



## Two different coordination geometries in polynuclear manganese(II) complexes with bis( $\mu$ -phosphinato) bridges

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This work is dedicated to Alfred Werner, who opened the door to an immense, exciting and still only superficially explored world.

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### ABSTRACT

Four new polynuclear phosphinato-bridged manganese(II) complexes, three dinuclear compounds [Mn( $\mu$ -dpp)(5-dmbpy)(NO<sub>3</sub>)<sub>2</sub>] (1), [Mn( $\mu$ -dpp)(Me-phen)(NO<sub>3</sub>)<sub>2</sub>] (2), [Mn( $\mu$ -bmp)(neocuproine)(NO<sub>3</sub>)<sub>2</sub>] (3) and a 1D compound [Mn( $\mu$ -bmp)<sub>2</sub>]<sub>n</sub> (4) where Hdpp is diphenylphosphinic acid, Hbmp is bis(4-methoxyphenyl)phosphinic acid, 5-dmbpy = 5,5'-dimethyl-2,2'-dipyridyl, Me-phen = methyl-1,10-phenanthroline and neocuproine = 2,9-dimethyl-1,10-phenanthroline, have been synthesized and structurally characterized by X-ray crystallography. In this series, the dinuclear structures consist in a bis(diphenylphosphinato) (dpp) or a bis(4-methoxyphenyl)phosphinato (bmp) anion bridging the two Mn(II) centers in a *syn-syn* coordination mode for 1–3. The monodimensional compound 4 is built from double bridging *syn-syn* bis(4-methoxyphenyl)phosphinato anions. The coordination geometry around the Mn(II) ions in 1–3 is six-coordinate with distorted octahedral environment. Moreover, the coordination geometry around the Mn(II) ions in 4 is tetrahedral. The magnetic behavior of these complexes is reported. The complexes show weak antiferromagnetic coupling with *J* in the range 0.05–0.43 cm<sup>-1</sup> for 1–3 and 0.88 cm<sup>-1</sup> for 4. The magnetic properties are discussed in relation to the structural data.

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### 1. Introduction

The RR'PO<sub>2</sub><sup>-</sup> phosphinato ligands can be an alternative for the carboxylate ligands in the synthesis of SMM compounds: manganese polynuclear cages with phosphinato and phosphonato ligands simultaneously but no slow magnetic relaxation [1] together with several Mn-RR' phosphinato cages with SMM behavior [2–4] have been yet reported. The RR'PO<sub>2</sub><sup>-</sup> phosphinato ligands, besides to be terminal ones, can act as bridging ligands through few coordination modes (Fig. 1) taking into account that only up to two oxygen atoms can act as coordinating atoms. Usually they can be found as  $\mu$ -O,O'-bridges (2.11 coordination mode in the Harris notation [5,6]) in polynuclear compounds [1–2,4–10], even though some examples of polynuclear transition metals with 3.21 [11–14] and 4.22 [15,16] coordination modes for phosphinato bridging ligands have been also reported (Fig. 1).

In a previous work [10] we have reported three compounds with general formula [Mn( $\mu$ -bmp)(L)(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, L = bidentate chelate ligand, Hbmp = bis(4-methoxyphenyl)phosphinic acid, where the phosphinato bridging ligands in all three compounds show the

2.11 coordination mode. All of them were weakly antiferromagnetically coupled according to the described observation that the  $\mu$ -O,O' O–P–O bridges give rise to low exchange interactions [17,18]. The found  $|J|$  values were tentatively correlated with the planarity of the dinuclear central eight membered ring [Mn(1)–O(1)–P(1)–O(2)]<sub>2</sub>: more planar, higher  $|J|$  value [10]. In this work, with the aim to increase the number of examples for the structure-coupling constant correlation, we explore the use of the anionic derivatives of two phosphinic acids, Hbmp and the structurally similar diphenylphosphinic acid (Hdpp), to generate new dinuclear manganese(II) compounds with L chelate ligands. We have synthesized three new dinuclear compounds: [Mn( $\mu$ -dpp)(5-dmbpy)(NO<sub>3</sub>)<sub>2</sub>] (1), [Mn( $\mu$ -dpp)(Me-phen)(NO<sub>3</sub>)<sub>2</sub>] (2) and [Mn( $\mu$ -bmp)(neocuproine)(NO<sub>3</sub>)<sub>2</sub>] (3), 5-dmbpy = 5,5'-dimethyl-2,2'-dipyridyl, Me-phen = methyl-1,10-phenanthroline and neocuproine = 2,9-dimethyl-1,10-phenanthroline (see Scheme S1 in supplementary material for the molecular structures of the ligands and phosphinic acids discussed in the manuscript). The phosphinato bridging ligands in the new dinuclear compounds show the 2.11 coordination mode and the skeleton is similar to the previously reported [10]. The magnetic properties of 1–3 are reported. All of them are weakly antiferromagnetically coupled according [10,16,17]. In the dinuclear compounds 1–3 the found  $|J|$  values can be tentatively correlated with the planarity of the dinuclear

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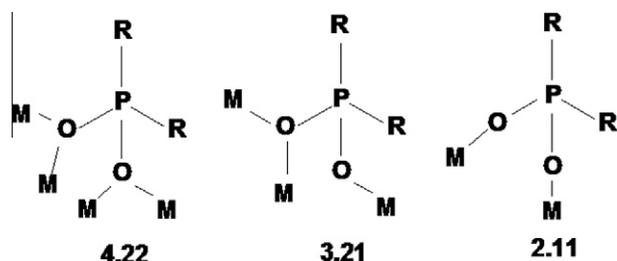


Fig. 1. Coordination modes for the bridging phosphinate ligands.

central eight membered ring  $[\text{Mn}(1)\text{--O}(1)\text{--P}(1)\text{--O}(2)]_2$ : more planar, higher  $|J|$  value [10].

