DALTON
FULL PAPER

$[Mn_2(bipym)(H_2O)_8]^{4+}$ and $[Fe(bipy)(CN)_4]^-$ as building blocks in designing novel bipym- and cyanide-bridged heterobimetallic complexes (bipym = 2,2′-bipyrimidine and bipy = 2,2′-bipyridine)

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Two new cyano complexes, $K[Fe(bipy)(CN)_4]\cdot H_2O$ (**1**) and $(\mu\text{-bipym})[Mn(H_2O)_3\{Fe(bipy)(CN)_4\}]_2[Fe(bipy)(CN)_4]_2\cdot 12H_2O$ (**2**), have been synthesised and their structures determined by single-crystal X-ray diffraction. Complex **1** is made up of mononuclear $[Fe(bipy)(CN)_4]^-$ anions, potassium cations and water molecules of crystallization. The iron(III) is six-coordinated, being surrounded by two nitrogen atoms of a chelating bipy and four carbon atoms of four cyanide groups [Fe–N and Fe–C 1.991(3)–1.990(3) and 1.958(5)–1.914(5) Å, respectively]. Complex **2** consists of centrosymmetric tetranuclear $(\mu\text{-bipym})[Fe(H_2O)_3\{Fe(bipy)(CN)_4\}]_2^{2+}$ cations, $[Fe(bipy)(CN)_4]^-$ anions and water molecules of crystallization. The cyano-containing iron(III) complex of **1** is present in **2** but in the latter it acts not only as a counterion but also as a monodentate ligand towards the manganese atom through one of its four cyanide groups. Bond lengths and angles around the iron atoms in **2** are practically identical to those observed in **1**. The manganese atom in **2** is six-coordinated with two bipym- and one cyanide-nitrogen atoms and three *mer*-water molecules comprising a distorted octahedral environment [Mn–N(bipym) 2.35(1) and 2.29(1) Å, Mn–N(cyanide) 2.19(2) and Mn–O 2.21(1)–2.12(2) Å]. The manganese–manganese and manganese–iron separations across the bis-chelating bipym and single-cyano bridge are 6.131(6) and 5.092(4) Å, respectively. Studies of the magnetic behaviour of **1** and **2** in the temperature range 1.9–300 K reveal that compound **1** is a magnetically isolated low-spin iron(III) complex with an important orbital contribution whereas significant antiferromagnetic interactions occur in **2** between the manganese(II) ions across bis-chelating bipym ($J = -1.2$ cm^{-1}) and between the manganese(II) and iron(III) ions through the single-cyano bridge ($j = -3.0$ cm^{-1}). The use of $[Fe^{III}(AA)(CN)_4]^-$ (AA = bidentate ligand) as a ligand towards metal ions appears very promising in designing new cyano-bridged polynuclear compounds.

Introduction

The most striking feature of the 2,2′-bipyrimidine ligand (bipym) is the easy access to stable dinuclear complexes of formula $[M_2(bipym)(H_2O)_8]^{m+}$ (M being a first row transition metal ion) where the ligand adopts the bis-bidentate coordination mode.[1] Magneto-structural studies on bipym-bridged metal complexes revealed the occurrence of large intramolecular antiferromagnetic interactions between the paramagnetic centers separated by more than 5 Å [singlet–triplet energy gap up to −236 cm^{-1} when M = Cu(II)].[2,3] The replacement of peripheral water molecules on each metal ion of this dinuclear unit by anionic bridging ligands allowed the rational design of exotic homometallic systems such as: (i) chains with a regular alternation of ferro- and antiferromagnetic interactions[4,5] and (ii) honeycomb layered materials which exhibit alternating intralayer antiferro–antiferro[6] and antiferro–ferro magnetic[7,8] interactions.

The use of stable anionic complexes as ligands towards the cationic dinuclear species $[M_2(bipym)(H_2O)_8]^{4+}$ would be a straightforward route to the preparation of heterometallic species whose nuclearity and dimensionality would be dependent on parameters such as the charge neutralization between the two interacting ions, the number of coordinated water molecules of the cation which are replaced by the coordinating anion and the coordinating capability on the anion. The recent availability of the stable cyano-containing mononuclear complexes $[Fe(AA)(CN)_4]^-$ (AA = neutral bidentate N-donor)[9,10] moved us to explore their use as ligands towards the preformed $[M_2(bipym)(H_2O)_8]^{4+}$ species in order to prepare novel bipym- and cyanide-bridged heterometallic complexes. In this work we present our first results which concern the synthesis, structural characterization and magnetic study of the compounds of formula $K[Fe(bipy)(CN)_4]\cdot H_2O$ (**1**) (bipy = 2,2′-bipyridine) and $(\mu\text{-bipym})[Mn(H_2O)_3\{Fe(bipy)(CN)_4\}]_2$-$[Fe(bipy)(CN)_4]_2\cdot 12H_2O$ (**2**).

Experimental

Materials

Chemicals were purchased from commercial sources and used as received. $K_2[Fe(bipy)(CN)_4]\cdot 3H_2O$ was prepared as described in the literature.[11] Elemental analysis (C,H,N) was performed by the Microanalyical Service of the Universidad Autónoma de Madrid. The values of the Fe : K (**1**) and Fe : Mn (**2**) molar ratios, 1 : 1 (**1**) and 2 : 1 (**2**) were determined by electron

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microscopy at the Servei de Microscopia Electrònica de la Universitat de València.

