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Preparation and single-crystal characterization of manganese(II) complexes of dichalcogenoimidodiphosphinato ligands. Monomeric versus dimeric $Mn[(OPPh_2)(XPPh_2)N]_2$ (X = S, O)

Ildiko Szekely^a, Cristian Silvestru^{a,*1}, John E. Drake^{b,*2}, Gabor Balazs^a, Sorin I. Farcas^c, Ionel Haiduc^a

^a Facultatea de Chimie, Universitatea 'Babes-Bolyai', RO-3400 Cluj-Napoca, Romania ^b Department of Chemistry and Biochemistry, University of Windsor Windsor, Ont., Canada N9B 3P4 ^c Institute for Isotopic and Molecular Technology, PO Box 700, RO-3400, Cluj-Napoca 5, Romania

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Abstract

Manganese(II) compounds of the type $Mn[(XPR_2)(YPR'_2)N]_2$ (X, Y = O, S; R, R' = Me, Ph), were prepared by metathesis reactions between $MnCl_2 \cdot 4H_2O$ and the alkaline salt of the corresponding ligand. IR data are consistent with the coordination of the phosphorus ligand in a deprotonated form. The ESR spectra exhibit resolved hyperfine structure only for the $Mn[(OPMe_2)(SPPh_2)N]_2$ derivative. The crystal and molecular structures of $Mn[(OPPh_2)(YPPh_2)N]_2$ (Y = O, S) were determined by X-ray diffractometry. The crystal of the tetraphenylthioimidodiphosphinato derivative contains monomeric, spiro-bicyclic $Mn[(OPPh_2)(SPPh_2)N]_2$ units, with a distorted tetrahedral MnO_2S_2 core, as a result of monometallic biconnective phosphorus ligands. By contrast, in the crystal of the tetraphenylimidodiphosphinato analogue distinct $[Mn\{(OPPh_2)_2N\}_2]_2$ dimers are present, in which the MnO_5 core has a trigonal bipyramidal geometry. The coordination pattern of the four imidodiphosphinato ligands differs. Two of them act as monometallic biconnective (chelating) units, leading to six-membered MnO_2P_2N rings. The other two ligands act as bimetallic triconnective units, which results in a fused tricyclic $Mn_2O_4P_4N_2$ system. The central four-membered Mn_2O_2 ring is slightly bent [Mn(1)O(5)O(8)/Mn(2)O(5)O(8) dihedral angle 23.9°]. The overall conformation of the $[Mn\{(OPPh_2)_2N\}_2]_2$ dimer might be described as *cis*, i.e. with six-membered MnO_2P_2N rings formed by ligands of the same type placed on the same side of the four-membered Mn_2O_2 ring. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Over the past several years ligands of the type $(XPR_2)(YPR'_2)NH$ (R, R' = Me, Prⁱ, Ph; X, Y = O, S, Se), which can be considered to be inorganic analogues of β -diketonates, enjoyed renewed interest in the coordination chemistry of both main group and transition metals [1–6]. In some cases significant structural differences were noted depending on the nature of the organic groups and chalcogens attached to phosphorus atoms. Thus, Ni[(SPR₂)(SPR'₂)N]₂ complexes contain-

ing symmetric ligands ($\mathbf{R} = \mathbf{R'} = \mathbf{Me}$ [7], Ph [8,9]), exhibit a tetrahedral NiS₄ core, while the complex of the related asymmetric ligand, Ni[(SPMe₂)(SPPh₂)N]₂, shows a square-planar NiS₄ core [8]. On the other hand, differences were also noted between the structures of [(XPR₂)(YPR'₂)N] metal complexes and the related β-diketonato derivatives, e.g. Co[(SPMe₂)(SPR₂)N]₂ ($\mathbf{R} =$ Me [10], Ph [11]) and Co[(SCMe)₂CH]₂ [12], which exhibit tetrahedral and square-planar CoS₄ cores, respectively. Conformational differences of the inorganic MXYP₂N rings have also been reported [13,14].

