Inorg. Chem. **2003**, *42*, 2695–2703

Inorganic Chemistry
Article

Structural Analyses and Magnetic Properties of 3D Coordination Polymeric Networks of Nickel(II) Maleate and Manganese(II) Adipate with the Flexible 1,2-Bis(4-pyridyl)ethane Ligand

Partha Sarathi Mukherjee,[†] Sanjit Konar,[†] Ennio Zangrando,[‡] Talal Mallah,[§] Joan Ribas,*[,||] and Nirmalendu Ray Chaudhuri*[,†]

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata-700032, India, Dipartimento di Scienze Chimiche, University of Trieste, 34127 Trieste, Italy, Laboratoire de Chimie Inorganique, UMR CNRS 8613, Universit de Paris-Sud, 91405 Orsay, France, and Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain

Received October 31, 2002

Two novel inorganic–organic hybrid 3D extended networks of Ni(II) and Mn(II) having molecular formulas $[(\mathrm{maleate})_2\mathrm{Ni}_3(\mathrm{bpe})_4(\mathrm{H_2O})_4](\mathrm{NO_3})_2\cdot\mathrm{H_2O}$ (**1**) and [(adipate)Mn(bpe)] (**2**) (bpe = 1, 2-bis(4-pyridyl)ethane), respectively, have been synthesized and characterized by single-crystal X-ray diffraction studies and low-temperature (300–2 K) magnetic measurements. Compound **1** crystallizes in the monoclinic system, space group *C*2/*c* (No. 15), with chemical formula $C_{56}H_{62}N_{10}Ni_3O_{19}$, $a = 30.955(4)$ Å, $b = 12.705(3)$ Å, $c = 17.058(5)$ Å, $\beta = 117.26(2)°$, and $Z = 4$. Compound **2** crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2), with chemical formula $C_{18}H_{20}MnN_2O_4$, $a = 8.492(2)$ Å, $b = 9.444(2)$ Å, $c = 11.533(3)$ Å, $\alpha = 97.19(1)°$, $\beta = 94.64(1)°$, $\gamma = 105.02(1)°$, and $Z = 2$. The structure determination reveals for both a 3D network. Compound **1** contains two crystallographically independent Ni(II) ions in different octahedral environments. Ni(1) lies on an inversion center, and its coordination environment comprises two chelating maleate anions and two bpe nitrogen donors, while the Ni(2) ion is surrounded by meridionally disposed three bpe N atoms, two water molecules, and one oxygen donor from the dicarboxylate anion. Of the three crystallographic independent bpe ligand, one presents an anti and the others a gauche conformation. The corresponding N-to-N distances are 9.344, 6.543, and 6.187 Å. Variable-temperature magnetic susceptibility measurement of the complex reveals the existence of a dominant ferromagnetic interaction within the molecule. Compound **2** is composed of Mn_2 dimer units linked by adipate anions to form corrugated 2D sheets which, on interconnection through bpe (anti conformation, N-to-N distance of 9.391 Å), produces an interpenetrated 3D α-polonium-related type net. Complex **2** reveals to be antiferromagnetic fitting data using a dimeric Mn(II) model that considers negligible magnetic transmission through the carbon skeleton of adipate and the bpe pathway.

Introduction

Metal–organic hybrid materials of paramagnetic metal ions may give rise to a series of novel inorganic frameworks with various crystal structures depending on the choice of bridging ligands and coordination geometries of transition metal ions.[1] Extended structures with polymeric networks have potential application in the field of molecular magnetism and material chemistry.[2–5] One commonly used strategy in building such networks with extended structures is to employ appropriate bridging ligands which can transmit magnetic interaction as well as bind metal ions.

There is an increase number of recently characterized interwoven nets incorporating metal ions and flexible ligands. In this respect, dicarboxylates are frequently used in the design of polynuclear complexes as efficient linkers/spacers, able to mediate magnetic interactions. The different coordination modes adopted by dicarboxylates accomplish the transmission of the magnetic coupling at different degrees. In general terephthalate, oxalate, malonate, fumarate, etc.,[5–9] are used in this purpose, but use of maleate[10] and adipate[11] is not very common. Recently 1,2-bis(4-pyridyl)ethane (bpe) has been employed for the construction of solid-state archi-

---

* To whom correspondence should be addressed. E-mail: icnrc@mahendra.iacs.res.in (N.R.C.); joan.ribas@qi.ub.es (J.R.). Fax: (91)(33) 2473-2805 (N.R.C.).

[†] Indian Association for the Cultivation of Science.

[‡] University of Trieste.

[§] Universit de Paris-Sud.

[||] Universitat de Barcelona.

10.1021/ic026150n CCC: $25.00

Table 1. Crystal Data and Refinement Details of Complexes $[(maleate)_2Ni_3(bpe)_4(H_2O)_4](NO_3)_2 \cdot H_2O$ (**1**) and [(adipate)Mn(bpe)] (**2**)

	1	**2**
empirical formula	$C_{56}H_{62}N_{10}Ni_3O_{19}$	$C_{18}H_{20}MnN_2O_4$
formula mass, g mol^{-1}	1355.29	383.30
cryst system	monoclinic	triclinic
space group	$C2/c$ (No. 15)	$P-1$ (No. 2)
a, Å	30.955(4)	8.492(2)
b, Å	12.705(3)	9.444(2)
c, Å	17.058(5)	11.533(3)
α, deg	90.00	97.19(1)
β, deg	117.26(2)	94.64(1)
γ, deg	90.00	105.02(1)
V, Å^3	5963(2)	880(2)
Z	4	2
D(calcd), g cm^{-3}	1.510	1.446
μ(Mo Kα), mm^{-1}	1.020	0.775
θ range, deg	2.40−26.37	1.79−25.89
no. of collcd data	12 092	5290
no. of unique data	6095	3117
R_{int}	0.0768	0.0813
refined params	415	225
R1[a] $[I > 2\sigma(I)]$	0.0540	0.0912
wR2[a] $[I > 2\sigma(I)]$	0.121	0.2572
GOF[b]	0.994	1.112

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [b] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

tectures for its flexibility in showing conformations. Only one single-crystal structure was reported to date based on Ni(II) using bpe ligand that exhibited an infinite chain of bridged bpe in anti conformation.[12] We have employed bpe along with maleate on Ni(II) and adipate on Mn(II) to construct mixed bridging networks. This contribution reports the synthesis, crystal structure, and variable-temperature magnetic behavior of two new 3D extended networks with metal ions different from Cu(II), owing to the scarce number of these complexes reported in the literature, compared to those of Cu(II). Magnetic results of both the complexes are corroborated with the structural parameters.

Experimental Section

Materials. High-purity (98%) 1,2-bis(4-pyridyl)ethane was purchased from the Aldrich Chemical Co. Inc. and was used as received. All others chemicals were of AR grade.

