# Synthesis, crystal structure and magnetic properties of the manganese(II) chains $[Mn(bipym)(NO_3)_2]$ and $[Mn(bipym)(NCO)_2]$ (bipym = 2,2′-bipyrimidine)

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Two new manganese(II) chains of formula $[Mn(bipym)(NO_3)_2]$ **1** and $[Mn(bipym)(NCO)_2]$ **2** (bipym = 2,2′-bipyrimidine) have been synthesized and their structures determined by single-crystal X-ray diffraction. Their structures consist of zigzag chains of bipym-bridged manganese(II) ions where electroneutrality is achieved by monodentate and chelating nitrate groups (**1**) and by *N*-bonded terminal cyanate ligands (**2**). The manganese atom in **1** is seven-co-ordinated being surrounded by four bipym nitrogens and three nitrato-oxygens [Mn–N and Mn–O 2.362(2)–2.330(2) and 2.205(2)–2.392(2) Å, respectively]. The manganese atom in **2** is six-co-ordinated with four bipym- and two cyanato-nitrogen atoms in *cis* position comprising a distorted-octahedral environment [average Mn–N (cyanato) and Mn–N (bipym) bond distances 2.097(3) and 2.355(3) Å, respectively]. In both structures the bipym group acts as a bis(bidentate) ligand forming two five-membered chelate rings, the values of the bite angle at the bipym being 69.5(1) and 69.3(1)° in **1** and 69.5(1)° in **2**. The intrachain metal–metal separations are 6.239(1) and 6.247(1) Å in **1** and 6.234(1) Å in **2**. Variable-temperature magnetic susceptibility data in the temperature range 290–4.2 K show the occurrence of a significant intrachain antiferromagnetic coupling between the local high-spin manganese(II) ions, the values of the exchange coupling parameter $J$ being −0.93 (**1**) and −1.1 (**2**) $cm^{-1}$. The efficiency of bis(chelating) ligands such as bipym and oxalate in mediating antiferromagnetic coupling between manganese(II) ions is analysed and discussed in the light of available magnetostructural data.

In previous works[1] we have shown how the chelating and bis(chelating) co-ordination modes of the heterocyclic 2,2′-bipyrimidine (bipym) allow the chemist to prepare nuclearity-tailored polynuclear complexes. Restricting ourselves to the case of the copper(II) complexes for simplicity, the great plasticity of its co-ordination sphere, the copper(II) to bipym molar ratio used, and the nature of counter ion and coligands appeared as very useful tools in designing mono-,[2] di-,[2c,f,g,3] hepta-nuclear,[4] one-,[3b,c,5] two-[2d,5b,d,6] and three-dimensional[5d,e] compounds.

Recently, a systematic study of complex formation between bipym and other first-row transition-metal ions led us to prepare bipym-bridged dinuclear compounds of general formula $[M_2(bipym)]^{4+}$ with M = $Fe^{II}$,[7] $Mn^{II}$,[8] $Co^{II}$,[9] $Ni^{II}$[10] or $Zn^{II}$.[11] In this series each metal atom is six-co-ordinated, four oxygen atoms from four water molecules (M = $Fe^{II}$, $Co^{II}$ or $Ni^{II}$) or from three water molecules and one unidentate sulfate counter ion (M = $Fe^{II}$ or $Mn^{II}$) comprise the octahedral metal environment. Given that these terminal aqua ligands can easily be replaced by suitable bridging groups, the next step consists of polymerizing these dinuclear units. Our first attempts in the case of manganese(II) yielded the new honeycomb layered materials of formula $[Mn_2(bipym)(ox)_2]\cdot 6H_2O$[8] and $[Mn_2(bipym)(N_3)_4]$[12] which behave as alternating magnetic planes with antiferromagnetic coupling through bis(chelating) bipym and oxalate ligands and ferromagnetic coupling through the double end-on azido bridge.

The present work concerns the preparation and structural characterization of the first bipym-bridged manganese(II) chains of formula $[Mn(bipym)(NO_3)_2]$ **1** and $[Mn(bipym)(NCO)_2]$ **2** where a 1:1 $Mn^{II}$:bipym molar ratio is involved. A study of their magnetic properties as a function of temperature is also presented.

