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Crystal and molecular structure of Mn[(OPPh₂)₂N]₃ · CH₂Cl₂, a new monomeric manganese(III) complex stabilized by oxygen chelating ligands

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Abstract—The reaction between $[Mn(CO)_5]Br$ and $Na[(OPPh_2)_2N]$ in argon atmosphere affords the preparation of $Mn(CO)_4[(OPPh_2)_2N]$ as a white powder. During attempts to grow X-ray diffraction quality crystals the tetracarbonylmanaganese(I) complex was oxidized and deep purplish-blue crystals were isolated. An X-ray diffractometry analysis has revealed the identity of the new product, i.e. the manganese(III) derivative, $Mn[(OPPh_2)_2N]_3 \cdot CH_2Cl_2$. The compound crystallizes in the triclinic space group *P*-1 and the crystal contains discrete, monomeric molecules of $Mn[(OPPh_2)_2N]_3$. The imidodiphosphinato groups are coordinated through both oxygen atoms of a ligand moiety to the central manganese atom. The resulted coordination octahedron exhibits a tetragonally elongated distortion as reflected by the Mn—O bond lengths [av. 2.130(16), 1.945(6) Å] and *cis* O—Mn—O bond angles [endocyclic (av.) 90.5(0.6)°; exocyclic (range) 87.2(0.1)–92.7(0.1)°]. The structure of the title compound is compared with those of other monomeric manganese(III) derivatives containing MnO₆ cores with various degrees of distortion. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: manganese(III) complexes; imidodiphosphinato.

Recently we have described the synthesis and the molecular structure of the monomeric complex Mn(CO)₄[(SPPh₂)₂N] [1]. Our interest in the investigation of metal complexes containing such ligands prompted us to attempt the preparation of the dioxo analog in order to establish structural changes which might be produced by changes in the chalcogen atoms attached to phosphorus. Several previous studies using phosphorus ligands have proved that modification in the organic groups or chalcogen atoms at phosphorus may result in dramatic structural changes [2] not only in the case of Main Group metal compounds [e.g. lead compounds, Pb(S₂PR₂)₂ [3,4], inorganic and organoantimony(III) and antimony(V) compounds [5], but also for transition metal compounds [e.g. Ni[$(SPR_2)_2N$]₂, R = Me [6], Ph [7,8] exhi-

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bit a tetrahedral NiS₄ core, Ni[(SPMe₂)(SPPh₂)N]₂, has a square-planar NiS₄ core [8], while the dinuclear $\{Ni_2[(OPPh_2)_2N]_4(H_2O)\}$ contains two different octahedral NiO₆ cores [9].

We wish to report here the molecular structure of the manganese(III) complex, $Mn[(OPPh_2)_2N]_3$. CH_2Cl_2 , produced via aerial oxidation during recrystallization of the product isolated by reacting $[Mn(CO)_5]Br$ and $Na[(OPPh_2)_2N]$. It should be noted that the oxygen-donor ligands are known to stabilize manganese(III) species [10].

EXPERIMENTAL

 $[Mn(CO)_{5}]Br$ [11] was obtained according to literature. IR spectra were obtained in KBr disk (4000–200 cm⁻¹) using a Perkin–Elmer 283B spectrometer. ¹H, ¹³C and ³¹P NMR spectra were recorded using Varian Gemini 200 and Varian VXR 300S instruments. The chemical shifts are reported in ppm relative to TMS and H₃PO₄ 85%, respectively.

Preparation of tetraphenylimidodiphosphinic acid, (OPPh₂)₂HN [12]

A slight excess of H_2O_2 30% (14 ml) was added dropwise to a suspension of (PPh₂)₂NH (20 g, 0.05 mol) in 200 ml THF, and the reaction mixture was stirred over night. The resulting white, solid product was filtered, washed with THF and dried in air. Yield : 21 g (97%), m.p. = 275–277°C (lit. [12] 268–269°C). IR (KBr, cm⁻¹) : v(PO) 1120 s, 1105 s; v_{as} (P₂NH) 920 s. ¹H NMR (CDCl₃, 200 MHz) : 7.35 m (3H, C₆H₅meta + para), 7.80 ddd [2H, C₆H₅-ortho, ³J(PH) 12.8, ³J(HH) 7.5, ⁴J(HH) 1.5 Hz]. ¹³C NMR (CDCl₃, 50 MHz) : 128.24 m [C_m, ³J(PC) 13.0 Hz], 131.96 s (C_p), 131.96 m [C_o, ²J(PC) 10.9 Hz], 134.33 d [C_i, ¹J(PC) 101.6 Hz]. ³¹P NMR (CDCl₃, 121.4 MHz) : 19.4 s.