Physical Measurements. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer (applied field = 0.3 T for complex **1** and 0.1 T for complex **2**) working in the temperature region 300−2 K. In case of complex **1** high applied field (0.3 T) was used to obtain a nice SQUID signal since the measurements were done on a 3 mg sample. It was however checked that no saturation is observed below 20 K by performing the measurements within an applied field of 0.05 T as well. Diamagnetic corrections were estimated from Pascal's table.[13]

Synthesis of $[(maleate)_2Ni_3(bpe)_4(H_2O)_4](NO_3)_2$ (H_2O) (1). A 5 mL aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.2908 g) was mixed with an aqueous solution (10 mL) containing Na_2 maleate (1 mmol, 0.1600 g). A methanolic solution (5 mL) of bpe (1 mmol, 0.1842 g) was added to the above solution with constant stirring. The resulting solution was filtered, and the green filtrate was kept in a $CaCl_2$ desiccator. Single crystals suitable for X-ray diffraction were obtained from the filtrate after several days. Yield: 80%. Anal. Found: C, 50.01; H, 4.80; N, 10.15. Calcd for $C_{56}H_{62}N_{10}Ni_3O_{19}$: C, 49.58; H, 4.57; N, 10.32. IR: $\nu(COO^-)$, 1575, 1666 cm^{-1}; ν(O−H), 3300−3400 cm^{-1}.

Synthesis of [(adipate)(Mn)(bpe)] (2). An aqueous solution (5 mL) of $MnCl_2 \cdot 4H_2O$ (1 mmol, 0.1970 g) was mixed with 5 mL of methanolic solution of bpe (1 mmol, 0.1842 g) with constant stirring. An aqueous (5 mL) solution of disodium adipate (1 mmol, 0.1760 g) was added to the above mixture. The resulting mixture turned turbid. It was then filtered, and the filtrate was kept in a $CaCl_2$ desiccator. The colorless single crystals, suitable for X-ray diffraction, were obtained from the filtrate after a few days. Yield: 72%. Anal. Found: C, 55.51; H, 4.89; N, 7.11. Calcd for $C_{18}H_{20}MnN_2O_4$: C, 56.35; H, 5.22; N, 7.30. IR: $\nu(COO^-)$, 1570, 1630 cm^{-1}.

Crystallographic Data Collection and Refinement. Data collection of the complexes **1** and **2** was carried out at 293(3) K, on a Nonius DIP-1030H system and on a modified STOE four-circle diffractometer equipped with a Mar-research image plate and Mo Kα radiation. A total of 30 frames were collected for **1**, each with an exposure time of 15 min, over a half of reciprocal space with a rotation of 6° about φ, the detector being at a distance of 90 mm from the crystal. For **2**, a total of 95 frames at 2° were collected with counting time 2 min. Cell refinement, indexing, and scaling of the data set were carried out using Mosflm and Scala.[14] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[15] For **1**, a Fourier-difference synthesis showed a residual assigned to a water oxygen with an occupancy of 0.5. The contribution of hydrogen atoms at calculated positions (except those of the disordered solvent in **1**) were included in the final cycles of refinements. The bpe carbon atoms of $-CH_2-$ groups in **2** were found disordered over two positions with an occupancy factor of 0.5 each. All the calculations were performed using the WinGX System, version 1.64.[16] The crystallographic data and

---

(1) (a) Cheetham, A. K.; Ferey, G.; Loiseu, T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3268. (b) Froster, M. P.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2002**, *41*, 457. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (d) Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (e) Fujita, M.; Oguru, D.; Milyazawa, M.; Oka, H.; Yamaguchi, K.; Oguru, K. *Nature* **1995**, *378*, 469.

(2) (a) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 653. (b) Stump, H. O.; Ouahab, L.; Pei, Y.; Gradjen, D.; Kahn, O. *Science* **1993**, *261*, 447. (c) Chaudhury, A.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3091.

(3) Chui, S. S.-Y.; Lo, S. M.-F.; Chatmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *238*, 1148.

(4) (a) Millange, F.; Serre, C.; Ferey, G. *Chem. Commun.* **2002**, 822. (b) Ayyappan, P.; Evans, O. R.; Lin, W. *Inorg. Chem.* **2001**, *40*, 4627.

(5) Konar, S.; Mukherjee, P. S.; Zangrando, E.; Lloret, F.; Ray Chaudhuri, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 1561.

(6) Deakin, L.; Arif, M. A.; Miller, J. S. *Inorg. Chem.* **1999**, *38*, 5072.

(7) (a) Bakalbassis, E.; Bergeret, P.; Kahn, O.; Jeannin, S.; Dromzee, Y.; Guilliot, M. *Inorg. Chem.* **1992**, *31*, 625. (b) Mukherjee, P. S.; Dalai, S.; Mostafa, G.; Zangrando, E.; Lu, T. H.; Rogez, G.; Mallah, T.; Ray Chaudhuri, N. *Chem. Commun.* **2001**, 1346.

(8) Mukherjee, P. S.; Konar, S.; Zangrando, E.; Diaz, C.; Ribas, J.; Ray Chaudhuri, N. *J. Chem. Soc., Dalton Trans.* **2002**, 3174.

(9) Girrerd, J. J.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1980**, *19*, 274.

(10) Cernak, J.; Chomic, J.; Kappenstein, C.; Robert, F. J. *Chem. Soc., Dalton. Trans.* **1997**, 2981.

(11) Kim, Y. J.; Jung. D.-Y. *Inorg. Chem.* **2000**, *39*, 1470.

(12) Rochon, F. D.; Andruh, M.; Melanson, R. *Can. J. Chem.* **1998**, *76*, 1564.

(13) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.

(14) Collaborative Computational Project: *Acta Crystallogr., Sect. D* **1994**, *4*, 760.

(15) Sheldrick, G. M. *SHELXL-97, Programs for Structure Analysis*; University of Gottingen: Gottingen, Germany, 1998.

Table 2. Bond Lengths (Å) and Angles (deg) for the Ni(1) and Ni(2) Coordination Spheres in Complex **1**[a]

Ni(1)−O(1) × 2	2.034(3)	Ni(2)−N(3)	2.113(4)
Ni(1)−O(4) × 2	2.058(3)	Ni(2)−O(2)	2.070(3)
Ni(1)−N(4) × 2	2.095(4)	Ni(2)−O(1w)	2.084(3)
Ni(2)−N(1)	2.115(4)	Ni(2)−O(2w)	2.123(4)
Ni(2)−N(2)	2.096(4)		
O(1)−Ni(1)−O(4)	91.5(1)	N(1)−Ni(2)−O(1w)	90.6(1)
O(1)−Ni(1)−O(4′)	88.5(1)	N(1)−Ni(2)−O(2w)	87.0(1)
O(1)−Ni(1)−N(4)	87.5(1)	N(2)−Ni(2)−N(3)	91.7(2)
O(1)−Ni(1)−N(4′)	92.5(1)	N(2)−Ni(2)−O(2)	89.7(1)
O(4)−Ni(1)−N(4)	87.4(1)	N(2)−Ni(2)−O(1w)	175.0(1)
O(4)−Ni(1)−N(4′)	92.6(1)	N(2)−Ni(2)−O(2w)	94.3(2)
O(1′)−Ni(1)−O(1)	180.0	N(3)−Ni(2)-O(2)	86.2(1)
O(4′)−Ni(1)−O(4)	180.0	N(3)−Ni(2)−O(1w)	92.3(2)
N(4)−Ni(1)−N(4′)	180.0	N(3)−Ni(2)−O(2w)	93.3(1)
N(1)−Ni(2)-N(2)	85.4(2)	O(2)−Ni(2)−O(1w)	93.5(1)
N(1)−Ni(2)−N(3)	177.1(2)	O(2)−Ni(2)−O(2w)	175.9(1)
N(1)−Ni(2)−O(2)	93.8(1)	O(1w)−Ni(2)−O(2w)	82.5(1)