So far, only the molecular structure of the monomeric $Mn[(SPPh_2)_2N]_2$ [15] and $Mn[(OPPh_2)_2N]_3$ [16], which exhibit tetrahedral MnS_4 and octahedral MnO_6 , respectively, have been reported. By contrast,

¹ *Corresponding author. Fax: +40-64-190 818; cristi@ chem.ubbcluj.ro

² *Corresponding author.

the Mn(II) acetylacetonate derivative is a trimer, all manganese atoms exhibiting octahedral MnO₆ cores as a result of the bimetallic triconnective coordination of the ligands [17]. Here we report the synthesis of Mn[(XPR₂)(YPR'₂)N]₂ (X, Y = O, S; R, R' = Me, Ph) complexes and the X-ray structures of monomeric Mn[(OPPh₂)(SPPh₂)N]₂ and dimeric [Mn{(OPPh₂)₂-N}₂]₂ [18]³.

2. Experimental

Sodium or potassium dichalcogenoimidodiphosphinates were prepared according to published methods: Na[(OPPh₂)₂N] [19], K[(SPPh₂)₂N] [20], K[(OPPh₂)-(SPPh₂)N] [21], K[(SPMe₂)(OPPh₂)N], Na[(OPMe₂)-(SPPh₂)N] [22]. The IR spectra were recorded using KBr pellets on a Specord 75 IR C. Zeiss–Jena (DDR) instrument, in the range 4000–400 cm⁻¹. ESR measurements were performed on powder compounds at room temperature (r.t.) on a Radiopan SE/X-2543 9GHz ESR spectrometer, using a 100 kHz field modulation.

2.1. Synthesis of $Mn[(XPR_2)(YPR'_2)N]_2$ (1-4)

K[(OPPh₂)(SPPh₂)N] (0.97 g, 2.05 mmol) was added to a solution of MnCl₂·4H₂O (0.20 g, 1.01 mmol) in methanol (50 ml), and the mixture was stirred for 24 h at r.t. The solvent was then completely removed in vacuo, and the remaining solid product was extracted with chloroform (30 ml). The filtrate was evaporated to dryness leading to a white solid. Then colourless crystals of Mn[(OPPh₂)(SPPh₂)N]₂ (1) were obtained from chloroform. Yield: 0.91 g (98%), m.p. 183–184°C. *Anal.* Found: C, 62.3; H, 4.1; N, 2.8. C₄₈H₄₀N₂O₂P₄S₂Mn requires: C, 62.7; H, 4.4; N, 3.0%. IR (cm⁻¹): $v_{as}(P_2N)$ 1250vs; v(PO) 1130vs; v(PS) 570vs. ESR (X band): g 1.932 ± 0.001.

Similarly were obtained:

Mn[(OPPh₂)₂N]₂ (**2**) from Na[(OPPh₂)₂N] (0.99 g, 2.25 mmol) and MnCl₂·4H₂O (0.24 g, 1.21 mmol); colourless crystals obtained from chloroform. Yield: 0.83 g (77%), m.p. 302–304°C. *Anal.* Found: C, 64.4; H, 4.2; N, 3.1. C₄₈H₄₀N₂O₄P₄Mn requires: C, 64.9; H, 4.5; N, 3.2%. IR (cm⁻¹): v_{as} (P₂N) 1240vs; v(PO) 1150vs; 1110vs. ESR (X band): g 1.932 ± 0.001.

 $Mn[(SPMe_2)(OPPh_2)N]_2$ (3) from $K[(SPMe_2)-(OPPh_2)N]$ (0.79 g, 2.27 mmol) and $MnCl_2 \cdot 4H_2O$ (0.22 g, 1.13 mmol); colourless crystals obtained from chloroform. Yield: 0.72 g (95%), m.p. 192–194°C. Anal.

Found: C, 49.9; H, 4.5; N, 3.9. $C_{28}H_{32}N_2O_2P_4S_2Mn$ requires: C, 50.1; H, 4.8; N, 4.2%. IR (cm⁻¹): $v_{as}(P_2N)$ 1200vs; v(PO) 1135vs; v(PS) 565vs, 550vs. ESR (X band): g 1.932 \pm 0.001.

