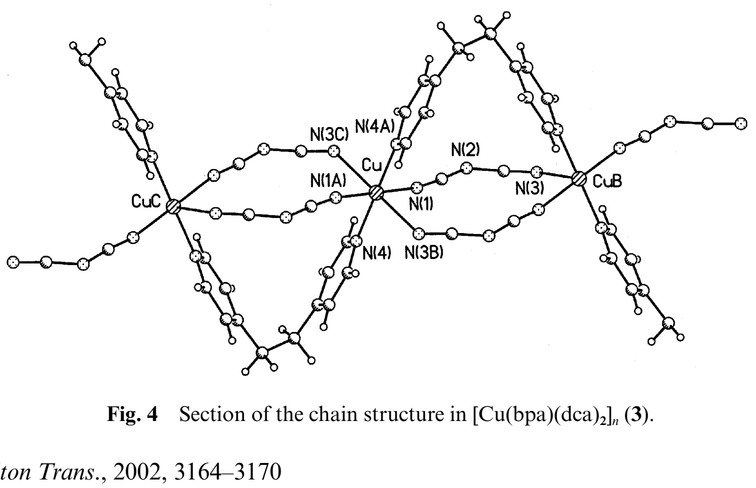


Fig. 4 Section of the chain structure in [Cu(bpa)(dca)$_2$]$_n$ (**3**).

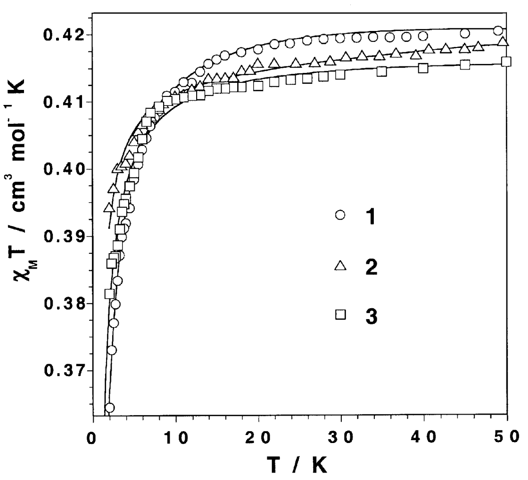


Fig. 5 $\chi_M T$ *versus* T plot for complexes **1**–**3**. The solid line is the best fit (see text).

smooth decrease of $\chi_M T$ occurs only in the low temperature range. The values of $\chi_M T$ at 1.9 K are 0.364 (**1**), 0.394 (**2**) and 0.382 (**3**) cm^3 mol^{-1} K. These features are characteristic of very weak antiferromagnetic interactions. Given that the structures of **1**–**3** consist of uniformly spaced chains of copper(II) ions, their magnetic data have been analysed through the theoretical expression (the Hamiltonian being $-J\Sigma_i \hat{S}_i \cdot \hat{S}_{i+1}$) proposed by Hall[29a] for a uniform chain of local spins $S = 1/2$, eqn. (1)

$$\chi_M = (N\beta^2 g^2/kT)[0.25 + 0.14995x + 0.30094x^2)/(1 + 1.9862x + 0.68854x^2 + 6.0626x^3) \quad (1)$$

where N, β and g have their usual meanings, $x = |J|/kT$ and J is the exchange coupling constant describing the magnetic interaction between two nearest-neighbour spin doublets. This expression, which derives from the numerical results from Bonner and Fisher,[29b] has been widely used for the treatment of the magnetic data of uniform copper(II) chains. Least-squares fit of the magnetic data of **1**–**3** through eqn. (1) leads to the following set of parameters: $J = -0.35$ cm^{-1}, $g = 2.14$ and $R = 2.5 \times 10^{-6}$ for **1**, $J = -0.10$ cm^{-1}, $g = 2.12$ and $R = 6.0 \times 10^{-6}$ for **2** and $J = -0.22$ cm^{-1}, $g = 2.11$ and $R = 1.1 \times 10^{-5}$ for **3** (R is the agreement factor defined as $\Sigma_i[(\chi_M T)_{\text{obs}(i)} - (\chi_M T)_{\text{calc}(i)}]^2/\Sigma_i[(\chi_M T)_{\text{obs}(i)}]^2$).