[a] Symmetry code for primed atoms: $-x + 1, -y + 1, -z + 1$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in Complex **2**[a]

Mn−N(11)	2.285(6)	Mn−O(33)	2.248(7)
Mn−N(22)	2.313(6)	Mn−O(51′)	2.123(5)
Mn−O(31)	2.355(7)	Mn−O(53)	2.115(6)
N(11)−Mn−O(31)	95.8(2)	O(31)−Mn−O(51′)	149.2(3)
N(11)−Mn−O(33)	94.0(2)	O(31)−Mn−O(53)	87.8(2)
N(11)−Mn−O(51′)	89.3(2)	O(33)−Mn−O(51′)	92.3(2)
N(11)−Mn−O(53)	92.8(2)	O(33)−Mn−O(53)	144.7(2)
N(22)−Mn−O(31)	89.8(2)	O(51′)−Mn−O(53)	122.4(2)
N(22)−Mn-O(33)	88.0(2)	C(32)−O(31)−Mn	88.7(5)
N(22)−Mn−O(51′)	85.2(2)	C(32)−O(33)−Mn	93.2(5)
N(22)−Mn−O(53)	88.6(2)	C(52′)−O(51′)−Mn	142.7(5)
N(11)−Mn−N(22)	174.3(2)	C(52)−O(53)−Mn	136.7(5)
O(31)−Mn−O(33)	57.1(2)		

[a] Symmetry code for O(51′): $-x, -y + 1, -z$.

details of refinements are given in Table 1, and selected geometrical parameters of complexes **1** and **2** are given in Tables 2 and 3, respectively.

Result and Discussion

Structure Description of Complex 1. The X-ray structure determination reveals a covalent bonded complicated 3D network of composition $[(\text{maleate})_2\text{Ni}_3(\text{bpe})_4(\text{H}_2\text{O})_4](\text{NO}_3)_2\cdot\text{H}_2\text{O}$ containing two crystallographically independent nickel(II) ions of different octahedral geometry. The metal coordination spheres are illustrated in Figures 1 and 2, and relevant bond lengths and angles are reported in Table 2. Ni(1) lies on an inversion center, and its coordination environment comprises two chelating maleate anions and two bpe nitrogen donors (Figure 1), while the distorted octahedron around Ni(2) ion shows meridionally disposed three bpe N atoms, two water molecules, and one oxygen donor of the dicarboxylate anion (Figure 2).

Thus, each maleate acts as a chelating ligand toward the former nickel ion (Ni(1)−O(1) = 2.034(3), Ni(1)−O(4) = 2.058(3) Å) and as unidentate with respect to Ni(2) (Ni(2)−O(2) = 2.070(3) Å). Despite the different environment with respect to maleate oxygens, all the C−O bond lengths are comparable within their estimated standard deviations and average 1.26 Å. The Ni−N bond distances fall in a range from 2.095(4) to 2.115(4) Å (Table 2), while the Ni−OH$_2$ bond lengths appear to be significantly different (Ni(2)−O(2w) = 2.123(4), Ni(2)−O(1w) = 2.084(3) Å). It is worth noting that, among the pyridyls, the N(2) ring sensibly deviates from a symmetrical coordination, as evidenced by the Ni−N(2)···C(8) angle of 169.1(2)°.

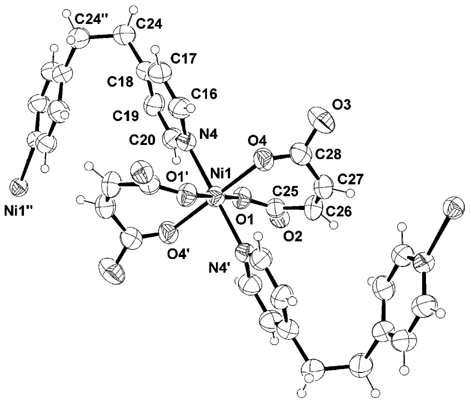


Figure 1. Coordination sphere about Ni(1) with atom labeling scheme (ORTEP drawing, 40% thermal ellipsoids).

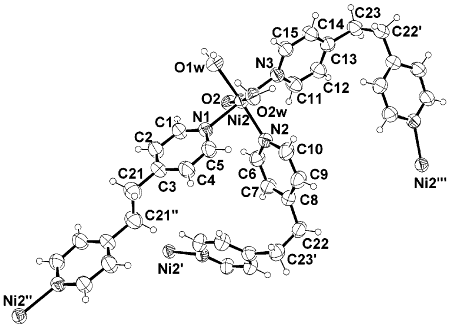


Figure 2. ORTEP view (40% thermal ellipsoids) of the "T-shaped" environment about Ni(2).

The overall 3D architecture is depicted in Figure 3, and it can be described in a stepwise manner starting from the molecular fragments depicted in Figures 1 and 2. The former affords 1D $[\text{Ni(maleate)(bpe)}]_n$ polymers with a zigzag arrangement running parallel to the *c* axis. Along the chains, the Ni(maleate) units are connected at 8.529(3) Å, i.e. half the *c* axis, by the flexible bpe linker in a gauche (angular) conformation (torsion angle about the ethyl bond = 63(1)°).

On the other hand, the "T-shaped" $(\text{bpe})_3\text{Ni(2)}$ unit gives rise to a 2D puckered structural motif with a (6,3) topology, where the nickel ions occupy the nodes of the distorted hexagons (Figure 4). This grid is unusual since it consists of centrosymmetric 66-membered rings (Figure 5) made up of six bpe ligands. Two of these are in anti and four in gauche conformation (torsion angles about the ethyl bond = 180.0 and 69.9(6)°) and span the metals at 13.548(3) and at 8.844(1) Å, respectively. It should be pointed out that an analogous 2D network in transition metal−bpe systems has never been documented previously. The polymers are connected to the 2D layers through the maleate oxygens O(2) that, as already mentioned, act as donors toward Ni(2) ions, leading Ni(1) and Ni(2) ions to be 5.180(2) Å far apart. The resulting novel three-dimensional architecture has a Ni(II):bpe composition of 3:4. Beside the coordinate bonds, H-bonds occur between

---

(16) Farrugia, L. J. *WinGX-A Windows Program for Crystal Structure Analysis*.; University of Glasgow: Glasgow, U.K., 1998.