Mn[(OPMe₂)(SPPh₂)N]₂ (4) from Na[(OPMe₂)-(SPPh₂)N] (0.79 g, 2.38 mmol) and MnCl₂·4H₂O (0.23 g, 1.16 mmol); colourless crystals obtained from chloroform. Yield: 0.65 g (83%), m.p. 156–158°C (dec.). *Anal.* Found: C, 49.8; H, 4.6; N, 3.8. $C_{28}H_{32}N_2O_2P_4S_2Mn$ requires: C, 50.1; H, 4.8; N, 4.2%. IR (cm⁻¹): $v_{as}(P_2N)$ 1200vs; v(PO) 1140vs; v(PS) 600vs. ESR (X band): g 1.98 ± 0.02, A 78 Gs.

2.2. Crystallographic structure determination

Details of the data collections and refinements are summarized in Table 1. Several attempts failed to produce high quality crystals. The results are those from the best collections that could be obtained from crystals that proved to be of relatively poor X-ray quality.

Table 1

Crystallographic data for $Mn[(OPPh_2)(SPPh_2)N]_2$ (1) and $Mn_2\mathchar`-[(OPPh_2)_2N]_4$ (2)

	1	2
Molecular formula	$C_{48}H_{40}N_2O_2P_4S_2Mn$	$C_{96}H_{80}N_4O_8P_8Mn_2$
M	919.81	1775.38
Crystal system	monoclinic	triclinic
Space group	$P2_{1}/c$	$P\overline{1}$
Radiation	Μο Κα	Μο Κα
a (Å)	12.6851(2)	14.335(3)
b (Å)	18.2333(1)	22.712(6)
<i>c</i> (Å)	19.4760(3)	14.308(3)
α (°)		96.60(2)
β (°)	100.611(1)	105.21(2)
γ (°)		81.78(2)
V (Å ³)	4427.6(1)	4434(1)
Ζ	4	2
Crystal size (mm)	$0.40 \times 0.38 \times 0.36$	$0.44 \times 0.40 \times 0.40$
$D_{\rm c}~({\rm g~cm^{-3}})$	1.38	1.33
F_{000}	1900.00	1836.00
2θ Range (°)	50	50
μ (Mo K α) (cm ⁻¹)	5.78	4.88
Max./min. transmission factors	1.00-0.45	1.00-0.77
Temperature (°C)	23	23
Reflections measured	10875	15591
Reflections observed $[F_o^3 \ge 3\sigma F_o)], N_o$	2814	4589
Parameters refined, $N_{\rm p}$	292	583
Largest shift/e.s.d. in final cycle	0.001	0.001
Max./min. residual density peaks (e Å ⁻³)	0.53, -0.41	0.42, -0.45
R ^a	0.0614	0.0693
<i>R</i> ′ ^b	0.0778	0.0603
Goodness of fit, ° S	1.37	2.04

^a $R = \Sigma |F_{o}| - |F_{c}| / \Sigma |F_{o}|.$

^b
$$R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2}$$
, where $w = 1/\sigma^2 (F_o)$.

 $^{\circ} S = [\Sigma(|F_{o}| - |F_{c}|)/\sigma]/(N_{o} - N_{p}).$

 $^{^{3}}$ A preliminary communication on the structure of [Mn-{(OPPh_2)_2N}_2]_2 was previously presented at The VIII International Symposium on Inorganic Ring Systems, Loughborough, UK, August 1997, Ref. [18].

Colourless block crystals of $Mn[(OPPh_2)(SPPh_2)N]_2$ (1) and $Mn_2[(OPPh_2)_2N]_4$ (2) were mounted on glass fibres and sealed with epoxy glue. Data were collected on a Siemens SMART/CCD system (for 1) and on a Rigaku AFC6S diffractometer (for 2) both with graphitemonochromated Mo Ka radiation, operating at 50 kV and 35 mA, the processed data for 1 being supplied by the X-ray services at the University of Windsor under the control of Dr D.W. Stephan. The data were corrected for Lorentz and polarization effects. Based on statistical analyses of intensity distributions and the successful solution and refinement of the structure, the space groups were determined to be $P2_1/c$ (no. 14) and $P\overline{1}$ (no. 2). The structures were solved by direct methods [23]. All of the non-hydrogen atoms except carbon were refined anisotropically. The positions of the hydrogens were idealized, with thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Refinements were by full-matrix least-squares based on F using the TEXSAN [24] crystallographic package of Molecular Structure Corporation. Neutralatom scattering factors were taken from Cromer and Waber [25]. Anomalous dispersion effects were included in F_c [26]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [27].

