Discrete Dinuclear Complexes and Two-Dimensional Architectures from Bridging Polynitrile and Bipyrimidine (bpym) Ligands: Syntheses, Structures and Magnetic Properties of $[M_2(bpym)(dcne)_4(H_2O)_2]$ ($M = Mn^{II}, Co^{II}$) and $[M_2(bpym)(dcne)_4(H_2O)_4]\cdot 2H_2O$ ($M = Fe^{II}, Cu^{II}$) ($dcne^- = [(CN)_2CC(O)OEt)]^-$)

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One-pot reactions in aqueous solutions of the polynitrile anion dcne⁻ {2,2-dicyano-1-ethoxyethenolate = $[(CN)_2CC(O)OEt)]^-$} with the M^{II} ions (M = Mn, Fe, Co, Cu) in the presence of bpym (2,2′-bipyrimidine) afford the first mixed dcne/bpym compounds $[M_2(bpym)(dcne)_4(H_2O)_2]$ (**1**: M = Mn; **2**: M = Co) and $[M_2(bpym)(dcne)_4(H_2O)_4]\cdot 2H_2O$ (**3**: M = Fe; **4**: M = Cu). The new compounds have been characterized by IR spectroscopy and X-ray crystallography. Compounds **1** and **2** are isostructural, with each metal ion being located in an MN_5O pseudo-octahedral environment with three N atoms coming from three dcne⁻ ligands, two nitrogen atoms from bpym and one oxygen atom from a water molecule. The extended structures of **1** and **2** are best described as dcne-bridged zigzag chains of M^{II} ions running along the [100] direction; connections of these chains in the [010] direction, by the bis(chelating) bpym ligand, afford 2D structures. Compounds **3** and **4** are isostructural, and consist of discrete dinuclear units involving MN_4O_2 octahedrally coordinated M^{II} ions bridged by bis(bidentate) 2,2′-bipyrimidine and terminal dcne ligands. Magnetic measurements for the 2D compounds **1** and **2** exhibit maxima in the χ_m vs. T plots (at about 4.5 K for **1** and about 20 K for **2**) which are characteristic of weak antiferromagnetic exchange interactions between the high-spin metal centres. While the dinuclear iron complex **3** presents a similar behaviour (maximum in χ_m vs. T plot at 12 K), the antiferromagnetic exchange interactions are stronger in the copper complex **4**. Fits of magnetic data for compounds **1**, **3** and **4** with appropriate models led to J values of –0.6, –1.5 and –99.0 cm^{-1} respectively.

Introduction

Polynitrile molecules are interesting ligands for the preparation of a large variety of discrete and extended molecular structures due to the fact that their cyano groups are disposed in such a way that they cannot coordinate to the same metal cation and that association of the π electronic system of the CN groups with the π system of the central fragment induces electronic delocalization that facilitates transmission of electronic effects between the metal centers (Scheme 1).[1,2] Reactions of dca⁻,[3,4] tcm⁻,[3,5] dcnm⁻,[6] dcne⁻,[7] tcnp⁻,[8] tcpd²⁻ [9] and hcazpd⁻ [10] with transition metal ions by us and others have led to the isolation of a variety of new compounds, many of which exhibit extended structures and interesting magnetic properties.

Taking into account the crucial role of the bridging ligands in the magnetic properties of such polynuclear or polymeric derivatives, we are interested in using polynitrile ligands in combination with other bridging ligands with the aim of generating new molecular architectures associated with new properties.[11] In this context, the 2,2′-bipyrimidine (bpym) ligand, which is known to transmit antiferromagnetic coupling between paramagnetic centers separated by more than 5.5 Å,[12] is a particularly interesting choice.[13–16] Recently reported results obtained for dca/bpym mixed-ligand complexes reveal that this combination affords a rich variation in molecular architectures. For example, $[M(dca)_2(bpym)(H_2O)]$ (M = Mn, Fe, Co) and $[Mn(dca)_2(bpym)]$ have 1D structures,[17,18]

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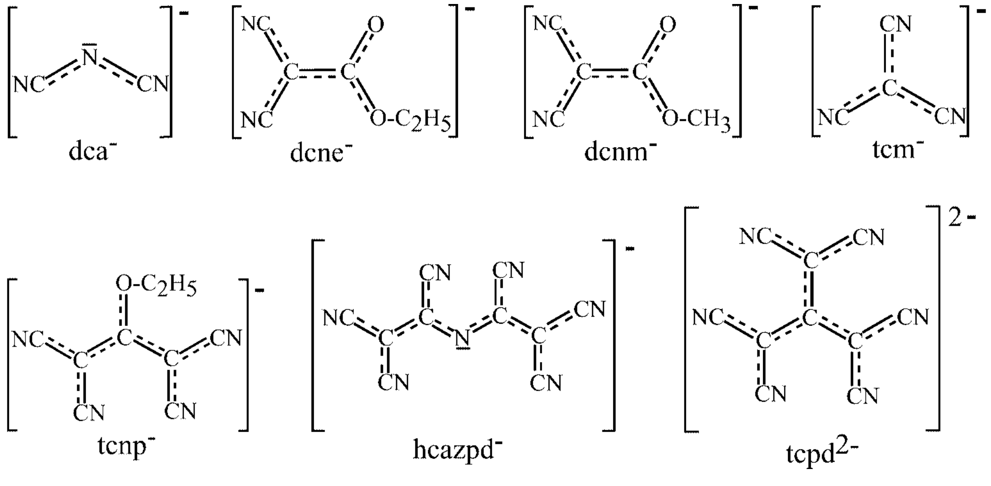


