$[Mn^{II}_2(bpym)(H_2O)_8]^{4+}$ and $[M^{IV}(CN)_8]^{4-}$ (M = Mo and W) as building blocks in designing bpym- and cyanide-bridged bimetallic three-dimensional networks (bpym = 2,2′-bipyrimidine)†

Juan Manuel Herrera,[a] Donatella Armentano,[b] Giovanni de Munno,[b] Francesc Lloret,[c] Miguel Julve*[c] and Michel Verdaguer*[a]

[a] *Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Université Pierre et Marie Curie, Unité CNRS 7071, 4 place Jussieu, 75252, Paris cedex 05, France*
[b] *Dipartimento de Chimica Inorganica, Università degli Studi della Calabria, 87030, Arcavacata di Rende (Cosenza), Italy*
[c] *Departament de Química Inorgànica, Instituto de Ciencia Molecular, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100, Burjassot (València), Spain.*
E-mail: miguel.julve@uv.es

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One-pot reaction between the dinuclear $[Mn^{II}_2(bpym)(H_2O)_8]^{4+}$ complex and the mononuclear $[M^{IV}(CN)_8]^{4-}$ unit (M = Mo and W; bpym = 2,2′-bipyrimidine) in aqueous solution yields the novel heterobimetallic complexes of formula $\{(\mu\text{-bpym})[Mn(H_2O)]_2\text{-}(\mu\text{-NC})_6M(CN)_2\}$ with M = Mo (**1**) and W (**2**). **1** and **2** are isostructural three-dimensional compounds where the manganese atoms are bridged by bisbidentate bpym and hexakismonodentate octacyanometalate units. Variable-temperature magnetic susceptibility data of **1** and **2** show the occurrence of a significant antiferromagnetic coupling between the high spin manganese(II) ions through bridging bpym (J *ca.* -1.1 cm^{-1}, the exchange Hamiltonian being defined as $H = -JS_A \cdot S_B$).

Introduction

The strategy based on the use of stable mononuclear complexes as ligands, which is known as the building block approach, is one of the best strategies in designing heterometallic compounds. Two recent illustrative examples are the tris-chelated $[M(ox)_3]^{(m-6)-}$ (m = oxidation state of the metal ion) species and the hexacyanometalate $[M(CN)_6]^{(m-6)-}$ unit (M = trivalent first-row transition metal ion).[1–5] Their high negative charge, great stability in solution and versatility as Lewis bases allowed the rational preparation of polyfunctional heterometallic assemblies such as high-T_c molecule-based magnets,[6,7] chiral magnets,[8–10] systems exhibiting photo-induced magnetic ordering[11,12] and high spin molecules.[13–15]

In the last decade, the stability of the bpym-bridged dinuclear species $\{[M(H_2O)_4]_2(bpym)\}^{2m+}$ (M = first row transition metal ion; bpym = 2,2′-bipyrimidine) in aqueous solution and the easy replacement of the terminally coordinated water molecules by potential bridging ligands allowed the design of extended homometallic compounds.[16,17] Focusing on the case where M = Mn(II), dinuclear complexes,[18–20] uniform chains,[20,21] honeycomb layered materials[18,20,22] and three-dimensional[22,23] networks were prepared and magneto-structurally characterised. A weak but significant antiferromagnetic coupling between the manganese(II) ions separated by more than 5 Å through bridging bpym was reported ($-J$ values varying in the range 0.9–1.2 cm^{-1}).[21] Very recently, we extended this strategy to the preparation of bpym- and cyanide-bridged heterobimetallic species using the mononuclear low-spin $[Fe^{III}(bipy)(CN)_4]^-$ as a ligand towards the dinuclear $\{[Mn(H_2O)_4]_2(bpym)\}^{4+}$ unit.[24] In our attempts to extend this strategy to other cyanide-bearing units, we obtained the isostructural three-dimensional heterobimetallic compounds $\{(\mu\text{-bpym})[Mn(H_2O)]_2(\mu\text{-NC})_6M(CN)_2\}$ with M = Mo (**1**) and W (**2**) where the manganese(II) ions are bridged by the bpym molecule and the $[M^{IV}(CN)_8]^{4-}$ units. Their preparation, crystal structure characterization and magnetic properties are presented here.