3. Results and discussion

Reaction of MnCl₂·4H₂O with tetraorganodichalcogenoimidodiphosphinate salts gave compounds 1–4 in very good yields. All compounds gave satisfactory elemental analyses and were characterized by IR spectroscopy. The strong IR absorptions observed for the Mn(II) complexes in the regions 1250–1200, 1150– 1110 and 600–550 cm⁻¹ were assigned to $v_{as}(P_2N)$, v(PO), and v(PS) stretching vibrations, respectively, by comparison with the spectra of the proligands and their alkaline salts. This behaviour is consistent with the coordination of the ligands in the deprotonated form through both chalcogens to the manganese atom.

All compounds exhibited a wide ESR spectrum (ca. 5000 Gs) of five fine structure lines as expected for Mn(II) ions. The line width was around 500 Gs and the distance between two fine structure lines is about 1000 Gs. The magnitude of these values is consistent with a strong crystal field around the paramagnetic ion. Only for the Mn[(OPMe₂)(SPPh₂)N]₂ (4) derivative was a hyperfine structure of 78 Gs observed on a line (413 Gs width), at a g factor of 1.98 ± 0.02 . This spectrum is superimposed on the wide, low intensity, fine structure spectrum, similar to those observed for the other manganese(II) compounds. This particular behaviour might suggest the presence of some paramagnetic ion clusters in this sample.

Table 2

Important bond lengths (Å) and angles (°) for $Mn[(OPPh_2)-(SPPh_2)N]_2$ (1)

Bond lengths			
Mn(1)–O(1)	2.041(6)	Mn(1)–O(2)	2.030(7)
Mn(1)-S(1)	2.448(4)	Mn(1)-S(2)	2.446(3)
P(1)–O(1)	1.559(7)	P(3)–O(2)	1.535(7)
P(1)–N(1)	1.582(9)	P(3)–N(2)	1.588(8)
P(2)–N(1)	1.577(9)	P(4)–N(2)	1.578(8)
P(2)-S(1)	2.012(4)	P(4)–S(2)	2.016(4)
O(1)…S(1) ^a	3.595(8)	O(2)…S(2) ^a	3.547(7)
Bond angles			
O(1)-Mn(1)-S(1)	106.0(2)	O(2)-Mn(1)-S(2)	104.5(2)
O(1)-Mn(1)-S(2)	114.6(2)	O(2)-Mn(1)-S(1)	113.2(2)
O(1)–Mn(1)–O(2)	108.9(3)	S(1)-Mn(1)-S(2)	109.9(1)
Mn(1)–O(1)–P(1)	125.7(4)	Mn(1)-O(2)-P(3)	125.6(4)
O(1) - P(1) - N(1)	118.5(4)	O(2) - P(3) - N(2)	117.6(4)
P(1)-N(1)-P(2)	134.2(6)	P(3)-N(2)-P(4)	136.1(5)
S(1)-P(2)-N(1)	118.5(4)	S(2)-P(4)-N(2)	118.2(3)
Mn(1)-S(1)-P(2)	98.5(2)	Mn(1)-S(2)-P(4)	95.7(1)

^a Non-bonding distances.

The crystal and molecular structure of Mn- $[(OPPh_2)(SPPh_2)N]_2$ and Mn $[(OPPh_2)_2N]_2$ were established by single-crystal X-ray diffractometry, revealing interesting differences on both the coordination patterns of the phosphorus ligands and the coordination geometry at the metal atom.

3.1. Molecular structure of $Mn[(OPPh_2)(SPPh_2)N]_2$ (1)

Selected bond distances and angles in Mn[(OPPh₂)-(SPPh₂)N]₂ are listed in Table 2 and Fig. 1 shows the ORTEP plot of the molecular structure with the atom numbering scheme.



Fig. 1. An ORTEP plot of the monomeric $Mn[(OPPh_2)(SPPh_2)N]_2$ (1). The atoms are drawn with 30% probability ellipsoids (hydrogen atoms are omitted for clarity).