Preparations

$K[Fe(bipy)(CN)_4]\cdot H_2O$ (1). This compound was obtained by bubbling chlorine gas through a warm aqueous solution (100 cm^3) of $K_2[Fe(bipy)(CN)_4]\cdot 3H_2O$ (2 mmol) under continuous stirring for half an hour. The resulting deep red solution was evaporated to dryness and the red solid of **1** recrystallized from hot water (yield 80%). Red parallelepipeds of **1** suitable for X-ray diffraction were obtained by slow evaporation of the mother liquor. Anal. calc. for $C_{14}H_{10}FeKN_6O$: C, 45.07; H, 2.68; N, 22.51. Found: C, 44.96; H, 2.59; N, 22.45%. IR (KBr disk), ν_{CN}/cm^{-1}: 2134s and 2124w.

(μ-bipym)$[Mn(H_2O)_3\{Fe(bipy)(CN)_4\}]_2[Fe(bipy)(CN)_4]_2\cdot 12H_2O$ (2). This compound was prepared by adding an aqueous solution of **1** (0.05 mmol, 20 cm^3) to a concentrated aqueous solution (5 cm^3) containing $Mn(NO_3)_2\cdot 4H_2O$ (0.05 mmol) and bipym (0.05 mmol). Red prisms of **2** separated from the resulting red solution in a few hours (yield 30%). Anal. calc. for $C_{64}H_{74}Mn_2Fe_4N_{28}O_{18}$: C, 41.40; H, 3.99; N, 21.13. Found: C, 41.31; H, 3.89; N, 21.04%. IR (KBr disk), ν_{CN}/cm^{-1}: 2141m, 2133s and 2119m.

Physical techniques

IR spectra were recorded on a Bruker IF S55 spectrometer with samples prepared as KBr pellets. Magnetic measurements were carried out on polycrystalline samples in the temperature range 1.9–300 K with a Quantum Design SQUID susceptometer under an applied magnetic field of 0.1 T. The diamagnetic corrections of the constituent atoms were estimated from Pascal constants[12] as -195×10^{-6} (**1**) and -1026×10^{-6} (**2**) cm^3 mol^{-1}.

Crystallography

X-Ray data collection and structure refinement. Crystals of dimensions 0.15 × 0.18 × 0.80 (**1**) and 0.12 × 0.16 × 0.40 mm (**2**) were mounted on an Enraf Nonius CAD-4 diffractometer and used for data collection. Intensity data were collected at 295 K by using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) with the ω–2θ scan method. Accurate unit-cell parameters and orientation matrices were determined from least-squares refinements of 25 well centered reflections in the θ range 12–12.5°. No significant variations were observed in the intensities of two checked reflections during data collections. The data were corrected for Lorentz and polarization effects. An empirical correction was performed using DIFABS.[13] The maximum and minimum transmission factors were 1.00 and 0.94 (**1**) and 1.00 and 0.78 (**2**). Of the 3127 (**1**) and 8086 (**2**) measured reflections in the θ range 1–25° (**1 and 2**) with index ranges $0 \le h \le 11$, $0 \le k \le 14$ and $-15 \le l \le 15$ (**1**) and $0 \le h \le 16$, $0 \le k \le 17$ and $-25 \le l \le 24$ (**2**), 2800 (**1**) and 7415 (**2**) were unique. From these, 1684 (**1**) and 1527 (**2**) were considered as observed $[I > 3\sigma(I)]$ and used for the structure refinements. Crystal parameters and some details of the structure refinements are summarized in Table 1.

The structures of **1** and **2** were solved by direct methods through SHELXS-86[14] and subsequently refined by Fourier recycling. All non-hydrogen atoms were refined anisotropically for compound **1** whereas they were left isotropic for compound **2** on account of the low amount of available data. In fact, the crystals of **2** poorly diffract and this is why only gross structural geometry is commented on for this compound. The hydrogen atoms of the bipy (**1 and 2**) and bipym (**2**) ligands were set in calculated positions whereas those of the water molecules were either located by means of a difference Fourier map (**1**) or not introduced (**2**). The coordinates of the hydrogen atoms were not refined, but only one overall isotropic thermal parameter was allocated and refined. The final full-matrix least-squares refinements on F through the PC version of CRYSTALS[15] reached convergence with values of the R and R' indices listed in Table 1. Selected interactomic bond distances and angles are listed in Tables 2 (**1**) and 3 (**2**).

Table 1 Summary of the crystal data and structure refinement for $K[Fe(bipy)(CN)_4]\cdot H_2O$ **1** and (μ-bipym)$[Mn(H_2O)_3\{Fe(bipy)(CN)_4\}]_2$-$[Fe(bipy)(CN)_4]_2\cdot 12H_2O$ **2**

	1	**2**
Formula	$C_{14}H_{10}FeKN_6O$	$C_{64}H_{74}Fe_4Mn_2N_{28}O_{18}$
M	373.2	1856.7
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	10.052(2)	13.624(3)
b/Å	12.345(2)	14.927(2)
c/Å	12.886(2)	21.767(5)
β/°	90.13(3)	107.30(2)
U/Å^3	1599.0(5)	4226(1)
Z	4	2
F(000)	756	1904
μ(Mo-Kα)/cm^{-1}	12.1	10.2
R[a]	0.0360	0.0671
R'[b, c]	0.0446	0.0803

[a] $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. [c] $w = w'$-$[1 - (||F_o| - |F_c||)/6\sigma(F_o)^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with three coefficients for a Chebyshev series [3.28, 1.18 and 2.38 (**1**) and 9.54, −1.99 and 7.80 (**2**)] for which $X = F_c/F_c$(max).