Experimental

Materials

$K_4[Mo(CN)_8]\cdot 2H_2O$ and $K_4[W(CN)_8]\cdot 2H_2O$ were prepared as previously described.[25] Bpym and $Mn(NO_3)_2\cdot 4H_2O$ were purchased from commercial sources and used as received. Elemental analyses (C, H, N) were carried out by the Microanalytical Service of the Universidad Autónoma de Madrid. The M:Mn [M = Mo (**1**) and W (**2**)] molar ratio was determined by electron probe X-ray microanalysis at the the Servicio Interdepartamental de Investigación de la Universitat de València.

Preparation of $\{\mu\text{-(bpym)}[Mn(H_2O)]_2\text{-}\mu\text{-(NC)}_6Mo(CN)_2\}$ (1). Compound **1** is obtained as a yellow solid in a practically quantitative yield by mixing concentrated aqueous solutions of $K_4[Mo(CN)_8]\cdot 2H_2O$ (0.5 mmol) and $Mn_2(bpym)(NO_3)_2$ (0.5 mmol) [mixture of stoichiometric amounts of $Mn(NO_3)_2\cdot 4H_2O$ and bpym] in the dark. Yellow needles of **1** suitable for single crystal X-ray diffraction were grown by slow diffusion in an H-shaped tube of aqueous solutions of the octacyanometalate salt in one arm and the Mn(II)/bpym mixture in the other one in the dark. The crystals were washed with water and ethanol and air dried. Yield *ca.* 90%. Anal. calc. for $C_{16}H_{10}Mn_2MoN_{12}O_2$ (**1**): C, 31.61; H, 1.64; N, 27.63. Found: C, 31.51; H, 1.57; N, 27.54%; Mo/Mn = 1/2.

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† Electronic supplementary information (ESI) available: $\chi_M T$ *vs.* T for **2**. See http://www.rsc.org/suppdata/nj/b2/b206124b/

Preparation of {μ-(bpym)[Mn(H_2O)]$_2$-μ-(NC)$_6$W(CN)$_2$} (2). The preparation of **2** is analogous to that of **1** except for the use of the octacyanotungstate(IV) anion as the cyano-bearing unit. **2** is obtained as an orange solid in a practically quantitative yield by mixing concentrated aqueous solutions of $K_4[W(CN)_8]\cdot 2H_2O$ (0.5 mmol) and $Mn_2(bpym)(NO_3)_2$ (0.5 mmol) [mixture of stoichiometric amounts of $Mn(NO_3)_2\cdot 4H_2O$ O and bpym] in the dark. Orange needles of **2** suitable for X-ray diffraction were grown by slow diffusion in an H-shaped tube in the dark as for **1**. The crystals of **2** were washed with water and ethanol and air dried. Yield *ca.* 90%. Anal. calc. for $C_{16}H_{10}Mn_2N_{12}O_2W$ (**2**): C, 27.61; H, 1.44; N, 24.14. Found: C, 27.49; H, 1.35; N, 23.98%; W/Mn = 1/2.

Physical techniques

IR spectra (4000–400 cm^{-1}) were recorded on a Bruker IF S55 spectrophotometer with samples prepared as KBr pellets. Variable-temperature (1.9–290 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design SQUID operating at 5000 Oe in the high temperature range (20–290 K) and at 250 Oe at $T < 20$ K in order to avoid saturation phenomena. Diamagnetic corrections for the molar units were estimated from Pascal's constants[26] as -275×10^{-6} (**1**) and -281×10^{-6} cm^3 mol^{-1} (**2**). The values of the temperature independent paramagnetism (TIP) estimated from the magnetic susceptibility data are 600×10^{-6} (**1**) and 1400×10^{-6} cm^3 mol^{-1} (**2**).

X-Ray data collection and structure refinement

Crystals of dimensions 0.45 × 0.09 × 0.13 (**1**) and 0.30 × 0.08 × 0.12 mm (**2**) were mounted on a Bruker R3m/V automatic diffractometer and used for data collection. Diffraction data were collected at room temperature by using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with the ω–2θ scan method. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range 15–30°. A summary of the crystallographic data and of the structure refinements is given in Table 1. Examination of two standard reflections, monitored after every 50 reflections, showed no sign of crystal deterioration. Lorentz-polarization and Ψ-scan absorption corrections[27] were applied to the intensity data. The maximum and minimum transmission factors were 0.736 and 0.574 for **1** and 0.342 and 0.270 for **2**.