The crystal contains discrete monomeric molecules of 1 exhibiting a distorted tetrahedral MnO₂S₂ core in a spiro-bicyclic NP2OSMnSOP2N system, as a result of the monometallic biconnective coordination pattern of the ligand. The bond angles at Mn are in the range $104.5(2)-114.6(2)^\circ$, with both endocyclic angles O(1)-Mn(1)-S(1) [106.0(2)°] and O(2)-Mn(1)-S(2) $[104.5(2)^{\circ}]$ less than the tetrahedral value (Table 2). The dihedral angle between the O(1)Mn(1)S(1) and O(2)Mn(1)S(2) planes is 86.7°. The Mn–S bond lengths [av. 2.447(1) Å] $[28]^4$ are of the same magnitude as observed for the dithio derivative $Mn\{(SPPh_2)_2N\}_2$ [av. 2.443(12) Å] [15], while the Mn-O bond lengths [av. 2.036(8) Å] are significantly shorter than those observed in the monomeric, octahedral complexes Mn[(OCMe)₂-CH]₂(1,10-Phen) [2.116(5), 2.152(5) Å] [29] or trans-Mn[(OCPh)₂CH]₂(THF)₂ [2.088(1), 2.136(1) Å] [30]. The P-N-P angles are slightly increased [av. 135.2(1.5)°] compared with those observed in the (OPPh₂)(SPPh₂)NH [av. 132.2(1.1)°] [31]. The phosphorus-sulfur [av. 2.014(1) Å] and phosphorus-oxygen [av. 1.547(17) Å] bond lengths in 1 are longer than those of the proligand [av. P–O 1.503(16) Å; av. P–S 1.925(14) Å] [31]. The phosphorus–nitrogen bonds are equivalent regardless of the nature of the chalcogen atom attached to phosphorus, and their magnitude [av. 1.581(5) Å] is clearly consistent with a considerable degree of double bond character [cf. (OPPh2)(SPPh2)NH [31]: av. P-N 1.680(12) Å; $[(Me_3Si)_2N-P(=NBu^t)S]_2$ [32]: P=N 1.529(2) Å, P-N 1.662(2) Å]. The two six-membered MnSOP₂N chelate rings are not planar, but display conformations, i.e. twisted boat and twisted chair with P(1)/S(1) and P(3)/S(2) atoms, respectively, in the apices.

3.2. Molecular structure of $Mn_2[(OPPh_2)_2N]_4$ (2)

Selected bond distances and angles for the imidodiphosphinato analogue **2** are listed in Table 3 and Fig. 2 shows the ORTEP plot of the molecular structure (only the *ipso* carbons are shown) with the atom numbering scheme.

In contrast to the monomeric $Mn[(OPPh_2)-(SPPh_2)N]_2$, the crystal of **2** contains distinct [Mn-{ $(OPPh_2)_2N$ }_2]_2 dimers, which are separated by normal van der Waals distances. All four imidodiphosphinato ligands coordinate through both oxygen atoms to manganese, but in a different mode. Two of them act as monometallic biconnective ligands (type A) [av. Mn–O 2.069(19) Å], leading to six-membered MnO_2P_2N rings. The other two act as bimetallic triconnective ligands

Table 3

Selected bond lengths (Å) and angles (°) for $Mn_2[(OPPh_2)_2N]_4$ (2)