## Experimental

### Materials

Manganese(II) nitrate tetrahydrate, sodium cyanate and 2,2′-bipyrimidine were obtained from commercial sources and used as received. Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Universidad Autónoma de Madrid (Spain). Manganese contents were determined by atomic absorption spectrometry.

### Preparations

**$[Mn(bipym)(NO_3)_2]$ 1.** This compound was isolated as pale yellow hexagonal prisms of X-ray quality by slow evaporation of a yellow aqueous solution containing stoichiometric amounts of $Mn(NO_3)_2\cdot 4H_2O$ (1 mmol) and bipym (1 mmol). Owing to its great solubility in water, evaporation of the solvent nearly to dryness is required to obtain the product in good yield (*ca.* 80%). The solid product was filtered off, washed with the minimum volume of cold water, ethanol and diethyl ether and kept over calcium chloride (Found: C, 28.4; H, 1.65; Mn, 16.1; N, 24.25. Calc. for $C_8H_6MnN_6O_6$: C, 28.5; H, 1.8; Mn, 16.3; N, 24.9%).

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**[Mn(bipym)(NCO)$_2$] 2.** This compound was isolated as a yellow polycrystalline powder solid by mixing warm concentrated aqueous solutions (total volume 10 cm$^3$) containing stoichiometric amounts of **1** (0.5 mmol) and NaNCO (1 mmol). The resulting precipitate was filtered off and washed with water, ethanol and diethyl ether. Yield 60% (Found: C, 40.3; H, 1.9; Mn, 18.3; N, 28.1. Calc. for $C_{10}H_6MnN_6O_2$: C, 40.45; H, 2.0; Mn, 18.5; N, 28.3%). Single crystals of complex **2** were grown from an aqueous solution (50 cm$^3$) containing **1** (1 mmol) and NaNCO (2 mmol) on standing at room temperature for 1 d. Hexagonal and polyhedral-shaped crystals were obtained in the same batch.

The infrared spectra of complexes **1** and **2** have in common the occurrence of a strong absorption at 1565 (**1**) and 1570 (**2**) cm$^{-1}$ (ring stretching mode of bipym) which is the signature of the presence of bis(chelating) bipym.[5d] The occurrence of co-ordinated nitrate[13,14] in **1** is associated with strong absorptions at 1455 (shoulder), 1450, 1375 and 1310 cm$^{-1}$ and sharp- and medium-intensity peaks at 1040, 1035, 1010, 840, 830, 810, 740w, 730w and 710w cm$^{-1}$. The cyanato absorptions in the IR spectrum are a strong doublet at 2220 and 2190 cm$^{-1}$ [ν(CN) asymmetric stretching vibration] and two sharp medium-intensity peaks at 630 and 610 cm$^{-1}$ [δ(NCO) bending mode]. The shift towards higher wavenumbers of the ν(CN) stretching in **2** when comparing with that of free cyanate (2170 cm$^{-1}$ for KNCO)[15] supports the co-ordination of cyanate in **2**. In addition, the split δ(NCO) of only a few wavenumbers suggests that **2** contains *N*-bonded cyanate.[16] All these spectroscopic indications on the co-ordination modes of the bipym, nitrate and cyanate ligands in **1** and **2** have been confirmed by the corresponding crystal structure determinations (see below).

## Physical techniques

Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the 4000–400 cm$^{-1}$ region. Magnetic susceptibility measurements were made on polycrystalline samples in the temperature range 4.2–290 K with a Metronique Ingenierie MS03 SQUID magnetometer (**1**) and a fully automatized pendulum-type susceptometer[17] (**2**) equipped with a TBT continuous-flow cryostat and a Bruker BE15 electromagnet operating at 1.8 T. The former was calibrated with $[NH_4]_2Mn(SO_4)_2\cdot6H_2O$ and the latter with $Hg[Co(NCS)_4]$. Diamagnetic corrections were estimated from Pascal's constants[18] as $-153 \times 10^{-6}$ (**1**) and $-151 \times 10^{-6}$ (**2**) cm$^3$ mol$^{-1}$.