Table 1 Crystallographic data for {μ-(bpym)[Mn(H_2O)]$_2$-μ-(NC)$_6$M(CN)$_2$} with M = Mo (**1**) and W (**2**)[a]

	1	**2**
Formula	$C_{16}H_{10}Mn_2MoN_{12}O_2$	$C_{16}H_{10}Mn_2N_{12}O_2W$
FW	608.18	696.09
a/Å	14.539(3)	14.542(2)
b/Å	12.620(2)	12.608(2)
c/Å	12.114(3)	12.126(2)
β/°	103.40(1)	103.46(1)
D_c/g cm^3	1.868	2.138
F(000)	1192	1320
μ(Mo-Kα)/cm^{-1}	17.63	64.99
Refl. colld./indep.	2019/1918	2018/1917
Refl. obs./param.	1918/156	1917/156
Goodness-of-fit[b]	0.997	1.002
R_1/wR_2[c d]	0.0326/0.0859	0.0244/0.0608
R_1/wR_2(all data)	0.0386/0.0877	0.0263/0.0613
Largest diff. peak/e $Å^{-3}$	0.608	1.007
Largest diff. hole/e $Å^{-3}$	−2.645	−0.875

[a] Details in common: monoclinic, $C2/c$, $Z = 4$, $U = 2162(1)$ $Å^3$ and $T = 295$ K. [b] Goodness-of-fit = $\{\sum[w(F_o^2 - F_c^2)^2/(N_o - N_p)]\}^{1/2}$. [c] $I > 2\sigma(I)$. [d] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$ with $P = [F_o^2 + 2F_c^2]/3$, $m = 0.0625$ (**1**) and 0.0444 (**2**) and $n = 0$ (**1** and **2**).

The structures of **1** and **2** were solved by standard Patterson methods through the SHELXTL NT package[28] and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecule were located on a ΔF map and refined with constraints whereas those of the bpym ligand were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The final full-matrix least-squares refinement on F^2, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, reached convergence with values of the discrepancy indices given in Table 1. The final geometrical calculations were carried out with the PARST program.[29] The drawings were performed using the XP utility of the SHELXTL NT system. Main interatomic bond distances and angles for **1** and **2** are listed in Table 2.

CCDC reference numbers 188051 (**1**) and 188052 (**2**). See http://www.rsc.org/suppdata/nj/b2/b206124b/ for crystallographic data in CIF or other electronic format.

Results and discussion

IR characterisation

The most relevant features of the IR spectra of **1** and **2** concern the presence of two main peaks at 2161m and 2118s cm^{-1} (**1**) and at 2160m and 2112s cm^{-1} (**2**) which are assigned to ν_{CN} stretching vibrations of the cyanide groups. Their significant shift towards higher frequencies when compared with the values in the corresponding mononuclear precursors, multiplets in the frequency ranges 2137–2103 cm^{-1} for $K_4[Mo(CN)_8]\cdot 2H_2O$ and 2138–2096 cm^{-1} for $K_4[W(CN)_8]\cdot 2H_2O$,[30] suggests the occurrence of bridging cyanide in both compounds.[31] The very asymmetric doublet at 1570s and 1530w cm^{-1} in the IR spectra of **1** and **2** (ring stretching vibrations of bpym) indicates the presence of bischelating bpym.[32] Finally, a strong and broad absorption centered at 3450 cm^{-1} in the spectra of both compounds with peaks at 3480 (**1** and **2**), 3395 (**1**) and 3385 cm^{-1} (**2**) is attributed to the OH stretching of coordinated water involved in hydrogen bonds. These spectral observations on **1** and **2** are confirmed by the X-ray structure determination (see below).