Scheme 1. Examples of polynitrile units with two to six CN groups

$[M_2(dca)_4(bpym)]\cdot H_2O$ (M = Fe, Co) and $[Fe_2(dca)_4(bpym)(H_2O)_2]$ 2D structures,[17,19] and $[M_2(dca)_4(bpym)]$ (M = Mn, Cu) 3D structures.[18,20]

Recently we described M^{II}−dcne binary derivatives of general formula $[M(dcne)_2(H_2O)_2]$ (M = Mn, Fe, Co, Ni, Zn) and $[Cu(dcne)_2(H_2O)]$ with the 2,2-dicyano-1-ethoxyethenolate ligand ($[(CN)_2CC(O)OEt)]^-$ = dcne⁻; Scheme 1). These compounds crystallize as one-dimensional structures with bridging polynitrile ligands.[7] Magnetic measurements indicated that very weak antiferromagnetic coupling occurs in these systems. In order to increase the dimensionality of the materials and therefore favour stronger magnetic coupling, we decided to introduce an auxiliary neutral bridging ligand in these binary systems. These efforts have resulted in the first examples of mixed M^{II}−dcne/bpym ternary compounds whose structures and properties are described herein.

Results and Discussion

Syntheses and IR Characterisation

One-pot reactions in aqueous solutions of the polynitrile anion dcne⁻ $\{[(CN)_2CC(O)OEt)]^-\}$ with M^{II} ions (M = Mn, Fe, Co, Cu) in the presence of bpym (2,2′-bipyrimidine) afforded new mixed dcne/bpym compounds of formula $[M_2(bpym)(dcne)_4(H_2O)_2]$ (**1**: M = Mn; **2**: M = Co) and $[M_2(bpym)(dcne)_4(H_2O)_4]\cdot 2H_2O$ (**3**: M = Fe; **4**: M = Cu).

It is well known that IR spectroscopy can be used as a diagnostic tool for identifying the coordination modes of the 2,2′-bipyrimidine (bpym) ligand, which can act as a single chelate or as a bis(chelate) ligand.[13,16] The former is typically characterised by two intense, absorption features of nearly equal intensities at about 1580 and 1560 cm^{-1}, while the latter is indicated either by an asymmetric doublet or by a single, strong broad feature near 1580 cm^{-1}.[13,16] The single strong band observed near 1580 cm^{-1} in the spectra of **1**−**4** points to a bis(chelate) coordination mode of the bpym ligand.

For the dcne ligand, two absorption bands assigned to ν(CN) are observed in the range 2180−2240 cm^{-1}. The first mode is very similar to that observed for the uncoordinated dcne⁻ moiety in K(dcne) (intense doublet centered at 2195 cm^{-1}), while the second feature is slightly shifted to higher wavenumbers.[7] These data are in good agreement with the presence of both coordinated and uncoordinated CN groups in compounds **1**−**4**, as confirmed by the X-ray structures.

For each compound, a broad feature indicative of the presence of water molecules [$\nu_s(OH)$ and $\nu_{as}(OH)$] is observed (from 3279 cm^{-1} in **2** to 3472 cm^{-1} in **4**); this observation does not allow for the assignment of free versus coordinated H_2O.

Single-Crystal X-ray Studies of Compounds 1−4

The four compounds were characterised by X-ray crystallography. Selected bond lengths and bond angles are provided in Tables 1−3 and the molecular structures are displayed in Figures 1−4.

Structures of $[M_2(bpym)(dcne)_4(H_2O)_2]$ [M = Mn^{II} (1), Co^{II} (2)]

Compounds **1** and **2** are isostructural (see Exp. Sect). Their asymmetric unit consists of one M^{II} ion, two dcne anions and a water molecule, all on general positions, and one bpym molecule centered on the special position (0,0,0). Each metal ion resides in an MN_5O pseudo-octahedral environment with three nitrogen atoms (N3, N4 and N5) coming from three dcne⁻ ligands, two nitrogen atoms (N1 and N2) from bpym and one oxygen atom (O5) from a water molecule (Figure 1). The metal-ion environment, which involves three dcne⁻ ligands in a *fac* arrangement, is highly distorted due to the small bite angle of the bpym ligand [71.71(6)° for **1**, 76.44(6)° for **2**] (Table 1). It is noteworthy that the two M−N(bpym) bonds (average: 2.309 Å for **1** and 2.169 Å for **2**) are longer than the other four M−L bonds (average: 2.178 Å for **1** and 2.085 Å for **2**), the difference being more pronounced in **1** (ca. 0.13 Å) than in **2** (ca. 0.08 Å).