Table 2 Selected bond lengths (Å) and angles (°) for $K[Fe(bipy)(CN)_4]\cdot H_2O$ **1**, with e.s.d.s in parentheses

Fe(1)–N(11)	1.991(3)	Fe(1)–N(12)	1.990(3)
Fe(1)–C(1)	1.952(2)	Fe(1)–C(2)	1.914(5)
Fe(1)–C(3)	1.924(4)	Fe(1)–C(4)	1.958(5)
C(1)–N(1)	1.134(5)	C(2)–N(2)	1.147(6)
C(3)–N(3)	1.122(6)	C(4)–N(4)	1.143(5)
N(11)–Fe(1)–N(12)	81.3(1)	N(11)–Fe(1)–C(1)	92.0(2)
N(11)–Fe(1)–C(2)	94.1(2)	N(11)–Fe(1)–C(3)	178.1(2)
N(11)–Fe(1)–C(4)	93.5(1)	N(12)–Fe(1)–C(1)	91.2(2)
N(12)–Fe(1)–C(2)	174.4(2)	N(12)–Fe(1)–C(3)	97.0(2)
N(12)–Fe(1)–C(4)	90.3(2)	C(1)–Fe(1)–C(2)	92.0(2)
C(1)–Fe(1)–C(3)	87.2(2)	C(1)–Fe(1)–C(4)	174.5(2)
C(2)–Fe(1)–C(3)	87.7(2)	C(2)–Fe(1)–C(4)	87.0(2)
C(3)–Fe(1)–C(4)	87.4(2)	Fe(1)–C(1)–N(1)	178.9(4)
Fe(1)–C(2)–N(2)	176.7(4)	Fe(1)–C(3)–N(3)	179.0(4)
Fe(1)–C(4)–N(4)	175.8(4)		

CCDC reference numbers 174231 and 174232.

See http://www.rsc.org/suppdata/dt/b2/b202422p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Description of the structures

$K[Fe(bipy)(CN)_4]\cdot H_2O$ (1). The crystallographic analysis of **1** shows that its structure consists of mononuclear $[Fe(bipy)(CN)_4]^-$ anions [Fig. 1(a)], potassium cations [Fig. 1(b)] and crystallization water molecules which are linked by electrostatic forces, hydrogen bonds and van der Waals interactions.

The iron atom is coordinated by two bipy nitrogen and four cyanide carbon atoms, taking a distorted octahedral geometry. The short bite of the chelating bipy [81.3(1)° for N(11)–Fe(1)–N(12)] is one of the main factors accounting for this distortion of the ideal geometry. The values of the Fe–N(bipy) bonds in **1** [1.991(3) and 1.990(3) Å, Table 2] are the same as those found in the parent low-spin iron(II) $K_2[Fe(bipy)(CN)_4]\cdot 2.5H_2O$ [1.987(4)–2.003(4) Å][16] and iron(III) $[Fe(bipy)_2(CN)_2]ClO_4$ [1.954(4)–1.993(5) Å],[17] $PPh_4[Fe(bipy)(CN)_4]\cdot H_2O$ [1.98(2) and

Table 3 Selected bond lengths (Å) and angles (°) for (μ-bipym)-$[Mn(H_2O)_3\{Fe(bipy)(CN)_4\}]_2[Fe(bipy)(CN)_4]_2\cdot 12H_2O$ **2**, with e.s.d.s in parentheses[a]