Description of the structures

1 and **2** are isostructural compounds where bpym-bridged aquamanganese(II) dinuclear entities are connected through octacyanometalate $[M^{IV}(CN)_8]^{4-}$ units [M = Mo (**1**) and W (**2**)] (Fig. 1) to afford a neutral three-dimensional arrangement of manganese and molybdenum (**1**)/tungsten (**2**) atoms (Fig. 2). Alternatively, the structure of **1** and **2** can be described as Mn(II)/M(IV) cyanide-bridged chains linked by bpym molecules adopting a bis-bidentate coordination mode towards the Mn(II) ions to afford a bidimensional arrangement (Fig. 3). Adjacent layers are joined by cyanide groups (Fig. 4) to form a three-dimensional network, the octacyanometalate anions acting as hexakismonodentate ligands through six of their eight cyanide ligands. The water molecule which is coordinated to the manganese atom is involved in hydrogen bonds with the cyanide-nitrogen atoms of the two terminally bound cyanides (see end of Table 2) contributing to the stabilization of the structure.

The manganese atom is six-coordinated: five nitrogen atoms, two from the bpym molecule and three from the cyanide groups, and an oxygen atom from a water molecule form a distorted octahedron around the metal atom. The small bite of the bridging bpym [70.5(1) for N(1)–Mn(1)–N(2a) in **1** and

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1** and **2**[a b]

	M = Mo (**1**)	M = W (**2**)
M(1)–C(5d)	2.155(4)	2.146(4)
M(1)–C(6b)	2.164(4)	2.163(5)
M(1)–C(7)	2.166(4)	2.175(5)
M(1)–C(8)	2.161(4)	2.171(5)
Mn(1)–O(1)	2.222(3)	2.229(4)
Mn(1)–N(1)	2.321(3)	2.319(4)
Mn(1)–N(2a)	2.360(3)	2.363(4)
Mn(1)–N(5)	2.186(3)	2.183(4)
Mn(1)–N(6)	2.196(3)	2.194(4)
Mn(1)–N(7)	2.155(3)	2.148(4)
C(5d)–M(1)–C(5e)	101.0(2)	100.9(3)
C(5d)–M(1)–C(6b)	92.2(1)	92.3(2)
C(5e)–M(1)–C(6b)	144.6(1)	144.5(2)
C(5d)–M(1)–C(7)	69.8(1)	70.1(2)
C(5e)–M(1)–C(7)	75.4(1)	75.3(2)
C(5d)–M(1)–C(8)	142.3(1)	142.5(2)
C(5e)–M(1)–C(8)	74.6(1)	74.2(2)
C(6b)–M(1)–C(6c)	95.7(2)	95.7(3)
C(6b)–M(1)–C(7)	78.8(1)	78.6(2)
C(6c)–M(1)–C(7)	145.6(1)	145.3(2)
C(7f)–M(1)–C(7)	124.0(2)	124.5(2)
C(8)–M(1)–C(6b)	75.0(1)	75.3(2)
C(8)–M(1)–C(6c)	72.8(1)	72.8(2)
C(8)–M(1)–C(7)	73.0(1)	72.7(2)
C(8)–M(1)–C(7f)	132.9(1)	132.7(2)
C(8)–M(1)–C(8f)	131.3(2)	131.7(3)
O(1)–Mn(1)–N(1)	90.8(1)	90.6(1)
O(1)–Mn(1)–N(2a)	80.7(1)	80.5(1)
N(1)–Mn(1)–N(2a)	70.5(1)	70.5(1)
N(5)–Mn(1)–O(1)	168.1(1)	167.8(1)
N(5)–Mn(1)–N(1)	81.1(1)	81.4(2)
N(5)–Mn(1)–N(2a)	88.2(1)	88.2(1)
N(5)–Mn(1)–N(6)	104.2(1)	104.7(2)
N(6)–Mn(1)–O(1)	85.4(1)	85.2(1)
N(6)–Mn(1)–N(1)	97.2(1)	97.4(2)
N(6)–Mn(1)–N(2a)	161.2(1)	161.0(2)
N(7)–Mn(1)–O(1)	89.0(1)	89.0(2)
N(7)–Mn(1)–N(1)	162.1(1)	162.0(2)
N(7)–Mn(1)–N(2a)	91.9(1)	91.7(1)
N(7)–Mn(1)–N(5)	96.0(1)	95.8(2)
N(7)–Mn(1)–N(6)	100.6(1)	100.6(2)

Hydrogen bonds[c]

