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Crystal and Molecular Structure of Bis(trimethylphosphite)octacarbonyldimanganese (Mn–Mn)

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Abstract

The crystal structure of $Mn_2(CO)_8[P(OCH_3)_3]_2$ was determined by the X-ray method. The complex crystallizes in the orthorhombic space group *Fdd*2 with eight molecules in a unit cell with dimensions of a = 38.778(4), b = 17.916(2), and c = 6.955(1) Å. The two manganese atoms bond directly to each other, each manganese atom being octahedrally coordinated by the counterpart manganese atom, four carbonyl carbon atoms and one trimethylphosphite phosphorus atom. The Mn–Mn bond distance, 2.912(3) Å, is slightly long in comparison with that of $Mn_2(CO)_8[P(C_2H_5)_3]_2$, while the Mn–P bond distance in the phosphite complex, 2.169(5) Å, is considerably shorter than the corresponding bond distance in the phosphine complex. Thus the *trans* effect for the Mn–Mn bond due to the axial ligands seems to be small.

Introduction

Distances of Mn–Mn single bonds in organomanganese complexes vary in a wide range (2.502–3.214 Å) [1]. For the factors that may influence the Mn–Mn bond distances, Bernal *et al.* cited several effects, *trans* effect of axial ligands, *cis* effect of equatorial ligands, influence of bridging groups, influence of η^5-cyclopentadienyl groups, and so on. They have, however, pointed out that it is not possible to observe any *trans* effects in geometries of $Mn_2(CO)_8L_1L_2$ type complexes (L_1 and L_2 = axial ligands). For the case of $L_1 = L_2$, recent X-ray structural analyses of dimanganese decacarbonyl, $Mn_2(CO)_{10}$ [2] and bis(triethylphosphine)octacarbonyldimanganese, $Mn_2(CO)_8[P(C_2H_5)_3]_2$ [3], have shown the Mn–Mn bond distances to be 2.9038(6) and 2.9032(14) Å, respectively. The bond distances are both quite similar, in spite of the differences in the axial ligands. We studied the structure of $Mn_2(CO)_8[P(OCH_3)_3]_2$, to examine geometric dependences of the $Mn_2(CO)_8$ core on the axial ligands.

Experimental

Preparation

$Mn_2(CO)_8[P(OCH_3)_3]_2$ was prepared by the method of Jackson and Poë [4]. Yellow prism single crystals were obtained by recrystallization from CH_3OH/H_2O mixture.

X-ray Structure Determination

Preliminary X-ray photographic examination established an orthorhombic unit cell containing eight molecules. The systematic absences of *hkl* for $h + k = 2n + 1$, $k + l = 2n + 1$, and $l + h = 2n + 1$, $0kl$ for $k + l = 4n + 1$, and $h0l$ for $h + l = 4n + 1$, led to the space group, Fdd2. A crystal with $0.1 \times 0.05 \times 0.05$ mm^3 was mounted on a Rigaku AFC-5 diffractometer with a graphite-monochromated Cu-Kα radiation ($\bar{\lambda}$ = 1.54178 Å). The unit cell dimensions refined by a least-squares treatment of the setting angles of 20 reflections are a = 38.778(4), b = 17.916(2), and c = 6.955(1) Å.

Intensity data of 3591 reflections in the range $2\theta < 120°$ were collected in the ω–2θ scan mode with a ω scan rate of 4° min^{-1}. During the course of data collection, three reflections were monitored every 56 reflections. The intensity data were converted to Fo data in the usual manner. Absorption correction was applied in the cylindrical approximation (μR = 0.27). The standard deviations $\sigma(F_o)$ were established by counting statistics. A

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total of 802 independent reflections with $F_o \geqslant 3\sigma(F_o)$ were retained as observed, and used in solving and refining the structure.