Fe(1)–N(11)	1.99(2)	Fe(1)–N(12)	2.00(2)
Fe(1)–C(1)	1.92(2)	Fe(1)–C(2)	1.83(2)
Fe(1)–C(3)	1.95(2)	Fe(1)–C(4)	1.94(2)
Mn(1)–N(1)	2.19(2)	Mn(1)–N(9)	2.29(1)
Mn(1)–N(10b)	2.35(1)	Mn(1)–O(1)	2.16(1)
Mn(1)–O(2)	2.12(2)	Mn(1)–O(3)	2.21(1)
Fe(2)–N(21)	1.98(2)	Fe(2)–N(22)	2.00(2)
Fe(2)–C(5)	1.95(2)	Fe(2)–C(6)	1.93(2)
Fe(2)–C(7)	1.94(2)	Fe(1)–C(8)	1.89(2)
C(1)–N(1)	1.13(2)	C(2)–N(2)	1.20(2)
C(3)–N(3)	1.12(2)	C(4)–N(4)	1.16(2)
C(5)–N(5)	1.09(2)	C(6)–N(6)	1.14(2)
C(7)–N(7)	1.13(2)	C(8)–N(8)	1.18(2)
N(11)–Fe(1)–N(12)	81.0(6)	N(11)–Fe(1)–C(1)	176.9(8)
N(11)–Fe(1)–C(2)	95.6(7)	N(11)–Fe(1)–C(3)	88.6(7)
N(11)–Fe(1)–C(4)	88.3(8)	N(12)–Fe(1)–C(1)	95.9(7)
N(12)–Fe(1)–C(2)	176.0(8)	N(12)–Fe(1)–C(3)	90.1(7)
N(12)–Fe(1)–C(4)	93.4(8)	C(1)–Fe(1)–C(2)	87.5(9)
C(1)–Fe(1)–C(3)	91.9(8)	C(1)–Fe(1)–C(4)	91.5(9)
C(2)–Fe(1)–C(3)	87.7(9)	C(2)–Fe(1)–C(4)	88.6(9)
C(3)–Fe(1)–C(4)	174.9(7)	Fe(1)–C(1)–N(1)	177.5(21)
Fe(1)–C(2)–N(2)	175.4(19)	Fe(1)–C(3)–N(3)	177.2(19)
Fe(1)–C(4)–N(4)	175.7(18)	O(1)–Mn(1)–O(2)	87.9(6)
O(1)–Mn(1)–O(3)	176.4(6)	O(1)–Mn(1)–N(9)	89.4(5)
O(1)–Mn(1)–N(1)	90.9(6)	O(1)–Mn(1)–N(10b)	90.8(5)
O(2)–Mn(1)–O(3)	93.6(6)	O(2)–Mn(1)–N(9)	160.0(6)
O(2)–Mn(1)–N(1)	101.7(6)	O(2)–Mn(1)–N(10b)	89.3(6)
O(3)–Mn(1)–N(9)	88.1(5)	O(3)–Mn(1)–N(1)	92.0(6)
O(3)–Mn(1)–N(10b)	85.9(5)	N(9)–Mn(1)–N(1)	98.1(6)
N(9)–Mn(1)–N(10b)	70.9(5)	N(1)–Mn(1)–N(10b)	168.9(6)
Mn(1)–N(1)–C(1)	154.1(18)	N(21)–Fe(2)–N(22)	80.3(6)
N(21)–Fe(2)–C(5)	174.0(8)	N(21)–Fe(2)–C(6)	96.6(7)
N(21)–Fe(2)–C(7)	93.1(7)	N(21)–Fe(2)–C(8)	90.5(8)
N(22)–Fe(2)–C(5)	95.2(7)	N(22)–Fe(2)–C(6)	175.1(8)
N(22)–Fe(2)–C(7)	90.7(7)	N(22)–Fe(2)–C(8)	91.0(8)
C(5)–Fe(2)–C(6)	88.1(9)	C(5)–Fe(2)–C(7)	91.1(8)
C(5)–Fe(2)–C(8)	85.5(9)	C(6)–Fe(2)–C(7)	85.7(8)
C(6)–Fe(2)–C(8)	92.8(9)	C(7)–Fe(2)–C(8)	176.3(9)
Fe(2)–C(5)–N(5)	175.9(20)	Fe(2)–C(6)–N(6)	175.3(20)
Fe(2)–C(7)–N(7)	177.1(18)	Fe(2)–C(8)–N(8)	174.3(21)
Short O ··· O and N ··· O interactions			
O(1) ··· O(10k)	2.792(21)	O(1) ··· O(13)	2.770(22)
O(2) ··· O(12c)	2.627(23)	O(3) ··· N(7d)	2.815(23)
O(3) ··· O(11d)	2.681(19)	N(3) ··· O(12f)	2.768(27)
N(3) ··· O(13g)	2.989(27)	N(4) ··· O(14c)	2.789(25)
N(5) ··· O(12j)	2.845(23)	N(6) ··· O(10)	2.938(24)
N(6) ··· O(15c)	2.953(36)	N(8) ··· O(11i)	2.829(24)
O(10) ··· O(11)	2.826(21)	O(10) ··· O(14)	2.700(23)
O(13) ··· O(15)	2.920(36)		

[a] Symmetry codes: (b) = 2 − *x*, −*y*, −*z*; (c) = 1 − *x*, 1 − *y*, −*z*; (d) 2 − *x*, 1 − *y*, −*z*; (e) = 3/2 − *x*, −1/2 + *y*, −3/2 − *z*; (f) = 3/2 − *x*, −1/2 + *y*, 1/2 − *z*; (g) 3/2 − *x*, 1/2 + *y*, 1/2 − *z*; (h) 1/2 + *x*, 1/2 − *y*, 1/2 + *z*; (i) −1/2 + *x*, 3/2 − *y*, −1/2 + *z*; (j) = 1/2 + *x*, 3/2 − *y*, −1/2 + *z*; (k) = *x*, −1 + *y*, *z*.

2.00(2)][10] complexes. This agreement is also observed between the Fe–C(cyano) bond lengths of **1** [1.914(5)–1.958(5) Å] and those reported for other cyano-containing mononuclear low-spin iron(III) [1.87(2)–1.95(1) Å][9,10,17] and iron(II) [1.891(5)–1.936(5) Å][16,18] complexes. The presence of potassium cations in the structure of **1** and the value of its magnetic moment (see below) clearly show that **1** is a low-spin iron(III) complex. Additional evidence of this low-spin iron(III) character comes from the significant shift towards higher frequency values of the cyanide stretching in the infrared spectrum of **1** [doublet at 2134s and 2124w cm^{-1}] when compared with the parent low-spin iron(II) complex $K_2[Fe(bipy)(CN)_4]\cdot 2.5H_2O$ [triplet at 2080m, 2055s and 2045w cm^{-1}]. The potassium atom is surrounded by four cyanide nitrogen atoms from four $[Fe(bipy)(CN)_4]^-$ units and a water molecule taking a distorted square pyramidal environment, the bond distances being 2.866(4) [K(1)–N(1b)], 2.803(4) [K(1)–N(2c)], 2.845(5) [K(1)–N(3d)], 2.788(4) [K(1)–N(4e)] and 2.606(4) Å [K(1)–O(1e)] [symmetry codes: (b) = 1/2 + *x*, 1/2 − *y*, 1/2 + *z*; (c) = 1/2 − *x*, −1/2 + *y*, 1/2 − *z*; (d) = *x*, *y*, 1 + *z*; (e) = −1/2 + *x*, 1/2 − *y*, 1/2 + *z*; (f) = 1 − *x*, −*y*, 1 − *z*]. A weak hydrogen bond occurs between the water molecule and one of the cyanide–nitrogen atoms [2.958(4) Å = O(1) ··· N(2b) = O(1e) ··· N(2d) = O(1f) ··· N(2c)].