Our results show that the magnetic coupling between copper(II) ions through the end-to-end dca bridge in **1**–**3** is very weak and antiferromagnetic, the observed trend of the values of $-J$ being **1** > **3** > **2**. Concerning the weakness of the magnetic coupling in this series, it deserves to be noted that in two very recent papers no magnetic coupling was observed in the dca-bridged copper(II) chains of formula $[\text{Cu(bpy)(dca)}_2]_n$[8] (bpy = 2,2′-bipyridine) and $[\text{Cu(apym)(dca)}_2]_n\cdot(\text{CH}_3\text{CN})$[9e] (apym = 2-aminopyrimidine) where single (bpy derivative) and double (apym complex) end-to-end dca groups act as bridges linking an equatorial position of one copper atom with an axial site of the adjacent copper atom. The weak coupling through this extended bridge can be understood as follows: the magnetic orbital describing the unpaired electron on a copper(II) ion in square pyramidal (**1** and **2**) or elongated distorted octahedral (**3**) geometries is of the $d_{x^2-y^2}$ type (the x and y axes being roughly defined by the short equatorial bonds). The overlap between two of these orbitals through the polyatomic μ-1,5-dca bridge is expected to be very weak and, consequently, the antiferromagnetic coupling which is proportional to the square of this overlap[30] is predicted to be a weak one, as observed. Concerning the trend of the $-J$ values of **1**–**3**, looking at the structures of **1**–**3**, simple structural considerations show that the largest antiferromagnetic coupling is expected for complex **1** where equatorial positions of adjacent copper atoms are connected through the dca bridge.

We would like to finish this contribution pointing out the variety of structures that can be obtained in the Cu(II) : dca^{2-} : L ternary system, L being a neutral chelating nitrogen donor. The magneto-structural reports concerning the uniform copper(II) chains of formula $[\text{Cu(pyim)(H}_2\text{O)(dca)}]_n(\text{NO}_3)_n$ (**1**) $[\text{Cu(dpa)(dca)}_2]_n$ (**2**) and $[\text{Cu(bpy)(dca)}_2]_n$ (**4**),[8] the ladder-like chain $[\text{Cu}_2\text{(bpm)(dca)}_4]_n$ (**5**)[8,14] and the sheetlike polymer $[\text{Cu(phen)(dca}_2)]_n$ (**6**)[31] (phen = 1,10-phenanthroline) are illustrative examples. The single end-to-end dca bridges which link adjacent copper atoms in **1**–**3** coexist with terminally bound dca groups (**2** and **4**) leading to either zig–zag (**1** and **4**) or linear (**2**) uniform chains. Very weak intrachain antiferromagnetic coupling (**1** and **2**) and Curie law behaviour (**4**) are observed. In **5** two parallel single dca-bridged chains of copper(II) ions (uprights) are linked through centrosymmetric bisbidentate bpm (rungs) leading to a ladder-like motif. In this case, the strong antiferromagnetic interaction observed is mediated by the bridging bpm. Finally, double and single end-to-end dca-bridges link the $[\text{Cu(phen)}]^{2+}$ units in **6** affording a neutral two-dimensional network. In this compound, a weak ferromagnetic coupling is observed between the copper(II) ions bridged by the single dca groups.

Conclusions

The combined use of dca and pyim, dpa and bpa as ligands towards copper(II) ions allowed us: firstly, to obtain three new single (**1** and **2**) and double (**3**) dca-bridged copper(II) chains with dca exhibiting the end-to-end bridging mode; secondly, to check and compare the efficiency of this coordination mode in mediating exchange interactions between copper(II) ions through the equatorial–equatorial (**1**) and equatorial-axial (**2** and **3**) pathways; and thirdly, to show how dca-bridged uniform copper(II) chains can result using as coligands bidentate (**1** and **2**) or bismonodentate (**3**) nitrogen donors.

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