Preparation of sodium tetraphenylimidodiphosphinate, Na[(OPPh₂)₂N] [13]

(OPPh₂)₂NH (4.5 g, 10.8 mmol) and NaOMe (0.6 g, 11 mmol) in 100 ml ethanol were stirred for 6 h, at room temperature. The insoluble solid product was filtered, and the solvent was removed from the clear filtrate in a rotary evaporator to dryness. The remaining white solid was extracted several times in a Soxhlet apparatus using MeCN as solvent. The white crystals of the title compound which deposited from the MeCN extract were filtered and dried in vacuo. Yield : 3.3 g (70%), m.p. = $335-338^{\circ}$ C. IR (KBr, cm⁻¹): $v_{as}(P_2N)$ 1260 vs, 1220 vs; v(PO) 1140 vs, 1120 s. ¹H NMR (CD₃OD, 300 MHz): 7.18 m (3H, C₆H₅meta + para), 7.72 ddd (2H, C_6H_5 -ortho, ³*J*(PH) 12.3, ³J(HH) 7.7, ⁴J(HH) 1.9). ¹³C NMR (CD₃OD, 75 MHz): 128.52 m [$C_{\rm m}$, ${}^{3}J(PC)$ 12.7 Hz], 130.64 s ($C_{\rm p}$), 132.50 t $[C_0, {}^2J(PC) 9.8 \text{ Hz}]$, 140.86 d $[C_i, {}^1J(PC) 134.5 \text{ Hz}]$ Hz]. ³¹P NMR (CD₃OD, 121.4 MHz): 11.3 s.

Reaction of [Mn(CO)₅]Br with Na[(OPPh₂)₂N]

A stoichiometric amount of Na[(OPPh₂)₂N] (1.1 g, 2.55 mmol) was added to a solution of [Mn(CO)₅]Br (0.7 g, 2.55 mmol) in 100 ml anhydrous THF. The reaction mixture was stirred under reflux until the IR spectrum of the crude solution remained unchanged in the region characteristic for CO stretching vibrations. After 0.5 h the formation of a white solid was noted. The NaBr was filtered off and the removal of the solvent from the clear filtrate under vacuum resulted in an oily product. Recrystallization of this material from a THF/*n*-hexane (1 : 1) solvent mixture resulted in isolation of Mn(CO)₄[(OPPh₂)₂N] as a white solid. IR

(KBr, cm⁻¹): $v_{as}(P_2N)$ 1243 vs; v(PO) 1126 vs, 1097 s; v(CO) 2035 vs, 2008 vs, 1983 vs, 1924 vs.

X-ray crystal determination of Mn[(OPPh₂)₂N]₃

Empirical formula $C_{72}H_{60}N_3O_6P_6Mn\cdot CH_2Cl_2$, M = 1388.9, triclinic, a = 13.572(1), b = 13.852(1), c = 18.761(2)Å, $\alpha = 95.44(2)$, $\beta = 98.50(2)$, $\gamma = 97.08(2)^{\circ}, \quad U = 3438.7(5) \quad \text{Å}^3, \quad F(000) = 1436,$ $Z = 2, D_{\rm C} = 1.341 \text{ g cm}^{-3}$, space group P-1, μ (Cu- K_{α}) = 4.031 mm⁻¹, crystal size 0.28 × 0.26 × 0.24 mm. Purplish blue prisms of Mn[(OPPh₂)₂N]₃. [Anal. Calc. for C₇₂H₆₀N₃O₆P₆Mn·CH₂Cl₂: C, 63.1; H, 4.5; N, 3.0; Found : C, 62.8; H, 4.4; N, 2.8%; ES (CH₂Cl₂, cm⁻¹): 32,570, 18,250] were obtained from CH₂Cl₂/nhexane solution. Data were collected at room temperature (293 K) on a Siemens P4/PC four-circle diffractometer with parallel-graphite crystal monochromator (Cu–K_{α} radiation, $\lambda = 1.54178$ Å), for 9660 reflections of which 9194 were independent reflections $[R_{int} = 6.20\%]$ and 7287 $(F^2 > 2.0\sigma(F^2))$ were used in the full-matrix least-squares refinement with the SHELXL-97 program system [14]. The structure was solved by Patterson methods [15] and difference Fourier synthesis revealed the positions for the other non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated as a riding model with isotropic U. Semi-empirical absorption correction was applied based on ψ -scan (transmission: min. 0.0128, max. 0.7645). The CH₂Cl₂ solvent molecule was distorted and was modeled [14] in two positions for each atom; the site occupation factors were 0.30/0.70 for C(1a)/C(1b), Cl(1)/Cl(1a) and Cl(2)/Cl(2a), respectively. The final R values are $R_1 = \Sigma |F_0 - F_c| / |\Sigma| F_0| =$ 6.24% and $wR_2 = [\Sigma(w|F_0 - F_c])^2 / \Sigma w |F_0|^2]^{1/2} = 15.83\%$ with weights $w^{-1} = \sigma^2 (F_o^2) + (0.1003P)^2 + 2.8031P$, where $P = (F_o^2 - 2F_c^2)/3$; goodness-of-fit 1.009. The residual electron density from a final difference Fourier synthesis was in the range of 0.523, $-0.753 \text{ e}\text{\AA}^{-3}$.