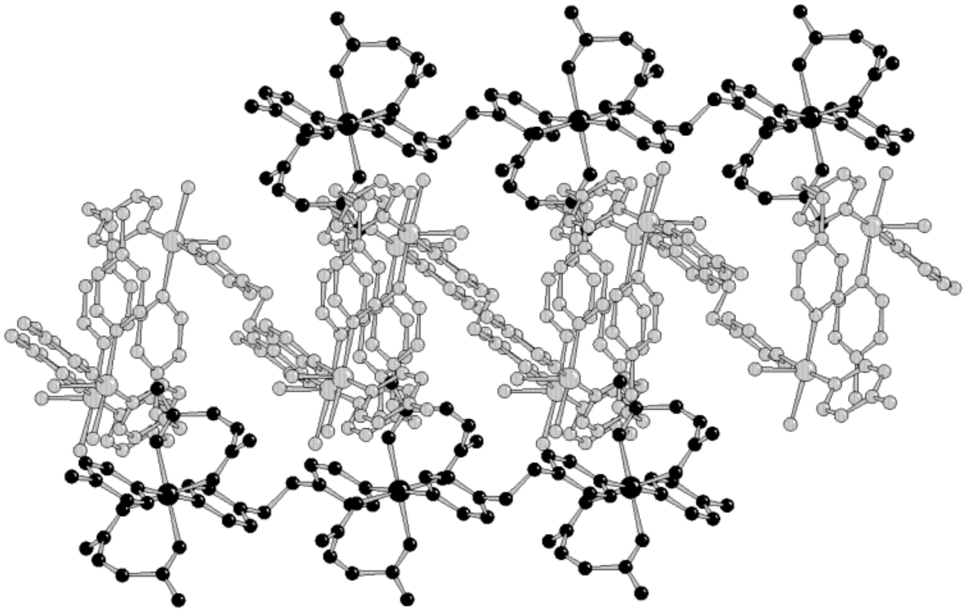


Figure 3. Representation of the three-dimensional crystal structure: 1D polymers (Ni(1), black fragment) alternate with the 2D grid (Ni(2)). Nitrate anions are not shown for the sake of clarity.

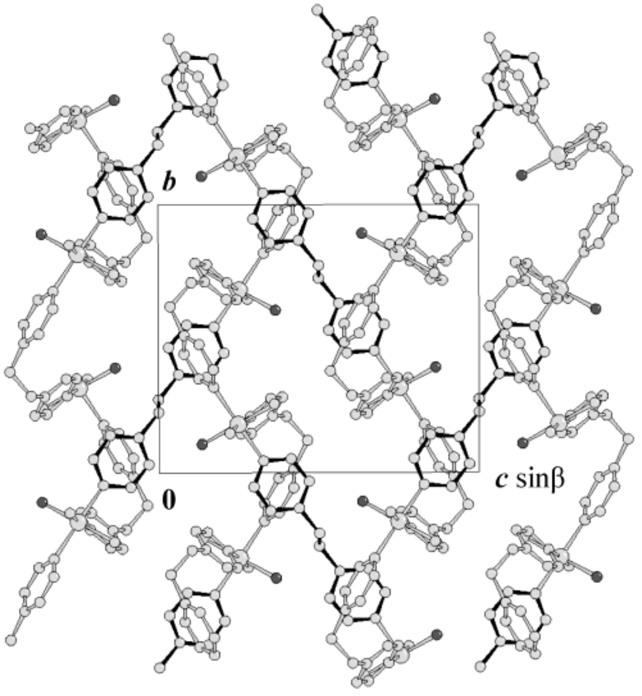


Figure 4. Puckered 2D layer viewed down the crystallographic *a* axis. Black bonds evidentiate bpe ligands in anti conformation, with shaded maleate oxygens O(2) that represent the connections to the Ni(1) polymers.

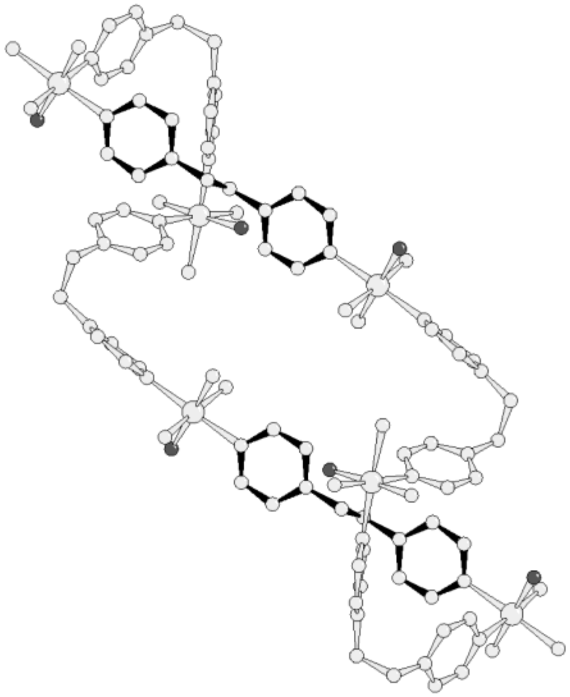


Figure 5. Perspective view of the 66-membered ring in the 2D layer. Ni−Ni distance = 8.844(1) Å for the two gauche bpe spacers and 13.548(3) Å for those with anti conformation.

the water molecules O(1w) and maleate O(1) that reinforce the framework, while O(2w) is linked to a nitrate oxygen with O···O distances of 2.750 and 2.835 Å, respectively.

In the only reported single-crystal structure featuring a nickel/bpe system, [Ni(μ-bpe)(bpe)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$, of the four bpe coordinated to the nickel center, two of these behave as monofunctional ligands.[12] The structure exhibits a 1D chain bridged by anti bpe at an internickel distance of 13.406 Å. So, to the best of our knowledge, complex **1** is the first 3D coordination polymer consisting of a Ni/bpe system with both gauche and anti bridging modes.

Structure Description of Complex 2. The crystal structure of **2** is formed by dinuclear manganese(II) units separated by 4.113 Å with a N$_2$O$_4$ chromophore about the metal ions. The distorted octahedral coordination geometry (Figure 6) comprises at the equatorial coordination plane four dicarboxylic oxygen atoms and at the axial position bpe N donors.

The Mn ions, in a centrosymmetric arrangement, are bridged by two opposite syn−syn carboxylate groups, and each metal is further chelated by a CO$_2^-$ group of another crystallographically independent adipate anion. To our knowledge this is the first example including adipate anions

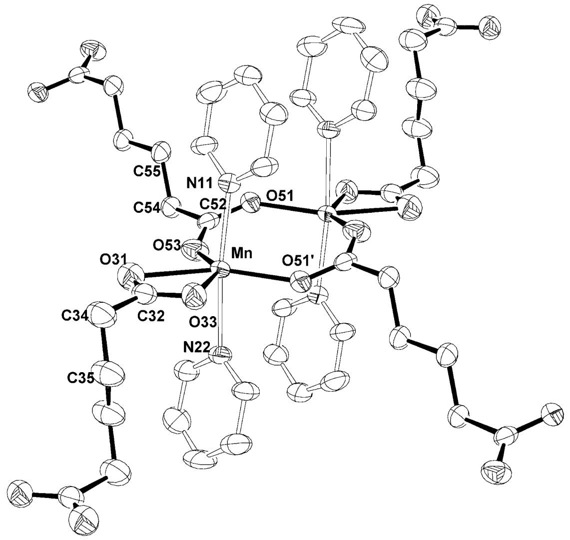


Figure 6. Centrosymmetric arrangement of the dimeric manganese(II) unit (thermal ellipsoids at 40% probability).

