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Carboxylate-Free Manganese(II) Phosphonate Assemblies: Synthesis, Structure, and Magnetism

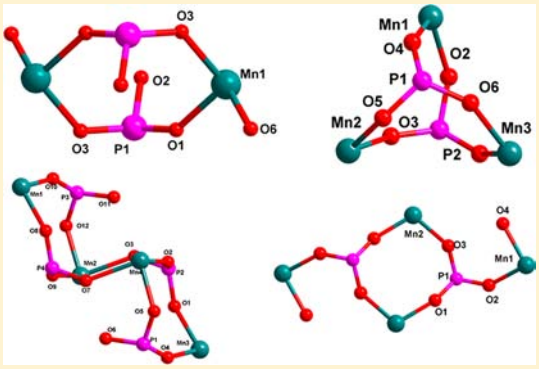
Vadapalli Chandrasekhar,*[,†] Joydeb Goura,[†] and E. Carolina Sañudo*[,‡]

[†]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

[‡]Departament de Química Inorgànica i Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Supporting Information

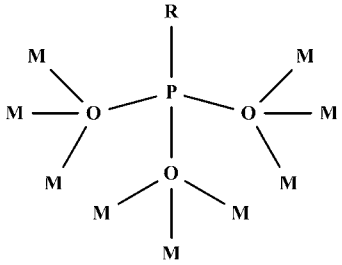
ABSTRACT: The reaction of manganese(II) salts with organophosphonic acid [*t*-BuPO$_3$H$_2$ or cyclopentyl phosphonic acid (C$_5$H$_9$PO$_3$H$_2$)] in the presence of ancillary nitrogen ligands [1,10-phenanthroline (phen) or 2,6-bis(pyrazol-3-yl)pyridine (dpzpy)], afforded, depending on the stoichiometry of the reactants and the reaction conditions, dinuclear, trinuclear, and tetranuclear compounds, [Mn$_2$(*t*-BuPO$_3$H)$_4$(phen)$_2$]·2DMF (**1**), [Mn$_3$(C$_5$H$_9$PO$_3$)$_2$(phen)$_6$](ClO$_4$)$_2$·7CH$_3$OH (**2**), [Mn$_3$(*t*-BuPO$_3$)$_2$(dpzpy)$_3$](ClO$_4$)$_2$·H$_2$O (**3**), [Mn$_4$(*t*-BuPO$_3$)$_2$(*t*-BuPO$_3$H)$_2$(phen)$_6$(H$_2$O)$_2$](ClO$_4$)$_2$ (**4**), and [Mn$_4$(C$_5$H$_9$PO$_3$)$_2$(phen)$_8$(H$_2$O)$_2$](ClO$_4$)$_4$ (**5**). Magnetic studies on **1**, **2**, and **4** reveal that the phosphonate bridges mediate weak antiferromagnetic interactions between the Mn^{II} ions have also been carried out.



INTRODUCTION

Organophosphonates [RP(O)$_2$OH]$^-$ and [RPO$_3$]$^{2-}$, obtained from the deprotonation of RP(O)(OH)$_2$, are good multidentate coordinating ligands and have the potential to rival and even exceed the coordination capabilities of the ubiquitous carboxylate ligand.[1] In principle, a single phosphonate ligand can bind to as many as nine metal centers (Chart 1), although this is rarely seen.[1] However, such a strong propensity of the phosphonate ligands to bind simultaneously to a large number of metal ions has, in fact, been a synthetic difficulty mostly because such a tendency leads to the formation, often, of insoluble compounds that possess extended structures.[2] While the value of compounds possessing extended structures is indisputable because of their potential applications in various areas including sorption,[3] catalysis,[4] cation exchange,[5] etc., phosphonate ligands appeared for a long time to be unsuitable for assembling molecular compounds. This difficulty has been circumvented by two strategies. First, the use of suitable ancillary ligands, along with the phosphonate ligands, limits the number of available coordination sites on the metal ions and thereby increases the chance of affording molecular compounds.[6] Second, an increase of steric bulk on the phosphonate ligand prevents agglomeration of the eventual metal ensemble and can lead to the isolation of molecular species.[7] Both of these synthetic strategies have been used either separately or together, leading to the realization of molecular phosphonates containing main-group,[8] transition-metal[9] and even lanthanide-metal[10] ions. However, in spite of this promise, this synthetic methodology remains underutilized, and molecular phosphonates of a large number of transition-metal ions are still sparse.[11−13] Thus, molecular phosphonates involving Mn^{II} ions are extremely limited. Herein we report the synthesis and structure of five examples of molecular manganese(II) phosphonates (with varying nuclearity, ranging from 2 to 4): [Mn$_2$(*t*-BuPO$_3$H)$_4$(phen)$_2$]·2DMF (**1**), [Mn$_3$(C$_5$H$_9$PO$_3$)$_2$(phen)$_6$](ClO$_4$)$_2$·7CH$_3$OH (**2**), [Mn$_3$(*t*-BuPO$_3$)$_2$(dpzpy)$_3$](ClO$_4$)$_2$·H$_2$O (**3**), [Mn$_4$(*t*-BuPO$_3$)$_2$(*t*-BuPO$_3$H)$_2$(phen)$_6$(H$_2$O)$_2$](ClO$_4$)$_2$ (**4**), and [Mn$_4$(C$_5$H$_9$PO$_3$)$_2$(phen)$_8$(H$_2$O)$_2$](ClO$_4$)$_4$ (**5**) [phen = 1,10-phenanthroline; dpzpy = 2,6-bis(pyrazol-3-yl)pyridine]. Among these, to the best of our knowledge, **2** and **3** represent the first examples of trinuclear manganese(II) phosphonates. Similarly, the structural form of **4** has been seen for the first time for

Chart 1. Possible Coordination Capability of a [RPO$_3$]$^{2-}$ Ligand



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molecular manganese(II) phosphonates. Magnetic studies on **1**, **2**, and **4** have also been carried out. These reveal that the phosphonate ligands mediate weak antiferromagnetic interactions between the Mn^{II} ions.