## Crystallography

Crystals of dimensions 0.26 × 0.31 × 0.38 (complex **1**) and 0.16 × 0.18 × 0.21 mm (**2**) were mounted on a Siemens R3m/V automatic four-circle diffractometer and used for data collection. Diffraction data were collected at room temperature by using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ 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 range 2θ 15–30°. Information concerning the crystallographic data collection and structure refinements is summarized in Table 1. Examination of two standard reflections, monitored after every 148, showed no sign of crystal deterioration. Lorentz-polarization and absorption corrections[19] were applied to the intensity data. The maximum and minimum transmission factors were 0.583 and 0.555 for **1** and 0.589 and 0.582 for **2**. Of the 2926 (**1**) and 1458 (**2**) measured reflections in the range 2θ 3–54° with index ranges $0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 16$ and $0 \leqslant l \leqslant 19$ (**1**) and $-9 \leqslant h \leqslant 8$, $0 \leqslant k \leqslant 18$ and $0 \leqslant l \leqslant 13$ (**2**), 2455 (**1**) and 1235 (**2**) were unique. From these, 1788 (**1**) and 1142 (**2**) were observed [$I > 3\sigma(I)$] and used for the refinement of the structures.

**Table 1** Summary of crystal data[a] for [Mn(bipym)(NO$_3$)$_2$] **1** and [Mn(bipym)(NCO)$_2$] **2**

| | **1** | **2** |
|---|---|---|
| Formula | $C_8H_6MnN_6O_6$ | $C_{10}H_6MnN_6O_2$ |
| $M$ | 337.1 | 297.1 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | *Pbca* | *C*2/*c* |
| $a$/Å | 10.905(2) | 7.322(2) |
| $b$/Å | 13.211(2) | 14.513(3) |
| $c$/Å | 15.543(2) | 10.743(2) |
| β/° | | 99.95(2) |
| $U$/Å$^3$ | 2239.2(6) | 1124.4(4) |
| $Z$ | 8 | 4 |
| $D_c$/g cm$^{-3}$ | 2.000 | 1.755 |
| $F$(000) | 1352 | 596 |
| μ(Mo-Kα)/cm$^{-1}$ | 12.2 | 17.6 |
| $R$[b] | 0.029 | 0.035 |
| $R'$[c] | 0.034 | 0.046 |
| $S$[d] | 1.06 | 1.39 |

[a] Details in common: $T = 25$ °C, $I > 3\sigma(I)$. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] Goodness of fit $= [\Sigma w(||F_o| - |F_c||)^2/\Sigma(N_o - N_p)]^{\frac{1}{2}}$.

**Table 2** Selected interatomic distances (Å) and angles (°) for compound **1** with estimated standard deviations (e.s.d.s) in parentheses*

| | | | |
|---|---|---|---|
| Mn(1)–N(1) | 2.352(2) | Mn(1)–N(3) | 2.330(2) |
| Mn(1)–O(1) | 2.205(2) | Mn(1)–O(4) | 2.325(2) |
| Mn(1)–O(5) | 2.392(2) | Mn(1)–N(2a) | 2.362(2) |
| Mn(1)–N(4b) | 2.394(2) | | |
| N(1)–Mn(1)–N(3) | 100.7(1) | N(1)–Mn(1)–O(1) | 101.5(1) |
| N(3)–Mn(1)–O(1) | 151.2(1) | N(1)–Mn(1)–O(4) | 125.5(1) |
| N(3)–Mn(1)–O(4) | 96.1(1) | O(1)–Mn(1)–O(4) | 85.6(1) |
| N(1)–Mn(1)–O(5) | 78.5(1) | N(3)–Mn(1)–O(5) | 80.5(1) |
| O(1)–Mn(1)–O(5) | 121.9(1) | O(4)–Mn(1)–O(5) | 53.8(1) |
| N(1)–Mn(1)–N(2a) | 69.5(1) | N(3)–Mn(1)–N(2a) | 94.0(1) |
| O(1)–Mn(1)–N(2a) | 77.0(1) | O(4)–Mn(1)–N(2a) | 159.5(1) |
| O(1)–Mn(1)–N(3) | 146.0(1) | N(1)–Mn(1)–N(4b) | 156.3(1) |
| N(3)–Mn(1)–N(4b) | 69.3(1) | O(1)–Mn(1)–N(4b) | 83.2(1) |
| O(4)–Mn(1)–N(4b) | 77.7(1) | O(5)–Mn(1)–N(4b) | 119.0(1) |
| N(2)–Mn(1)–N(4b) | 89.4(1) | | |