On the other hand, we have prepared the 1D compound  $[\text{Mn}(\mu\text{-bmp})_2]_n$  (**4**) which is built from double bridging *syn-syn* bis(4-methoxyphenyl)phosphinato anions. The coordination of the manganese(II) ions is tetrahedral, yielding a non usual chain of  $\text{Mn}(\text{II})\text{O}_4$  tetrahedra. The magnetic properties of **4**, which show antiferromagnetic coupling, are also reported.

## 2. Experimental

### 2.1. Materials and methods

The compounds were purchased from Aldrich Chem. Co. All other materials were reagent grade quality. Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded from KBr pellets on a Perkin-Elmer 380-B spectrophotometer. Elemental analyses were performed at the Scientific-Technical services of the University of Barcelona. Magnetic susceptibility measurements under a magnetic field of 0.3 T in the temperature range 2–300 K and magnetization measurements in the field range of 0–5 T were performed with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona. All measurements were performed on polycrystalline samples. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the corrected molar magnetic susceptibilities.

### 2.2. Synthesis of the compounds

#### 2.2.1. $[\text{Mn}(\mu\text{-dpp})(5\text{-dmbpy})(\text{NO}_3)_2]$ (**1**)

To a solution of Mn(II) nitrate hexahydrate (0.155 g, 0.54 mmol) in methanol was added 5-dmbpy (5,5'-dimethyl-2,2'-dipyridyl) (0.096 g, 0.52 mmol), diphenylphosphinic acid (Hdpp) (0.117 g, 0.54 mmol) and triethylamine (1 mmol). A yellow precipitate was obtained one week later. It was then recrystallized in  $\text{CH}_2\text{Cl}_2$  and layered in hexane. After two weeks compound **1** was obtained as yellow prism crystals. *Anal.* Calc. for  $\text{C}_{48}\text{H}_{44}\text{Mn}_2\text{P}_2\text{N}_6\text{O}_{14}$ : C, 55.61; H, 4.28; N, 8.11%. Found: C, 55.2; H, 4.3; N, 8.3%. Selected IR bands ( $\text{cm}^{-1}$ ): 3434 (br) (st. -OH); 1291 (m), 1207 (m), 1195 (m), 1133 (s), 1059 (m), 726 (m), 705 (m), 557 (s), 543 (m) (dpp); 1486 (m), 1437 (m) (5-dmbpy) and 1384 (vs) ( $\text{NO}_3$ ).

#### 2.2.2. $[\text{Mn}(\mu\text{-dpp})(\text{Me-phen})(\text{NO}_3)_2]$ (**2**)

To a solution of Mn(II) nitrate hexahydrate (0.168 g, 0.58 mmol) in 60 ml of methanol was added Me-phen (methyl-1,10-phenanthroline) (0.097 g, 0.52 mmol), diphenylphosphinic acid (Hdpp) (0.109 g, 0.50 mmol) and triethylamine (0.5 mmol). After two weeks compound **2** was obtained as yellow prism crystals. *Anal.* Calc. for  $\text{C}_{50}\text{H}_{40}\text{Mn}_2\text{N}_6\text{O}_{10}\text{P}_2$ : C, 56.82; H, 3.79; N, 7.95. Found: C, 56.3; H, 3.8; N, 7.8%. Selected IR bands ( $\text{cm}^{-1}$ ): 3427 (br) (st. -OH); 1305 (s), 1198 (s), 1132 (s), 1052 (s), 1031 (m), 998 (m),

858 (m), 759 (m), 725 (vs), 700 (s), 562 (vs), 539 (s) (dpp); 1463 (s), 1437 (s), 1426 (s) (Mephen) and 1384 (s) ( $\text{NO}_3$ ).

#### 2.2.3. $[\text{Mn}(\mu\text{-bmp})(\text{neocuproine})(\text{NO}_3)_2]$ (**3**)

To a solution of Mn(II) nitrate hexahydrate (0.151 g, 0.53 mmol) in methanol was added neocuproine (2,9-dimethyl-1,10-phenanthroline) (0.107 g, 0.51 mmol), bis(4-methoxyphenyl)phosphinic acid (Hbmp) (0.139 g, 0.50 mmol) and triethylamine (0.5 mmol). After two weeks of slow evaporation compound **3** was obtained as yellow prism crystals. *Anal.* Calc. for  $\text{C}_{57}\text{H}_{55}\text{Mn}_2\text{P}_2\text{N}_6\text{O}_{15}$ : C, 55.34; H, 4.32; N, 6.86. Found: C, 55.4; H, 4.4; N, 6.8%. Selected IR bands ( $\text{cm}^{-1}$ ): 3434 (br) (st. -OH); 1295 (m), 1251 (m), 1197 (m), 1127 (s), 1049 (m), 1030 (m), 803 (m), 549 (m) (bmp); 1504 (m) (neocuproine) and 1384 (vs) ( $\text{NO}_3$ ).