Compound	A	D	H	A···D	A···H	A···H–D
1	O(1)	N(8g)	H(1w)	2.930(5)	2.06(3)	152(4)
2				2.917(6)	2.00(3)	158(6)
1	O(1)	N(8b)	H(2w)	3.006(5)	2.08(2)	163(5)
2				3.001(6)	2.07(2)	163(6)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] Symmetry code: (a) = $-x+3/2$, $-y+3/2$, $-z+2$; (b) = $-x+3/2$, $-y+1/2$, $-z+2$; (c) $x+1/2$, $-y+1/2$, $z+1/2$; (d) = x, $-y+1$, $z+1/2$; (e) = $-x+2$, $-y+1$, $-z+2$; (f) = $-x+2$, y, $-z+5/2$; (g) = $x-1/2$, $y+1/2$, z. [c] A = acceptor, D = donor.

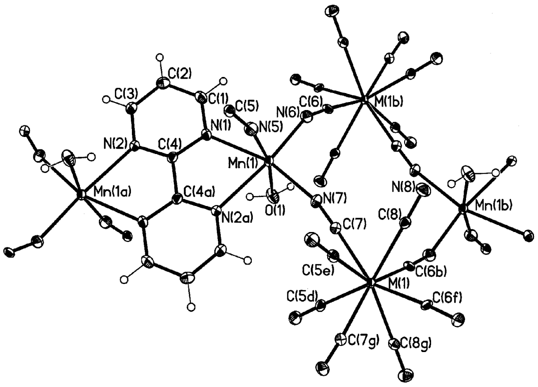

Fig. 1 Perspective view of a fragment of **1** (M = Mo) and **2** (M = W) with the atom numbering. The thermal ellipsoids are drawn at the 30% probability level.

2] is the main factor accounting for this distortion. The Mn–N(bpym) bond lengths [2.340(3) (**1**) and 2.341(4) Å (**2**)] are significantly longer than those of the Mn–N(cyanide) [average values 2.179(3) (**1**) and 2.175(4) A (**2**)] and that involving the coordinated water molecule [2.222(3) (**1**) and 2.229(4) Å (**2**)]. A comparison of the bpym-bridged manganese(II) dinuclear unit of **1** and **2** with the structure of the related dinuclear complex μ-(bpym)[$Mn(H_2O)_3(SO_4)]_2$[18] (**3**) reveals a slight increase in the Mn–bpym bonds in this last species [av. value 2.312(3) Å in **3**] but a shorter manganese–manganese separation across bridging bpym [6.123(2) Å in **3** *vs.* 6.201(3) (**1**) and 6.203(4) Å (**2**)]; the larger value of the bite of bpym in **3** [71.4(1)°] accounts for the reduction of the metal–metal separation in this compound.

The Mo(IV) (**1**) and W(IV) (**2**) ions show the same distorted dodecahedron geometry, being coordinated to eight cyanide-carbon atoms. Two of these cyanide ligands are monodentate whereas the other six act as bridges towards the manganese atoms. The main differences between the M(IV) cores in **1** and **2** are the values of the metal–carbon bonds which vary in the ranges 2.155(4)–2.166(4) (**1**) and 2.146–2.175(5) Å (**2**). These values are close to those observed in other reported structures containing octacyanomolydate(IV)[33] and octacyanotungstate(IV)[34] units. Structurally characterized polynuclear complexes based on the use of the $[M(CN)_8]^{4-}$ unit (M = Mo Mo or W) as a ligand are still rare. In fact, as far as we are aware, structural reports of cyanide-bridged Mn(II)M(IV) (M = Mo or W) bimetallic compounds are very recent and