where carboxylate act as bis-chelating and as bis-bridging toward the metal centers.[17]

The distortions in the Mn(II) coordination geometry can be denoted by the dihedral angles that the plane through the four bridging oxygens makes with the chelating carboxylic group (O(31)/C(32)/O(33)) of 19.8° and with the pyridine rings N(11) and N(22) of 83.2 and 77.7°, respectively. An analysis of coordination bond lengths and angles (Table 3) evidences shorter Mn−O distances in the bridging (Mn−O(51′) = 2.123(5), Mn−O(53) = 2.115(6) Å) with respect to those detected in the chelating dicarboxylate (Mn−O(33) = 2.248(7), Mn−O(31) = 2.355(7) Å). These distances compare well with those found in the coordination polymer which includes two-dimensional MnO_6 polyhedra interconnected by adipate bidentate anions.[11]

The connectivities between metal atoms and adipate ligands give rise to corrugated sheets of rhomboid meshes of dimensions 13.578 × 10.942 Å^2, illustrated in Figure 7. These values are effected by the coordination modes adopted by the anions but also by their different conformations. In fact, the torsion angles along the C−C−C−C skeleton for the bis-chelating and bis-bridging ligand are 58.3, 180.0, −58.3° and 177.2, 180.0, −177.2°, respectively.

Such layers are interconnected by bpe spacers with an anti conformation that span the metals at 13.962 Å (coordination Mn−N bond lengths of 2.285(6) and 2.313(6) Å). The overall structure results in a covalently bonded 3D architecture, where the wide net dimensions in the $[Mn(adipate)]_n$ layer allow the formation of an interpenetrated α-polonium-related type structure,[18] where the nodes are characterized by the dinuclear Mn(II) units (Figure 8).

Magnetic Properties

Complex 1. Considering the structure of complex **1**, made by quasi-isolated trinuclear Ni_3 entities (Chart 1) linked by long bis(4-pyridyl)ethane (bpe) ligands, all calculations are made by assuming a Ni_3 unit. The plot of $1/\chi_M$ (χ_M, molar magnetic susceptibility) vs T given per Ni(II) ion shows a straight line down to 9 K; it can be fitted by the Curie−Weiss expression, giving a Curie constant $C = 1.08$ and $\Theta = +1.6$ K, indicating the presence of a weak ferromagnetic interaction within the compound. The Curie constant corresponds well to the expected value for one Ni(II) ion with a g-value of 2.08. Below 9 K, $1/\chi_M$ deviates from the straight line indicating the presence of a very weak antiferromagnetic interaction within the compound that occurs at very low

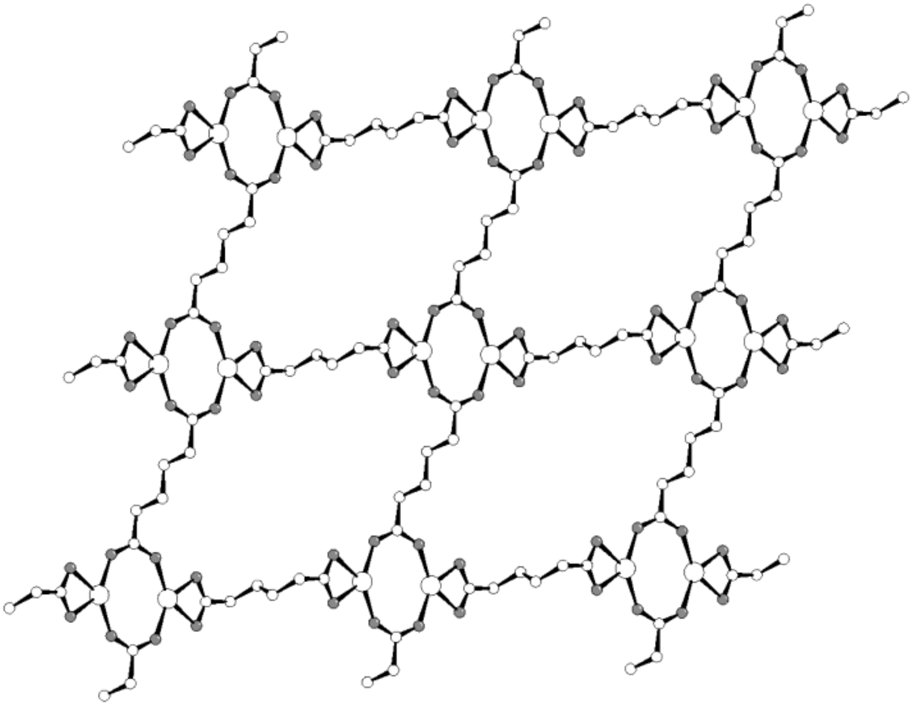


Figure 7. Layered architecture formed by the Mn(II) ions and dicarboxylate adipate anions along the [110] direction. Both the anions are located on an inversion center.

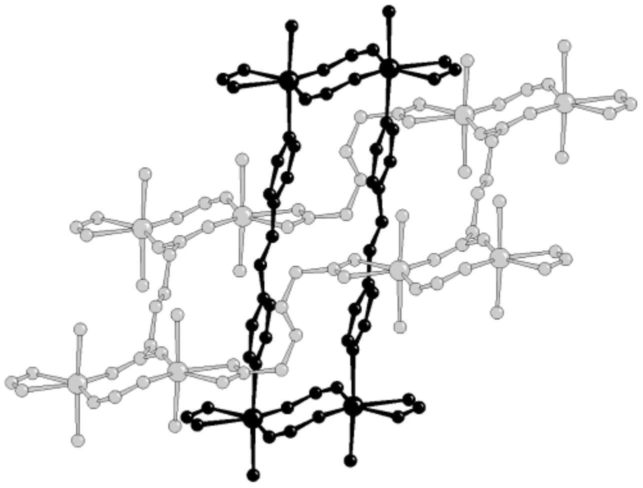
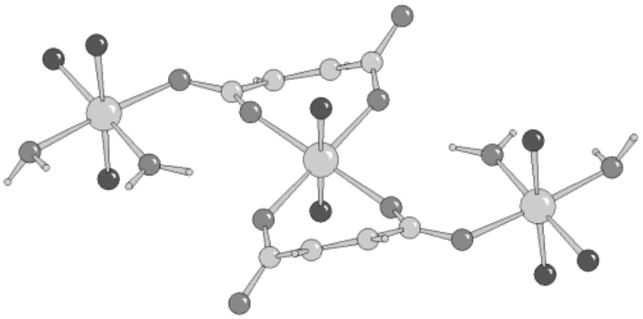


Figure 8. View of the interpenetrated nets in the [(adipate)Mn(bpe)] compound. Each dinuclear Mn unit individuates a node of a α-polonium-related net.