EXPERIMENTAL SECTION

Reagents and General Procedures. Solvents and other general reagents used in this work were purified according to standard procedures.[15] $MnCl_2·4H_2O$ (S.D. Fine Chemicals, India), $Mn(ClO_4)_2·4H_2O$ (Aldrich, U.S.A.), C_5H_9Cl (Aldrich, U.S.A.), 1,10-phenanthroline (phen; Aldrich, U.S.A.), $AlCl_3$ (S.D. Fine Chemicals, India), PCl_3 (S.D. Fine Chemicals, India), 2,6-diacetylpyridine (Aldrich, U.S.A.), *N*,*N*-dimethylformamide diethyl acetal (Aldrich, U.S.A.), and hydrazine hydrate ($N_2H_4·H_2O$; S.D. Fine Chemicals, India) were used as received. The phosphonic acids $C_5H_9P(O)(OH)_2$ and *t*-BuP(O)$(OH)_2$ and the pyrazole ligand 2,6-bis(pyrazol-3-yl)pyridine (dpzpy) were prepared according to literature procedures.[16−18]

Instrumentation. ^1H and ^{31}P NMR were recorded on a JEOL-JNM Lambda 400 model NMR spectrometer operating at 400.0 and 161.7 MHz, respectively, in $CDCl_3$ solutions. Chemical shifts are referenced with respect to tetramethylsilane. IR spectra were recorded as KBr pellets on a Bruker Vector 22 Fourier transform infrared spectrophotometer operating from 400 to 4000 cm^{-1}. Elemental analyses of the compounds were obtained using a Thermoquest CE instrument CHNS-O, model EA/110. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Micromass QUATTRO II triple-quadrupole mass spectrometer. Thermogravimetric analysis (heating rate of 10 °C min^{-1}) were carried out on a Perkin-Elmer Pyris 6 machine. Magnetic measurements were carried out in the Unitat de Mesures Magnètiques at the Universitat de Barcelona on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. Diamagnetic corrections were calculated using Pascal's constants, and an experimental correction for the sample holder was applied.

Synthesis. *$[Mn_2(t\text{-}BuPO_3H)_4(phen)_2]·2DMF$ (**1**).* $MnCl_2·4H_2O$ (0.200 g, 1.01 mmol) was taken in methanol (20 mL). To this was added a solution of phen (0.182 g, 1.01 mmol) and *tert*-butylphosphonic acid (0.139 g, 1.01 mmol) in methanol (15 mL), and the resulting mixture was stirred at room temperature for 2 h. At this stage, triethylamine (0.36 g, 3.557 mmol) was added to the reaction mixture. A yellow precipitate formed immediately. The reaction mixture was stirred for an additional 6 h. The reaction mixture was filtered, and the precipitate was dissolved in *N*,*N*-dimethylformamide (DMF), filtered, and kept for crystallization to afford yellow crystals of **1** after 1 week. Yield: 0.140 g, 24% (based on phosphorus). Anal. Calcd for $C_{46}H_{70}N_6O_{14}P_4Mn_2$ (**1**; 1164.84): C, 47.43; H, 6.06; N, 7.22. Found: C, 47.55; H, 5.88; N, 7.02. IR (KBr, ν, cm^{-1}): 3383(s), 2971(s), 2865(w), 2500(w), 2000(w), 1676(s), 1623(m), 1590(s), 1516(s), 1479(s), 1460(s), 1427(w), 1391(m), 1360(w), 1227(s), 1129(s), 1070(s), 1023(s), 922(s), 864(s), 852(s), 831(s), 775(m), 730(s), 651(s), 492(s), 410(s). ESI-MS: m/z = 510.0978 ($[(1,10\text{-phen})Mn(t\text{-}BuPO_3H_2)(t\text{-}BuPO_3H)]^+$). Synthesis of **1** could also be carried out using experimental conditions similar to those above by varying the stoichiometry ($MnCl_2·4H_2O$:phen:*tert*-butylphosphonic acid:triethylamine ratio = 1:1:2:4.5). No significant changes in the yields of **1** were observed.

*$[Mn_3(C_5H_9PO_3)_2(phen)_6](ClO_4)_2·7CH_3OH$ (**2**).* $Mn(ClO_4)_2·4H_2O$ (0.128 g, 0.393 mmol) was taken in methanol (15 mL). To this was added a solution of phen (0.09 g, 0.499 mmol) and cyclopentylphosphonic acid (0.056 g, 0.373 mmol) in a dichloromethane solution (15 mL), and the resulting mixture was stirred at room temperature for 6 h. At this stage, triethylamine (0.114 g, 1.134 mmol) was added to the reaction mixture. The resulting clear yellow solution was stirred for an additional 12 h. The solution was evaporated, and the residue obtained was redissolved in methanol, filtered, and kept for crystallization. After a few days, yellow crystals of **2** were obtained. Yield: 0.104 g, 28% (based on phosphorus). Anal. Calcd for $C_{90}H_{93}Cl_2N_{12}O_{21}P_2Mn_3$ (**2**; 1976.43): C, 54.69; H, 4.74; N, 8.50. Found: C, 54.75; H, 4.63; N, 8.71. IR (KBr, ν, cm^{-1}): 3754(s), 3423(s), 3065(w), 2948(s), 2871(m), 2375(m), 2276(w), 1622(m), 1581(s), 1513(s), 1422(s), 1091(s), 986(s), 849(s), 773(m), 725(s), 624(s), 579(m), 532(s). ESI-MS: m/z 384.1317 ($[(1,10\text{-phen})Mn(C_5H_9PO_3H)]^+$), 564.1195 ($[(1,10\text{-phen})_2Mn(C_5H_9PO_3H)]^+$), 714.1615 ($[(1,10\text{-phen})Mn(C_5H_9PO_3H_2)(C_5H_9PO_3H)]^+$). The synthesis of **2** was attempted by varying the stoichiometry [$Mn(ClO_4)_2·4H_2O$:phen:cyclopentylphosphonic acid:triethylamine ratio = 3:6:2:4.5]. Although **2** could be obtained, pure crystals of **2** could not be isolated.

*$[Mn_3(t\text{-}BuPO_3)_2(dpzpy)_3](ClO_4)_2·H_2O$ (**3**).* $Mn(ClO_4)_2·4H_2O$ (0.165 g, 0.506 mmol) was taken in methanol (15 mL). To this was added a solution of dpzpy (0.137 g, 0.649 mmol) and *tert*-butylphosphonic acid (0.060 g, 0.435 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred at room temperature for 6 h. At this stage, triethylamine (0.203 g, 2.008 mmol) was added to the reaction mixture. The resulting clear yellow solution was stirred for an additional 12 h. The solution was evaporated, and the residue obtained was redissolved in methanol, filtered, and kept for crystallization. After 2 days, yellow blocks of crystals of **3** were obtained. Yield: 0.115 g, 42% (based on phosphorus). Anal. Calcd for $C_{41}H_{47}Cl_2Mn_3N_{15}O_{15}P_2$ (**3**; 1287.60): C, 38.25; H, 3.68; N, 16.32. Found: C, 38.07; H, 3.50; N, 16.05. IR (KBr, ν, cm^{-1}): 3280(br), 2952(m), 1610(s), 1573(s), 1460(s), 1431(s), 1360(s), 1307(s), 1271(m), 1221(m), 1091(s), 1047(s), 985(s), 966(s), 822(s), 784(s), 661(s), 622(s), 514(s), 427(s). ESI-MS: m/z 212.0936 ($[(dpzpy) + H]^+$), 476.1018 ($[(dpzpy)Mn(dpzpy\text{-}H)]^+$). The synthesis of **3** was attempted by varying the stoichiometry [$Mn(ClO_4)_2·4H_2O$:dpzpy:*tert*-butylphosphonic acid:triethylamine ratio = 3:3:2:4.5]. Although **3** could be obtained, pure crystals of **3** could not be isolated.