* Symmetry codes: a $-x, -y, -z$; b $1 - x, -y, -z$.

The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. The full-matrix least-squares refinement was based on $|F_o|$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of bipym were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Full-matrix least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1.000/[\sigma^2(F_o) + 0.0010(F_o)^2]$ (**1**) or $1.000/[\sigma^2(F_o) + 0.0017(F_o)^2]$ (**2**). Models reached convergence with values of the $R$ and $R'$ indices listed in Table 1. The number of refined parameters was 190 for **1** and 89 for **2**. Criteria for satisfactory complete analysis were the ratios of the root-mean-square shift to standard deviation being less than 0.002 : 1 and no significant features in final difference maps. The residual maxima and minima in the final Fourier-difference maps were 0.29 and −0.76 e Å$^{-3}$ for **1** and 0.55 and −0.52 e Å$^{-3}$ for **2**. Solutions and refinements were performed with the SHELXTL PLUS system.[20] The final geometrical calculations were carried out with the PARST program.[21] Graphical manipulations were performed using the XP utility of the SHELXTL PLUS system. Main interatomic bond distances and angles are listed in Tables 2 (**1**) and 3 (**2**).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the

**Table 3** Selected interatomic distances (Å) and angles (°) for compound **2** with e.s.d.s in parentheses*

| | | | |
|---|---|---|---|
| Mn(1)-N(1) | 2.358(2) | Mn(1)–N(3) | 2.097(3) |
| Mn(1)–N(2a) | 2.349(2) | | |
| N(1)–Mn(1)–N(3) | 86.6(1) | N(1)–Mn(1)–N(1b) | 160.6(1) |
| N(3)–Mn(1)–N(1b) | 105.7(1) | N(1)–Mn(1)–N(2a) | 69.5(1) |
| N(3)–Mn(1)–N(2a) | 155.6(1) | N(1b)–Mn(1)–N(2a) | 96.2(1) |
| N(3)–Mn(1)–N(2c) | 89.4(1) | N(2a)–Mn(1)–N(2c) | 88.5(1) |
| N(3)–Mn(1)–N(3b) | 102.0(1) | | |

* Symmetry codes: a $-x, -y, -z$; b $-x, y, \frac{1}{2} - z$; c $x, -y, \frac{1}{2} + z$.

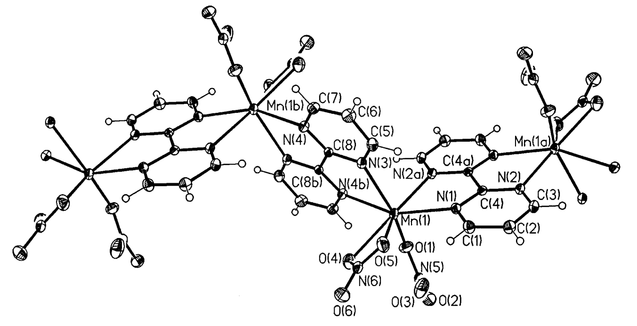

**Fig. 1** Perspective view of compound **1** with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level

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## Results and Discussion

### Crystal structures

**[Mn(bipym)(NO$_3$)$_2$] 1.** The structure of complex **1** consists of neutral zigzag chains of manganese(II) ions bridged by bipym. The electroneutrality is achieved by the presence of monodentate and chelating nitrato groups. A perspective view of the asymmetric unit and three symmetry-related units is depicted in Fig. 1. Inversion centres positioned at the middle of the C(4)–C(4a) and C(8)–C(8a) bonds lead to chains of metal atoms running parallel to the *x* axis. The chains are well isolated from each other, the average bipym planes of neighbouring chains are not parallel and π interchain interactions are precluded.