The structure was solved by the heavy-atom method. The two manganese atoms were located by a sharpened Patterson synthesis. The complete structure was elucidated through the iterative applications of a Fourier synthesis, and was refined by a full-matrix least-squares method. Several cycles of the refinement, including the anisotropic thermal parameters, were carried out with the weighting scheme of $w^{-1} = (\sigma^2(F_o) + (0.023\ F_o)^2)$. Atomic scattering factors [5a] and anomalous dispersion terms [5b] were taken from the International Tables for X-Ray Crystallography IV. The hydrogen atoms were included as a fixed contribution in the last cycles; their positions were obtained from the difference Fourier synthesis, and their temperature factors were assumed to be isotropic (B = 8.00 Å). The final R and R_w values were 0.069 and 0.078. The final difference Fourier maps showed no peak greater than 0.3 e/Å^3; most of the largest peaks were around the manganese atom. All computations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University, using the KPAX program system. Positional parameters of the non-hydrogen atoms are given in Table I.[†]

Results and Discussion

The geometry of $Mn_2(CO)_8[P(OCH_3)_3]_2$ is shown in Fig. 1 with the numbering of atoms. Each manganese atom is octahedrally coordinated by the other manganese atom, the four carbonyl carbon atoms, and the phosphorus atom of trimethylphosphite group, the phosphorus atom and the complementary manganese atom locating at the axial positions, and the carbonyl carbon atoms occupying the equatorial positions. A view of the molecule along the Mn–Mn bond is presented in Fig. 2. The crystallographic two-fold axis passes through the center of the molecule across the Mn–Mn bond, and the carbonyl groups are arranged about the Mn–Mn bond in the most stable staggered conformation.

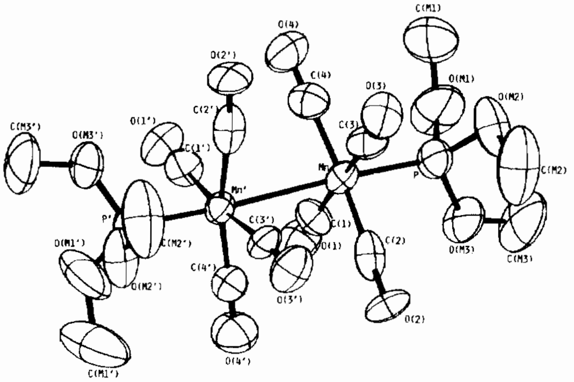

Fig. 1. Computer-drawn model in perspective of the $Mn_2(CO)_8[P(OCH_3)_3]_2$ complex. The thermal ellipsoids are drawn at the 50% probability level.

TABLE I. Positional and Thermal Parameters for Non-hydrogen Atoms of $Mn_2(CO)_8[P(OCH_3)_3]_2$ and Their e.s.d.s. in Parentheses.

Atom	x	y	z	B_{eq} (Å^2)
Mn	0.0276(1)	0.0551(1)	0.0	3.80(8)
P	0.0704(1)	0.1330(2)	0.0052(11)	5.22(12)
C(1)	0.0405(5)	0.0171(11)	−0.2306(28)	4.76(72)
C(2)	0.0535(5)	−0.0179(12)	0.1326(26)	4.93(79)
C(3)	0.0133(4)	0.0837(10)	0.2500(34)	4.83(68)
C(4)	−0.0040(5)	0.1177(10)	−0.0847(32)	5.33(78)
O(1)	0.0486(3)	−0.0037(9)	−0.3610(25)	6.68(74)
O(2)	0.0715(3)	−0.0634(7)	0.1999(21)	5.97(69)
O(3)	0.0029(4)	0.1065(8)	0.3994(23)	6.65(68)
O(4)	−0.0242(3)	0.1581(8)	−0.1459(25)	7.71(75)
C(M1)	0.0463(9)	0.2622(14)	−0.1312(73)	13.29(89)
C(M2)	0.0902(8)	0.1484(20)	0.3528(43)	11.78(89)
C(M3)	0.1377(5)	0.1328(15)	−0.0648(67)	11.22(90)
O(M1)	0.0693(5)	0.1974(11)	−0.1425(49)	12.91(92)
O(M2)	0.0788(5)	0.1865(10)	0.1790(20)	7.12(76)
O(M3)	0.1053(3)	0.0948(7)	−0.0445(45)	9.36(87)

[†] Thermal parameters, fractional coordinates of the hydrogen atoms, and observed and calculated structure factors are deposited with the Editor. The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the Hamilton's expression [6].