*$[Mn_4(t\text{-}BuPO_3)_2(t\text{-}BuPO_3H)_2(phen)_6(H_2O)_2](ClO_4)_2$ (**4**).* $Mn(ClO_4)_2·4H_2O$ (0.138 g, 0.423 mmol) was taken in methanol (15 mL). To this was added a solution of phen (0.098 g, 0.544 mmol) and *tert*-butylphosphonic acid (0.05 g, 0.362 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred at room temperature for 12 h. At this stage, triethylamine (0.11 g, 1.07 mmol) was added to the reaction mixture. The resulting clear yellow solution was stirred for an additional 12 h. The solution was evaporated, and the residue obtained was redissolved in methanol, filtered, and kept for crystallization to afford yellow crystals of **4**. Yield: 0.110 g, 58% (based on phosphorus). Anal. Calcd for $C_{88}H_{90}Cl_2N_{12}O_{22}P_4Mn_4$ (**4**; 2082.26): C, 50.76; H, 4.36; N, 8.07. Found: C, 50.61; H, 4.20; N, 7.95. IR (KBr, ν, cm^{-1}): 3758(s), 3395(w), 3069(s), 2955(s), 2865(s), 2677(s), 2374(m), 1622(m), 1585(s), 1513(s), 1422(s), 1345(s), 1159(s), 1094(s), 969(s), 901(s), 852(s), 726(s), 625(s), 556(m), 502(s), 420(s). ESI-MS: m/z 552.1113 ($[(1,10\text{-phen})_2Mn(t\text{-}BuPO_3H)]^+$), 690.1567 ($[(1,10\text{-phen})_2Mn(t\text{-}BuPO_3H_2)(t\text{-}BuPO_3H)]^+$), 959.1288 ($[(1,10\text{-phen})_3Mn_2(t\text{-}BuPO_3)(t\text{-}BuPO_3H)(H_2O) + (H_2O)]^+$). The synthesis of **4** was attempted by varying the stoichiometry [$Mn(ClO_4)_2·4H_2O$:phen:*tert*-butylphosphonic acid:triethylamine ratio = 4:6:4:6.5]. Although **4** could be obtained, pure crystals of **4** could not be isolated.

*$[Mn_4(C_5H_9PO_3)_2(phen)_8(H_2O)_2](ClO_4)_4$ (**5**).* $Mn(ClO_4)_2·4H_2O$ (0.171 g, 0.525 mmol) was taken in methanol (15 mL). To this was added a solution of phen (0.121 g, 0.672 mmol) and cyclopentylphosphonic acid (0.075 g, 0.496 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred at room temperature for 12 h. At this stage, triethylamine (0.153 g, 1.515 mmol) was added to the reaction mixture. The resulting clear yellow solution was stirred for an additional 12 h. The solution was evaporated, and the residue obtained was redissolved in methanol, filtered, and kept for crystallization to afford yellow crystals of **5**. Yield: 0.120 g, 20% (based on phosphorus). Anal. Calcd for $C_{106}H_{86}Cl_4Mn_4N_{16}O_{24}P_2$ (**5**; 2391.41): C, 50.81; H, 4.26; N, 8.08. Found: C, 53.24; H, 3.62; N, 9.37. IR (KBr, ν, cm^{-1}): 3429(s), 2952(w), 2868(w), 1622(s), 1576(s), 1515(s), 1451(s), 1425(s), 1342(w), 1301(m), 1222(s), 1148(s), 1116(s), 1089(s), 1056(s), 987(s), 931(s), 863(s), 852(s), 842(m), 779(s), 765(s), 728(s), 622(s), 578(s), 534(s), 418(s). ESI-MS: m/z 384.1354 ($[(1,10\text{-phen})Mn(C_5H_9PO_3H)]^+$), 564.2029 ($[(1,10\text{-phen})_2Mn(C_5H_9PO_3H)]^+$). The synthesis of **5** was attempted

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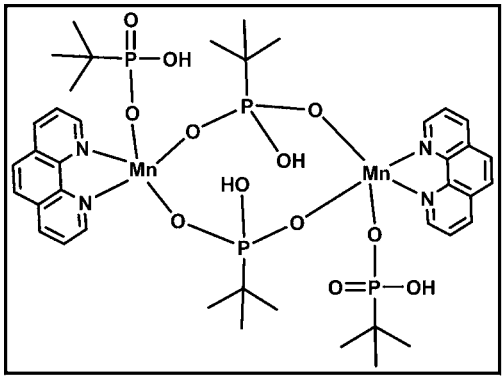
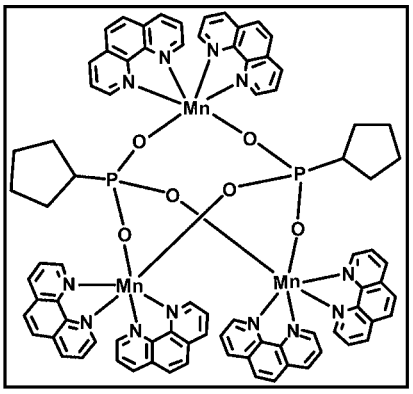
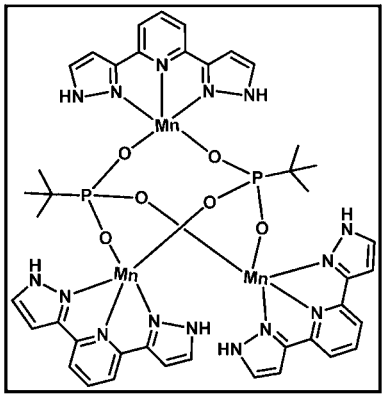
Chart 2. Schematic Diagrams of Compounds 1−5



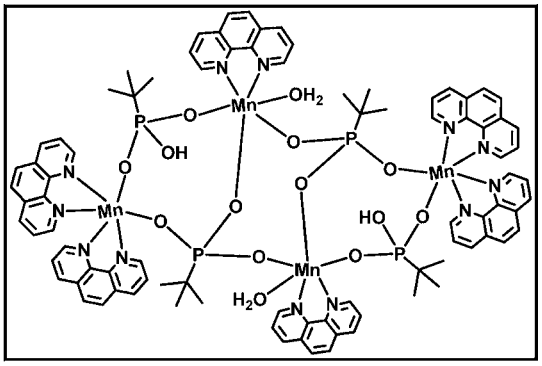
Compound 1



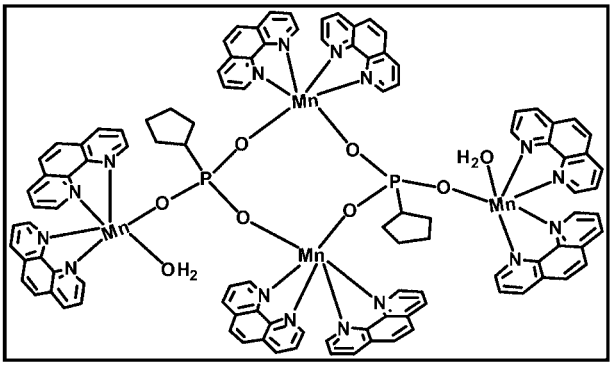
Compound 2



Compound 3



Compound 4



Compound 5

by varying the stoichiometry [$Mn(ClO_4)_2 \cdot 4H_2O$:phen:cyclopentylphosphonic acid:triethylamine ratio = 4:8:2:4.5]. Although **5** could be obtained, pure crystals of **5** could not be isolated.