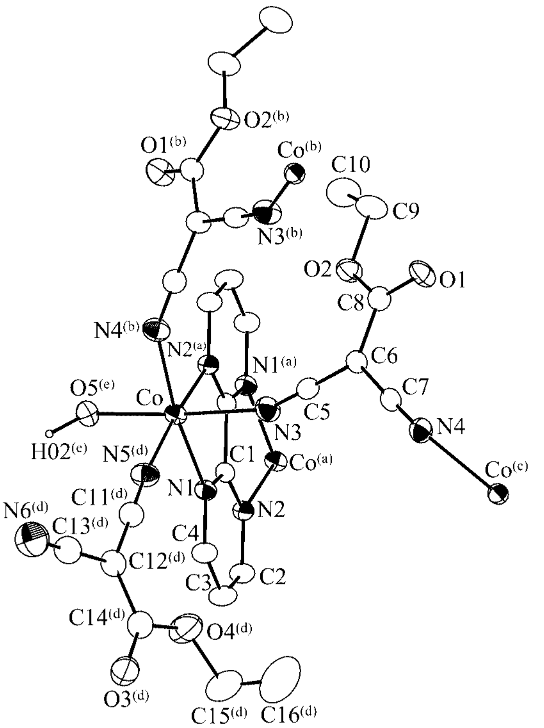


Figure 1. ORTEP view showing the metal environment and the atom labelling scheme in compound **1** (similar to compound **2**); codes of equivalent positions: (a): $-x, -y, -z$; (b): $1/2 + x, 1/2 - y, z$; (c): $-1/2 + x, 1/2 - y, z$; (d): $-1/2 + x, 1/2 - y, -1 + z$; (e): $1/2 - x, -1/2 + y, -z$

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**

	1	2
M−N1	2.292(2)	2.153(2)
M−N2	2.326(2)	2.185(2)
M−N3	2.208(2)	2.108(2)
M−N5	2.146(2)	2.063(2)
M−O5	2.152(2)	2.054(2)
M−N4	2.207(2)	2.117(2)
N1−M−N2	71.71(6)	76.44(6)
N1−M−N3	90.94(8)	90.02(8)
N1−M−N4	165.50(7)	170.02(7)
N1−M−N5	93.00(8)	94.13(7)
N1−M−O5	88.58(7)	90.90(7)
N2−M−N3	87.70(8)	90.03(8)
N2−M−N4	93.88(7)	94.16(7)
N2−M−N5	164.65(8)	170.26(7)
N2−M−O5	85.32(6)	86.26(7)
N3−M−N4	86.78(9)	86.60(8)
N3−M−N5	94.02(9)	92.44(8)
N3−M−O5	172.79(7)	175.86(7)
N4−M−N5	101.44(8)	95.39(8)
N4−M−O5	91.88(8)	91.83(7)
N5−M−O5	93.19(8)	91.52(7)

The two crystallographically equivalent dcne ligands exhibit μ_2-coordination modes while the other one is monodentate; the bpym ligand acts as a bis(bidentate) ligand. The extended structure resulting from these coordination modes is best described as dcne-bridged zigzag chains of M^{II} ions running along the [100] direction; connections of these chains, in the [010] direction, by the bis(chelating) bpym ligand afford the 2D structure shown in Figure 2. The metal−metal distances across the bpym bridges [6.1152(5) in **1** and 5.7853(4) Å in **2**] are close to those observed in other Mn^{II}−bpym (6.1−6.3 Å)[13] and Co^{II}−bpym (5.76−5.95 Å)[15] derivatives. The M···M distances across

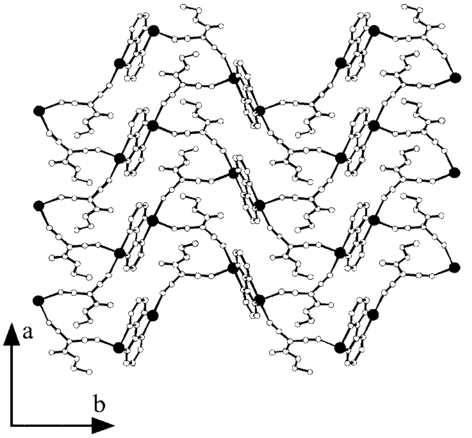


Figure 2. ORTEP view of compound **1** showing the two-dimensional structure (similar to compound **2**); the terminal dcne ligands have been omitted for the sake of clarity

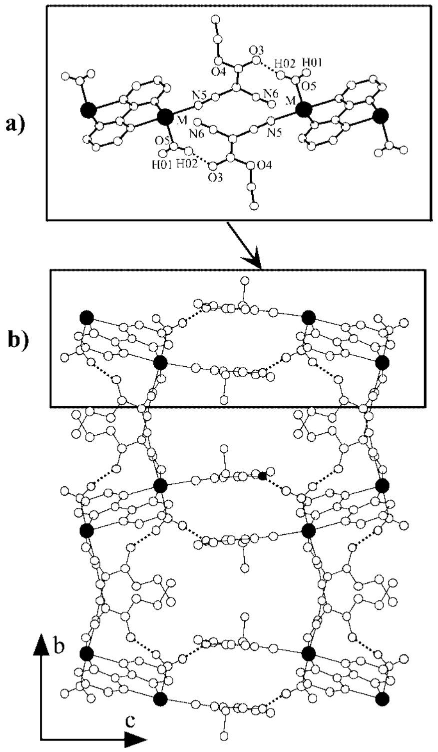


Figure 3. ORTEP view of compound **1** showing the hydrogen bonds between two adjacent sheets (similar to compound **2**)

the span of the dcne bridges [8.1420(5) in **1** and 8.0867(4) Å in **2**] are longer than the analogous distances observed in the 1D binary compounds $[Co(dcne)_2(H_2O)_2]$ [7.4270(2) Å][7] and $[Mn(dcne)_2(H_2O)_2]$ [7.5906(3) Å].[21]

Careful examination of the inter-layer distances revealed the presence of hydrogen bonds between the terminal oxygen atom of the $dcne^-$ ligands (O3) and the oxygen atom of the water molecule (O5). These hydrogen bonds occur between adjacent sheets [O3···H02 1.731(2) Å and O3···H02−O5 157.6(1)° for **1**; 1.731(2) Å and 164.9(1)° for **2**] as shown in Figure 3, giving rise to overall 3D structures.