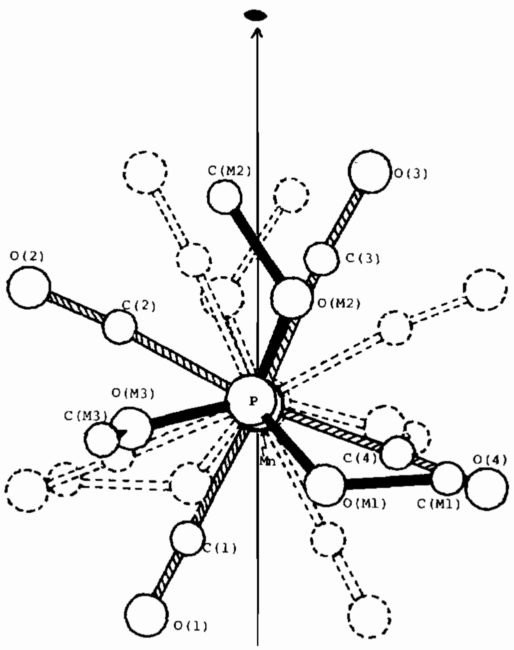

Fig. 2. Projection of the complex along the Mn–Mn bond. The two halves of the dimeric complex are symmetrically related by the indicated crystallographic 2-fold axis.

Bond distances and bond angles are listed in Table II. The Mn–Mn single bond distance is 2.912(3) Å, and the P–Mn–Mn–P bond is in an almost linear array (Mn–Mn–P = 177.2(2)°). The valence angles about the phosphorus atom (116.6, 124.2, 112.3°) show the large deviations from the regular tetrahedral values, as observed in those of $Mn_2(CO)_8[P(C_2H_5)_3]_2$ [3]. Geometries about the manganese atoms in $Mn_2(CO)_8L_2$ type complexes are compared in Table III. A significant increase of the Mn–P bond distance of the phosphine complex in comparison with that of the phosphite complex accompanies a slight decrease of the Mn–Mn distance. However, the *trans* effect for the Mn–Mn bond is fairly small. Although the $\sigma_{MnMn}\sigma_{MnMn}^*$ transition energies in $Mn_2(CO)_8L_2$ type complexes increase in the order of L = $P(C_2H_5)_3$, $P(OCH_3)_3$ and CO [8], the Mn–Mn bond distances are not in parallel with this order. The $Mn_2(CO)_8$ core is rather rigid for the perturbations exerted by the axial ligands, and it keeps an irregular octahedral structure. The four equatorial Mn–CO bonds with the bond distances (1.76–1.89 Å) are bent towards the other half of the molecule; the manganese atom is displaced by 0.11 Å out of the plane defined by the four carbonyl carbons, the Mn–Mn–C angles being 85.4–88.2° and the Mn–C=O angles being 173.7–178.1°. The Mn···C(O) non-bonding distances are 3.28–3.40 Å, as given in Table IV with the other selected non-bonded intramolecular distances. The distorted $Mn_2(CO)_8$ core may be stabilized by the attractive interactions between the

TABLE II. Bond Distances (Å) and Bond Angles (Degree), with Their e.s.d.s in Parentheses.