X-ray Crystallography. Single-crystal X-ray structural studies of **1**−**5** were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). Crystals did not degrade/decompose during data collection. Data collection, structure solution, and refinement were performed using *SMART*, *SAINT*, and *SHELXTL* programs, respectively.[19a−f] All calculations for data reduction were done using the Bruker *SADABS* program. All non-H atoms were refined anisotropically using full-matrix least-squares procedures. All H atoms were included in idealized positions, and a riding model was used. All mean-plane analyses as well as molecular drawings were obtained from *DIAMOND* (version 3.1).

RESULTS AND DISCUSSION

Synthesis. Most of the molecular manganese phosphonates either contain exclusively Mn^{III} or contain both Mn^{II} and Mn^{III} [representative examples: $\{Mn^{III}_6(O)_2(O_3PPh)_2(OH\text{-}(O)_2PPh)(O_2CPh)_8(py)_2\}$[6a] and $\{Mn^{II}_4Mn^{III}_{18}(O)_{12}\text{-}(O_3PC_6H_{11})_8(O_2CCH_3)_{22}(H_2O)_6(py)_2\}$.[6c] Invariably, all such complexes seem to contain carboxylate ligands in addition to phosphonate ligands. Discrete manganese(II) complexes containing only phosphonate ligands (without carboxylate ligands) are, in fact, only a handful: $[Mn(t\text{-}Bu\text{-}PO_3H)_2(phen)_2]\cdot MeCOOH]$,[20] $[Mn_2(HL)_2(phen)_4]$,[2b] $[Mn_2(HL)_2(phen)_4][Mn_2(HL)_2(phen)_4(H_2O)]_2\cdot 6H_2O$,[2b] $[Mn_4(L)_2(phen)_8(H_2O)_2][ClO_4]_2\cdot 3H_2O$,[2b] $[Mn_6(L)_4(phen)_8\text{-}(H_2O)_2]\cdot 4H_2O$,[2b] $[Mn_6(L)_4(phen)_8(H_2O)_2]\cdot 24H_2O$,[2b] and

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Table 1. Crystal Data and Structure Refinement Parameters of 1−5

	1	2	3	4	5
formula	$C_{46}H_{70}Mn_2N_6O_{14}P_4$	$C_{90}H_{93}Cl_2Mn_3N_{12}O_{21}P_2$	$C_{41}H_{47}Cl_2Mn_3N_{15}O_{15}P_2$	$C_{88}H_{90}Cl_2Mn_4N_{12}O_{22}P_4$	$C_{106}H_{86}Cl_4Mn_4N_{16}O_{24}P_2$
fw	1164.84	1976.43	1287.60	2082.26	2391.41
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
unit cell dimens					
a (Å)	11.710(3)	14.0405(5)	13.022(3)	14.392(3)	10.688(2)
b (Å)	12.262(4)	14.656(5)	13.089(3)	14.431(3)	15.235(3)
c (Å)	12.390(4)	14.828(5)	14.816(3)	14.844(3)	27.509(5)
α (deg)	119.457(4)	96.125(5)	81.374(4)	67.009(3)	95.281(4)
β (deg)	99.910(5)	91.886(5)	85.103(4)	62.565(3)	97.824(4)
γ (deg)	105.641(5)	116.226(5)	65.466(3)	88.285(3)	94.734(4)
volume (Å^3); Z	1389.7(7); 1	4398.2(15); 2	2710.5(16) ; 2	2270.6(8); 1	2476.1(8); 1
density (Mg m^{-3})	1.392	1.492	1.578	1.523	1.604
abs coeff (mm^{-1})	0.635	0.602	0.924	0.753	0.726
F (000)	610	2048	1314	1072	1224
cryst size (mm)	0.09 × 0.07 × 0.05	0.14 × 0.12 × 0.11	0.14 × 0.12 × 0.11	0.12 × 0.11 × 0.09	0.14 × 0.12 × 0.11
θ range (deg)	2.03−25.49	1.93−25.50	1.67−25.50	2.18−26.00	1.99−25.50
limiting indices	$-13 \le h \le 14$	$-12 \le h \le 12$	$-17 \le h \le 16$	$-15 \le h \le 11$	$-17 \le h \le 16$
	$-14 \le k \le 14$	$-18 \le k \le 18$	$-14 \le k \le 17$	$-16 \le k \le 16$	$-17 \le k \le 17$
	$-14 \le l \le 6$	$-33 \le l \le 16$	$-17 \le l \le 16$	$-17 \le l \le 18$	$-14 \le l \le 17$
reflns collected	7419	23537	14518	12612	13088
unique reflns [R_{int}]	5057 [0.0236]	15899 [0.0636]	9740 [0.0287]	8694 [0.0404]	8925 [0.0409]
completenes (%) to θ	97.9 (25.49°)	97.1 (25.50°)	96.6 (25.50°)	97.3 (26.00°)	96.7 (25.50°)
data/restraints/param	5057/0/341	15899/1/1183	9740/2/724	8694/0/606	8925/0/704
GOF on F^2	1.122	0.982	1.029	1.029	1.015
final R indices [$I > 2\sigma(I)$]	R1 = 0.0496, wR2 = 0.1341	R1 = 0.0871, wR2 = 0.2023	R1 = 0.0615, wR2 = 0.1555	R1 = 0.0625, wR2 = 0.1540	R1 = 0.0620, wR2 = 0.1313
R indices (all data)	R1 = 0.0603, wR2 = 0.1682	R1 = 0.1570, wR2 = 0.2554	R1 = 0.0823, wR2 = 0.1772	R1 = 0.0963, wR2 = 0.2053	R1 = 0.0996, wR2 = 0.1546
largest residual peaks (e Å^{-3})	1.212 and −0.513	1.093 and −0.769	1.875 and −0.494	1.100 and −1.035	0.883 and −0.737