Structures of $[M_2(bpym)(dcne)_4(H_2O)_4]\cdot 2H_2O$ (M = Fe^{II}(3), Cu^{II} (4)]

Compounds **3** and **4** are isostructural (see Exp. Sect.). Their asymmetric unit consists of one M^{II} ion, two dcne anions and three water molecules, all on general positions, as well as one bpym molecule centered on the special position (0,1/2,1/2). Each metal ion resides in a *trans*-MN_4O_2 pseudo-octahedral geometry (Figure 4). The four nitrogen atoms are from bpym (N1 and N2) and from two independent *cis*-$dcne^-$ ligands (N3 and N5); the two oxygen atoms arise from water molecules (O5 and O6) in a *trans* arrangement.

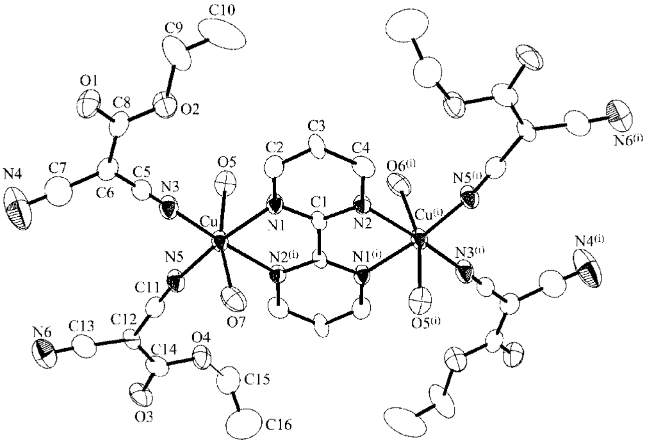


Figure 4. ORTEP view showing the metal environment and the atom labelling scheme in compound **3** (similar to compound **4**); code of equivalent position: (i): $-x$, $1 - y$, $1 - z$

As in the cases of **1** and **2**, the metal-ion environments are highly distorted due to the small bite angle of the bpym ligand [75.4(1)° for **3** and 80.8(2)° for **4**], but this distortion is more pronounced in compound **4** since the axial Cu−O bonds [2.338(3) and 2.494(3) Å] are much more longer than the four equatorial Cu−N ones (averaged $Cu-N_{bpym}$: 2.06 Å and averaged $Cu-N_{dcne}$: 1.96 Å; Table 2).

Table 2. Selected bond lengths [Å] and angles [°] for compounds **3** and **4**

	3	4
M−N1	2.212(4)	2.064(4)
M−N2	2.201(4)	2.045(4)
M−N3	2.121(4)	1.955(4)
M−N5	2.087(5)	1.965(5)
M−O5	2.117(4)	2.338(3)
M−O6	2.106(4)	2.494(3)
N1−M−N2	75.4(1)	80.8(2)
N1−M−N3	92.6(2)	92.0(2)
N1−M−N5	170.1(2)	172.7(1)
N1−M−O5	90.2(2)	87.2(1)
N1−M−O6	84.3(1)	80.0(1)
N2−M−N3	167.9(2)	171.7(2)
N2−M−N5	94.9(2)	92.3(2)
N2−M−O5	87.5(2)	89.3(1)
N2−M−O6	85.8(1)	84.6(1)
N3−M−N5	97.0(2)	94.6(2)
N3−M−O5	94.3(2)	94.5(2)
N3−M−O6	91.5(2)	90.2(1)
N5−M−O5	91.5(2)	95.2(2)
N5−M−O6	93.0(2)	97.1(1)
O5−M−O6	172.2(2)	166.5(1)

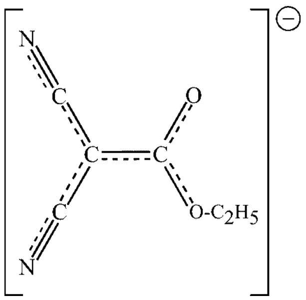
While the bpym ligand acts as a bis(bidentate) bridge as in **1** and **2**, all of the dcne ligands in this structure are monodentate, which results in the formation of discrete dinuclear units (Figure 4). The intradinuclear M···M distances through the bpym bridges [5.881(1) in **3** and 5.506(1) Å in **4**] are in the same range observed for other Fe^{II}−bpym (5.5−6.0 Å)[14] and Cu^{II}−bpym (5.3−5.7 Å)[16] derivatives. Careful examination of the inter-dinuclear distances clearly reveals an absence of hydrogen bonding.

Structure of the dcne Ligand

An examination of bond lengths and angles of the dcne ligand in **1−4** reveals that the metrical parameters of the dcne ligands are not significantly different in the series (Table 3). Apart from the terminal ethyl group, each dcne ligand is essentially planar within a maximum deviation of 0.1 Å (0.08, 0.10, 0.08 and 0.06 Å for **1−4**, respectively) from the corresponding mean plane. The two central carbon atoms of each dcne unit (C6−C8 and C12−C14) exhibit an sp^2 hybridization whereas the carbon atoms of the cyano groups are sp-hybridized, which permits a strong electronic delocalization as indicated by the C−C bonds with bond lengths from 1.390 to 1.436 Å in **1−4**. This delocalization is also evident from the rather short terminal C−O bond (range 1.223−1.248 Å), which deviates from a typical C−O single bond (1.50 Å), and by a C−OEt bond (range 1.334−1.350 Å) that also indicates some degree of multiple bonding. As previously reported for the binary system M^{II}−dcne,[7] the structural data in this work are in agreement with the electronic structure depicted in Scheme 2.

