

Preliminary communication

SYNTHESIS AND CRYSTAL STRUCTURE OF THE NOVEL HEXANUCLEAR MANGANESE COMPLEX $[\text{Mn}_6(\text{CO})_9 \{ \text{OP}(\text{OEt})_2 \}_3]$

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Summary

The crystal structure of the first hexanuclear manganese complex has revealed the presence of two different types of manganese atoms. The three on the interior (Mn^{2+}) are each coordinated in an approximately trigonal bipyramidal fashion to five oxygen atoms from the $[\text{OP}(\text{OEt})_2]^-$ ligands, while the three on the exterior (Mn^+) are each bonded to three phosphorus atoms and three carbonyl groups. There is no metal—metal interaction.

Crystallographic evidence for the existence of discrete molecules which contain more than three manganese atoms has not been forthcoming. This is surprising in view of the extensive effort devoted to Mn_3 systems [1, 2]. In an attempt to prepare polynuclear manganese complexes with phosphite ligands, we have isolated a new hexanuclear complex in which the metal atoms are bridged together by $[\text{OP}(\text{OEt})_2]^-$ groups.

$[\text{Mn}(\text{CO})_2 \{ \text{P}(\text{OEt})_3 \}_3 \text{Br}]$ was prepared by reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with $\text{P}(\text{OEt})_3$ according to the literature procedure [3]. 1.5 g of $[\text{Mn}(\text{CO})_2 \{ \text{P}(\text{OEt})_3 \}_3 \text{Br}]$ was placed in a reaction vessel and put under vacuum (10^{-5} Torr). The sample was slowly heated to 155°C where vigorous evolution of gas from the molten compound was observed. The sample was held at 155°C until gas evolution had ceased (~ 2 h) and the color had changed from orange to light yellow. The weight loss was approximately 40%. Initial purification was effected by recrystallization from toluene/hexane. The product was colorless and soluble in toluene, diethyl ether, THF, methylene chloride, etc. The complex does not

*Supplementary Material. The following supplementary material has been deposited with the National Auxiliary Publications Service as NAPS Document: Table 1, Final Fractional Coordinates and Thermal Parameters for $\text{Mn}_6[\text{P}(\text{OEt})_2\text{O}]_3(\text{CO})_9$. Table 2, Bond Lengths for $\text{Mn}_6[\text{P}(\text{OEt})_2\text{O}]_3(\text{CO})_9$. Table 3, Bond Angles for $\text{Mn}_6[\text{P}(\text{OEt})_2\text{O}]_3(\text{CO})_9$. Observed and Calculated Structure Factors for $\text{Mn}_6[\text{P}(\text{OEt})_2\text{O}]_3(\text{CO})_9$.

melt up to 240°C. Attempts to record the NMR showed the complex to be paramagnetic. The infrared spectrum in toluene showed absorptions at 2030 w, 1990 s, and 1950 s. Crystals suitable for X-ray diffraction were grown by slow evaporation of a 1/1 toluene/hexane solution.

Crystal data: $C_{45}H_{90}Mn_6P_9O_{36}$, Molecular weight 1815.6, Monoclinic, $a = 20.201$ (7), $b = 12.512$ (5), $c = 34.780$ (9) Å, $\beta = 95.57$ (3)°, $V = 8749.3$ Å³, $Z = 4$, $D_c = 1.38$ g cm⁻³, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 12.6$ cm⁻¹, space group $P2_1/n$. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the $\omega-2\theta$ scan technique. All reflections in one independent quadrant out to $2\theta = 36^\circ$ were measured; 4180 reflections were considered observed ($I > 3\sigma(I)$). The structure was solved with the aid of the direct methods program MULTAN, and refined with anisotropic thermal parameters for Mn, P, and bridging O to a conventional R value of 0.068. The structure of the molecule is shown in Fig. 1.

There are two different kinds of manganese atoms in the molecule. Those on the interior, Mn(1), Mn(2), and Mn(3), are each bonded to five oxygen atoms in a distorted trigonal bipyramidal fashion. The ones on the exterior, Mn(4), Mn(5), and Mn(6), are each bonded to three phosphorus atoms and three car-