$Mn_6(L)_4(phen)_6(H_2O)_4]\cdot 5H_2O$ [LH_3 = (*m*-$HO_3SC_6H_4PO_3H_2$); phen = 1,10-phenanthroline].[2b] Recently, we have utilized chelating nitrogen ligands such as bpy, phen, and dipyridylamine in conjunction with organophosphonic acids and copper(II) salts and were able to modulate the nuclearity of the resulting assembly from 2 to 6.[14] We wished to explore whether such a strategy could also be applied to the synthesis of manganese(II) phosphonates. Accordingly, the reaction of manganese(II) salts [$MnCl_2\cdot 4H_2O$ or $Mn(ClO_4)_2\cdot 4H_2O$] with organophosphonic acids (cyclopentylphosphonic acid or *tert*-butylphosphonic acid) and chelating nitrogen ligands (phen or dpzpy) afforded di-, tri-, and tetranuclear derivatives **1**−**5** (Chart 2). Compounds **1**−**5** were isolated only in moderate yields, suggesting the formation of other compounds also under these conditions. In view of this, we would not like to comment on modulation of the nuclearity in the present instance. Attempts to optimize the yields of **1**−**5** using crystal structure stoichiometries were not successful (see the Experimental Section). ESI-MS studies on these compounds reveal that all of them decompose in solutions to various fragments, and in no case, we were able to detect parent ion peaks (see the Experimental Section).

Molecular Structures of 1−5. The molecular structures of **1**−**5** were determined by X-ray crystallography. The crystallographic parameters of these compounds are given in Table 1.

The molecular structure of **1** reveals that it is a dimer (Figure 1). The two manganese centers are bridged to each other by two bridging isobidentate phosphinate ligands, [*t*-BuP-

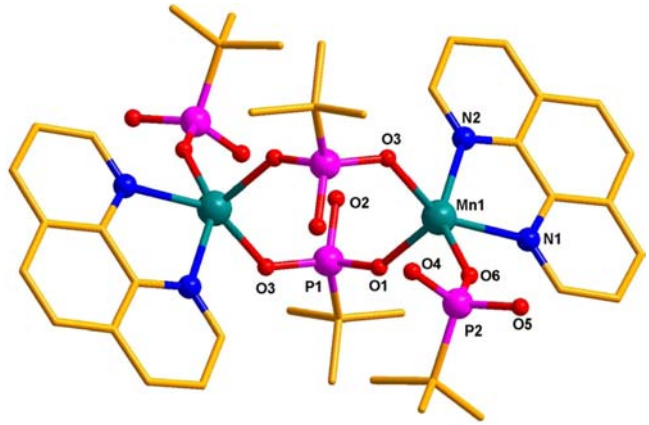

Figure 1. Molecular structure of **1**. All H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): Mn1−O1, 2.024(2); Mn1−O6, 2.063(2); Mn1−O3, 2.090(2); Mn1−N1, 2.284(3); Mn1−N2, 2.275(3); P1−O1, 1.498(2); P1−O2, 1.579(2); P1−O3, 1.510(2); P2−O4, 1.515(2); P2−O5, 1.573(2); P2−O6, 1.495(2); O1−Mn1−O6, 103.05(9); O1−Mn1−O3, 105.4(1); O3−Mn1−N2, 88.58(9); N2−Mn1−N1, 72.2(1); O1−P1−O3, 116.1(1); O1−P1−O2, 107.6(1); O3−P1−O2, 110.6(1); O6−P2−O4, 115.2(1); O6−P2−O5, 106.6(1).

$(O)_2OH]^-$, resulting in an eight-membered ($Mn_2P_2O_4$), puckered, ring. The two P−O bond distances involved in the bridging coordination mode are nearly similar [average: 1.500(2) Å]. The third P−O(H) distance is longer than

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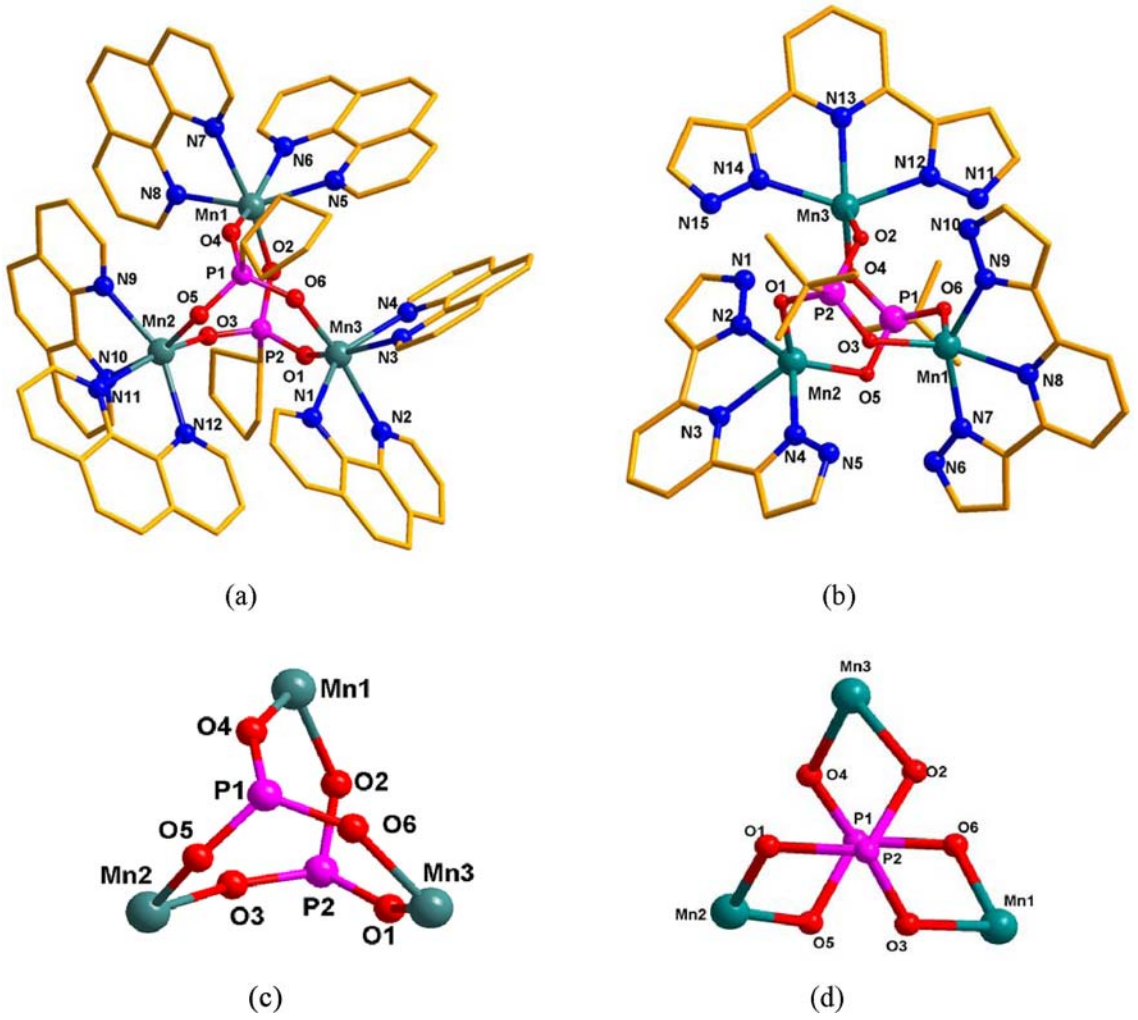