Table 3. Selected bond lengths [Å] and angles [°] for the dcne ligands in compounds **1**−**4**

	1	**2**	**3**	**4**
O1−C8	1.223(3)	1.224(3)	1.227(6)	1.242(7)
O2−C8	1.340(3)	1.341(3)	1.334(7)	1.334(8)
N3−C5	1.147(4)	1.151(3)	1.147(7)	1.153(7)
N4−C7	1.149(3)	1.150(3)	1.154(9)	1.14(1)
C5−C6	1.397(4)	1.399(3)	1.395(7)	1.397(8)
C6−C7	1.403(3)	1.399(3)	1.402(9)	1.42(1)
C6−C8	1.435(3)	1.436(3)	1.428(7)	1.407(7)
O3−C14	1.226(3)	1.232(3)	1.248(6)	1.230(7)
O4−C14	1.350(3)	1.348(3)	1.343(7)	1.342(7)
N5−C11	1.143(3)	1.142(3)	1.160(7)	1.145(7)
N6−C13	1.135(4)	1.136(4)	1.130(8)	1.155(9)
C11−C12	1.390(3)	1.399(3)	1.392(7)	1.398(8)
C12−C13	1.414(4)	1.415(4)	1.420(8)	1.413(9)
C12−C14	1.419(4)	1.416(3)	1.415(8)	1.433(8)
C5−C6−C7	119.3(2)	120.0(2)	121.1(5)	118.6(5)
C5−C6−C8	122.1(2)	121.4(2)	121.2(5)	122.9(6)
C7−C6−C8	118.1(2)	118.0(2)	117.5(5)	118.4(5)
O1−C8−O2	123.8(2)	123.9(2)	123.0(5)	122.2(5)
O1−C8−C6	123.8(2)	123.4(2)	124.6(5)	124.5(6)
O2−C8−C6	112.3(2)	112.7(2)	112.5(4)	113.3(5)
C11−C12−C13	118.7(2)	118.7(2)	121.0(5)	120.4(5)
C11−C12−C14	121.2(2)	121.2(2)	119.5(5)	120.0(5)
C13−C12−C14	120.0(2)	120.2(2)	119.4(5)	119.5(5)
O3−C14−O4	121.8(3)	122.1(2)	120.8(5)	121.9(5)
O3−C14−C12	125.6(3)	125.1(2)	125.2(5)	124.8(6)
O4−C14−C12	112.6(2)	112.8(2)	113.9(4)	113.4(5)



Scheme 2. Mean electronic structure of the dcne ligand

It is particularly noteworthy that the negative charge is not located on the terminal oxygen atom for the dcne ligand and therefore it is not surprising that this atom does not enter in the coordination sphere of the metal atom.

Magnetic Properties

The magnetic properties for compounds **1** (Figure 5), **2** (Figure 6), and **3** (Figure 7) are displayed as the thermal dependence of χ_m and the $\chi_m T$ product, where χ_m is the magnetic susceptibility per formula unit (2 mol of metal ions). These compounds exhibit similar behaviour in the temperature range 2−300 K. The room-temperature $\chi_m T$ values (8.4, 5.4 and 6.0 emu·K·mol^{-1} for **1**, **2** and **3**, respectively) are in good agreement with the expected values for two magnetically isolated high-spin ions [two Mn^{II} (S = 5/2), two Co^{II} (S = 3/2), and two Fe^{II} (S = 2) for **1**, **2** and **3**, respectively].[7,8,13−15] Upon cooling, the $\chi_m T$ products for **1** and **3** remain constant down to approximately 100 K, at which temperature the value decreases sharply and

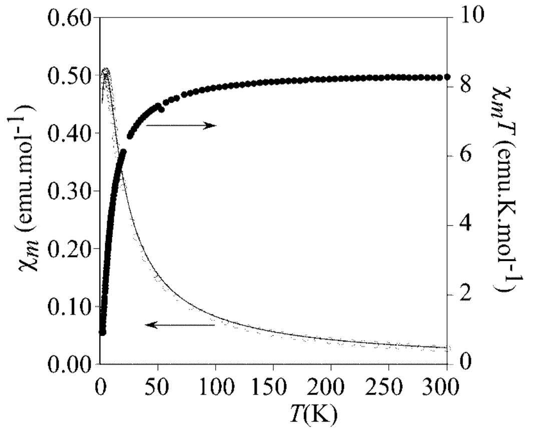


Figure 5. Thermal variations of the magnetic susceptibility in the form $\chi_m T$ (•••) and χ_m (ooo) for compound **1** (solid lines represent the best fit)

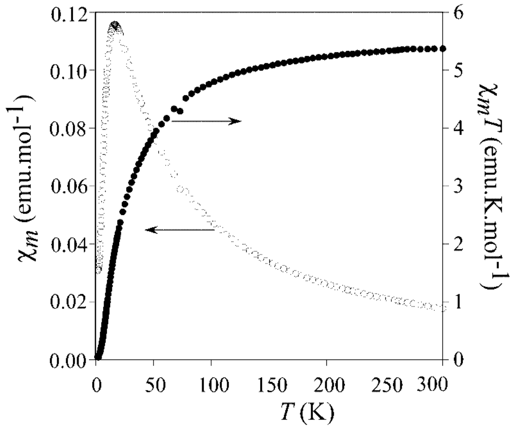


Figure 6. Thermal variations of the magnetic susceptibility in the form $\chi_m T$ (•••) and χ_m (ooo) for compound **2**