#### 2.2.4. $[\text{Mn}(\mu\text{-bmp})_2]_n$ (**4**)

To a solution of Mn(II) perchlorate hydrate (0.255 g, 1.0 mmol) in methanol was added salicylaldehyde (salox) (0.138 g, 1.0 mmol), bis(4-methoxyphenyl)phosphinic acid (Hbmp) (0.278 g, 1.0 mmol) and triethylamine (1 mmol). After a few days compound **4** was obtained as light-yellow prism crystals. *Anal.* Calc. for  $\text{C}_{28}\text{H}_{28}\text{Mn}_2\text{P}_2\text{O}_8$ : C, 54.10; H, 4.78. Found: C, 55.2; H, 4.6%. Selected IR bands ( $\text{cm}^{-1}$ ): 3427 (br) (st. -OH); 1295 (m), 1256 (m), 1149 (s), 1133 (vs), 1061 (m), 1024 (m), 823 (m), 803 (m), 670 (m), 546 (s) (bmp) and 1133 (vs), 725 (m) ( $\text{ClO}_4$ ).

### 2.3. Crystal structure analysis

The X-ray single-crystal data of compounds **1**, **3** and **4** were collected on a Bruker-AXS SMART APEX CCD diffractometer and for **2** on a MAR345 diffractometer with image plate detector. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. Intensities were collected with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Lorentz-polarization and absorption corrections using the SADABS computer program [19] were applied. The structures were solved by direct methods using the SHELXS-97 [20] computer program, and refined by full-matrix least-squares methods on  $F^2$ , using the SHELXL-97 [20] program incorporated in the SHELXTL [20] program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on calculated positions, and their isotropic displacement factors were set 1.2 (or 1.5) times the value of the equivalent isotropic displacement parameter of the parent atom. The molecular plots were obtained using XP [18] and Mercury programs [21].

## 3. Results and discussion

### 3.1. Synthetic discussion

Compounds **1–3** of general formula  $[\text{Mn}(\mu\text{-phos})(\text{L})(\text{NO}_3)_2]$ , phos = phosphinate and L = blocking ligand) were obtained by mixing the stoichiometric quantities of manganese(II) nitrate (1 mmol), phosphinic acid (1 mmol), chelate ligand (1 mmol) and triethylamine (1 mmol) in methanol in the same predictable way that was used by us in reference [10]. Compound **4** of formula  $[\text{Mn}(\mu\text{-bmp})_2]_n$  was obtained by mixing the stoichiometric quantities of manganese(II) perchlorate (1 mmol), bis(4-methoxyphenyl)phosphinic acid (1 mmol), salicylaldehyde (1 mmol) and triethylamine (1 mmol). In this case we have used not a neutral chelate ligand but a ligand which needs to be deprotonated (salicylaldehyde). Probably, the low stoichiometric quantity of triethylamine (only 1 mmol to deprotonate 1 mmol of salicylaldehyde and 1 mmol of phosphinic acid) is the cause of the not presence of salicylaldehyde in the final product **4**.

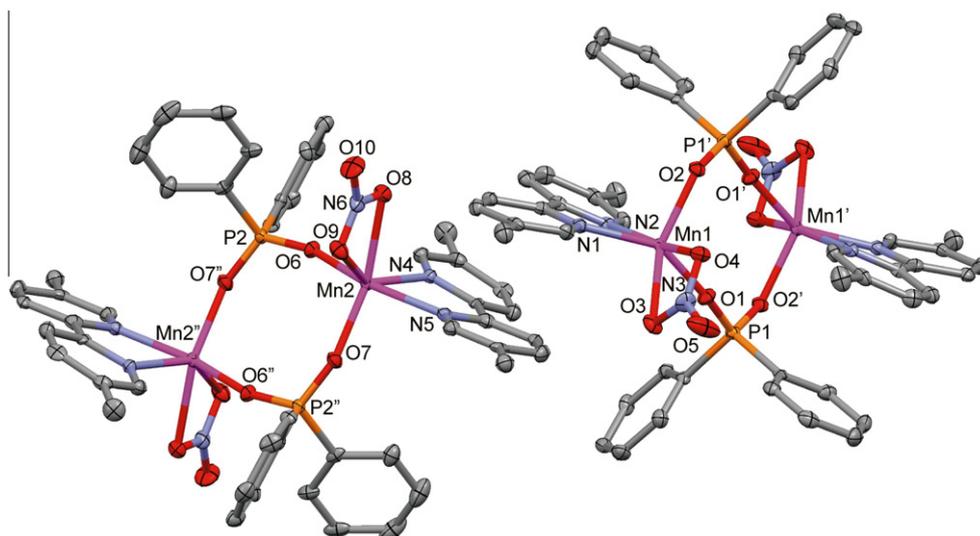
**Table 1**  
Crystallographic data and processing parameters.