Figure 2. (a) Molecular structure of **2**. All H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): Mn1−O4, 2.044(3); Mn1−O2, 2.105(4); Mn3−O1, 2.047(3); Mn2−O3, 2.052(3); Mn2−O5, 2.082(3); Mn3−O6, 2.061(4); Mn3−N1, 2.288(4); Mn3−N2, 2.349(5); P2−O3, 1.517(3); P2−O1, 1.518(4); P2−O2, 1.541(4); O4−Mn1−O2, 106.6(1); N5−Mn1−N8, 148.9(2); O6−P1−O5, 112.4(2); O6−P1−O4, 112.1(2); O5−P1−O4 112.2(2). (b) Molecular structure of **3**. All H atoms have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): Mn2−O1, 2.064(2); Mn2−O5, 2.092(2); Mn2−N2 2.243(3); Mn2−N4, 2.257(3); Mn2−N3, 2.280(3); P2−O3, 1.529(2); P2−O2, 1.539(2); P2−O1, 1.541(2); O1−Mn2−O5, 122.67(9); O3−P2−O2, 111.55(13); O3−P2−O1, 109.19(12); O2−P2−O1, 111.24(13). (c) Mn−O−P core of **2**. (d) Mn−O−P core of **3**.

1.579(2) Å. The Mn−O bond distances involved with the bridging phosphinate ligands involved are also nearly similar [average: 2.064(2) Å]. Each of the Mn centers is also bound with a unidentate phosphinate ligand, $[t\text{-BuP(O)}_2\text{OH}]^-$. Expectedly, in this instance, three types of P−O bond distances are seen, with the shortest distance of 1.496(2) Å associated with O6, which is bound to the metal ion. The other important bond parameters for this compound are summarized in the caption of Figure 1. In addition to the phosphinate ligands, each of the Mn centers is also bound with a chelating phen ligand. Thus, each Mn^{II} center in **1** is five-coordinate (two N and three O atoms) and is present in a distorted square-pyramidal configuration (Supporting Information). The molecular structure of **1** is similar to some metal phosponates such as $[Mn_2(m\text{-}HO_3SC_6H_4PO_3H_2)_2(phen)_4]$,[2b] $[Cu_2(\mu_2\text{-}C_5H_9PO_3)_2(bpya)_2(H_2O)_2](H_2O)_4$[14a] (bpya = 2,2-bipyridylamine), and $[Cd_2(ArPO_3H)_4(bpy)_2](CH_3OH)(H_2O)$[7d] (bpy = 2,2-bipyridine).

The trinuclear compounds **2** and **3** possess nearly similar structural cores (Figure 2). In **2**, manganese is six-coordinate (four N and two O atoms), while in **3**, it is five-coordinate (three N and two O atoms; Supporting Information). This difference in the coordination number and geometry arises because of the fact that, in **2**, two phen ligands serve as the ancillary ligands, while in **3**, one tripodal dpzpy ligand alone is present. The core structures in both of these compounds are comprised of a triangular Mn_3 platform held together by two bicapping tripodal phosphonate ligands from the top and bottom of the manganese plane. Such a structural motif, although unprecedented in manganese(II) phosphonates, has been noticed earlier, for example, in the trinuclear zinc(II) complex $[Zn_3Cl_2(3,5\text{-}Me_2Pz)_4(t\text{-}BuPO_3)_2]$.[21] In **2** and **3**, each of the phosphonate ligands are involved in a 3.111 (Harris notation)[22] coordination mode, binding to all three Mn centers. This results in the formation of a propellane-type bicyclic structure (Figure 2c,d). An interesting feature of the molecular structure of these trinuclear comounds is that, in **2**, the Mn−Mn interdistances are nearly similar [average: 4.654(2) Å], while in **3**, the corresponding distances are not only dissimilar but also shorter [4.005(2), 4.007(2), and 4.431(1) Å;

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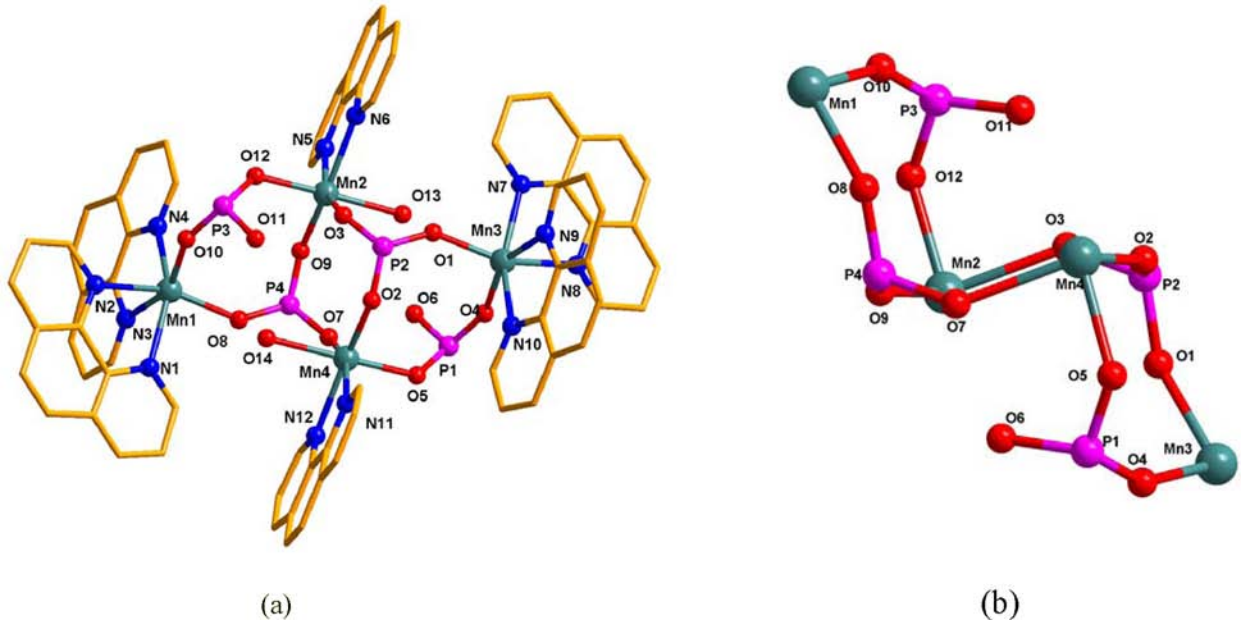
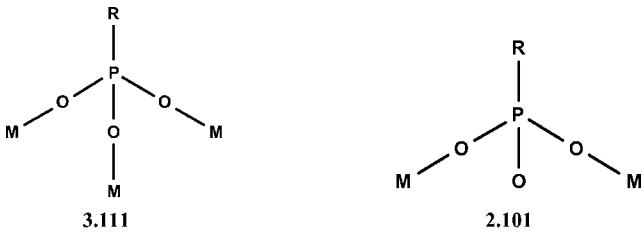