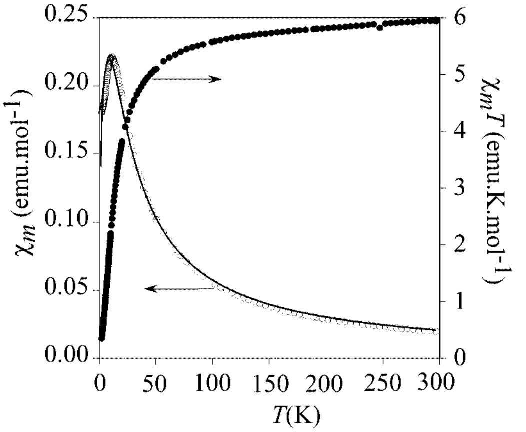


Figure 7. Thermal variations of the magnetic susceptibility in the form $\chi_m T$ (•••) and χ_m (ooo) for compound **3** (solid lines represent the best fit)

reaches values of 0.92 and 0.36 emu·K·mol^{-1} at 2 K for **1** and **3**, respectively. For the Co derivative **2**, the decrease in the $\chi_m T$ product begins at higher temperatures due to the well-known orbital contribution for this ion,[22] and tends to a value close to zero at 2 K (Figure 6). These data are characteristic of antiferromagnetic exchange interactions between the metal ions and is corroborated by the presence of susceptibility maxima at 4.5, 20 and 12 K for **1**, **2** and **3**, respectively.

A perusal of magnetic data for various related compounds indicates that magnetic interactions through the dcne bridge are weaker ($-J_{\text{dcne}} \approx 0.04-0.40$ cm^{-1})[7,13–15] than those observed through a bis(bidentate) bpym ligand ($-J_{\text{bpym}} \approx 0.6-10$ cm^{-1} for M = Mn, Fe, Co).[7,13–15] This conclusion led us to fit the magnetic data with a model that only takes into account interactions through the bpym ligand. Thus, to treat the magnetic data we used the susceptibility expressions derived from the spin pairs (5/2-5/2, 3/2-3/2 and 2-2 for **1**–**3**, respectively) coupled through an isotropic exchange interaction J (the Hamiltonian is written as $H = -2JS_aS_b$).[22] This isotropic model cannot be used for the Co derivative **2**, however, due to the important zero-field splitting for this ion, as previously reported for $[Co_2(dca)_4(bpym)]·H_2O$.[17] The analytical expressions are given in Equations (1) and (2) with $C = Ng^2\mu_B^2/(k_B)$, $x = J/(k_BT)$, and the parameters N, g, μ_B and k_B having their usual meanings.

$$\text{for } \mathbf{1}: \chi_m = 2(C/T)\{[e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x}]/[1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}]\} \quad (1)$$

$$\text{for } \mathbf{3}: \chi_m = 2(C/T)\{[e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x}]/[1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x}]\} \quad (2)$$

For both compounds, a satisfactory agreement with the experimental data were observed over the entire temperature range (solid lines in Figures 5 and 7) with the sets of parameters displayed in Table 4. The J values are very similar to those reported for other dinuclear Mn^{II} (−0.4 to −0.6 cm^{-1})[13] and Fe^{II} (−1.5 to −2.1 cm^{-1})[14] derivatives with a bis(bidentate) bpym bridge.

For the Cu derivative **4**, the thermal variation of the magnetic susceptibility presents a broad susceptibility maximum at approximately 150 K (Figure 8) which is higher than the values observed for **1**–**3**, an indication of the presence of strong antiferromagnetic coupling between the two metal ions. The increase observed below 50 K is attributed to the presence of paramagnetic impurities. As for compounds **1** and **3**, the magnetic data were modelled using the susceptibility expression derived from the spin pair 1/2-1/2, by adding in this case a term to take into account a paramagnetic contribution. The analytical expression is given in Equation (3) where $\chi_D = 2(C/T)[1/(3 + e^{-2x})]$ and ρ represents the fraction of uncoupled impurities for which the molecular weight is the same as that of the investigated compound. The best fit, obtained with the values given in Table 4, is plotted as solid lines in Figure 8a.