Compound	1	2	3	4
Empirical formula	C <sub>48</sub> H <sub>44</sub> Mn <sub>2</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>50</sub> H <sub>40</sub> Mn <sub>2</sub> N <sub>6</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>57</sub> H <sub>56</sub> Mn <sub>2</sub> N <sub>6</sub> O <sub>15</sub> P <sub>2</sub>	C <sub>112</sub> H <sub>113</sub> Mn <sub>4</sub> O <sub>32.50</sub> P <sub>8</sub>
Formula mass	1036.71	1056.70	1236.90	2446.55
T (K)	100(2)	293(2)	100(2)	100(2)
System	triclinic	monoclinic	monoclinic	triclinic
Space group	P1	P2 <sub>1</sub> /c	C2/c	P1
a (Å)	11.2638(12)	12.595(4)	15.2770(11)	12.2919(12)
b (Å)	11.9899(12)	12.158(3)	18.3853(14)	15.6102(13)
c (Å)	17.3669(14)	18.009(5)	20.861(2)	17.8941(15)
α (°)	82.279(7)	90	90	111.073(14)
β (°)	87.837(8)	119.956(19)	105.995(7)	95.050(12)
γ (°)	83.956(8)	90	90	112.847(14)
V (Å <sup>3</sup> )	2310.6(4)	2389.3(12)	5632.4(8)	2847.2(7)
Z	2	2	4	1
μ (Mo Kα) (mm <sup>-1</sup> )	0.682	0.661	0.579	0.624
D <sub>calc</sub> (Mg/m <sup>3</sup> )	1.490	1.469	1.459	1.427
Crystal size (mm)	0.38 × 0.30 × 0.21	0.21 × 0.14 × 0.11	0.38 × 0.32 × 0.24	0.40 × 0.28 × 0.22
θ maximum (°)	26.34	30.55	26.37	26.37
Reflections collected	17744	6400	21577	22766
Independent reflections (R <sub>int</sub> )	9058/0.0433	6400/0.0481	5730/0.0293	11449/0.0220
Parameters	617	318	385	720
Goodness-of-fit (GOF) on F <sup>2</sup>	1.316	1.106	1.302	1.081
R <sub>1</sub> /wR <sub>2</sub> (all data)	0.0900/0.1736	0.0658/0.1950	0.0546/0.1162	0.0410/0.1031
Residual extrema (e Å <sup>-3</sup> )	0.782/−0.676	1.186/−0.685	0.600/−0.365	0.572/−0.293

**3.2. Description of the crystal structures of [Mn(μ-dpp)(5-dmbpy)(NO<sub>3</sub>)<sub>2</sub>] (1), [Mn(μ-dpp)(Me-phen)(NO<sub>3</sub>)<sub>2</sub>] (2), [Mn(μ-bmp)(neocuproine)(NO<sub>3</sub>)<sub>2</sub>] (3)**

Partially labeled perspective views of **1–3** are depicted in Figs. 2–4, and relevant bond parameters are given in the Supplementary Section (Tables S1–S3), respectively. The crystal structures consist of centrosymmetric dimeric neutral complexes, [Mn(μ-dpp)(5-dmbpy)(NO<sub>3</sub>)<sub>2</sub>] (1), [Mn(μ-dpp)(Me-phen)(NO<sub>3</sub>)<sub>2</sub>] (2) and [Mn(μ-dmp)(neocuproine)(NO<sub>3</sub>)<sub>2</sub>](MeOH) (3), (Hdpp = diphenylphosphinic acid, Hbmp = bis(4-methoxyphenyl)phosphinic acid, 5-dmbpy = 5,5'-dimethyl-2,2'-dipyridyl, Me-phen = methyl-1,10-phenanthroline and neocuproine = 2,9-dimethyl-1,10-phenanthroline). The structure of compound **3** crystallizes with a disordered MeOH solvent molecule (molar ratio of metal/solvent: 2/1). In compounds **1–3** every Mn(II) center is six-coordinated by two O atoms of a chelating nitrate group, two O atoms of different μ-dpp or μ-dmp bridging anions and two N atoms of a chelate ligand. The

MnN<sub>2</sub>O<sub>4</sub> chromophore has a distorted cis-octahedral geometry mainly derived from the small O–Mn–O<sup>#</sup> angle of 54.68(13)° and 55.42(13)° (**1**), 53.77(7)° (**2**) and 53.93(7)° (**3**) imposed by the chelating nitrate ligand. The Mn–N bond lengths are in the range from 2.217(4) to 2.275(4) Å. The shorter Mn–O(bmp) or Mn–O(bpp) bonds are in the range from 2.033(4) to 2.0893(19) Å, whereas the longer Mn–O(nitrate) bonds vary from 2.2056(18) to 2.433(4) Å. By applying inversion symmetry two Mn(II) centers are pairwise connected by the oxygen atoms of two substituted phosphinate ligands, thus acting as μ-O,O'-bridges, to form dimeric units. The core of each dimeric unit consists of an eight-membered corrugated ring of sequence [Mn–O–P–O<sup>#</sup>]<sub>2</sub> with intra-ring geometrical parameters summarized in Table 2. The disordered MeOH solvent molecule of **3** forms a hydrogen bond of type O–H...O to non-coordinated O atom of nitrate group with O(8)...O(6)[1/2 + x, 1/2 + y, z] distance of 2.722(7) Å. The packing of the dimeric complex units is further stabilized by ring–ring interactions between aromatic rings of adjacent dimers.