Mn–Mn′	2.912(3)	Mn–P	2.169(5)
Mn–C(1)	1.813(20)	Mn–C(2)	1.889(20)
Mn–C(3)	1.896(23)	Mn–C(4)	1.763(19)
C(1)–O(1)	1.030(26)	C(2)–O(2)	1.171(24)
C(3)–O(3)	1.187(27)	C(4)–O(4)	1.148(24)
P–O(M1)	1.545(27)	P–O(M2)	1.577(17)
P–O(M3)	1.555(14)	O(M1)–C(M1)	1.466(35)
O(M2)–C(M2)	1.457(35)	O(M3)–C(M3)	1.436(25)
Mn′–Mn–P	177.2(2)	Mn′–Mn–C(1)	87.0(6)
Mn′–Mn–C(2)	85.5(6)	Mn′–Mn–C(3)	88.2(5)
Mn′–Mn–C(4)	85.4(6)	Mn–C(1)–O(1)	178.1(15)
Mn–C(2)–O(2)	173.7(16)	Mn–C(3)–O(3)	174.4(16)
Mn–C(4)–O(4)	177.8(19)	C(1)–Mn–C(2)	91.4(8)
C(1)–Mn–C(3)	173.6(8)	C(1)–Mn–C(4)	97.8(9)
C(2)–Mn–C(3)	84.0(8)	C(2)–Mn–C(4)	166.7(9)
C(3)–Mn–C(4)	86.1(9)	P–Mn–C(1)	92.6(7)
P–Mn–C(2)	91.8(6)	P–Mn–C(3)	92.0(5)
P–Mn–C(4)	97.4(6)	Mn–P–O(M1)	116.6(9)
Mn–P–O(M2)	124.2(7)	Mn–P–O(M3)	112.3(5)
P–O(M1)–C(M1)	124.9(27)	P–O(M2)–C(M2)	114.5(18)
P–O(M3)–C(M3)	125.1(14)	O(M1)–P–O(M2)	93.5(12)
O(M1)–P–O(M3)	101.8(13)	O(M2)–P–O(M3)	105.0(12)

TABLE III. Comparison of Geometries in $Mn_2(CO)_8L_2$ Type Complexes.

L	Av. dist. (Å)			Av. angl. (deg)
	Mn–Mn	Mn–$C(O)_{eq}$	Mn–L	Mn'–Mn–$C(O)_{eq}$
CO[a]	2.9038(6)	1.86	1.811(3)	86
$P(OCH_3)_3$[b]	2.912(3)	1.84	2.169(5)	87
$P(C_2H_5)_3$[c]	2.9032(14)	1.83	2.253(2)	87

[a] Ref. 2. [b] Present work. [c] Ref. 3.

TABLE IV. Selected Intramolecular Non-bonded Contacts (Å)[a].

Mn–C(1)'	3.350(20)	O(1)–C(1)'	3.580(12)
Mn–C(2)'	3.344(20)	O(1)–O(1)'	3.772(12)
Mn–C(3)'	3.424(19)	O(1)–C(4)'	3.295(15)
Mn–C(4)'	3.282(18)	O(1)–O(4)'	3.284(16)
Mn–O(M1)	3.178(22)	O(2)–C(3)'	3.327(12)
Mn–O(M2)	3.322(18)	O(2)–O(3)'	3.293(12)
Mn–O(M3)	3.111(13)	O(2)–C(4)'	3.423(13)
P–C(1)	2.889(20)	O(2)–O(4)'	3.468(13)
P–C(2)	2.920(21)	O(3)–C(2)'	3.278(15)
P–C(3)	2.929(20)	O(3)–C(3)'	3.617(15)
P–C(4)	2.965(20)	O(3)–O(3)'	3.823(14)
P–C(M1)	2.670(31)	O(4)–C(1)'	3.256(14)
P–C(M2)	2.552(31)	O(4)–C(2)'	3.369(15)
P–C(M3)	2.655(21)	O(M1)–C(1)	3.472(28)
C(1)–C(2)	2.651(27)	O(M1)–C(4)	3.206(28)
C(1)–C(4)	2.694(27)	O(M1)–O(M2)	2.275(37)
C(2)–C(3)	2.532(27)	O(M1)–O(M3)	2.407(26)
C(3)–C(4)	2.498(32)	O(M2)–C(2)	3.805(28)
C(1)–C(1)'	3.200(27)	O(M2)–C(3)	3.176(25)
C(1)–C(4)'	2.978(27)	O(M2)–C(4)	3.898(27)
C(2)–C(3)'	2.961(26)	O(M2)–O(M3)	2.484(27)
C(2)–C(4)'	3.027(28)	O(M3)–C(1)	3.151(26)
C(3)–C(3)'	3.172(25)	O(M3)–C(2)	3.103(26)

[a] The atoms with and without a prime superscribed are related by the crystallographic 2-fold axis.

non-bonding manganese orbitals and the adjacent carbonyl π^* orbitals as mentioned by Brown *et al.* [7].

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