Figure 3. (a) Molecular structure of **4**. All H atoms and *tert*-butyl groups of phosphonic acid have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): Mn3−O1, 2.0882(7); Mn3−O4, 2.1220(8); Mn3−N10, 2.2970(8); Mn3−N8, 2.310(1); P1−O4, 1.480(1); P1−O5, 1.506(1); P1−O6, 1.598(1); O1−Mn3−O4, 97.0(1); N10−Mn3−N8,100.0(1); O4−P1−O5, 116.7(1); O4−P1−O6, 109.8(1); O5−P1−O6, 107.8(4); O2−P2−O1, 113.3(1); O2−P2−O3, 111.3(1); O1−P2−O3 108.8(1). (b) Mn−O−P core of **4** showing the tricyclic framework. The anti disposition of the terminal rings is shown.

Supporting Information). Additionally, the two phosphonate ligands are anti with respect to each other in **3**, while their relationship is nearly syn in the case of **2** (Supporting Information). The bond parameters of **2** and **3** are summarized in the caption of Figure 2.

The molecular structure of **4** is shown in Figure 3, the caption of which contains information about selected bond parameters for this compound. The tetranuclear compound **4**, containing four Mn^{2+} ions, two phosphonate lignads $[RPO_3]^{2-}$, and two phosphinate ligands $[RP(O)_2(OH)]^-$, is a tricyclic system that contains three fused $Mn_2P_2O_4$ eight-membered rings (Chart 3). All of the rings are puckered, and the

Chart 3. Coordination Modes Shown by the $[RPO_3]^{2-}$ and $[RP(O)_2(OH)]^-$ Ligands in the Present Study



R = *tert*-butyl or cyclopentyl

relationship of the two terminal rings vis-à-vis the central ring is trans (Figure 3b). While **4** represents a new structural form for manganese(II) phosphonates, a similar composition exists in a zinc(II) phosphonate, $[Zn_4\{ArPO_3\}_2\{ArPO_2(OH)\}_2\{DMPZH\}_4(DMPZ)_2]\cdot 5MeOH$ [Ar = 2,4,6-isopropylphenyl][7c] although in the latter, an open-book conformation with a cis arrangement of the terminal rings vis-à-vis the central ring is present. Unlike in compounds **1**−**3**, in **4** two different types of Mn^{II} centers are present. The terminal Mn^{II} centers, Mn1 and Mn3, have two chelating phen ligands each, while the central Mn^{II} centers, Mn2 and Mn4, possess only one phen ligand. A phosphinate ligand (2.101, Harris notation[22]) and a phosphonate ligand (3.111, Harris notation[22]) bind a terminal ion and a central Mn^{II} ion (Mn1 and Mn2; Mn3 and Mn4). On the other hand, the central Mn^{II} ions (Mn2 and Mn4) are bound to each other by the coordination action of two phosphonate ligands. Interestingly, each of the central Mn^{II} centers possesses one molecule of coordinating water each, whose disposition is anti with respect to each other. The molecular dimensions of **4** reveals that it is a nanosized entity: the Mn3−Mn1 interdistance is about 9.5 Å, while the end-to-end distance, as measured between the two H atoms of the phen group, is 20.7 Å.

The molecular structure of **5** reveals a central dinuclear motif present as an eight-membered $Mn_2P_2O_4$ ring, on either end of which are attached mononuclear Mn^{II} motifs (Figure 4). The two terminal Mn^{II} centers possessing two phen ligands and a coordinating water molecule are attached to the central portion of the molecule by a phosphonate ligand. Unlike other compounds described in this study, particularly compounds **1** and **4**, compound **5** is *phosphonate-poor* in that it possesses only two phosphonate ligands for the four Mn^{II} centers. The central eight-membered ring possesses two Mn^{II} centers, each of which are six-coordinate (four N and two O atoms) and are bound to each other by the phosphonate ligand coordination. Overall, in this compound, the phosphonate coordination is 3.111. The molecular structure of **5** is reminiscent of a literature precedent.[2b]

Magnetic Studies. The χT product for complex **1** has a value of 8.9 cm^3 K mol^{-1} at 300 K at an applied field of 0.3 T. This is well in agreement with the expected value for two isolated Mn^{II} ions with $S = {}^5/_2$ and $g = 2.0$ (4.375 cm^3 K mol^{-1} per Mn^{II} ion). As the temperature decreases, the χT product slightly decreases, remaining nearly constant. Below 15 K, a sharp decrease is observed to a value of 8.3 cm^3 K mol^{-1}. An

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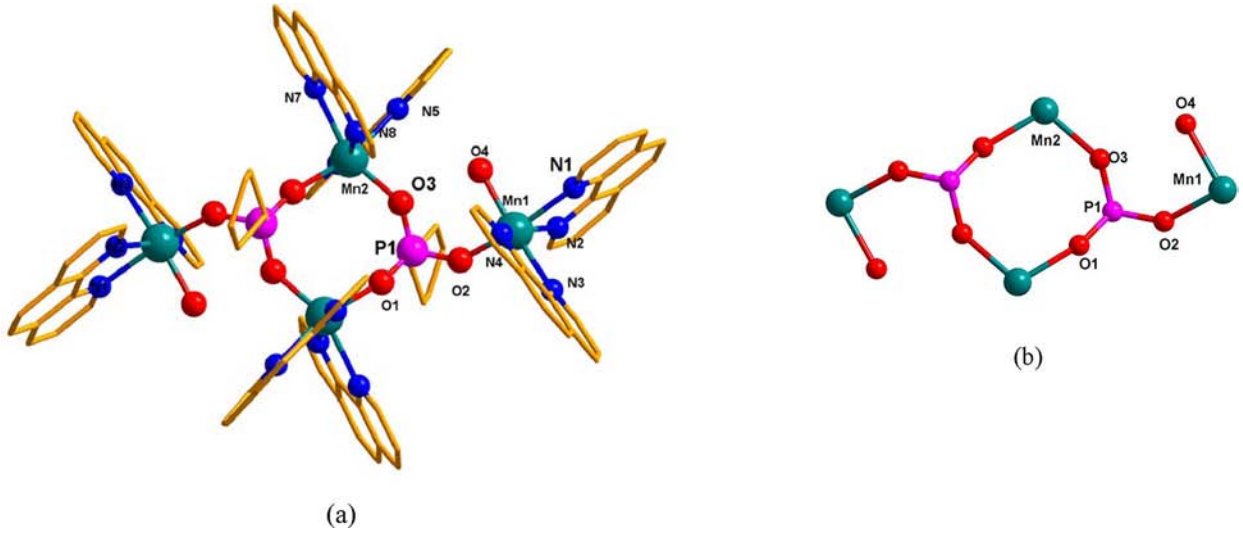