**Fig. 2.** Perspective view of **1** together with the atom numbering scheme.

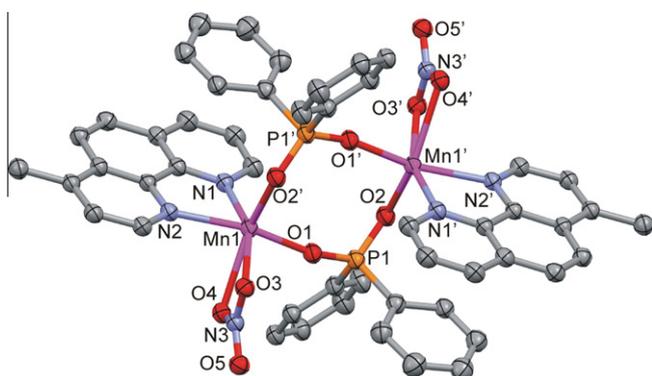


Fig. 3. Perspective view of dinuclear subunit of **2** together with the atom numbering scheme.

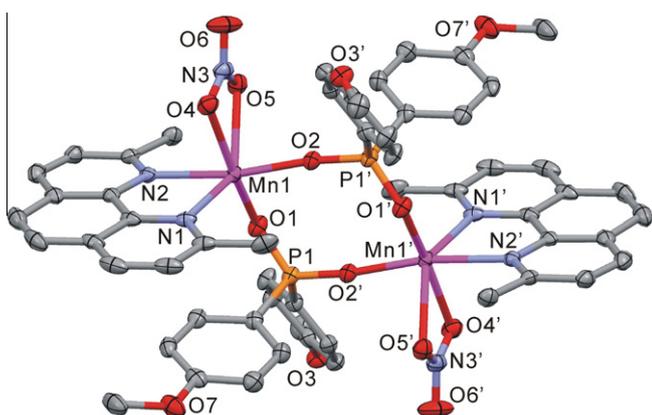


Fig. 4. Perspective view of **3** together with the atom numbering scheme.

### 3.3. Description of the crystal structure $[Mn(\mu\text{-bmp})_2 \cdot 1/4H_2O]_n$ (**4**)

The structure of complex **4** features a polymeric 1D system, consisting of  $[Mn(\mu\text{-bmp})_2]$  subunits, oriented along the x-axis of the triclinic unit cell and lattice water molecules (molar ratio: Mn/H<sub>2</sub>O = 8/1). A partially labeled perspective view of a section of the polymeric chain of  $[Mn_2(\mu\text{-bmp})_2]_n$  is presented in Fig. 5 and relevant bond parameters are given in the Supplementary Section (Table S4). Each Mn(II) center is tetrahedrally coordinated by

four O atoms of two different  $\mu\text{-bmp}$  anions, thus acting as  $\mu\text{-O,O'}$ -bridges [Mn–O: from 2.0068(15) to 2.0318(15) Å; O–Mn–O: from 102.02(6)° to 116.78(7)°] to form the polymeric chains of polyhedra. The core of the  $[Mn(\mu\text{-bmp})_2]_n$  chains consists of three crystallographic different eight-membered corrugated rings of sequence  $[Mn\text{-O-P-O}^\#]_2$  with common Mn(II) centers. Two of them are centrosymmetric with chair conformation, the third is acentric with distorted boat conformation. Their intra-ring geometrical parameters are summarized in Table 2.

### 3.4. Infrared spectra

In the three complexes we find several  $\nu\text{PO}_2$  absorption bands in the region 1200–1000  $\text{cm}^{-1}$ , which are diagnostic of bidentate coordination mode of the phosphinate group [22]. Also in all complexes there is an absorption at ca. 1260  $\text{cm}^{-1}$ , very characteristic for  $\mu(\text{P}=\text{O})$  as evidenced in metal phosphates [23]. Complexes **3** and **4** also show the characteristic pattern between 1300 and 500  $\text{cm}^{-1}$  of the bmp ligand [24]. In complexes **1–3** we can also observe bands at ca. 1450  $\text{cm}^{-1}$  corresponding to the bpy or phen derivatives and a very strong band at 1384  $\text{cm}^{-1}$  due to the nitrate group.

### 3.5. Conformation of the $Mn_2P_2O_4$ rings

In the present crystal structures of compounds **1–4**, seven eight-membered  $Mn_2P_2O_4$  core rings have been observed with the following Mn(II) centers: four of them in the dimeric complexes: ring 1A (Mn1..Mn1') and ring 1B (Mn2..Mn2'') in **1**, ring 2 and ring 3 in complexes **2** and **3**, respectively. Three crystallographic different  $Mn_2P_2O_4$  core units are present in the polymeric chain of compound **4**: ring 4A (Mn1..Mn1''), ring 4B (Mn2..Mn2') and ring 4C (Mn1..Mn2). Only ring 4C is acentric with distorted boat conformation, the other six are centrosymmetric with distorted chair conformation. Their intra-ring geometrical parameters are summarized in Table 2.