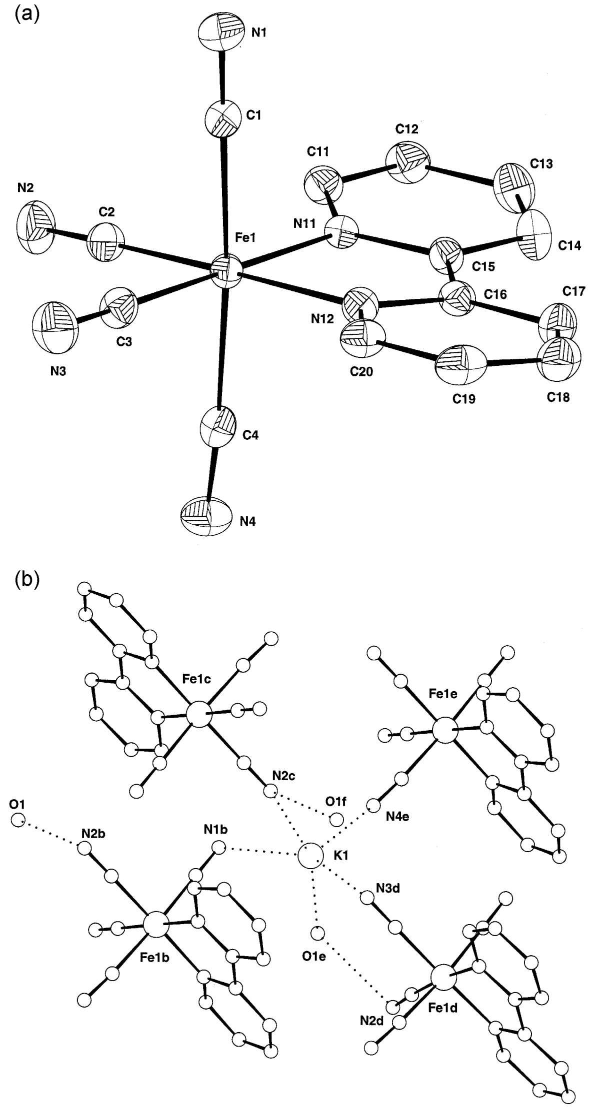

Fig. 1 (a) Perspective view of the anionic complex $[Fe(bipy)(CN)_4]^-$ of **1** showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity. (b) A view of the environment of the potassium atom in **1** including the hydrogen bonds (see text). Symmetry codes: (b) = 1/2 + *x*, 1/2 − *y*, 1/2 + *z*; (c) = 1/2 − *x*, −1/2 + *y*, 1/2 − *z*; (d) = *x*, *y*, 1 + *z*; (e) = −1/2 + *x*, 1/2 − *y*, 1/2 + *z*; (f) = 1 − *x*, −*y*, 1 − *z*.

The bipy ligand as a whole exhibits a deviation from planarity, the dihedral angle between the two planar pyridyl rings being 7°. Bond lengths and angles within this ligand are in agreement with those reported for free bipy.[19] The N(11)C(15)C(16)N(12)Fe(1) set of atoms defining the five-membered chelate at the iron atom are practically coplanar, the largest deviation from their mean plane being 0.04 Å. The triatomic Fe–C–N set of atoms at each cyanide are almost linear [values in the range 175.8(4)–179.0(4) Å]. The values of the cyanide C–N bonds [values in the range 1.122(6)–1.147(6) Å] compare well with those reported for other cyano-containing low-spin mononuclear iron(III) compounds.[9,10,17,20] The $[Fe(bipy)(CN)_4]^-$ anions which are grouped in the structure around the potassium cations, are well separated from each