RESULTS AND DISCUSSION

The tetraphenylimidodiphosphinic acid and its sodium salt were prepared using previously described procedures [12,13], and were characterized by IR and multinuclear NMR spectroscopy. The resonance signals observed in the ¹H and ¹³C NMR spectra of both compounds exhibit the expected pattern due to the proton-proton and proton-phosphorus, and carbonphosphorus couplings, respectively. A significant increase in the ${}^{1}J(PC)$ coupling constant from 101.6 Hz in the free acid to 134.5 Hz in the sodium salt was noted. In addition, when the ¹³C NMR spectrum of $Na[(OPPh_2)_2N]$ was recorded in DMSOd₆, the resonance for the *ipso* carbon was further split due to the coupling to the second phosphorus atom of the ligand unit $[{}^{1}J(PC) = 129.0 \text{ Hz}, {}^{3}J(PC) = 4.3 \text{ Hz}]$. However, ³¹P NMR spectra show only one broad resonance for

both phosphorus atoms, in the sodium salt the signal being shifted about 10 ppm to lower field due to delocalization of the electrons over the OPNPO fragment.

 $\begin{array}{ccc} The & carbonylmanganese(I) & complex, \\ Mn(CO)_4[(OPPh_2)_2N], \mbox{ was prepared by methatesis} \\ according to eq (1) \mbox{ and isolated as a white solid :} \end{array}$

$$[Mn(CO)_5]Br + Na[(OPPh_2)_2N] \rightarrow$$

$$Mn(CO)_4[(OPPh_2)_2N] + CO + NaBr$$
 (1)

Its IR spectrum shows a strong absorption assigned to $v_{as}(P_2N)$ stretching vibration at about 1243 cm⁻¹ which is consistent with the coordination of the ligand in its deprotonated form (cf $v_{as}(P_2NH)$ 920 cm⁻¹ in (OPPh₂)₂NH, and $v_{as}(P_2N)$ 1260, 1220 cm⁻¹ in Na[(OPPh₂)₂N]). In the carbonyl stretching region the expected four bands were observed (2035 vs, 2008 vs, 1983 vs, 1924 vs cm⁻¹, in KBr pellet, and 2051 vs, 2012 vs, 1980 m, and 1932 m cm⁻¹, in *n*-hexane solution), corresponding to non-degenerate v(CO) vibrations (2A₁+B₁+B₂) [16]. This behavior is characteristic of psuedooctahedral complexes with a carbonyl C_{2v} local symmetry, and is consistent with the coordination of the imidodiphosphinato ligand through both oxygen atoms.

A monomeric structure (**a**) might be proposed for this carbonylmanganese complex in solid state, similar to that established for the dithio analog [1]. However, a dimeric structure of type (**b**) cannot be ruled out.