Chart 1



temperature. The $\chi_M T = f(T)$ plot is given per three Ni(II) ions. The temperature dependence of the $\chi_M T$ plot is shown in Figure 9. The $\chi_M T$ value is 3.25 cm^3 mol^{-1} K at 300 K, a typical value for three quasi-isolated Ni(II) ions with $g > 2.00$, as usual in this kind of system. $\chi_M T$ increases with decreasing temperature (4.75 cm^3 mol^{-1} K at 3.0 K) and then decreases to a minimum value of 4.50 cm^3 mol^{-1} K at 2.01 K. This curve suggests that ferromagnetic coupling, with the presence of the D parameter for Ni(II) ions and/or antiferromagnetic intermolecular interactions, acts at low temperature. It must be pointed out that the theoretical value for $\chi_M T$ at low temperature for an $S = 3$ ground state (ferromagnetic coupling) would be 6.00 for $g = 2.00$. The actual value is less than this expected one indicating, thus, the existence of D and/or J' (intertrinuclear interactions).

The theoretical calculation of the thermal accessible energy levels of the magnetic properties of linear Ni(II) trimer can be performed using the well-known Kambe's method[19] but without considering the single-ion anisotropy of the Ni(II) ion (D parameter). This calculation was first made by Ginsberg et al.,[20] from the Hamiltonian

$$H = -2J[S_1S_2 + S_2S_3] - 2J_{31}S_3S_1$$

1 and 3 being the terminal Ni(II) atoms and 2 the central one. In the present case the linearity and symmetry of the trinuclear complex allow us to simplify the Hamiltonian eliminating the coupling between the two terminal Ni(II) ions

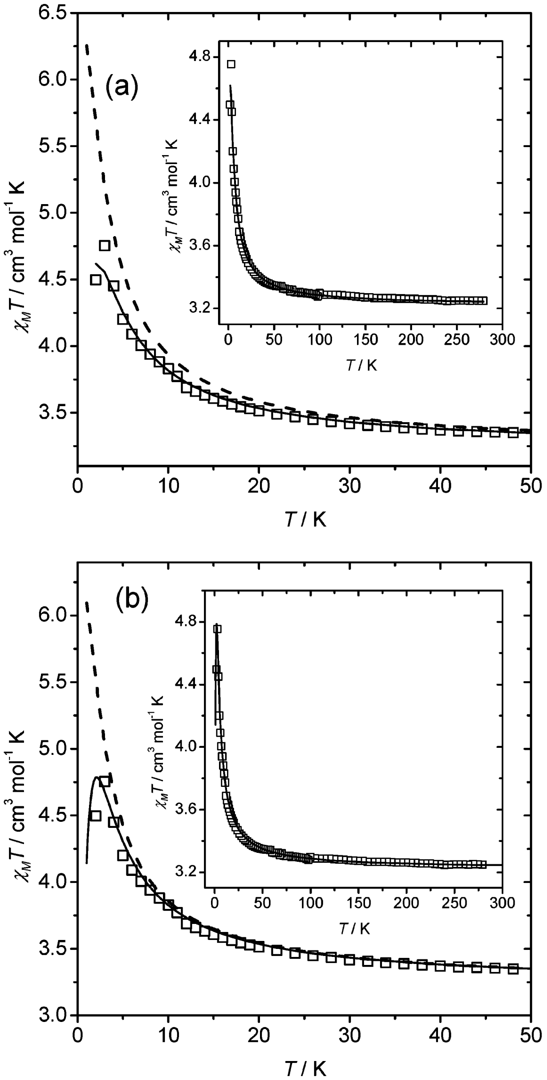


Figure 9. (a) Inset: Plot of $\chi_M T$ vs T for **1**, applying the Ginsberg formula. The curve represents the best fit, and the points represent the experimental data. Theoretical behavior of the system with $J' = 0$ in the range 50−2 K is shown as a dotted line. (b) Inset: Plot of $\chi_M T$ vs T for complex **1**, applying the MAGPACK program. The curve represents the best fit, and the points represent the experimental data. Theoretical behavior of system considering a fully isotropic Ni$_3$ cluster is shown as a dotted line.

and, thus, reducing it to

$$H = -2J[S_1S_2 + S_2S_3]$$

With this hypothesis, the formula of $\chi_M T$ vs T is as follows:

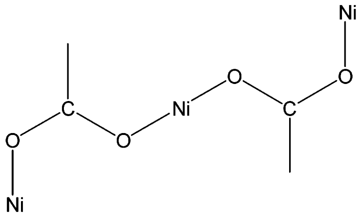
$$\chi_M T = Ng^2\beta^2(F(J))T/(kT - J'F(J)) \tag{1}$$

where

$$\begin{aligned} F(J) = {} & 28 + 10\exp(-J/kT) + 2\exp(-2J/kT) + \\ & 2\exp(-3J/kT) + 10\exp(-3J/kT) + 2\exp(-5J/kT)/7 + \\ & 5\exp(-J/kT) + 3\exp(-2J/kT) + 3\exp(-3J/kT) + \\ & 5\exp(-3J/kT) + \exp(-4J/kT) + 3\exp(-5J/kT) \end{aligned}$$

In the formula of Ginsberg, a new parameter, J', has been introduced, following the theory of the molecular-field approximation,[21] to take into account the small intermolecular interactions between the trinuclear entities, due to the

Chart 2



presence of the bpe bridging ligands. The best J parameters obtained with this model are as follows: $J_1 = 1.75$ cm^{-1}; $J' = -0.09$ cm^{-1}; $g = 2.07$; $R = 1.2 \times 10^{-5}$.

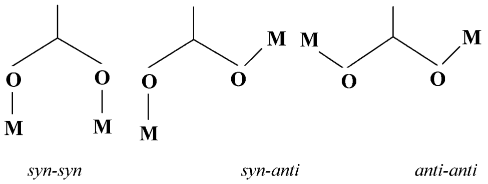
Unfortunately, this method does not take into account the important D parameter (zero-field-splitting) of the Ni(II) ions. To consider the anisotropic terms of the electronic Hamiltonian (anisotropic and antisymmetric exchanges, single ion anisotropy), Clemente and co-workers developed a general procedure (MAGPACK program)[22] that allows treating spin clusters formed by an arbitrary number of magnetic sites. The Hamiltonian used for **1** is $H = -2J_{ij}\Sigma S_iS_j + DS_{iz}^2$. As in the prior procedure, the possible coupling between the two terminal Ni(II) ions has been assumed to be nil. Thus, a rigorous treatment has been carried out which considers both isotropic exchange interactions and an axial single ion anisotropy of the type DS_{iz}^2, where $|D|$ represents the zero-field splitting parameter. The best J parameters simulated with this computing model are as follows: $J_1 = 1.74$ cm^{-1}; $|D| = 2.5$ cm^{-1}; $g = 2.07$ (Figure 9). The coincidence in J and g, applying the two different methods, is total. The $|D|$ value is of the same order of magnitude as in other nickel complexes reported recently in the literature.[23]

The exchange pathway connecting the Ni(II) ions can be illustrated as shown in Chart 2.

The Ni−Ni interactions between the spins $S = 1$ are transmitted through the syn−anti carboxylate bridges.

Magneto−Structural Correlation. The carboxylate group is one of the most widely used bridging ligands for designing polynuclear complexes with interesting magnetic properties. Its versatility as a ligand is illustrated by the variety of its coordination modes acting as a bridge,[24] the most common being the syn−syn, syn−anti, and anti−anti modes (Chart 3).