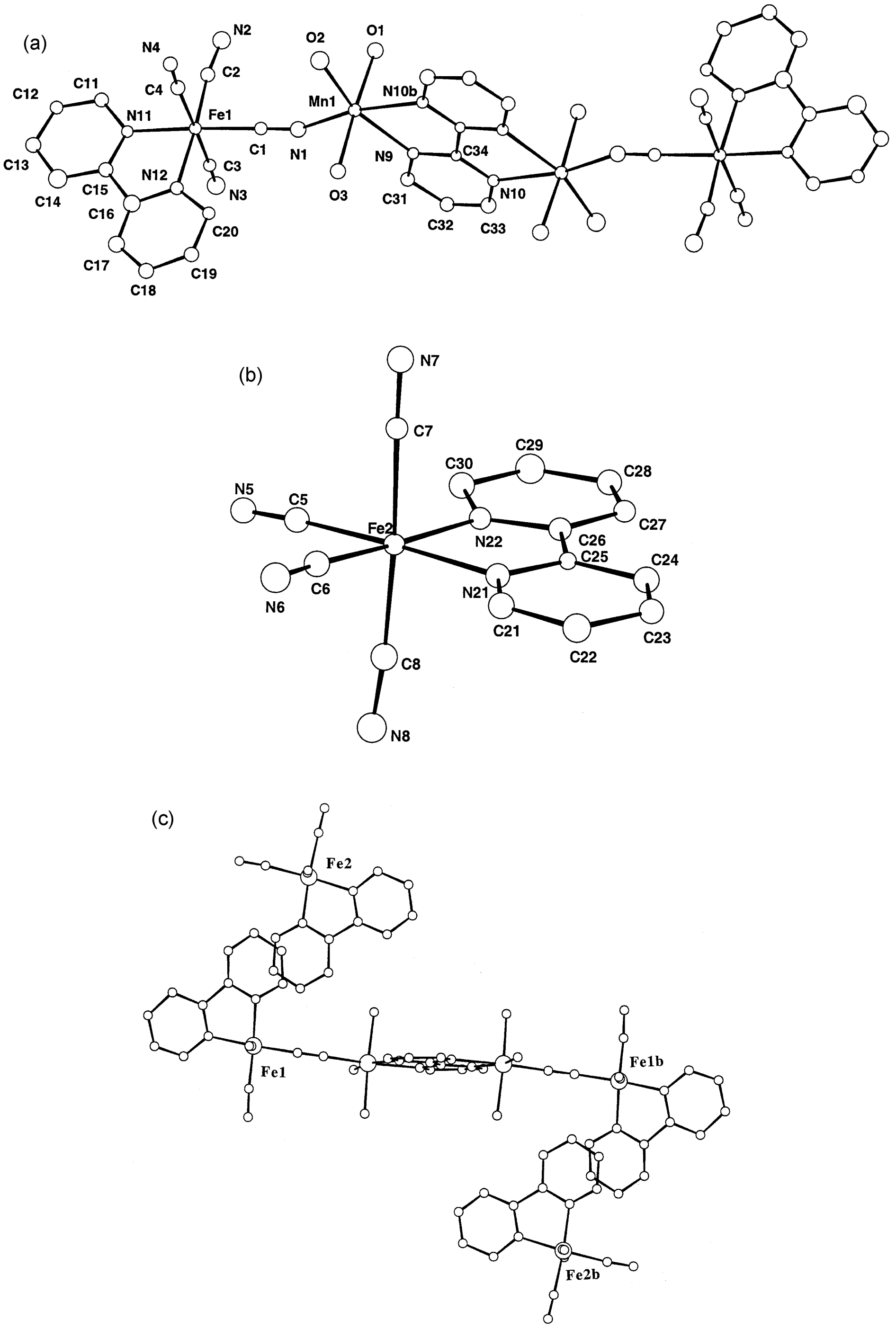

Fig. 2 (a) Crystal structure of the cationic complex [Mn$_2$(bipym)(H$_2$O)$_6${Fe(bipy)(CN)$_4$}$_2$]$^{2+}$ of **2** showing the atom numbering. (b) Crystal structure of the anionic complex [Fe(bipy)(CN)$_4$]$^-$ of **2**. (c) Perspective view of **2** showing the π–π stacking interactions.

other as indicated by the large value of the shortest intermolecular iron–iron separations: 6.498(1), 7.540(1) and 8.379(1) Å for Fe(1) ··· Fe(1h), Fe(1) ··· Fe(1g) and Fe(1) ··· Fe(1i), respectively [symmetry code: (g) = $-x$, $-y$, $-z$; (h) = $-x$, $1 - y$, $-z$; (i) = $1/2 - x$, $1/2 + y$, $1/2 - z$].

(μ-bipym)[Mn(H$_2$O)$_3${Fe(bipy)(CN)$_4$}]$_2$[Fe(bipy)(CN)$_4$]$_2$·12H$_2$O (2). The X-ray crystal structure of **2** reveals that this compound is made up of centrosymmetric heterotetranuclear [(μ-bipym)-[Mn(H$_2$O)$_3${Fe(bipy)(CN)$_4$}]$_2$]$^{2+}$ cations [Fig. 2(a)], mononuclear [Fe(bipy)(CN)$_4$]$^-$ anions [Fig. 2(b)] and crystallization water molecules. These units are held together by electrostatic forces, van der Waals interactions and an extensive network of hydrogen bonds involving nine water molecules and seven cyanide nitrogen atoms (see end of Table 3, the hydrogen atoms of the water molecules were not located). The mononuclear cyano-containing unit of **1** is also present in **2**, but here apart from its role as counterion, it also acts as a monodentate ligand towards the bipym-bridged dimanganese(II) unit through one of its four peripheral cyanide groups. This leads to the unprecedented cyano- and bipym-bridged heterotetranuclear Fe$^{III}_2$Mn$^{II}_2$ unit. Additional evidence of the occurrence of bridging cyanide and bipym is provided by the infared spectroscopy. So, the cyanide stretching frequency in the infrared spectrum of **2** consists of three peaks at 2141m, 2133s and 2119m cm^{-1}, the two higher frequency absorptions being attributed to terminal cyanide and the lower frequency one to the bridging cyanide. An asymmetric doublet at 1580s and 1570m cm^{-1} (ring stretching modes of bipym) supports the bis-chelating coordination mode of bipym.[3,6b,8b,22]

As in **1**, the iron atoms in **2** [Fe(1) and Fe(2)] are coordinated by two bipy nitrogen atoms and four cyanide carbon atoms, in a distorted octahedral geometry. The values of the Fe–N(bipy) bond distances [1.98(2)–2.00(2) Å] and that of the angle subtended by the chelating bipy {81.0(6)° [Fe(1)] and 80.3(6)° [Fe(2)]} at the two iron atoms in **2** are practically the same as those observed in **1**. This agreement also applies to the Fe–C(cyano) bonds {values varying in the ranges 1.83(2)–1.95(2) [Fe(1)] and 1.89(2)–1.95(2) Å [Fe(2)]}. The values of the cyanide C–N bonds at Fe(1) [1.12(2)–1.20(2) Å] and Fe(2) [1.09(2)–1.18(2) Å] are equal within error. The manganese atom has a six-coordinate MnN_3O_3 chromophore with distorted octahedral coordination; it is bound to three water molecules in a *mer* orientation [Mn–O bonds varying in the range 2.12(2)–2.21(1) Å], two bipym nitrogen atoms [2.29(1) and 2.35(1) Å for Mn(1)–N(9) and Mn(1)–N(10b), respectively] and a cyanide nitrogen [2.19(2) Å for Mn(1)–N(1)]. The angle subtended by bipym at the manganese atom is 70.9(5)°. Bond distances and angles within the bipym-bridged dimanganese(II) unit are close to those previously observed in the dinuclear compound $[Mn_2(bipym)(H_2O)_6(SO_4)_2]$.[6b] The values of the Fe(1)–C(1)–N(1) and Mn(1)–N(1)–C(1) bond angles are 177.5(2) and 154.1(2)°, respectively. The metal–metal separations through cyano- and bipym-bridges are 5.092(4) [Fe(1) ··· Mn(1)] and 6.131(6) Å [Mn(1) ··· Mn(1b); (b) = 2 − *x*, −*y*, −*z*] whereas the shortest intermolecular iron–iron and manganese–iron distances are 6.772(4) [Fe(1) ··· Fe(2d)] and 6.451(4) Å [Mn(1) ··· Fe(2d)].