$$\chi_m = (1 - \rho)\chi_D + (C/2T)\rho \quad (3)$$

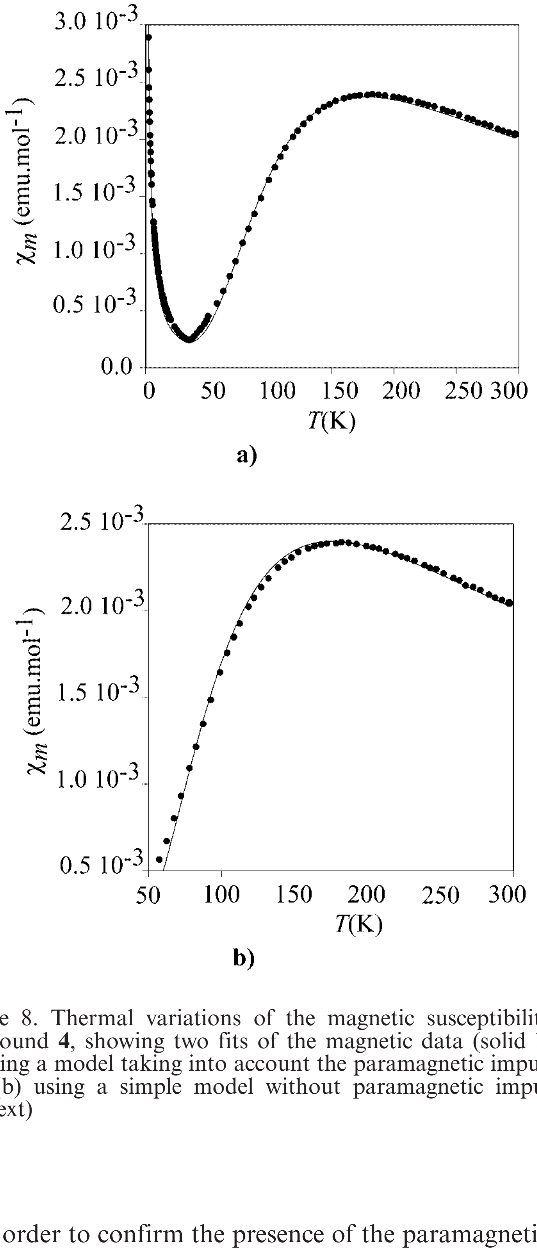


Figure 8. Thermal variations of the magnetic susceptibility for compound **4**, showing two fits of the magnetic data (solid lines): (a) using a model taking into account the paramagnetic impurities, and (b) using a simple model without paramagnetic impurities (see text)

In order to confirm the presence of the paramagnetic impurities, a second fit was carried out in the range 50–300 K using the same model but with no paramagnetic impurities ($\rho = 0$; $\chi_m = \chi_D$). The best agreement was obtained with $g = 2.12$ and $J = -98$ cm^{-1} (Figure 8b); these values are very similar to those obtained for the first fit (Table 4),

Table 4. Magnetic parameters for compounds **1**, **3** and **4**.

Compound	S	J [cm^{-1}]	g	ρ
$[Mn_2(bpym)(dcne)_4(H_2O)_2]$ (**1**)	5/2	−0.6	2.00	
$[Fe_2(bpym)(dcne)_4(H_2O)_4]·2H_2O$ (**3**)	2	−1.5	2.05	
$[Cu_2(bpym)(dcne)_4(H_2O)_4]·2H_2O$ (**4**)	1/2	−99.0	2.12	0.008

which corroborates the hypothesis that the increase in χ_m below 50 K is due to paramagnetic impurities. Finally, it is worth pointing out that the magnetic coupling is much more stronger in the Cu derivative than in other compounds; such a difference has been reported previously in several other compounds with bpym bridges.[16]

Conclusion

This study, which reports a new series of transition-metal derivatives with two types of bridging ligands, confirms the ability of such mixed systems to generate a variety of molecular architectures. The combination of dcne with bpym as ligands afforded both 2D derivatives $[M_2(bpym)(dcne)_4(H_2O)_2]$ (**1**: M = Mn; **2**: M = Co) and discrete dinuclear compounds $[M_2(bpym)(dcne)_4(H_2O)_4]\cdot 2H_2O$ (**3**: M = Fe; **4**: M = Cu). Since compounds without the bpym ligand, such as $[M(dcne)_2(H_2O)_2]$ (M = Mn, Fe, Co, Ni, Zn) and $[Cu(dcne)_2(H_2O)]$, are known to exhibit 1D structures, it is obvious that the introduction of an additional bridging ligand induces significant structural modifications. In an effort to increase the dimensionality of these mixed polynitrile/co-ligand compounds, further work is in progress that involves a similar synthetic strategy with polynitrile anions that possess more than two nitrile substituents.

Experimental Section

Materials and Physical Measurements: All reagents were purchased from commercial sources and used as received (2,2′-bipyrimidine from Lancaster). The potassium 2,2-dicyano-1-ethoxyethenolate {K(dcne) = $K[(CN)_2CC(O)OEt)]$} was prepared according to a recently reported procedure.[7] Elemental analyses were obtained from the Service Central d'Analyses (Vernaison) and Service de Microanalyses de ICSN-CNRS (Gif-sur-Yvette). Infrared spectra were recorded in the range 4000−200 cm^{-1} as KBr pellets on a FT-IR NEXUS NICOLET Spectrometer. Magnetic studies were carried out on powder samples at 0.1 T after zero-field cooling, in the temperature range 2−300 K with an MPMS-XL SQUID magnetometer from Quantum Design housed in the Chemistry Department at Texas A&M University. The susceptibilities were corrected for the sample holder and the diamagnetic contributions of all atoms.

Syntheses: All syntheses were performed under aerobic conditions using the following procedure: 2,2′-Bipyrimidine (20 mg, 0.126 mmol) and K(dcne) (89 mg, 0.504 mmol) were successively added with continuous stirring to a hot aqueous solution of the hydrated metal(II) chloride (0.252 mmol). The resulting solution was filtered and then slowly concentrated to yield crystals which were removed by filtration and air-dried.

Compound 1: Yield 74% (79 mg). $C_{32}H_{30}Mn_2N_{12}O_{10}$ (852.54): calcd. C 45.08, H 3.55, N 19.72; found C 44.92, H 3.61, N 19.59. Colorless crystals. IR (KBr): $\tilde{\nu}$ = 3348 br. and 3290 br. ν(OH), 3114 s, 3082 w, 2996 w, 2980 w, 2229 m, 2219 s and 2194 s ν(CN), 1623 m, 1580 m, 1462 w, 1413 m, 1401 w, 1372 m, 1320 m, 1163 w, 1142 w, 1116 m, 1102 w, 760 w, 693 w, 673 w, 559 w, 550 w, 366 w.