The solid state conformational preferences in the  $[M(\mu\text{-OPO})_2]$  core in transition metal complexes double bridged by phosphate and related ligands (phosphates, phosphonates and phosphinates) have been extensively studied taking into account that the conformational preferences can play an important role, between others, in the magnetic or biological properties of the complexes [25,26]. The most probable conformation for each eight-membered  $Mn_2P_2O_4$  ring were C<sub>2</sub> for compound **1**, TC<sub>3</sub> for compound **2**, and C<sub>1</sub> for compound **3**. **1–3** show a conformation belonging to the chair family

Table 2  
Geometrical parameters of  $[Mn\text{-O-P-O}]_2$  eight-membered rings in complexes **1–4**.

	Ring 1A	Ring 1B	Ring 2	Ring 3	Ring 4A	Ring 4B	Ring 4C
<i>Dist./angle (Å/°)</i>							
Mn...Mn'	4.776	5.194	4.855	5.186	4.462	4.796	4.667
P...P'	4.785	4.693	4.672	4.441	4.991	4.863	4.430
Mn...P	3.514	3.528	3.210	3.287	3.376	3.461	3.400/3.232
Mn...P'	3.241	3.471	3.521	3.537	3.319	3.369	3.397/3.355
Mn..P..Mn'	89.9	95.8	92.2	98.9	83.6	89.2	86.7/90.2
P..Mn..P'	90.1	84.2	87.8	81.1	96.4	90.8	83.8/82.0
O–Mn–O	107.0	101.1	101.4	94.7	114.6	112.5	114.9/109.1
O–P–O	116.8	118.2	117.8	118.2	116.3	116.0	116.6/117.6
Mn–O–P	168.9	163.3	162.7	130.7	140.0	156.2	149.3/143.1
Mn–O–P'	129.0	152.5	126.3	172.7	145.1	144.0	149.4/130.9
<i>Deviation from mean Plane (Å)</i>							
Mn	0.193	0.004	0.289	0.220	0.280	0.024	0.494/0.339
P	0.094	0.097	0.143	0.197	0.004	0.158	0.394/0.593
O1	0.138	0.071	0.204	0.337	0.239	0.146	0.158/0.056
O2	0.223	0.074	0.349	0.098	0.255	0.086	0.115/0.140
Mean	0.162	0.062	0.246	0.213	0.195	0.105	0.286
Mean comp.	0.112		0.246	0.213		0.195	
Conformat.	Chair	Chair	Twist chair	Chair	Chair	Chair	Boat

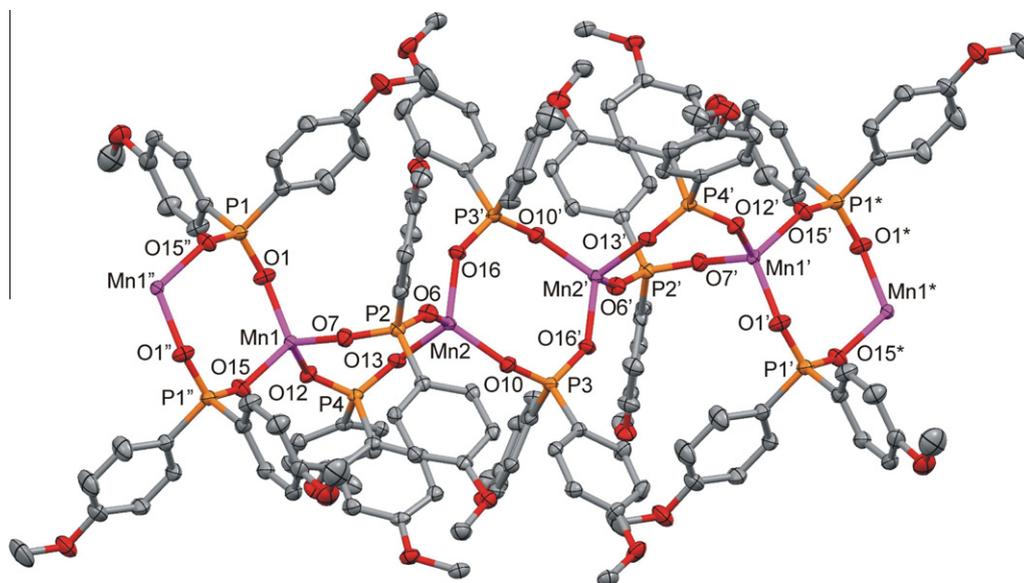


Fig. 5. Perspective view of a section of the polymeric chain of **4** together with the atom numbering scheme.

(*chair* or *twist chair* conformation) as the 64% of the data in which the  $[M(\mu\text{-OPO})_2]$  core has not constraints imposed by polycyclic systems or internal bridges [7]. While in compound **4** two conformations are observed  $BC_1$  and  $C_1$  where the (*boat chair*) conformation is much less known in these systems [9]. The conformations were established by using the classification method appealing to RingConf software with  $\sigma = 10^\circ$  [25].