Bond lengths			
Mn(1) - O(1)	2.057(8)	Mn(2)–O(3)	2.097(8)
Mn(1)–O(2)	2.056(8)	Mn(2)–O(4)	2.065(8)
Mn(1)–O(7)	2.063(8)	Mn(2)–O(6)	2.026(8)
Mn(1)–O(8) (bridging)	2.267(7)	Mn(2)–O(5) (bridging)	2.382(7)
Mn(1)–O(5) (bridging)	2.109(7)	Mn(2)–O(8) (bridging)	2.107(7)
P(1)-O(1)	1.508(8)	P(3)-O(3)	1.516(8)
P(1)–N(1)	1.58(1)	P(3)–N(2)	1.59(1)
P(2)–N(1)	1.60(1)	P(4)–N(2)	1.594(9)
P(2)–O(2)	1.498(8)	P(4)–O(4)	1.513(8)
P(5)-O(5)	1.526(7)	P(7)–O(7)	1.524(8)
P(5)-N(3)	1.57(1)	P(7)–N(4)	1.584(9)
P(6)-N(3)	1.60(1)	P(8)–N(4)	1.571(9)
P(6)-O(6)	1.508(8)	P(8)–O(8)	1.535(7)
O(1)…O(2) ^a	2.91(1)	O(3)…O(4) ^a	3.00(1)
O(5)…O(6) ^a	3.07(1)	O(7)…O(8) ^a	3.10(1)
Bond angles			
O(1) - Mn(1) - O(2)	90.1(3)	O(3) - Mn(2) - O(4)	92.3(3)
O(1)-Mn(1)-O(7)	97.1(3)	O(3)-Mn(2)-O(6)	97.3(3)
O(1)-Mn(1)-O(5)	95.9(3)	O(3)-Mn(2)-O(8)	95.4(3)
O(2)-Mn(1)-O(8)	87.1(3)	O(4) - Mn(2) - O(5)	91.4(3)
O(7)-Mn(1)-O(8)	91.2(3)	O(5)-Mn(2)-O(6)	87.8(3)
O(5)-Mn(1)-O(8)	79.2(3)	O(5)-Mn(2)-O(8)	76.6(3)
O(1)-Mn(1)-O(8)	171.5(3)	O(3)-Mn(2)-O(5)	171.9(3)
O(2)-Mn(1)-O(5)	124.7(3)	O(4)-Mn(2)-O(8)	126.0(3)
O(2)–Mn(1)–O(7)	119.9(4)	O(6)-Mn(2)-O(8)	118.2(3)
O(5)-Mn(1)-O(7)	113.8(3)	O(4)-Mn(2)-O(6)	113.6(3)
Mn(1)-O(5)-Mn(2)	97.4(3)	Mn(1)-O(8)-Mn(2)	101.1(3)
Mn(1)-O(1)-P(1)	133.8(5)	Mn(2)–O(3)–P(3)	129.9(5)
O(1) - P(1) - N(1)	117.2(5)	O(3)-P(3)-N(2)	118.4(5)
P(1)-N(1)-P(2)	126.8(6)	P(3)–N(2)–P(4)	123.5(6)
O(2)-P(2)-N(1)	118.0(5)	O(4)-P(4)-N(2)	118.5(5)
Mn(1)-O(2)-P(2)	133.3(5)	Mn(2)–O(4)–P(4)	127.5(5)
Mn(1)-O(7)-P(7)	126.3(5)	Mn(2)-O(5)-P(5)	120.8(4)
O(7)–P(7)–N(4)	116.9(5)	O(5)-P(5)-N(3)	116.6(5)
P(7)-N(4)-P(8)	133.8(6)	P(5)-N(3)-P(6)	129.6(6)
O(8)-P(8)-N(4)	116.2(5)	O(6)-P(6)-N(3)	117.9(5)
Mn(1)-O(8)-P(8)	121.1(4)	Mn(2)–O(6)–P(6)	134.1(5)
Mn(1)-O(5)-P(5)	141.6(5)	Mn(2)-O(8)-P(8)	137.1(4)

^a Non-bonding distances.

(type **B**), resulting in a fused tricyclic $Mn_2O_4P_4N_2$ system. The Mn-O(bridging) distances differ and are longer than those involving the non-bridging oxygen atom (Table 3). For a given OPNPO fragment the P-O and P-N bond lengths are equivalent regardless of the coordination pattern of the oxygen atoms, i.e. av. P-O 1.511(9), P-N 1.593(10) Å for the A-type ligands and av. P-O 1.531(5), P-N 1.571(10) Å for the B-type ligands, respectively. The four six-membered MnO₂P₂N inorganic rings display different conformations. For the monometallic biconnective A-type ligands the rings are quasi-planar [deviations from the $Mn(1)O_2P_2N$ plane are: Mn(1) - 0.009, O(1) 0.039, O(2) = 0.005, P(1) = 0.051, P(2) = 0.006, N(1) 0.033Å] and twisted chair [with Mn(2)/N(2) atoms in the apices]. The MnO₂P₂N rings formed by the bimetallic triconnective **B**-type ligands are slightly distorted from

⁴ E.s.d.s for average bond lengths are calculated from the equation $\sigma = [\Sigma_{i=l}^{i=N}(x_i - x)^2/(N-1)]^{1/2}$, where x_i is ith bond length and x is the mean of the N equivalent bond lengths. An analogous formula is used for the calculation of e.s.d.s for average bond angles.