Chart 3



Whereas for copper(II) system, the number of complexes with these three kind of conformations is very high, for nickel(II) the number is much more less, mainly if we consider only complexes without other bridges, which impede a complete interpretation of the magnetic data through the carboxylate bridge. For copper(II) the syn−syn conformation mediates large antiferromagnetic interactions (singlet−triplet energy gap ≈ -300 cm^{-1}).[25] Weak antiferro- or ferromagnetic interactions are observed for carboxylato-bridged copper(II) complexes in which the carboxylate adopts the syn−anti conformation.[26] The small overlap between the magnetic orbitals of the copper atom through the anti−syn carboxylate bridge, for a Cu−O−C−O−Cu skeleton which is planar, accounts for the weak coupling observed. This overlap is significantly reduced for cases in which the Cu−O−C−O−Cu skeleton deviates from planarity (out-of-phase exchange pathway), thus reducing the antiferromagnetic contribution, and the ferromagnetic term becomes dominant.[26,27] Theoretical DFT calculations also corroborate this weak ferromagnetic coupling for syn−anti conformation.[27] In the anti−anti carboxylate bridge the coupling is always small antiferromagnetic.[27] For Ni(II) the syn−syn carboxylato complexes are also antiferromagnetically coupled although the number of these complexes reported in the literature is very poor,[28] because the great tendency of nickel(II) ions to have, together with the carboxylate bridging ligands, other bridging ligands, like μ−oxo,[29] μ-hydroxo,[30] or μ-alkoxo.[31] To the best of our knowledge, only one complex has been reported with syn−anti configuration, showing ferromagnetic coupling ($J = 0.22$ cm^{-1}).[23] This complex presents the inconvenience of having two other magnetic pathways, with syn−syn and di-μ-oxo bridges, also ferromagnetic, making it difficult to give an accurate calculation of the syn−anti pathway Very recently, a nickel(II) complex derived from the malonic acid has been reported with syn−anti configuration but, unfortunately, without magnetic studies.[32] Thus,

---

(17) A search in the Cambridge Data Base retrieved about 20 structures containing coordinated adipate anions: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res*. **1983**, *16*, 146−153.

(18) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460−1494.

(19) Kambe, K. *J. Phys. Soc. Jpn*. **1950**, *5*, 48.

(20) Ginsberg, A. P.; Martin, R. L.; Brookes, R. W.; Sherwood, R. C. *Inorg. Chem.* **1972**, *11*, 2884. (b) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 244.

(21) Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem*. **1968**, *7*, 932.

(22) (a) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *Inorg. Chem*. **1999**, *38*, 6081. (b) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerbalt, B. S. *J. Comput. Chem.* **2001**, *22*, 985.

(23) Du, M.; Bu, X.-H.; Guo, Y.-M.; Zhang, L.; Liao, D.-Z.; Ribas, J. *Chem. Commun.* **2002**, 1478 and references therein.

(24) (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev*. **1980**, *33*, 227. (b) Melnik, M.; *Coord. Chem. Rev*. **1981**, *36*, 1. (c) Kato, M.; Muto, Y.; *Coord. Chem. Rev*. **1988**, *92*, 45. (d) Oldham, C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, p 435.

(25) (a) Doedens, R. J. *Prog. Inorg. Chem*. **1990**, *38*, 97. (b) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451. (c) Figgis, B. N.; Martin, R. L. *J. Chem. Soc*. **1956**, 3837.

(26) Ruiz-Pérez, C.; Sanchiz, J.; Molina, M. H.; Lloret, F.; Julve, M. *Inorg. Chem*. **2000**, *39*, 1363 and references therein.

(27) Rodríguez-Fortea, A.; Alemany, P.; Alvarez, S.; Ruiz, E. *Chem.*−*Eur. J.* **2001**, *7*, 627.

(28) Husebye, S.; Kato, M.; Maartman-Moe, K.; Muto, Y.; Nakashima, M.; Tokii, T. *Acta Chem. Scand.* **1994**, *48*, 628.

(29) (a) Wages, H. E.; Taft, K. L.; Lippard, S. J. *Inorg. Chem*. **1993**, *32*, 4985. (b) Nanda, K. K.; Das, R.; Thompson, L. K.; Venkatsubramanian, K.; Nag, K. *Inorg. Chem*. **1994**, *33*, 5934.

(30) Chaudhuri, P.; Küpers, H. J.; Wieghardt, K.; Gehring, S.; Haase, W.; Nuber, B.; Weiss, J. *J. Chem. Soc., Dalton Trans.* **1988**, 1367.

(31) Buchanan, R. M.; Mashuta, M. S.; Oberhausen, K. J.; Richardson, J. F. *J. Am. Chem. Soc*. **1989**, *111*, 4497.

(32) Zhou, Z.-H.; Ye, J.-J.; Deng, Y.-F.; Wang, G.; Gao, J.-X.; Wao, H.-L. *Polyhedron* **2002**, *21*, 787.

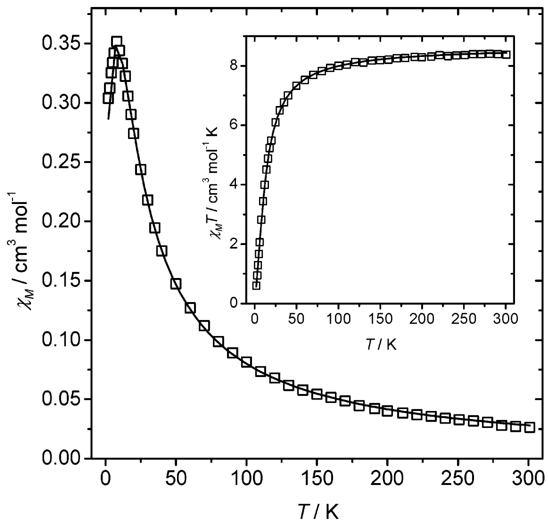
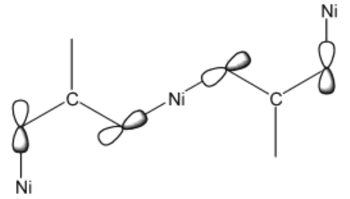


Figure 10. Plot of χ_M vs T data for complex **2**. Inset: Plot of $\chi_M T$ vs T. The solid line shows the best fit obtained by considering the model of the Mn(II) dimer (see text).

Chart 4



the ferromagnetic coupling of the first isolated syn−anti carboxylate configuration seems to be in agreement with the results reported for copper(II) complexes, even if the magnetic pathways is more complicated due to the presence of two electrons in the nickel(II) ions in the orbitals d_{z^2} and $d_{x^2-y^2}$. In any case, independently of the metal ion, the syn−anti configuration reduces drastically the overlap between the magnetic orbitals, thus diminishing the antiferromagnetic coupling and enhancing the ferromagnetic pathway (Chart 4).