The manganese atom exhibits a seven-co-ordinate stoichiometry which is far from the common pentagonal-bipyramidal (ideal $D_{5h}$ symmetry) environment found for seven-co-ordinated Mn$^{II}$.[22] Each metal atom is bound to four nitrogen atoms from two adjacent bipym groups and three nitrato-oxygens from two nitrate ligands, one being uni- and the other bi-dentate. The resulting metal geometry can be regarded as distorted octahedral, where the equatorial positions are occupied by the N(1), O(1), N(3) and N(4b) atoms, one axial position is filled by N(2a) and the other axial site, which is split, is occupied by O(4) and O(5) from the chelating nitrate. The two adjacent bipym molecules are not equivalent: that containing the N(1) and N(2) atoms is almost symmetrically co-ordinated to the metal atom [average Mn–N 2.357(2) Å] whereas distances of 2.330(2) and 2.394(2) Å are observed for Mn(1)–N(3) and Mn(1)–N(4b), respectively. However, these Mn–N (bipym) distances are in the range found in other bipym-bridged manganese(II) complexes.[8,23] The values of the bite angle at the bipym ligands are 69.5(1) and 69.3(1)° for N(1)–Mn(1)–N(2a) and N(3)–Mn(1)–N(4b), respectively. The Mn–O distance concerning the monodentate nitrate [2.205(2) Å for Mn(1)–O(1)] is significantly shorter than that involving the bidentate chelating one, which is bound to Mn$^{II}$ in an almost symmetrical bidentate fashion [2.392(2) and 2.325(2) Å for Mn(1)–O(5) and Mn(1)–O(4), respectively].

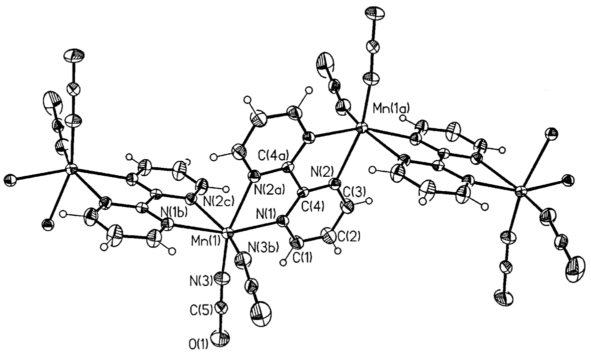

**Fig. 2** Perspective view of the asymmetric unit and three symmetry-related units of compound **2**. Details as in Fig. 1

The pyrimidine rings are planar, as expected, with deviations not greater than 0.005(2) and 0.014(2) Å from the mean planes containing atoms N(1) and N(2) and N(3) and N(4), respectively. The bipym ligands are also planar and the metal atom is 0.0321(1) and 0.0334(1) Å out of these planes. The dihedral angle between adjacent bipym planes is 108.1(1)°. No significant differences are observed in the carbon–carbon and –nitrogen intra-ring bonds of the two bridging bipym ligands and their values are in agreement with that of both free[24] and co-ordinated bipym.[2,6a,b,7–12] The carbon–carbon inter-ring bond lengths [1.486(4) and 1.482(4) Å for C(8)–C(8b) and C(4)–C(4a), respectively] are somewhat longer than the average carbon–carbon intra-ring bond distance (1.379 Å), as expected.

Both monodentate bidentate nitrates are planar, as expected. The lengthening of some of the N–O nitrate bonds [1.269(2) Å for N(5)–O(1) *versus* 1.229(3) and 1.228(3) Å for N(5)–O(2) and N(5)–O(3); 1.261(2) and 1.254(3) Å for N(6)–O(5) and N(6)–O(4) *versus* 1.221(2) Å for N(6)–O(6)] is due to their co-ordination to Mn$^{II}$. The chelating co-ordination of the nitrate containing the N(6) atom causes a significant reduction of the magnitude of the O(4)–N(6)–O(5) bond angle [116.3(2)°] with respect to the ideal value of 120°.