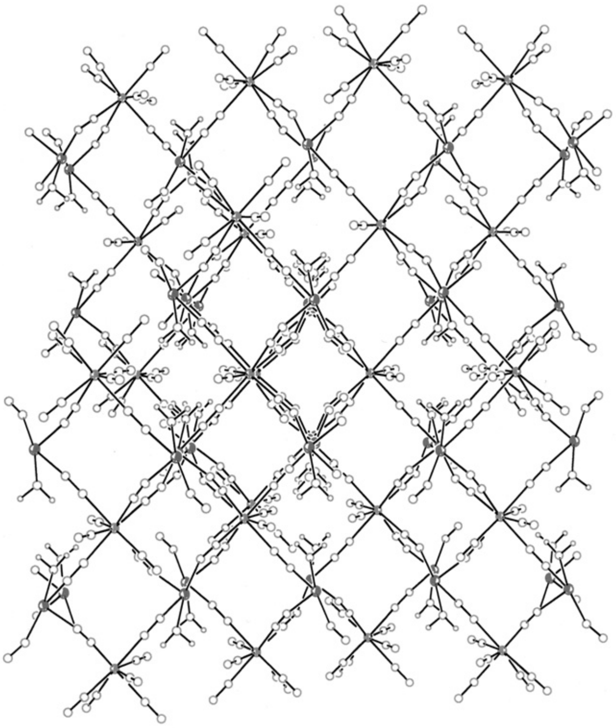

Fig. 2 Projection of the three-dimensional rhombic array of the M(IV) (cross-hatched circles) and Mn(II) ions in **1** (M = Mo) and **2** (M = W) along the [001] direction. The bpym ligand has been omitted for clarity.

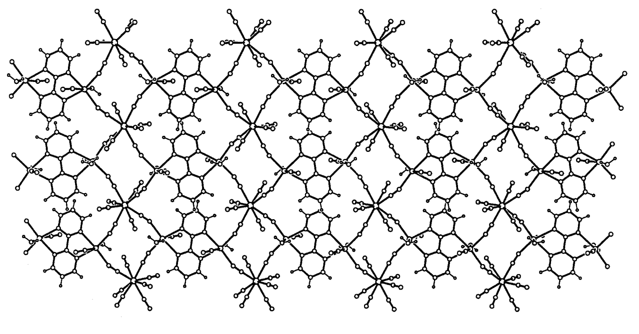

Fig. 3 A view of the two-dimensional arrangement of the Mn(II) and M(IV) metal ions from **1** and **2** extending in the (−1 0 1) plane.

concern the following examples: the hexanuclear complex $\{[Mn(bipy)_2]_2(\mu\text{-}CN)_2[Mo(CN)_6]_2[(\mu\text{-}CN)_2[Mn(bipy)_2]_2\}\cdot 8H_2O$,[33c] the chain $\{[Mn_2(L)_2(H_2O)][Mo(CN)_8]\}\cdot 5H_2O$[33b] and the two-dimensional compound $\{[Mn(L)]_6[Mo^{III}(CN)_7][Mo(CN)_8]_2\}\cdot 19.5H_2O$[33d] (L = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene) in the molybdenum series and the three-dimensional compound $[W\{(\mu\text{-}CN)_4Mn(H_2O)_2\}_2]\cdot 4H_2O$[35] in the tungsten family.

Within the experimental error, there are no significant differences between the mean values for the bridging and terminal cyanide ligands [the values of the C–N bond distance vary in the ranges 1.135(5)–1.159(5) (**1**) and 1.132(6)–1.150(6) Å (**2**)]. The M(IV)–C–N angles for both terminal [178.5(3)° (**1**) and 178.6(4)° (**2**)] and bridging [175.5(3)–178.6(3)° (**1**) and 175.1(4)–178.6(4)° (**2**)] cyanides are almost in a line, whereas the Mn(1)–N–C(cyanide) linkages depart significantly from 180° [151.2(3)–166.0(3)° (**1**) and 151.9(4)–166.7(4)° (**2**)]. The values of the metal-metal separation through bridging cyanide are 5.400(5) (**1**) and 5.412(5) Å (**2**) for Mn(1)···M(1), 5.316(5) (**1**) and 5.305(6) Å (**2**) for Mn(1)···M(1b) [(b) = $-x+3/2$, $-y+1/2$, $-z+2$] and 5.390(6) (**1**) and 5.397(6) Å (**2**) for Mn(1)···M(1e) [(e) = $-x+2$, $-y+1$, $-z+2$].