Compound 2: Yield 69% (75 mg). $C_{32}H_{30}Co_2N_{12}O_{10}$ (860.53): calcd. C 44.66, H 3.51, N 19.53; found C 44.74; H 3.51; N 19.49. Orange crystals. IR (KBr): $\tilde{\nu}$ = 3347 br. and 3279 br. ν(OH), 3084 w, 2996 w, 2979 w, 2228 m and 2196 s ν(CN), 1622 s, 1584 m, 1462 w, 1418 m, 1402 w, 1372 m, 1321 m, 1163 w, 1113 m, 1012 w, 760 w, 693 w, 679 w, 547 w, 368 w.

Compound 3: Yield 64% (75 mg). $C_{32}H_{38}Fe_2N_{12}O_{14}$ (926.42): calcd. C 41.49, H 4.13, N 18.14; found C 41.22, H 4.22, N 17.99. Red

Table 5. Crystal data for compounds **1**−**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{32}H_{30}Mn_2N_{12}O_{10}$	$C_{32}H_{30}Co_2N_{12}O_{10}$	$C_{32}H_{38}Fe_2N_{12}O_{14}$	$C_{32}H_{38}Cu_2N_{12}O_{14}$
Formul mass[a]	852.55	860.54	926.43	941.81
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
a [Å]	8.2320(2)	8.1772(2)	7.1857(4)	7.0670(3)
b [Å]	19.3486(5)	19.0699(5)	12.2737(6)	12.5536(5)
c [Å]	12.9429(3)	12.7165(4)	12.8907(7)	12.6724(5)
α [°]	90	90	102.2(1)	103.265(7)
β [°]	96.38(7)	96.9(1)	102.4(2)	102.941(6)
γ [°]	90	90	100.2(1)	102.612(7)
V (Å^3)	2048.7(4)	1968.6(6)	1055(2)	1022.4(2)
Z[a]	2	2	1	1
$D_{calcd.}$ [g·cm^{-3}]	1.38	1.45	1.46	1.53
μ [mm^{-1}]	0.654	0.906	0.759	1.117
F(000)	872	880	478	484
Refl. measured	6735	10157	6271	6122
2θ range [°]	5.0−50.70	5.0−60.10	5.0−51.0	5.0−52.02
Refl. unique/R_{int}	3623/0.026	5502/0.031	3675/0.051	3714/0.05
Refl. with [$I > n\sigma(I)$]	2459 (n = 3)	2904 (n = 3)	2141 (n = 2)	2150 (n = 2)
N_v	253	253	271	271
$R(F_o)$[b]/$R_w(F_o)$[c]	0.033/0.039	0.034/0.039	0.055/0.060	0.050/0.053
Goodness-of-fit[d]	1.146	1.300	1.229	1.053
$\Delta\rho_{max,/min}$ [e/Å^3]	+0.194/−0.329	+0.205/−0.388	+0.602/−0.450	+0.500/−0.492

[a] For compounds **1**−**4** the asymmetric unit contains half of the chemical formula. [b] $R = \Sigma|F_o - F_c|/F_o$. [c] $Rw = [\Sigma w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2}$. [d] G.O.F = $[(\Sigma w|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$.

crystals. IR (KBr): $\tilde{\nu}$ = 3349 br. ν(OH), 3090 w, 2994 w, 2980 w, 2214 m and 2187 s ν(CN), 1647 m, 1607 s, 1582 s, 1471 w, 1425 m, 1400 w, 1378 m, 1329 m, 1170 w, 1120 m, 1012 w, 755 w, 692 w, 667 w, 553 w, 365 w.

Compound 4: Yield 76% (90 mg). $C_{32}H_{38}Cu_2N_{12}O_{14}$ (941.82): calcd. C 40.81, H 4.07, N 17.85; found C 40.57, H 4.15, N 17.64. Brown crystals. IR (KBr): $\tilde{\nu}$ = 3472 br. ν(OH), 3082 w, 2990 w, 2971 w, 2209 s and 2181 s ν(CN), 1643 s, 1587 m, 1471 w, 1413 w, 1404 w, 1375 m, 1321 s, 1144 m, 1113 w, 1024 w, 754 w, 692 w, 685 w, 553 w, 364 w.

X-ray Structural Determinations: Data were collected at 288 K with a Nonius KappaCCD Diffractometer, equipped with an Oxford Cryosystem Cryostream cooler device and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods and successive Fourier difference syntheses, and were refined on F^2 by weighted anisotropic full-matrix least-squares methods (Table 5).[23] The positions of all hydrogen atoms of the dcne ligands were calculated [d(C–H) = 0.95Å]; the thermal parameters were taken as $U_{\mathrm{iso}} = 1.3U_{\mathrm{equ}}$(C) and therefore included as isotropic fixed contributors to F_c in the four structures. The hydrogen atoms of the water molecules were not observed, except those of the coordinated water molecule O5 of compounds **1** and **2**, which were located by difference Fourier maps and refined isotropically. Scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography.[24] All calculations were performed with an Alphastation 255 4/233 computer. Selected bond lengths and angles are listed in Tables 1–3, pertinent crystal data in Table 5. CCDC-232956 to -232959 (**1–4**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat. + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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