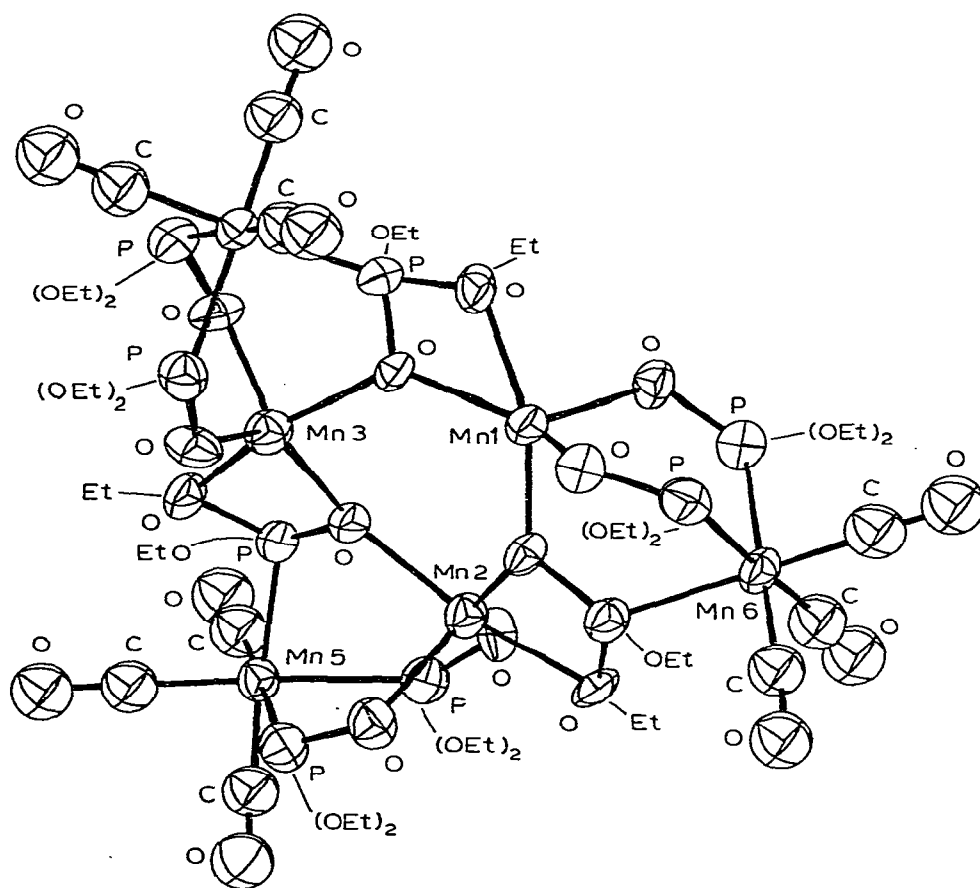
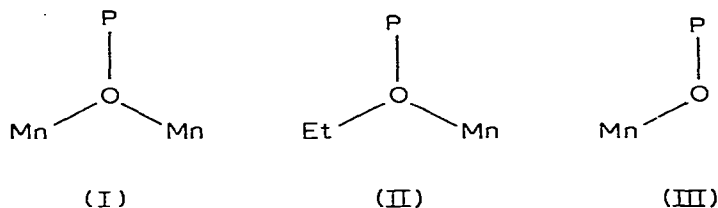


Fig. 1. Molecular Structure of $[Mn_6(CO)_6\{OP(OEt)_2\}_3]_2$.

bonyl groups. Mn(4)→Mn(6) are formally in the 1+ oxidation state, and Mn(1)→Mn(3) carry a charge of 2+.

Examination of Fig. 1 reveals that there are also two different kinds of $[\text{OP}(\text{OEt})_2]^-$ ligands. The three associated with the "core" have the lone oxygen atom bridging two metals (I) and one oxygen of an OEt unit coordinated to a metal (II) in a terminal manner. The phosphorus atoms are bonded to an exterior manganese atom. Thus, each of these ligands is bonded to three metals.



The lone oxygen atom is bonded (III) to an interior manganese atom, and the phosphorus atom to an exterior one. The oxygen atoms of the OEt groups are not coordinated to a metal atom.

The general pattern of bond lengths may be rationalized in terms of the coordination mode of the ligand involved. The Mn—O lengths of type III are shortest, 2.01 Å, those for I are intermediate at 2.15 Å, and II, longest at 2.28 Å. Smaller variations are seen in the Mn—P distances: those for P corresponding to I and II average 2.25 Å, and for P of type III, 2.30 Å. There is no Mn—Mn bonding interaction. The metal—metal separations are 3.88 Å between interior and exterior manganese atoms, and 3.98 Å between interior metal atoms.

This complex represents a new type of bonding for trialkylphosphites which could be important in stabilizing unsaturated intermediates during catalytic reactions [4]. Triarylphosphines [5, 6], triarylphosphites [7], and trialkylphosphines [8] have been observed to undergo metallation, but this capability had not previously been observed for trialkylphosphites. Bonding of type II could well be involved in the reactions of trialkylphosphites with metal carbonyls leading to acylmetal complexes [9, 10].

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