This qualitative approach was already introduced by Kahn and co-workers while studying this syn−anti configuration in mixed Mn(II)−Cu(II) complexes.[33]

Complex 2. Considering the structure of complex **2**, made by quasi-isolated dinuclear Mn_2 entities linked by adipate and bpe ligands, all calculations are made by assuming a Mn_2 unit. The χ_M and $\chi_M T$ vs T plots are given per two Mn(II) ions. The temperature dependence of the magnetic susceptibility is shown in Figure 10. The χ_M value is 0.0262 cm^3 mol^{-1} at 300 K, which increases when decreasing the temperature reaching a maximum of 0.3516 cm^3 mol^{-1} at 8 K and then decreases to 0.3037 cm^3 mol^{-1} at 2 K. The presence of a maximum at 8 K is indicative of small antiferromagnetic coupling. The $\chi_M T$ value is 8.37 cm^3 mol^{-1} K at 300 K, a typical value for two quasi-isolated Mn(II) ions with $g = 2.00$, as usual in this kind of systems. $\chi_M T$ decreases with decreasing temperature (0.60 cm^3 mol^{-1} K at 2.0 K). This curve also suggests small antiferromagnetic coupling between the Mn(II) centers.

The theoretical calculation of the thermally accessible energy levels of the magnetic properties of a dinuclear Mn(II) complex has a very easy solution, using the Hamiltonian

$$H = -JS_1S_2$$

The mathematical formula is[13]

$$\chi_M = (2Ng^2\beta^2/kT)\,F(J) \tag{2}$$

where

$$F(J) = e^x + 5e^{3x} + 14e^{6x} + 30e^{10x} + 55e^{15x}/1 + 3e^x + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x}$$

The best J parameters obtained with this model are as follows: $J_1 = -1.84 \pm 0.015$ cm^{-1}; $g = 2.00 \pm 0.007$; $R = 1.1 \times 10^{-5}$ (Figure 10).

Magneto−Structural Correlation. From magnetic point of view it is important to point out some structural features: the 3D systems is made by bpe ligands which link two Mn(1) ions at very long distance (13.962 Å). The adipate anion bridges the Mn(II) ions in two different forms: (a) in a chelated manner to two Mn(1) through the O(31) and O(33) atoms, with Mn−Mn distance of 9.775 Å; (b) in a bis-bidentate manner to four Mn(II) ions through the O(51) and O(53) atoms. In this case the distance of the Mn atoms through the carbon skeleton is 10.942 Å and through the carboxylate in syn−syn configuration is only 4.113 Å. In this case, these two Mn(II) ions are linked by two opposite syn−syn carboxylate bridges (Figure 6).

Taking into consideration these structural pathways, only the syn−syn carboxylate bridge will be magnetically active. All other possible magnetic pathways correspond to long carbon-chains, making nil the coupling. Thus, the exchange pathway connecting the Mn(II) ions ($S = 5/2$) is transmitted only through the syn−syn carboxylate bridges.

For Mn(II) complexes the syn−syn carboxylato complexes are also antiferromagnetically coupled although the number of these complexes reported in the literature, i.e. dinuclear complexes with only carboxylate bridge in syn−syn configuration[34] (this kind of complex usually shows the syn−anti conformation),[35] trinuclear complexes normally with also a μ-oxo bridge,[35,36] one-dimensional complexes,[37] and a few three-dimensional systems,[38] is limited. An important repetitive feature of all these complexes with syn−syn carboxylate bridges is that their antiferromagnetic coupling is very small,

---

(33) Pei, Y.; Nakatani, K.; Kahn, O.; Sletten, J.; Renard, J. P. *Inorg. Chem.* **1989**, *28*, 3170.

(34) (a) Fernández, G.; Corbella, M.; Mahía, J.; Maestro, M. A. *Eur. J. Inorg. Chem*. **2002**, 2502 and references therein. (b) Albela, B.; Corbella, M.; Ribas, J.; Castro, I.; Sletten, J.; Stoeckli-Evans, H. *Inorg. Chem*. **1998**, *37*, 788.

(35) Romero, I.; Dubois, L.; Collomb, M.-N.; Deronzier, A.; Latour, J. M.; Pécaud, J. *Inorg. Chem.* **2002**, *41*, 1795

(36) Tangoulis, V.; Malamatari, D. A.; Soulti, K.; Stergiou, V.; Raptopoulou, C. R.; Terzis, A.; Kabanos, T. A.; Kessissoglou, D. P. *Inorg. Chem*. **1996**, *35*, 4974 and references therein.

(37) Tan, X. S.; Xiang, D. F.; Tang, W. X.; Yu, K. B. *Polyhedron* **1997**, *16*, 1411 and references therein.

(38) Lin, W.; Chapman, M. E.; Wang, Z.; Yee, G. T. *Inorg. Chem.* **2000**, *39*, 4169 and references therein.

compared to analogous Cu(II) systems: in all cases the |*J*| values are < 5 cm^{-1}. To the best of our knowledge, only one Mn(II) complex with syn−syn carboxylate bridges has been reported showing weak ferromagnetically coupling which is a double carboxylato bridged together with isophthalate bridging anion.[39] The authors do not have any explanation to rationalize this experimental feature.

Concluding Remarks

In this paper we have presented the syntheses, crystal structures, and variable temperature magnetic studies of two novel 3D coordination polymers. Dicarboxylate anions are frequently used in the design of polynuclear complexes as efficient linker to mediate magnetic interactions and, as they have different coordination modes, accomplish the transmission of magnetic coupling to different degrees. In this work, the use of bpe ligands beside the dicarboxylate anions allows the construction of extended magnetic three-dimensional networks. In complex **1** two crystallographically independent nickel(II) ions give rise to two different structural motifs: 1D $[\mathrm{Ni(maleate)(bpe)}]_\infty$ parallel polymers and 2D corrugated layers that alternate in the crystal to form a novel covalent-bonded 3D architecture. The maleate, acting as a chelating ligand toward one metal ion and simultaneously as a monodentate toward the other, represents the linker between the two structural motifs. Variable-temperature (300−2 K) magnetic study reveals the existence of dominant ferromagnetic interaction within the complex.

On the other hand, complex **2** exhibits an interpenetrated 3D α-polonium-related type net obtained by interconnection of several 2D Mn(II) adipate sheets linking through bpe spacers. Of the two crystallographic independent adipate anions in **2**, one behaves as a bis-chelating ligand and the other exhibits a syn−syn bridging mode toward the Mn_2 unit. Low-temperature susceptibility measurements reveal the existence of a weak antiferromagnetic interaction within the molecule. Thus, in **1** the maleate acts as five-membered chelating ring and unidentate toward two different nickel ions, while in **2** two crystallographic independent adipate anions exhibit three membered chelation and a syn−syn bridging mode toward the Mn_2 unit.

Acknowledgment. Funding for the work described here provided by the CSIR (New Delhi) Grant Scheme (Granted to N.R.C.) is gratefully acknowledged

Supporting Information Available: X-ray crystallographic data, in CIF format, and tables giving crystal data and details of the structure determination, bond lengths and angles, atomic and hydrogen coordinates, isotropic displacement parameters, and anisotropic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026150N

---

(39) Tan, X. S.; Sun, J.; Feng, D.; Xiang, D. F.; Tang, W. X. *Inorg. Chim. Acta* **1997**, *255*, 157.