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Di- μ -iodo-bis[tetracarbonylmanganese(I)]

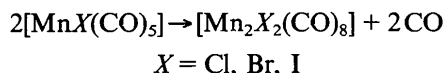
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Abstract. $[\text{Mn}_2\text{I}_2(\text{CO})_8]$, $M_r = 587.77$, monoclinic, $P2_1/c$, $a = 9.759$ (1), $b = 12.252$ (2), $c = 13.017$ (2) Å, $\beta = 108.65$ (1)°, $V = 1474.8$ (1.7) Å³, $Z = 4$, $D_x = 2.65$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 58.2$ cm⁻¹, $F(000) = 1072$, $T = 294$ (1) K, $R = 0.032$ for 1877 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ of 3212 total data. The I atoms form the dimer. There is pseudo octahedral geometry around the Mn atoms. Ranges of bond lengths and angles: I—Mn 2.691 (1)–2.710 (1), Mn—C_{eq} 1.797 (9)–1.815 (8), Mn—C_{ax} 1.865 (9)–1.882 (8), Mn...Mn 3.986 (1), C_{eq}—O 1.122 (9)–1.16 (1), C_{ax}—O 1.108 (9)–1.127 (9) Å, Mn—C—O 177.6 (6)–180 (1), I—Mn—C_{ax} 88.0 (2)–89.7 (2), I—Mn—C_{eq} 91.2 (3)–92.7 (2), Mn—I—Mn 95.09 (3)–95.10 (3), I—Mn—I 84.61 (3)–85.16 (3)°.

Introduction. Since the first synthesis of manganese pentacarbonyl iodide in 1954 (Brimm, Lynch & Sesny, 1954), other carbonyl halides of manganese (Cl, Br) have been prepared and their utility in organometallic synthesis has become apparent (Wimmer & Snow, 1978). These compounds undergo thermal dissociation of coordinated carbon monoxide and dimerization to produce bis[halotetracarbonylmanganese(I)] (Brimm, Lynch & Sesny, 1954), according to the following stoichiometry



It is known that the thermal decomposition of manganese pentacarbonyl iodide to the correspond-

ing bis[iodotetracarbonylmanganese(I)] is easier (Abel & Wilkinson, 1959) than the corresponding dimerization of the rhenium analog, whose X-ray structure has been reported previously (Darst, Lenhart, Lukehart & Warfield, 1980). Although both $[\text{Mn}_2\text{Cl}_2(\text{CO})_8]$ (Clegg & Morton, 1978) and $[\text{Mn}_2\text{Br}_2(\text{CO})_8]$ (Dahl & Wei, 1963) have been characterized crystallographically $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ has not. In order to complete the series of manganese dimers and to allow comparisons with $[\text{Re}_2\text{I}_2(\text{CO})_8]$, we describe here the structural characterization of $[\text{Mn}_2\text{I}_2(\text{CO})_8]$.

Experimental. The complex $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ was prepared by the reaction of $[\text{Mn}(\text{CO})_5]^-$ with diiodoacetylene as reported previously (Davies, El-Ghanam, Pinkerton & Smith, 1990). This compound was isolated with other products of the reaction and then separated. $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ was first identified by infrared and mass spectroscopy. IR (KBr disk): $\nu(\text{CO})$ 1844 (vw), 1868 (w), 1890 (w), 1951 (m), 1960 (w), 1978 (s), 2004 (m), 2026 (m), 2036 (m), 2087 (vs) cm⁻¹; MS (70 eV; EI): M^+ (558), $M^+ - 3\text{CO}$ (504), $M^+ - 4\text{CO}$ (476), $M^+ - 5\text{CO}$ (448), $M^+ - 6\text{CO}$ (420), $M^+ - 7\text{CO}$ (392), Mn_2I_2^+ (364), Mn_2I^+ (237), MnI^+ (182), I^+ (127), Mn^+ (55). $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ was crystallized from hexane to give a brown crystalline material found to be suitable for X-ray analysis. Crystal 0.34 × 0.14 × 0.08 mm; Enraf-Nonius CAD-4 computer-controlled κ -axis diffractometer, graphite monochromator; cell dimensions from setting angles of 25 reflections, $10 < \theta <$