The bipy molecules coordinated to Fe(1) and Fe(2) are practically planar (max. deviation from their mean planes are 0.02 and 0.05 Å, respectively) and the mean plane of the former makes a dihedral angle of 94° with the plane of the bipym. There are π–π stacking interactions between one of the pyridyl rings of the bipy groups coordinated to Fe(1) [N(12)–C(16)–C(17)–C(18)–C(19)–C(20)] and Fe(2) [N(21)–C(21)–C(22)–C(23)–C(24)–C(25)], the interplanar separation being 3.54 Å [see Fig. 2(c)]. The mononuclear cations and the tetranuclear anions are well isolated from each other, the shortest iron–iron separations between cations and between anions being larger than 8.2 Å [8.456 Å for Fe(1) ··· Fe(1f) and 8.267 Å for Fe(2) ··· Fe(2l); (f) = 3/2 − *x*, −1/2 + *y*, 1/2 − *z*; (l) = 3/2 − *x*, 1/2 + *y*, −1/2 − *z*].

Magnetic properties

The susceptibility measurements for **1** and **2** are shown in Fig. 3 as a $\chi_M T$ *versus* T plot, χ_M being the molar magnetic susceptibility. $\chi_M T$ for **1** exhibits a quasi linear dependence with T in the temperature range 300–25 K, its value at room temperature being 0.475 $cm^3\ mol^{-1}$ K (μ_{eff} = 1.95 μ_B). $\chi_M T$ decreases smoothly in the lower temperature region and it attains a value of 0.35 $cm^3\ mol^{-1}$ K at 1.9 K. This behaviour is the expected one for a low-spin distorted octahedral iron(III) system with spin–orbit coupling of the $^2T_{2g}$ ground term.[23] This term for a low-spin iron(III) ion in O_h symmetry is split under a rhombic distortion (C_{2v} symmetry) into a singlet ground state ($^2A_1$) and two excited doublets ($^2B_1 + {}^2B_2$) which are separated by an energy gap, denoted Δ. We have analyzed the magnetic data of **1** through a Hamiltonian which takes into account the rhombic distortion, spin–orbit coupling and the Zeeman effect.[24] Best-fit parameters are $\Delta = 900$ cm^{-1}, $\lambda = -75.5$ cm^{-1}, $\kappa = 0.76$ and $\theta = 0.31$ K where λ is the spin–orbit coupling, κ is the orbital reduction factor and θ is the Weiss constant (introduced as $T - \theta$) which accounts for the intermolecular interactions at low temperatures.

The $\chi_M T$ product of **2** at room temperature is 10.5 $cm^3\ mol^{-1}$ K, a value which is as expected for two high-spin manganese(II) and four low-spin iron(III) ions. Upon cooling, $\chi_M T$ continuously decreases and attains a value of 1.70 $cm^3\ mol^{-1}$ K at 1.9 K. This variation is consistent with the occurrence of an intramolecular antiferromagnetic coupling. An antiferromagnetic coupling of *ca.* −1 cm^{-1} was previously reported in the case of bipym-bridged manganese(II) compounds[6b,21,25] and also an antiferromagnetic coupling between low-spin Fe(III) ($t_{2g}^5e_g^0$) and high-spin Mn(II) ($t_{2g}^3e_g^2$) through bridging cyano is expected on simple symmetry considerations (net overlap of the metal centered magnetic orbitals through the π t_{2g}–t_{2g} pathway). No maximum is observed in the susceptibility curve of **2** because of the presence of the two uncoupled low-spin iron(III) units. In order to have a rough estimate of the values of the magnetic couplings through bipym- (J) and cyano-bridges (j) in the tetranuclear unit of **2**, we have analyzed its magnetic data by the spin-only formalism through the Hamiltonian [eqn. (1)]

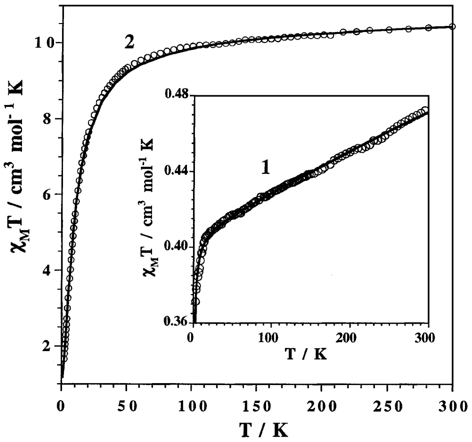

Fig. 3 Temperature dependence of $\chi_M T$ product for **1** and **2**: (○) experimental; (—) best-fit (see text).