The metal–metal separations across the bridging bipym are 6.239(1) [Mn(1)···Mn(1a)] and 6.247(1) Å [Mn(1)···Mn(1b)], somewhat longer than those reported for other structurally characterized bipym-bridged manganese(II) compounds.[8,12,23] The shortest interchain metal–metal distance [Mn(2)···Mn(1i); i $x - \frac{1}{2}, -y + \frac{1}{2}, -z$] is 6.516(1) Å.

**[Mn(bipym)(NCO)$_2$] 2.** The structure of complex **2** is made up of neutral zigzag chains of manganese(II) atoms which are bridged by bipym molecules. The electroneutrality is achieved by terminally bound cyanato groups in *cis* positions. A perspective view of the asymmetric unit and three-symmetry related units is shown in Fig. 2. An inversion centre positioned at the middle of the C(4)–C(4a) bond leads to chains of metal atoms running parallel to the *z* axis which are well separated from each other: bipym planes from neighbouring chains are parallel but slipped and separated by a distance of 3.609(3) Å, no π overlap being observed. This chain is very close to that reported for the compound [Fe(bipym)(NCS)$_2$] where manganese(II) and cyanate are replaced by iron(II) and thiocyanate.[25] The most striking difference is the chirality of the iron(II) chain (it crystallizes in the tetragonal space group $P4_1$, no. 76 and both Δ and λ enantiomers are obtained in the same batch).

Each manganese atom is in a distorted-octahedral environment, being bonded to six nitrogen atoms (four from two bipym molecules and two from two *N*-bonded cyanate groups). A

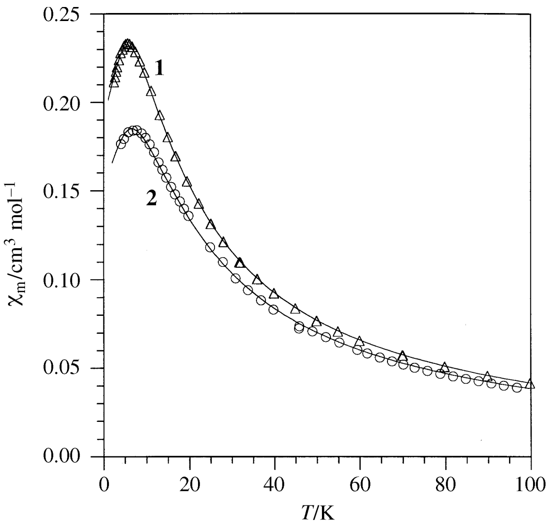

**Fig. 3** Temperature dependence of the molar magnetic susceptibility for compounds **1** (△) and **2** (○); the continuous lines are the best fits (see text)

comparison of the values of $R$ and $R'$ indices assuming either $N$- ($R = 0.035$ and $R' = 0.046$) or $O$- ($R = 0.050$ and $R' = 0.064$) cyanate co-ordination allow us to conclude that the first possibility is the correct one. The Mn–N (cyanate) bond [2.097(3) Å for Mn(1)–N(3)] is much shorter than those concerning the bipym ligands [2.358(2) Å for Mn(1)–N(1) and Mn(1)–N(1b) and 2.349(2) Å for Mn(1)–N(2a)] which are in the range found for complex **1**. This feature together with the small bite angle of the bipym ligand [69.5(1)° for N(1)–Mn(1)–N(2a)] and large value of the angle subtended at the metal by the two cyanato groups [102.0(1)° for N(3)–Mn(1)–N(3b)] are the main distortions of the octahedral surrounding of the manganese atom. The best equatorial plane is defined by atoms N(2c), N(3b), N(1) and N(1b) or N(2a), N(3), N(1) and N(1b) atoms [largest deviation from the mean basal plane is 0.104(3) Å either at N(3b) or N(3)].