15° ; $\omega-2\theta$ scan; max. $2\theta = 52^\circ$; h 0 to 12, k 0 to 15, l -16 to 15; empirical absorption (from 0.61–0.99 on λ); three standard reflections, decay 7.7%, intensities adjusted accordingly; 3212 data, 3033 unique, $R_{\text{int}} = 2.2\%$, structure solved by direct and Fourier methods; refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(F_o)^2$, 182 parameters; final $R = 0.032$, $wR = 0.039$ for 1877 reflections with $F_o^2 > 3\sigma F_o^2$; max. shift to e.s.d. = 0.19; max. and min. of difference Fourier synthesis 0.70 (16) and -0.78 (16) $e \text{ \AA}^{-3}$, e.s.d. of observations of unit weight = 1.12, atomic scattering factors for neutral Mn, I, C and O atoms, and values of f' and f'' for all atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2 and 2.3.1); computer programs *SDP/VAX* (Frenz, 1978). The figure was prepared using *ORTEP* (Johnson, 1971).

Discussion. The compound (Fig. 1) was prepared by the reaction of $[\text{Mn}(\text{CO})_5]^-$ and $\text{IC}\equiv\text{CI}$. The reaction proceeds by formal I^+ abstraction to give $[\text{Mn}(\text{CO})_5\text{I}]$ which undergoes dimerization to $[\text{Mn}_2\text{I}_2(\text{CO})_8]$, a major product of this reaction. Structure refinement was completed in order to make comparisons with $[\text{Mn}_2\text{Br}_2(\text{CO})_8]$ (Dahl & Wei, 1963), $[\text{Mn}_2\text{Cl}_2(\text{CO})_8]$ (Clegg & Morton, 1978) and $[\text{Re}_2\text{I}_2(\text{CO})_8]$ (Darst, Lenhart, Lukehart & Warfield, 1980). Final atomic coordinates are listed in Table 1 and derived bond lengths and angles in Table 2.*

The coordination geometry around the Mn atoms in $[\text{Mn}_2\text{I}_2(\text{CO})_8]$ is formally octahedral with the two iodide ligands bridging the manganese centers. Inspection of Table 3 shows that the $M-X$ distances in $[\text{M}_2\text{X}_2(\text{CO})_8]$ follow the expected trend, *i.e.* where $M = \text{Mn}$, $M-X$ increases in the order $X = \text{Cl} < \text{Br} < \text{I}$ and where $X = \text{I}$, $M-X$ increases in the order M

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53879 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

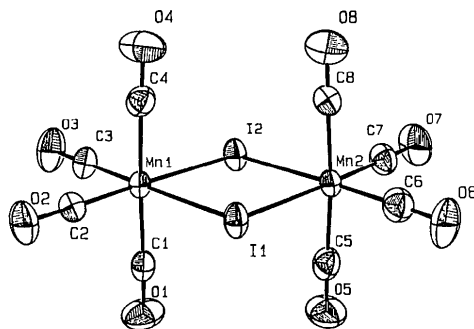


Fig. 1. *ORTEP* (Johnson, 1971) drawing showing the atom-numbering scheme and 50% probability ellipsoids.

Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	$B(\text{\AA}^2)$
I1	-0.11491 (5)	0.01455 (4)	0.34614 (4)	3.05 (1)
I2	-0.11238 (5)	0.25218 (4)	0.17825 (4)	3.09 (1)
Mn1	0.1029 (1)	0.13117 (9)	0.31261 (8)	2.44 (2)
Mn2	-0.3281 (1)	0.13217 (8)	0.20810 (8)	2.49 (2)
O1	0.1052 (7)	0.2787 (5)	0.4976 (5)	5.4 (2)
O2	0.3272 (6)	-0.0082 (4)	0.4593 (5)	4.4 (1)
O3	0.3312 (6)	0.2636 (5)	0.2720 (5)	5.2 (2)
O4	0.0884 (7)	-0.0109 (5)	0.1226 (5)	5.4 (2)
O5	-0.3254 (7)	0.2800 (5)	0.3914 (5)	5.6 (2)
O6	-0.5524 (6)	-0.0061 (5)	0.2512 (6)	5.5 (2)
O7	-0.5492 (7)	0.2672 (5)	0.0524 (5)	5.5 (2)
O8	-0.3136 (7)	-0.0167 (5)	0.0301 (5)	5.7 (2)
C1	0.1012 (7)	0.2230 (6)	0.4279 (6)	2.9 (2)
C2	0.2378 (8)	0.0449 (6)	0.4023 (6)	3.2 (2)
C3	0.2425 (8)	0.2140 (6)	0.2867 (6)	3.2 (2)
C4	0.0941 (8)	0.0423 (6)	0.1943 (6)	3.3 (2)
C5	-0.3237 (8)	0.2253 (6)	0.3241 (6)	3.5 (2)
C6	-0.4641 (8)	0.0468 (6)	0.2327 (7)	3.8 (2)
C7	-0.4621 (8)	0.2156 (6)	0.1133 (6)	3.6 (2)
C8	-0.3174 (8)	0.0395 (7)	0.0972 (6)	3.5 (2)

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $B_{\text{eq}} = 8\pi^2/3 \times \text{trace of the orthogonalized } U \text{ tensor}$.

Table 2. *Distances (Å) and angles (°) with e.s.d.'s in parentheses*

I1	Mn1	2.710 (1)	Mn2	C7	1.802 (8)		
I1	Mn2	2.691 (1)	Mn2	C8	1.866 (9)		
I2	Mn1	2.706 (1)	O1	C1	1.127 (9)		
I2	Mn2	2.696 (1)	O2	C2	1.150 (9)		
Mn1	C1	1.880 (8)	O3	C3	1.122 (9)		
Mn1	C2	1.797 (8)	O4	C4	1.126 (9)		
Mn1	C3	1.815 (8)	O5	C5	1.108 (9)		
Mn1	C4	1.865 (9)	O6	C6	1.16 (1)		
Mn2	C5	1.882 (8)	O7	C7	1.149 (9)		
Mn2	C6	1.797 (9)	O8	C8	1.122 (9)		
Mn1	I1	Mn2	95.10 (3)	I1	Mn2	C7	176.3 (3)
Mn1	I2	Mn2	95.09 (3)	I1	Mn2	C8	88.2 (2)
I1	Mn1	I2	84.61 (3)	I2	Mn2	C5	88.1 (2)
I1	Mn1	C1	88.8 (2)	I2	Mn2	C6	176.7 (3)
I1	Mn1	C2	92.0 (2)	I2	Mn2	C7	91.2 (3)
I1	Mn1	C3	177.3 (2)	I2	Mn2	C8	88.9 (2)
I1	Mn1	C4	89.7 (2)	C5	Mn2	C6	92.2 (4)
I2	Mn1	C1	89.1 (2)	C5	Mn2	C7	91.8 (3)
I2	Mn1	C2	176.5 (2)	C5	Mn2	C8	175.7 (3)
I2	Mn1	C3	92.7 (2)	C6	Mn2	C7	92.1 (4)
I2	Mn1	C4	88.0 (2)	C6	Mn2	C8	90.6 (4)
C1	Mn1	C2	91.4 (3)	C7	Mn2	C8	91.3 (4)
C1	Mn1	C3	90.7 (3)	Mn1	C1	O1	177.6 (7)
C1	Mn1	C4	176.9 (3)	Mn1	C2	O2	177.9 (7)
C2	Mn1	C3	90.7 (3)	Mn1	C3	O3	178.4 (7)
C2	Mn1	C4	91.4 (3)	Mn1	C4	O4	180. (1)
C3	Mn1	C4	90.7 (3)	Mn2	C5	O5	177.9 (7)
I1	Mn2	I2	85.16 (3)	Mn2	C6	O6	177.8 (8)
I1	Mn2	C5	88.5 (2)	Mn2	C7	O7	178.7 (8)
I1	Mn2	C6	91.5 (3)	Mn2	C8	O8	178.7 (8)