### 3.6. Magnetic properties

Variable-temperature (2–300 K) magnetic susceptibility data were collected on polycrystalline samples for **1–4**. The magnetic behavior of the manganese(II) compounds **1–4** are represented in Figs. 6 and 7 in the form of  $\chi_M T$  versus  $T$  plots for **1–3** (Fig. 6) and of  $\chi_M$  versus  $T$  plot for **4** (Fig. 7). The structurally related dinuclear compounds **1–3** show similar behavior with slight differences. At 300 K, the  $\chi_M T$  product are 9.00, 8.90 and  $8.90 \text{ cm}^3 \text{ K mol}^{-1}$  for complexes **1**, **2** and **3**, respectively. These values are slightly higher than the expected for two uncoupled  $S = 2.5$  spins ( $8.750 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $g = 2.0$ ). Upon cooling, the  $\chi_M T$  values

remain nearly constant and only decreases clearly from approximately  $T < 25 \text{ K}$  indicating antiferromagnetic coupling. The  $\chi_M T$  values at 2 K are 3.21, 7.92 and  $7.04 \text{ cm}^3 \text{ K mol}^{-1}$  for complexes **1**, **2** and **3**, respectively. The corresponding  $\chi_M$  versus  $T$  plots for **1–3** increase on cooling and exhibit no maximum in  $\chi_M$  in the temperature range studied. Based on this situation, the experimental magnetic data have been fitted using the expression derived through the Hamiltonian  $\hat{H} = -J\hat{S}_A\hat{S}_B$  with  $S_A = S_B = 2.5$  (Eq. (1)):

$$\chi_M = (2Ng^2\mu_B^2/kT)[(\exp(J/kT) + 5\exp(3J/kT) + 14\exp(6J/kT) + 30\exp(10J/kT) + 55\exp(15J/kT))/(1 + 3\exp(J/kT) + 5\exp(3J/kT) + 7\exp(6J/kT) + 9\exp(10J/kT) + 11\exp(15J/kT))] \quad (1)$$

The parameters  $N$ ,  $\mu_B$  and  $k$  in Eq. (1) have their usual meanings. Least-squares fitting of all experimental data leads to the following parameters:  $J = -0.43 \text{ cm}^{-1}$ ,  $g = 2.03$  for **1**,  $J = -0.05 \text{ cm}^{-1}$ ,  $g = 2.02$  for **2** and  $J = -0.11 \text{ cm}^{-1}$ ,  $g = 2.02$  for **3**.

The coupling constants for **1–3** can be roughly correlated with the planarity of the dimeric units consisting of the eight-membered ring of sequence  $[Mn(1)\text{-}O(1)\text{-}P(1)\text{-}O(2)]_2$  the

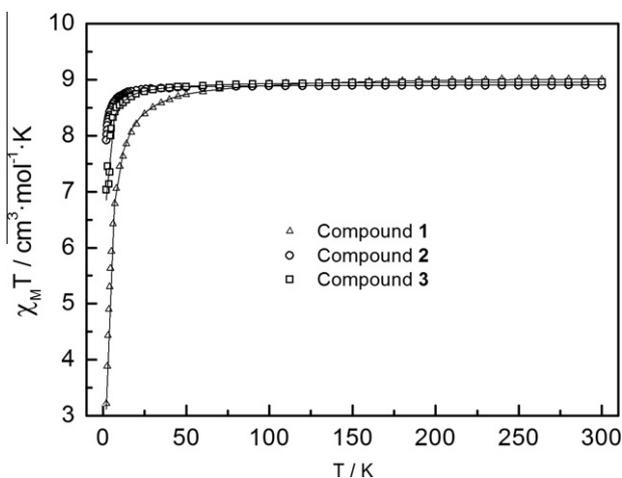


Fig. 6. Temperature dependence of  $\chi_M T$  of a solid sample of compounds **1–3**. The solid lines represent the best fit (see text).

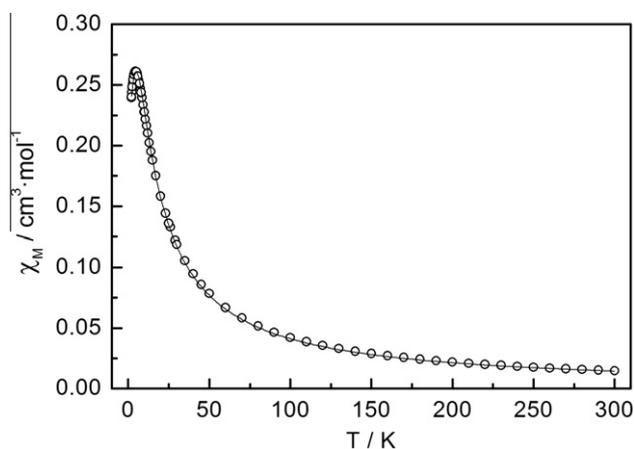


Fig. 7. Temperature dependence of  $\chi_M$  of a solid sample of complex **4**. The solid lines represent the best fit (see text).

**Table 3**

Values of the arithmetic mean value of the absolute deviations for the mean planes of the eight-membered rings of sequence  $[\text{Mn}(1)\text{-O}(1)\text{-P}(1)\text{-O}(2)]_2$  and calculated  $|J|$  values.