The pyrimidyl rings are planar as expected [largest deviation not greater than 0.006(2)° from the mean planes]. The bipym molecule as a whole is also planar and the metal atom is 0.220(1) Å out of this plane. The dihedral angle between the adjacent bipym planes is 96.4(1)°. The cyanato group is almost linear [179.3(4)° for N(3)–C(5)–O(1)] whereas the Mn–N–C(O) linkages are bent [155.9(5)°]. The bond lengths within the cyanate ligand are significantly different [1.127(3) and 1.174(4) Å for N(3)–C(5) and C(5)–O(1), respectively]. Comparable structural features have been found in other transition-metal complexes containing terminally $N$-bonded cyanate.[26–29]

The metal–metal separation across bipym [Mn(1) ⋯ Mn(1a)] is 6.234(1) Å, very similar to that observed in complex **1**. The shortest interchain metal–metal distance [Mn(1) ⋯ Mn(1i); i $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$] is 7.226(1) Å.

## Magnetic properties

The magnetic properties of complexes **1** and **2** in the form of $\chi_m$ (molar magnetic susceptibility) for complexes **1** and **2** are shown in Fig. 3. Both curves are quite similar and they are characteristic of an antiferromagnetic interaction between local single-ion sextuplet states: the value of $\chi_m$ at room temperature is in the range expected for an $S = \frac{5}{2}$ state ($\chi_m T$ 4.30 (**1**) and 4.20 (**2**) cm$^3$ K mol$^{-1}$; calculated value for an isolated high-spin manganese(II) ion 4.33 cm$^3$ K mol$^{-1}$], increases as the temperature is lowered until a maximum is reached [$T_{max} = 6$ (**1**) and 7.5 K (**2**)], and finally decreases. The magnetic susceptibility of these compounds was analysed by using Fisher's nearest-neighbour classical Heisenberg coupling model for infinite linear chains[30] through the expression (1) which has been derived from the Hamiltonian (4) with $S_i = S_{i+1} = \frac{5}{2}$. Least-squares

$$\chi_m = \frac{35N\beta^2 g^2}{12kT} \cdot \frac{1 + u(K)}{1 - u(K)} \qquad (1)$$

$$u(K) = \coth K - (1/K) \qquad (2)$$

$$K = 35J/4kT \qquad (3)$$

$$\hat{H} = -J\sum_{i=1}^{n} \hat{S}_i \cdot \hat{S}_{i+1} - g\beta \sum_{i=1}^{n} \hat{H} \cdot \hat{S}_i \qquad (4)$$

analysis of the susceptibility data led to $J = -0.93$ cm$^{-1}$, $g = 2.00$ and $R = 1.1 \times 10^{-4}$ (**1**) and $J = -1.1$ cm$^{-1}$, $g = 1.99$ and $R = 5.8 \times 10^{-5}$ (**2**); $R$ is the agreement factor defined as $\Sigma_i[(\chi_m)_{obs}(i) - (\chi_m)_{calc}(i)]^2/[(\chi_m)_{obs}(i)]^2$. An excellent agreement between the experimental and theoretical curves is achieved as seen in Fig. 3. The introduction of an additional parameter to account for the interchain interactions in **1** and **2** was discarded because of the lack of them (see above).