Table 3. *Crystallographic data (Å, °) for some $[\text{M}_2\text{X}_2(\text{CO})_8]$ complexes*

	$[\text{Mn}_2\text{Cl}_2(\text{CO})_8]$	$[\text{Mn}_2\text{Br}_2(\text{CO})_8]$	$[\text{Mn}_2\text{I}_2(\text{CO})_8]$	$[\text{Re}_2\text{I}_2(\text{CO})_8]$
$M-C$ trans to halogen	1.816 (2)	1.76 (4)	1.803 (4)	1.91 (3)
$M-C$ cis to halogen	1.888 (2)	1.87 (4)	1.874 (3)	2.00 (3)
$M-X$	2.395 (1)	2.526 (5)	2.7007 (5)	2.820 (2)
$M...M$	3.569 (1)	3.743 (8)	3.986 (1)	4.218 (2)
$X-M-X$	83.7 (1)	84.4 (2)	84.884 (2)	83.18 (4)

= Mn < Re. The $X-M-X$ angles increase in the order $X = \text{Cl} < \text{Br} < \text{I}$, where $M = \text{Mn}$ and in the order $\text{Re} < \text{Mn}$ where $X = \text{I}$, entirely as expected based on covalent radii. The $M-\text{CO}$ distances for the carbonyl groups *cis* to X in $[\text{M}_2\text{X}_2(\text{CO})_8]$ differ significantly from the $M-\text{CO}$ distances *trans* to X ; in every case the *cis* bonds are longer as anticipated based on the known *trans*-influences of the groups involved. The C—O bond lengths shorten as $M-C$ lengthens owing to less effective back bonding from manganese. Unfortunately, comparisons of $M-\text{CO}$ bond distances as X is varied are hindered by the low accuracy of the bond lengths for $[\text{Mn}_2\text{Br}_2(\text{CO})_8]$, whose structure was solved from photographic data. The nonbonded $\text{Mn}\cdots\text{Mn}$ distances in $[\text{Mn}_2\text{X}_2(\text{CO})_8]$ (all > 3.5 Å) are significantly longer than the Mn—Mn distance of 2.923 (3) Å in $[\text{Mn}_2(\text{CO})_{10}]$ (Dahl & Rundle, 1963) confirming the absence of any metal-metal interaction.

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Structure of Synthetic Perryite, $(\text{Ni,Fe})_8(\text{Si,P})_3$

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Abstract. $(\text{Ni}_{0.97}\text{Fe}_{0.03})_8(\text{Si}_{0.79}\text{P}_{0.21})_3$, $M_r = 550$, trigonal, $R3c$, hexagonal axes, $a = 6.640$ (2), $c = 37.982$ (7) Å, $V = 1450.3$ (7) Å³, $Z = 12$ [96 Ni(Fe) and 36 Si(P) per unit cell], $D_x = 7.63$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 31.07$ mm⁻¹, $F(000) = 3194$, $T = 295$ K, final $R = 0.027$, $wR = 0.019$ for 333 independent reflections. The structure was found to be isomorphous with that of Pd_8Sb_3 , and also a stacking variant of $\text{Ni}_{31}\text{Si}_{12}$ and Pd_5Sb_2 structures.

Introduction. In the highly reduced stony meteorites, *i.e.* enstatite chondrites and enstatite achondrites, it has been known that a nickel silicide mineral called perryite occurs as thin rims around and as thin

lamellae within metallic nickel-iron grains. The chemical composition of perryite as determined by electron probe microanalysis is Ni 75.5–83.7, Fe 1.7–9.4, Si 9.7–15.0 and P 2.4–5.2 wt% (Fredriksson & Henderson, 1965; Okada, Keil & Taylor, 1988; Reed, 1968; Wai, 1970).

Natural perryite crystals in meteorites which are usually less than 20 μm are too small to be used for single-crystal structure analysis. This is the main reason why the crystal structure and the accurate chemical formula of perryite have not been clarified. We synthesized the crystal by melting the materials, the composition obtained is almost the same as that of perryite in the Norton County enstatite achondrite