The pyrimidyl rings are planar as expected [the largest deviation from the mean planes is 0.023(5) Å at C(2)]. The bpym molecule as a whole is also planar and the manganese atom is 0.180(1) Å out of this plane. The value of the inter-ring carbon–carbon bond length [C(4)–C(4a) = 1.479(8) (**1**) and 1.472(10) Å (**2**)] is very close to that observed in the free bpym in the solid state [1.497(4) Å].[36] The value of the bite distance of the bis-chelating coordination mode of bpym in **1** and **2** [2.702(5) Å for N(1)···N(2a)] is practically identical to that found for the uncoordinated molecule [2.70 and 2.71 Å].[36] The bond distances and angles of the pyrimidyl rings of the bpym molecule fall within the range of values found in other bpym-bridged manganese(II) complexes.

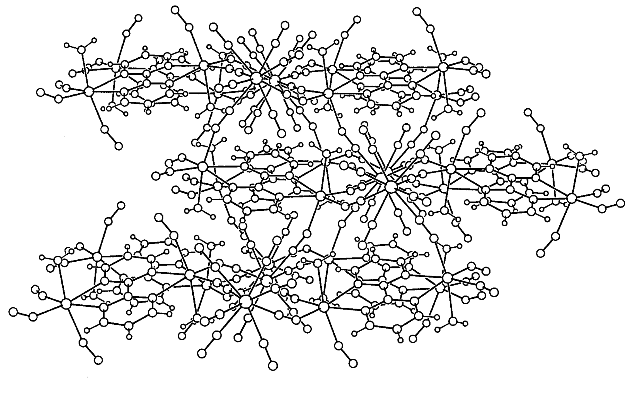

Fig. 4 View along the [010] direction showing the interlayer connection through bridging cyanide groups in the three dimensional network of **1** and **2**.

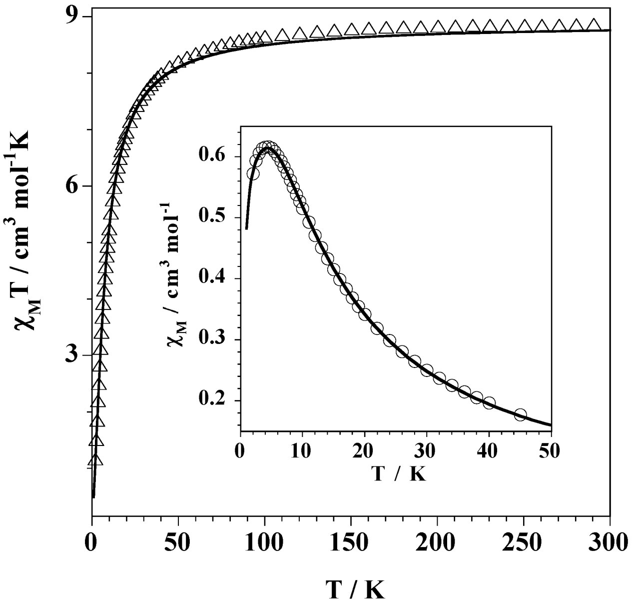

Fig. 5 $\chi_M T$ (●) *vs.* *T* plot for complex **1**. The insert shows the χ_M *vs.* *T* plot in the vicinity of the maximum. The solid line is the best-fit through eqn. (2) (see text).

Magnetic properties

The temperature dependence of $\chi_M T$ for **1** [χ_M is the magnetic susceptibility per $Mn^{II}_2M^{IV}$ unit] is shown in Fig. 5. A quasi identical curve is obtained for **2** (Fig. S1 in ESI†). At room temperature, $\chi_M T$ is 8.70 (**1**) and 8.40 (**2**) cm^3 mol^{-1} K, values which are as expected for two magnetically isolated high spin manganese(II) ions ($S_{Mn} = 5/2$). Upon cooling, $\chi_M T$ decreases continuously, slowly until 100 K and more and more steeply at lower temperature to reach 1.1 (**1**) and 0.98 (**2**) cm^3 mol^{-1} K at 2.0 K. The suceptibility curve shows a maximum at 4.3 (**1**) and 4.5 K (**2**) (see insert of Figs. 5 and S1 for **1** and **2**, respectively). These features are consistent with a weak but significant antiferromagnetic interaction between two single-ion sextuplet states of the manganese(II) ions. The susceptibility data of **1** and **2** were analyzed in terms of an isotropic exchange interaction for a dinuclear species:

$$H = -JS_A\cdot S_B \text{ with } S_A = S_B = 5/2 \qquad (1)$$

through the expression:

$$\chi_M = \frac{2N_A\mu_B^2 g^2}{kT}\,\frac{x+5x^3+14x^6+30x^{10}+55x^{15}}{1+3x+5x^3+7x^6+9x^{10}+11x^{15}} \qquad (2)$$

with $x = \exp(J/kT)$. The parameters N_A, μ_B and k have their usual meanings. The values of J and g were determined by least-squares fit minimizing $R = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma[(\chi_M)_{obs}]^2$. The values obtained were $J = -1.05$ cm^{-1}, $g = 2.0$ and $R = 1.9\times10^{-5}$ for **1** and $J = -1.10$ cm^{-1}, $g = 1.98$ and $R = 2.3\times10^{-5}$ for **2**. The calculated curve matches very well the experimental data in both cases.

The values of J in **1** and **2** are very close to those reported for other bpym-bridged manganese(II) compounds, as shown in Table 3. It is therefore likely that the main exchange interaction occurs within the bpym-bridged manganese(II) dinuclear fragments occurring in **1** and **2** and not through the diamagnetic octacyanomolybdate (**1**) or tungstate (**2**) bridging units [the manganese–manganese separation through the octacyanometalate bridging units is larger than 10.6 Å]. The antiferromagnetic coupling observed is mediated by the bis-chelating bpym and the exchange pathways involved are as mentioned in previous works:[18,19,21] the main contribution is due to the σ* in-plane overlap between the two $d_{x^2-y^2}$ type magnetic orbitals of each manganese(II) ion through the bpym N–C–N

Table 3 Selected magneto-structural data for bpym-bridged manganese(II) complexes[a]

Compound	Nuclearity	Donor set[b]	$-J/\mathrm{cm}^{-1}$ [c]	Mn–N(bpym)/Å[d]	Mn···Mn/Å[e]	Ref.
$[Mn_2(bpym)(H_2O)_4(SO_4)_2]$	Dinuclear	N_2O_4	1.1	2.31	6.123(2)	18
$[Mn_2(bpym)_3(NCS)]_4$	Dinuclear	N_2N_4	1.19	2.36	6.223(1)	19
$[Mn_2(bpym)_3(NCSe)]_4$	Dinuclear	N_2N_4	1.20	2.35	6.211(1)	19
$\{[Mn_2(bpym)(H_2O)_6][Fe(bipy)(CN)_4]_2\}$-$[Fe(bipy)(CN)_4]_2\cdot 12H_2O$	Tetranuclear	N_2NO_3	1.2	2.32	6.131(6)	24
$[Mn(bpym)(NCO)_2]_n$	Chain	N_2N_4	1.1	2.35	6.234(1)	21
$[Mn(bpym)(NO_3)_2]_n$	Chain	$N_2N_2O_3$	0.93	2.36	6.239(1) 6.247(1)	21
$[Mn_2(bpym)(dca)_4]_n$	Three-dimensional	N_2N_4	0.86	2.33	6.156	23
1	Three-dimensional	N_2N_3O	1.05	2.34	6.201(3)	This work
2	Three-dimensional	N_2N_3O	1.10	2.34	6.203(4)	This work

[a] Abbreviations used: bipy = 2,2′-bipyridine and dca = dicyanamide anion. [b] The two first atoms are those of the bridging bpym. [c] Magnetic coupling between the Mn(II) ions across bridging bpym. [d] Average bond distances are given for each structure. [e] Manganese–manganese separation through bridging bpym.

bridging skeleton [the x and y axis being roughly defined by the Mn–N(bpym) bonds].

The main conclusion of the present work concerns the synthetic possibilities opened by the availability and stability of the dinuclear $\{[M(H_2O)_4]_2(bpym)\}^{4+}$ units in aqueous solution (M being a divalent first-row transition metal ion). These complexes have been prepared and magneto-structurally characterized.[18–22,37–40] The easy replacement of the peripheral water molecules by complexes which can act as ligands, as shown in **1** and **2**, allows a plethora of n-dimensional (n = 0–3) bimetallic arrays to be foreseen, where the bpym-bridged dinuclear motif could interact magnetically with paramagnetic octacyanometalate entities used as bridging units (work in progress).

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