$$\hat{H} = -J[\hat{S}_{Mn1}\cdot\hat{S}_{Mn2}] - j[\hat{S}_{Fe1}\cdot\hat{S}_{Mn1} + \hat{S}_{Mn2}\cdot\hat{S}_{Fe2}] \qquad (1)$$

where $\hat{S}_{Mn}$ and $\hat{S}_{Fe}$ are spin operators associated with the interacting local spins ($\hat{S}_{Mn1} = \hat{S}_{Mn2} = 5/2$ and $\hat{S}_{Fe1} = \hat{S}_{Fe2} = 1/2$). It is important to note that there is no analytical expression for the magnetic susceptibility of this system through the vector coupling model[26] and to treat the magnetic data we used numerical matrix diagonalization techniques.[27,28] Previously to that, and in order to avoid the orbital contribution of the T_{2g} term of the two coordinated low spin iron(III) centers as well as to remove the magnetic contribution of the two uncoordinated $[Fe(bipy)(CN)_4]^-$ anions, we corrected the values of $\chi_M T$ of **2** as follows: we subtracted first the $\chi_M T$ data of **1** (four times) to that of **2** and then, a value of 0.75 $cm^3\ mol^{-1}$ K (twice the value of the Curie law term for a magnetically isolated spin doublet with g = 2.0) was added to the difference data. In so doing, the corrected magnetic data correspond to a tetranuclear Fe–Mn–Mn–Fe unit with interacting spins $S_{Fe} = 1/2$ and $S_{Mn} = 5/2$ and a common g factor of 2.0. The resulting corrected $\chi_M T$ *versus* T plot for the tetranuclear Fe–CN–Mn–bipym–Mn–NC–Fe unit is shown in Fig. 4. The presence of a maximum of susceptibility at 6.5 K (see insert of Fig. 4) is the signature of intramolecular antiferromagnetic interactions within the tetranuclear unit entity. Best-fit parameters of the corrected data through numerical matrix diagonalization techniques leads to $J = -1.2$ cm^{-1}, $j = -3.0$ cm^{-1} and $R = 3.0 \times 10^{-5}$ (R is the agreement factor defined as $\Sigma_i[(\chi_M)_{obs}(i) - (\chi_M)_{calc}(i)]^2/[(\chi_M)_{obs}(i)]^2$). A common value of 2.0 was fixed for the Lande factor g.

The magnetic interaction through bis-chelating bipym and the single cyanide bridge are antiferromagnetic, as predicted on orbital considerations. Although the values of the magnetic couplings we have obtained must be regarded with caution because of the crude approach used to determine them, one can see that value of the magnetic coupling through bipym lies in the range of those previously reported for bipym-bridged manganese(II) compounds [values of $-J$ varying in the range 0.93–1.2 cm^{-1}].[6b,21,25] As far as the value of the magnetic

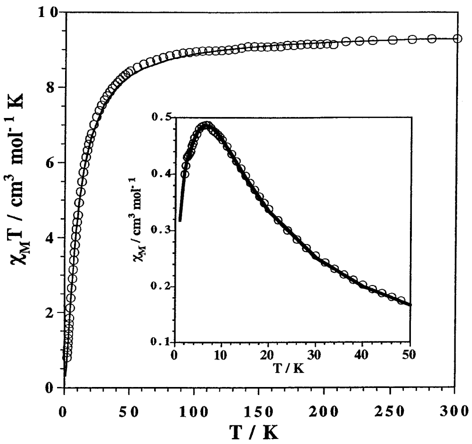

Fig. 4 Temperature dependence of the corrected $\chi_M T$ product for the tetranuclear unit Fe–CN–Mn–bipym–Mn–NC–Fe of **2**. The insert shows the temperature dependence of the corrected χ_M in the low temperature region. The solid lines are the best fit curves.

coupling within the Fe(III)–μ-CN–Mn(II) unit is concerned (-3.0 cm^{-1}), it can only be compared with that recently observed in the centrosymmetric trinuclear complex [{Fe(bipy)(CN)$_4$}$_2$Mn(H$_2$O)$_4$]·4H$_2$O (-0.9 cm^{-1}).[10] The somewhat shorter iron–manganese separation through the bridging cyanide [5.092(4) Å in **2** *versus* 5.126(1) Å in the trinuclear complex] and different chromophore around the manganese atom [MnN_3O_3 in **2** *versus* MnN_2O_4 in the trinuclear complex][29] would favour a larger antiferromagnetic coupling in **2**. Other parameters such as the deviation of the linearity in the Fe–C–N–Mn set of atoms and the tilting at the cyanide bridge also influence the magnetic coupling as shown recently for cyano-bridged homodinuclear copper(II) and nickel(II) complexes.[30] Finally, we would like to briefly discuss the relative magnitude of the magnetic couplings through bipym ($J = -1.2$ cm^{-1}) and cyanide ($j = -3.0$ cm^{-1}) bridges in **2**. At first sight, it seems surprising that the the σ exchange pathway involved in the case of the Mn(II)–bipym–Mn(II) unit appears as less efficient than the π one which is operative in the Fe(III)–CN–Mn(II) entity. The answer to this apparent anomaly lies in the fact that when several unpaired electrons are present on each interacting center (n_A and n_B in an A–B unit), the magnetic interaction is not properly described by J but by $n_A n_B J$.[31] In the case of **2**, given that the values of $n_{Mn} = 5$ and $n_{Fe} = 1$, the values of J and j become -30 ($= n_A n_B J$) and -15 cm^{-1} ($= n_A n_B j$), respectively. These values support the greater efficiency of the σ exchange pathway *versus* the π one, as expected.

In the near future, the systematic use of partially blocked cyanide-containing complexes of formula $[M(AA)(CN)_4]^{(4-m)-}$ (M = transition metal ion) as a ligand towards other d and f spin carriers could afford new cyanide-bridged heterometallic systems with different dimensionalities and new spin topologies.

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