Figure 4. (a) Molecular structure of **5**. All H atoms groups have been omitted for clarity. Important bond lengths (Å) and bond angles (deg): Mn1−O2, 2.055(3); Mn1−O4, 2.170(3); Mn2−O3, 2.108(3); Mn1−N2, 2.287(4); Mn1−N1, 2.319(4); P1−O1, 1.513(3); P1−O2, 1.526(3); P1−O3, 1.540(3); O2−Mn1−O4, 84.6(1); O1−Mn2−O3, 106.1(1); N3−Mn1−N4, 73.7(1); O1−P1−O2 111.3(2); O1−P1−O3, 112.2(2); O2−P1−O3, 110.6(2). (b) Core framework of **5** showing the interconnected Mn, O, and P atoms.

analytical van Vleck equation can be derived using the spin Hamiltonian $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2)$. This equation can be used to fit the experimental data, giving the best-fitting parameters g = 2.01 and $J = -0.015$ cm^{-1}. The best fit is shown in Figure 5 as a solid line.

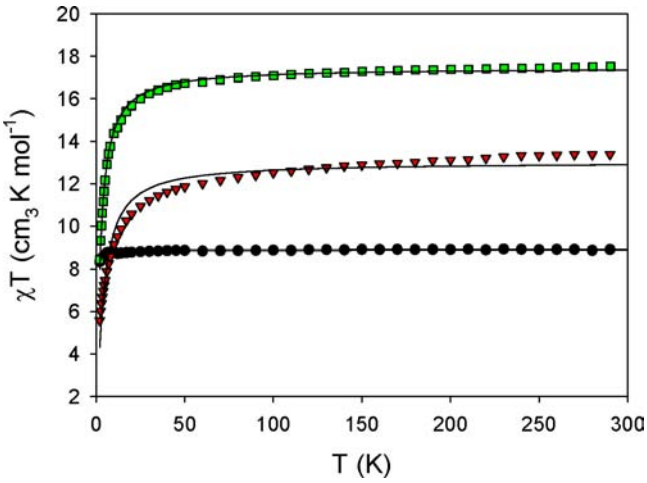

Figure 5. $\chi_M T$ vs T plot for complexes **1** (black), **2** (red), and **4** (green). The solid lines are the best fits to the experimental data.

The χT product for complex **2** has a value of 13.4 cm^3 K mol^{-1} at 300 K at an applied field of 0.3 T, in agreement with the expected value for two isolated Mn^{II} ions with $S = {}^5/_2$ and g = 2.0 (4.375 cm^3 K mol^{-1} per Mn^{II} ion). As the temperature decreases, the χT product slightly decreases, remaining nearly constant. Below 50 K, a sharp decrease is observed to a value of 5.5 cm^3 K mol^{-1}. An analytical van Vleck equation can be derived using the spin Hamiltonian $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3)$. This equation can be used to fit the experimental data, giving the best-fit parameters g = 1.99 and $J = -0.17$ cm^{-1}. The best fit is shown in Figure 5 as a solid line.

The χT product for complex **4** has a value of 17.5 cm^3 K mol^{-1} at 300 K at an applied field of 0.3 T, in agreement with the expected value for two isolated Mn^{II} ions with $S = {}^5/_2$ and g = 2.0 (4.375 cm^3 K mol^{-1} per Mn^{II} ion). As the temperature decreases, the χT product slightly decreases, remaining nearly constant. Below 50 K, a sharp decrease is observed to a value of 8.2 cm^3 K mol^{-1}. An analytical van Vleck equation can be derived using the spin Hamiltonian $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4 + \hat{S}_3 \cdot \hat{S}_4]$. This equation can be used to fit the experimental data, giving the best-fitting parameters g = 1.99 and $J = -0.09$ cm^{-1}. The best fit is shown in Figure 5 as a solid line.

In all of the three cases, the data corroborate the already expected weak coupling between Mn^{II} ions linked by organic phosphonato bridges. The calculated exchange couplings are all very weak and antiferromagnetic; thus, the spin ground state S = 0 for complexes **1**, **2**, and **4** is not isolated (Figure 6).

CONCLUSION

In summary, we have synthesized five different kinds of discrete manganese phosphonate clusters with different kinds of

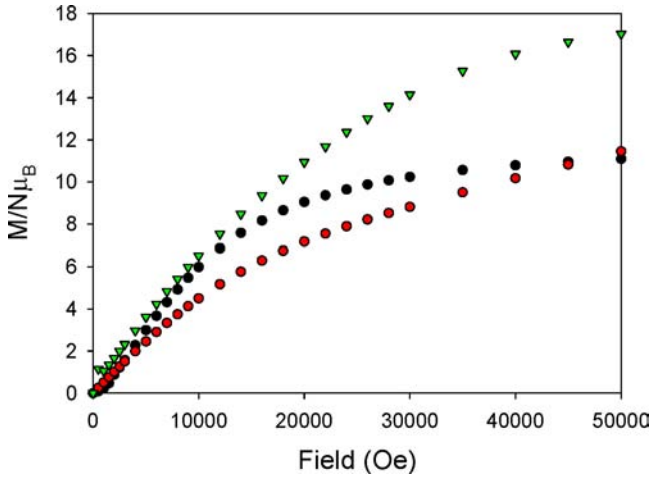

Figure 6. Reduced magnetization vs field plot for complexes **1** (black), **2** (red), and **4** (green) at 2 K.

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phosphonic acids in the presence of phen or dpzpy as the coligand at room temperature. Magnetic studies reveal that manganese(II) phosphonate complexes display weak antiferromagnetic coupling mediated by the phosphonate ligands. This is similar to what has been previously observed for other metal ions when using phosphonate ligands: the relative strength of the coupling mediated by phosphonato ligands is always weaker than that mediated by a carboxylate group.[23,24]

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, bond lengths and angles and coordination geometry for **1**−**5**, coordination environment and degree of trigonality values for **1** and **3**, Mn−O−P cores for **1**−**5**, ESI-MS spectra, thermogravimetric and DSC analyses, and reduced magnetization versus field plot. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vc@iitk.ac.in (V.C.), esanudo@ub.edu (E.C.S.).

Notes

The authors declare no competing financial interest.

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