Several attempts to grow X-ray quality crystals of $Mn(CO)_4[(OPPh_2)_2N]$ were performed using $CHCl_3/hexane$ and $CH_2Cl_2/hexane$ solutions but always decomposition of the starting material was achieved. The initial colorless solution became violet within few days and deposited purplish-blue crystals of the manganese(III) complex $Mn[(OPPh_2)_2N]_3$ (as proved by X-ray diffractometry—see below) together with an amorphous brown solid (probably MnO_2). The decomposition process might be described by eqn (2):

 $3 \operatorname{Mn}(\operatorname{CO}_4[(\operatorname{OPPh}_2)_2 N] + 2 \operatorname{O}_2 \rightarrow$

$$Mn[(OPPh_2)_2N]_3 + 2MnO_2 + 12CO$$
 (2)

Attempts to obtain the same manganese(III) compound by oxidizing the manganese(II) complex, $Mn[(OPPh_2)_2N]_2$ [17], with hydrogen peroxide both in water suspension or chloroform solution have failed. No color change was observed when air was bubbled about out 6 h through a CHCl₃ solution of Mn[(OPPh₂)₂N]₂. However after a long period of time during which the solvent was slowly evaporated a purplish-blue solid was finally obtained. This was soluble in chloroform and was proved to be the corresponding manganese(III) complex. The compound was very stable and no decomposition was observed after several weeks in open atmosphere.

Table 1 contains selected bond distances and angles in $Mn[(OPPh_2)_2N]_3$ and Fig. 1 shows the ORTEP-like view [15] of the molecular structure with the atom numbering scheme.

The crystal contains discrete molecules of the manganese(III) complex, in which the imidodiphosphinato ligands act as bidentate moieties. As expected the PNP fragment, which in the free acid has a linear orientation, becomes now angular [av. $124.6(6)^{\circ}$ to allow the coordination of both oxygen atoms to the metal. Although significant differences in the manganese-oxygen bond lengths are noted (see below), the corresponding phosphorus-oxygen distances are equivalent [av. 1.518(9) Å] as are the phosphorus-nitrogen bonds [av. 1.587(7) Å]. These values might be considered of intermediate magnitude between single and double phosphorus-oxygen [cf $Ph_2P(=S)OMe [18]: P=O 1.60(2) Å; Ph_3P(=O)$ [19]: P=O 1.487(2) Å] and phosphorus-nitrogen bonds [cf Me—S—PPh₂=N—Ph₂P=S [20]: P—N 1.610(4), P=N 1.568(4) Å]. However the considerable double bond character of both bond types is evident.

The six-membered MnO₂P₂N inorganic rings thus formed are not planar despite the averaging in bond lengths due to some delocalization of π -electrons over the OPNPO fragment. They exhibit a twisted boat conformation as reflected by the torsion angles and the deviations from the MnO₂ planes within a MnO₂P₂N ring, respectively (Table 2).

For 6-coordinate complexes the octahedral geometry is the most common. However in many cases different degrees of distortion from the octahedron have been established [21], and this is the case for various manganese(III) complexes with chelating oxo ligands, MnL₃, resulting in a MnO₆ core (Fig. 2). A first type of distortion is the tetragonal distortion, that is either elongation or compression along one of the fourfold rotational axes of the octahedron, resulting in a reduction of symmetry from O_h to D_{4h}. This is the case of the previously reported β - and γ -forms of Mn(acetilacetonato)₃ and the distortion has been



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Mn(1) - O(1)	2.141(3)	cis-O—Mn—O angles						
Mn(1) - O(2)	1.953(3)	O(1) - Mn(1) - O(2)	89.9(1)	O(2) - Mn(1) - O(6)	92.0(1)			
Mn(1) - O(3)	1.941(3)	O(1) - Mn(1) - O(3)	92.7(1)	O(3) - Mn(1) - O(4)	91.2(1)			
Mn(1) - O(4)	1.939(3)	O(1) - Mn(1) - O(4)	88.4(1)	O(3) - Mn(1) - O(5)	87.9(1)			
Mn(1) - O(5)	2.118(3)	O(1) - Mn(1) - O(6)	88.9(1)	O(4) - Mn(1) - O(5)	92.4(1)			
Mn(1) - O(6)	1.950(3)	O(2) - Mn(1) - O(3)	87.2(1)	O(4) - Mn(1) - O(6)	89.7(1)			
., .,		O(2)—Mn(1)—O(5)	89.2(1)	O(5)—Mn(1)—O(6)	90.4(1)			
			trans-O-Mn-O angles					
		O(1) - Mn(1) - O(5)	178.9(1)	O(3) - Mn(1) - O(6)	178.2(1)			
		O(2) - Mn(1) - O(4)	177.6(1)					
P(1)—O(1)	1.513(3)	O(1) - P(1) - N(1)	117.7(2)	Mn(1) - O(1) - P(1)	124.0(2)			
P(2) - O(2)	1.514(3)	O(2) - P(2) - N(1)	117.9(2)	Mn(1) - O(2) - P(2)	131.2(2)			
P(1) - N(1)	1.588(4)							
P(2) - N(1)	1.595(4)	P(1) - N(1) - P(2)	123.9(2)					
P(3)—O(3)	1.520(3)	O(3) - P(3) - N(2)	116.6(2)	Mn(1) - O(3) - P(3)	131.1(2)			
P(4)—O(4)	1.530(3)	O(4) - P(4) - N(2)	116.4(2)	Mn(1) - O(4) - P(4)	130.1(2)			
P(3) - N(2)	1.584(4)							
P(4)—N(2)	1.584(4)	P(3) - N(2) - P(4)	124.9(2)					
P(5)—O(5)	1.505(3)	O(5) - P(5) - N(3)	117.8(2)	Mn(1) - O(5) - P(5)	128.5(2)			
P(6)—O(6)	1.524(3)	O(6)—P(6)—N(3)	117.3(2)	Mn(1)—O(6)—P(6)	129.3(2)			
P(5)—N(3)	1.592(4)							
P(6)—N(3)	1.576(4)	P(5)—N(3)—P(6)	124.9(3)					