Compound	Mean value (Å)	$ J $ , $\text{cm}^{-1}$	Ref.
$[\text{Mn}(\mu\text{-bmp})(\text{bpy})(\text{NO}_3)_2]$	0.227	0.41	[8]
$[\text{Mn}(\mu\text{-bmp})(\text{phen})(\text{NO}_3)_2]$	0.256	0.11	[8]
$[\text{Mn}_2(\mu\text{-bmp})_2(5\text{-dmbpy})_2(\text{NO}_3)_2]$	0.055	0.61	[8]
<b>1</b>	0.112	0.43	This work
<b>2</b>	0.246	0.05	This work
<b>3</b>	0.213	0.11	This work

arithmetic mean value of the absolute deviations for the three mean planes are 0.112, 0.246 and 0.213 for **1**, **2** and **3**, respectively and the  $|J|$  values are 0.43, 0.05 and  $0.11 \text{ cm}^{-1}$ , respectively. More planar, higher  $|J|$  value. The same result has been observed in [10]. In Table 3 are reported the values of the arithmetic mean value of the absolute deviations for the three mean planes with the  $|J|$  values for the compounds **1–3** and the previously reported similar compounds [10].

The 1D compound **4** has a different behavior: at 300 K, the  $\chi_{\text{MT}}$  product is  $4.44 \text{ cm}^3 \text{ K mol}^{-1}$ . This value is slightly higher than the expected for one uncoupled  $S = 2.5$  spin ( $4.375 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $g = 2.0$ ). Upon cooling, the  $\chi_{\text{MT}}$  values remain nearly constant and only decrease clearly from approximately  $T < 25 \text{ K}$  indicating antiferromagnetic coupling. The corresponding  $\chi_{\text{M}}$  values for **4** (Fig. 7) increase on cooling and exhibit a maximum at 4.5 K, indicative of an antiferromagnetic coupling. The  $\chi_{\text{MT}}$  value at 2 K is  $0.48 \text{ cm}^3 \text{ K mol}^{-1}$ . Based on this situation, the experimental magnetic data have been fitted by using the Fisher equation [27] derived through the Hamiltonian  $H = -J \sum_i S_i S_{i+1}$ . Least-squares fitting of all experimental data leads to the following parameters:  $J = -0.80 \text{ cm}^{-1}$ ,  $g = 2.01$ . A structurally similar 1D compound,  $[\text{Mn}_2(\text{Ph}_2\text{PO}_2)_2]_n$ , where  $\text{HPh}_2\text{PO}_2$  is diphenylphosphinic acid, has been also structurally reported with a  $J$  value of  $-0.17 \text{ cm}^{-1}$  [28].

#### 4. Conclusion

A series of three dinuclear complexes of composition,  $[\text{Mn}(\mu\text{-dpp})(5\text{-dmbpy})(\text{NO}_3)_2]$  (**1**),  $[\text{Mn}(\mu\text{-dpp})(\text{Me-phen})(\text{NO}_3)_2]$  (**2**) and  $[\text{Mn}(\mu\text{-dmp})(\text{neocuproine})(\text{NO}_3)_2(\text{MeOH})]$  (**3**), ( $\text{Hdpp} = \text{diphenylphosphinic acid}$ ,  $\text{Hbmp} = \text{bis}(4\text{-methoxyphenyl})\text{phosphinic acid}$ ,  $5\text{-dmbpy} = 5,5'\text{-dimethyl-2,2'-dipyridyl}$ ,  $\text{Me-phen} = \text{methyl-1,10-phenanthroline}$  and  $\text{neocuproine} = 2,9\text{-dimethyl-1,10-phenanthroline}$ ) have been synthesized and structurally characterized. The centrosymmetric neutral dimers feature common octahedral Mn(II) centers, chelating nitrate groups, chelating chelate ligands L, and  $\mu\text{-O,O'}$ -bridging substituted phosphinato anions. **1–3** are slightly antiferromagnetically coupled according with the described observation that the  $\mu\text{-O,O'}$  O–P–O bridges give rise to negligible exchange interactions. [17,18] The coupling constants can be roughly correlated with the planarity of the dimeric units consisting of the eight-membered ring of sequence  $[\text{Mn}(1)\text{-O}(1)\text{-P}(1)\text{-O}(2)]_2$ : the arithmetic mean value of the absolute deviations for the three mean planes are 0.112, 0.246 and 0.213 for **1**, **2** and **3** respectively and the  $|J|$  values are 0.43, 0.05 and  $0.11 \text{ cm}^{-1}$  respectively. More planar, higher  $|J|$  value. We have also synthesized the 1D compound of formula  $[\text{Mn}(\mu\text{-bmp})_2]_n$  (**4**) which is built from double bridging *syn-syn* bis(4-methoxyphenyl)phosphinato

anions, showing a not usual chain of Mn(II) $\text{O}_4$  tetrahedra. **4** shows also antiferromagnetic coupling with a  $J$  value of  $-0.88 \text{ cm}^{-1}$ .

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#### Appendix A. Supplementary data

CCDC-881355 to CCDC-881358 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2012.07.028>.

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