Fig. 2. An ORTEP plot of the dimeric $[Mn\{(OPPh_2)_2N\}_2]_2$ (2). The atoms are drawn with 30% probability ellipsoids (for clarity, only the *ipso* carbons are shown).

planarity towards a boat conformation, with O(5)/P(6) and Mn(1)/N(4) atoms, respectively, in the apices.

The coordination geometry of central manganese atom is distorted trigonal bipyramidal as reflected by the bond angles: O_{ax} -Mn- O_{ax} (av.) 171.7(1)°, O_{eq} -Mn- O_{eq} (range) 113.6(3)–126.0(3)°, O_{ax} -Mn- O_{eq} (range) 76.6(3)–97.3(3)°. The equatorial MnO₃ systems are quasi-planar [deviations from Mn(1)O(2)O(5)O(7) and Mn(2)O(4)O(6)O(8) are Mn(1) – 0.119, O(2) 0.042, O(5) 0.39, O(7) 0.038 Å, and Mn(2) – 0.137, O(4) 0.046, O(6) 0.043, O(8) 0.048 Å, respectively], with the manganese atoms slightly out-of-plane towards the axial non-bridging oxygen atom. The sum of O_{eq} -Mn- O_{eq} is close to 360° [$\Sigma(O_{eq}$ -Mn- $O_{eq})_e$ = 358.4° for Mn(1), and 357.8° for Mn(2)].

The central four-membered Mn₂O₂ ring is slightly folded [Mn(1)O(5)O(8)/Mn(2)O(5)O(8) dihedral angle 23.9°], with a non-bonding Mn(1)...Mn(2) distance of 3.378(3) A. The overall conformation of the $[Mn\{(OPPh_2)_2N\}_2]_2$ dimer might be described as *cis*, i.e. with six-membered MnO₂P₂N rings formed by ligands of the same type placed on the same side of the four-membered Mn₂O₂ ring, resulting in a 'butterfly'like structure (Fig. 3(a)). This contrasts with the overall trans conformation observed for the ladder structure of the $[Mn(S_2PEt_2)_2]_2$ dimer [33] (Fig. 3(b)), which also contains five-coordinate metal atoms. The dimeric structure of $[Mn\{(OPPh_2)_2N\}_2]_2$ also contrasts with that of the Mn(II) acetylacetonate, which is associated into trimeric units in the solid state [17] (Fig. 3(c)). The decrease in the degree of association and the coordination number at the metal atom is probably due to the bulky imidodiphosphinato ligand. It should be noted here that dimeric, i.e. [Mn{(OCMe)₂CH}₂(NH₂CH₂-CH=CH₂)]₂ [34], and monomeric structures, i.e. trans- $Mn[(OCR)_2CH]_2(L)_2$ (R = Ph, L = THF [30]; R = CF₃, $L = H_2O$ [35]), have also been reported and in all these cases the manganese atom is exhibiting an octahedral core.



Fig. 3. View of (a) $Mn_2[(O_2P_2N]_4$ core in the dimeric $[Mn\{(OPPh_2)_2N\}_2]_2$; (b) dimeric $[Mn(S_2PEt_2)_2]_2$ structure; (c) $Mn_3[(O_2C_3]_6$ core in the trimeric $[Mn\{(OCMe)_2CH\}_2]_3$.

4. Supplementary material

The complete listing of the crystal data is provided in the Supporting Information which contains tables giving final fractional coordinates and B_{eq} for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates and B_{eq} for hydrogen atoms, all bond lengths and angles and OR-TEP drawings for Mn[(OPPh₂)(SPPh₂)N]₂ and Mn[(OPPh₂)₂N]₂ (19 pages). Structure factor tables are available from the authors (J.E.D.).

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