Table 1. Selected bond distances (Å) and angles (°) in $Mn[(OPPh_2)_2N]_3$



Fig. 1. Three dimensional representation of the molecular structure of $Mn[(OPPh_2)_2N]_3$ (for clarity only *ipso* carbons attached to phosphorus atoms are shown).

A new monomeric manganese (III) complex

27.5	N(2)P(3)O(3)Mn(1)	-12.5	N(3)P(5)O(5)Mn(1)	9.6
11.2	O(3)P(3)N(2)P(4)	-11.9	O(5)P(5)N(3)P(6)	-22.5
-26.6	O(4)P(4)N(2)P(3)	8.1	O(6)P(6)N(3)P(5)	3.1
0.3	N(2)P(4)O(4)Mn(1)	20.7	N(3)P(6)O(6)Mn(1)	33.4
25.9	O(3)Mn(1)O(4)P(4)	-33.3	O(5)Mn(1)O(6)P(6)	-36.7
40.1	O(4)Mn(1)O(3)P(3)	29.1	O(6)Mn(1)O(5)P(5)	14.0
•	Mn(1)O(3)O(4) plane		Mn(1)O(5)O(6) plane	
-0.809	P(3)	0.556	P(5)	0.287
-0.498	P(4)	0.643	P(6)	0.707
-1.155	N(2)	0.988	N(3)	0.866
	$27.5 \\ 11.2 \\ -26.6 \\ 0.3 \\ 25.9 \\ -40.1 \\ e \\ -0.809 \\ -0.498 \\ -1.155 \\ end{tabular}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccc} 27.5 & N(2)P(3)O(3)Mn(1) & -12.5 \\ 11.2 & O(3)P(3)N(2)P(4) & -11.9 \\ -26.6 & O(4)P(4)N(2)P(3) & 8.1 \\ 0.3 & N(2)P(4)O(4)Mn(1) & 20.7 \\ 25.9 & O(3)Mn(1)O(4)P(4) & -33.3 \\ -40.1 & O(4)Mn(1)O(3)P(3) & 29.1 \\ \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$









(b)



Fig. 2. $MnO_6 \text{ cores in } (\mathbf{a}) \beta - Mn[(OCMe)_2CH]_3, (\mathbf{b}) \gamma - Mn[(OCMe)_2CH]_3, (\mathbf{c}) Mn[O_2C_7H_5]_3 \text{ (molecule 2), } (\mathbf{d}) Mn[(OPPh_2)_2N]_3 \text{ [for clarity only carbons attached to oxygen and phosphorus atoms are shown in } (\mathbf{c}) \text{ and } (\mathbf{d}), \text{ respectively]}.$