The values of $J$ for the two compounds are almost identical, as expected in the light of their closely related crystal structures. It should be noted that values of $J$ ranging from $-1.1$ to $-1.2$ cm$^{-1}$ were observed for related bipym-bridged manganese(II) dimers of formula [Mn$_2$(bipym)(H$_2$O)$_4$(SO$_4$)$_2$][8] and [Mn$_2$(bipym)$_3$(NCX)$_4$] (X = S or Se).[31] The remarkable ability of bis(chelating) ligands such as bipym to mediate antiferromagnetic coupling between metal centres separated by more than 5.5 Å has been analysed previously.[5b] The observed antiferromagnetic coupling in this family of complexes arises from the $\sigma^*$ overlap between the $d_{x^2-y^2}$ magnetic orbitals centred on each metal ion (the $x$ and $y$ axes are roughly defined by the metal–bipym nitrogen bonds) through the bipym N–C–N bridging skeleton. In the case of Cu$^{II}$ (only one unpaired electron per metal atom and located in a $d_{x^2-y^2}$ magnetic orbital) this exchange pathway is the only one operative, whereas for Mn$^{II}$ (five unpaired electrons per metal atom) the $\pi$-exchange pathway is also operative. Symmetry considerations indicate that the number of ferromagnetic terms $J_{\mu\nu}$ ($\mu$ and $\nu$ denoting pairs of orthogonal magnetic orbitals) increases when going from Cu$^{II}$ to Mn$^{II}$. However, given that the manganese–manganese separation across bipym is larger than 6 Å, the ferromagnetic terms are expected to be negligible,[32] and the good $\sigma^*$ overlap between the $d_{x^2-y^2}$ magnetic orbitals through the bipym N–C–N bridging skeleton accounts mainly for the antiferromagnetic coupling observed. The same exchange pathway is operative in the related bis(chelating) oxalate. The remarkable efficiency of both bipym and oxalate to transmit antiferromagnetic interactions between manganese(II) ions is shown in Table 4. As inferred from this table, the coupling through oxalate ($J_{ox}$) in this family of complexes is about twice that observed through bipym ($J_{bipym}$). These values are to be compared with magnetic coupling between manganese(II) ions through the monoatomic chloride bridge: $J = -0.33$ cm$^{-1}$ in the chain MnCl$_2$·2H$_2$O,[40] the intrachain metal–metal separation being 3.7 Å.

We would like to finish this contribution by pointing out that the determination of the exchange coupling constants through bis(chelating) assembling units such as bipym or oxalate in chain compounds is very important because from a topologic viewpoint the chains are closer to two- and three-dimensional compounds than to simple dimers. It should be noted that the magnetic properties of structurally characterized bipym- and oxalate-containing two- and three-dimensional materials which have been isolated by different research teams in the last few years[2d,6c,8,12,41] cannot be analysed because of the lack of suitable theoretical models. Undoubtedly, the values of $J_{bipym}$

**Table 4** Selected magnetostructural data for bipym- and oxalato-bridged manganese(II) complexes[a]

| Compound | Nuclearity | $d(\mathrm{M}\cdots\mathrm{M})^b$/Å | $-J^c$/cm$^{-1}$ | Ref. |
|---|---|---|---|---|
| [Mn$_2$(bipym)(H$_2$O)$_4$(SO$_4$)$_2$] | Dimer | 6.123(2) | 1.1 | 8 |
| [Mn$_2$(bipym)$_3$(NCS)$_4$] | Dimer | 6.223(1) | 1.2 | 31 |
| [Mn$_2$(bipym)$_3$(NCSe)$_4$] | Dimer | 6.211(1) | 1.2 | 31 |
| **1** | Chain | 6.239(1)<br>6.247(1) | 0.93 | This work |
| **2** | Chain | 6.234(1) | 1.1 | This work |
| [Mn$_2$L$^1{}_2$(ox)][ClO$_4$]$_2$ | Dimer | 5.626(4) | 1.91 | 33 |
| [Mn$_2$L$^2{}_2$(ox)][ClO$_4$]$_2$ | Dimer | 5.610(1) | 2.04 | 33 |
| [Mn(bipy)(ox)] | Chain | 5.622(1) | 2.4–2.14 | 34, 35 |
| [Mn(H$_2$O)$_2$(ox)] | Chain | 5.64$^d$ | 1.7–1.8 | 34, 36–39 |

[a] Abbreviations used: bipy = 2,2′-bipyridine; L$^1$ = *N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine; L$^2$ = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)-ethane-1,2-diamine. [b] Metal–metal separation across bipym or ox. [c] Value of the exchange coupling interaction through the bridging bipym or ox ligands. [d] Calculated through X-ray diffraction data from ref. 37.

and $J_{\mathrm{ox}}$ listed in Table 4 will be a good basis to check the reliability of ones obtained from corresponding fits on higher-dimensionality systems.

*Note added at proof:* Upon correcting proofs of the present work, we became aware that the crystal structure and magnetic susceptibilities of complex **1**, [Mn(bipym)(NO$_3$)$_2$], had been reported by D. M. Hong *et al.* (*Polyhedron*, 1996, **15**, 2335). Our magnetostructural results on **1** fully agree with theirs.

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