	$Mn[(OPPh_2)_2N]_3$	$\beta - \mathrm{Mn}[(\mathrm{OCMe})_2 \mathrm{CH}]_3$ [22]	γ -Mn[(OCMe) ₂ CH] ₃	$Mn[O_2C_7H_5]_3 [24]^b$	
	[this work]		[23]	molecule 1	molecule 2
MnO_6 core geometry ^c	tetragonally elongated MnO_6 distortion	tetragonally compressed MnO_6 distortion	tetragonally elongated MnO_6 distortion	tetragonally elongated MnO_6 distortion	orthorhombic MnO ₆ distortion
$b (\text{\AA})^d$	1.42	1.41	1.40	1.27	1.27
θ (degree) ^e	29.1	30.1	29.6	24.5	24.5
Mn—O (average)	1.946(7)	1.944(18)	1.935(5)	1.942(15)	1.944(7)
	2.130(16)	2.000(16)	2.111(2)	2.127(24)	1.990(4) 2.052(16)
O ··· O bite (average)	2.85(7)	2.79(2)	2.80(4)	2.56(5)	2.54(3)
O—Mn—O (endocyclic, average)	90.5(0.6)	89.6(0.5)	89.2(1.5)	79.2(1.5)	79.0(1.9)
O—Mn—O (endocyclic, <i>cis</i> , range) O—Mn—O (endocyclic, <i>trans</i> , range) Mn—O—X (average)	87.2(0.1)-92.7(0.1) 117.6(0.1)-178.9(0.1) 129.0(2.7)	88.8(0.3)-91.7(0.3) 178.0(0.4)-179.0(0.4) 127.2(0.4)	$\begin{array}{c} 87.5(0.1) - 92.5(0.1) \\ 174.6 - 178.9^{e} \\ 127.1(1.4) \end{array}$	86.8(0.6)-104.1(0.6) 162.9(0.6)-173.5(0.6) 115.0(4.1)	90.0(0.6)–97.4(0.6) 169.1(0.6)–171.4(0.6) 115.4(2.0)

Table 3. Comparative structural data in Mn[(OPPh₂)₂N]₃ and related MnO₆ core-containing derivatives^a

^{*a*} Esds for average bond length are calculated from the equation $\sigma = \left\{ \left[\sum_{i=1}^{i=N} (x_i - x)^2 / (N-1) \right]^{1/2} \right\}^{1/2}$, where x_i is *i*th bond length and x is the mean of the N equivalent bond lengths. An analogous

formula is used for the calculation of esds for average bond angles [25]

 ${}^{b}O_{2}C_{7}H_{5} = tropolonato.$

 c TD = tetrahedral, SP = square-planar.

^{*d*}Normalized bite of the bidentate ligand [21].

^e Twist angle between the upper and lower triangular faces of the MnO₆ octahedron [20].

^e Calculated from published atomic coordinates.

discussed in connection with the Jahn-Teller effect. The title compound, Mn[(OPPh₂)₂N]₃, exhibits a similar tetragonal elongation of the MnO₆ octahedral core (for comparative molecular parameters see Table 3): the axial Mn-O bond distances [av. 2.130(16) Å] are about 0.18 Å longer than the equatorial Mn-O bond distances [av. 1.946(7) Å]. The distortion of the oxygen atom arrangement around the metal is also reflected in the magnitude of the O-Mn-O angles. An elongation or compression along one of the threefold rotational axes of the octahedron might also be expected and results in a trigonal antiprism (D_{3h}) . The Mn(tropolonato)₃ complex shows an unusual feature, i.e. there are two crystallographically independent molecules : one is tetragonal elongated, while the other one was described as orthorhombical distorted with three pairs of different Mn-O distances [24]. It should be mentioned here that Keppert has considered an orthorhombical distortion of β -Mn[(OC-Me)₂CH]₃, while the two independent molecules in the unit cell of the Mn(tropolonato)₃ complex were both described as exhibiting different degrees of tetragonal elongation (4% and 10%) [21].

Another possibility of distorsion might be considered for complexes containing MX₆ cores the coordination polyhedron being intermediate between a perfect octahedral symmetry and a trigonal prismatic coordination. For M(bidentate ligand)₃ complexes this type of distortion is completely defined by the normalized bite of the bidentate ligand b and the twist angle θ between two opposite triangular faces [21]: the shorter the bite distance, the smaller the twist angle. For manganese(III) complexes containing bidentate dioxo ligands (Table 3), if any Jahn-Teller distortions are ignored and the O-Mn-O bond angles are averaged assuming a three fold axis, then the calculated values of b and θ are consistent with the repulsion-energy calculations [21]. The flexibility of the OPNPO skeleton can allow smaller or larger O...O bite values as required by the coordination geometry around the metal atom. Therefore the tetragonal elongation observed in the case of Mn[(OP- Ph_2 ₂N₃ adds further evidence that the distortion of the molecular structure of Mn(III) complexes is due to the Jahn-Teller effect.

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