

# Octacarbonylbis{ $\mu$ -[iodo(pentacarbonylmanganio)germanium(IV)]}-dimanganese

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**Abstract.**  $[\text{Mn}_2(\text{CO})_8\{\text{GeMn}(\text{CO})_5\text{I}\}_2]$ ,  $M_r = 1122.93$ , monoclinic,  $P2_1/c$ ,  $a = 8.987(2)$ ,  $b = 12.190(3)$ ,  $c = 15.659(3)$  Å,  $\beta = 61.4(1)^\circ$ ,  $U = 1506$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.343$  Mg m<sup>-3</sup>,  $F(000) = 1044$ , Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 5.06$  mm<sup>-1</sup>. The final  $R = 0.053$  for 2279 unique diffractometer data ( $I > 3\sigma$ ). The core of the molecule is formed by a planar  $\text{Mn}_2\text{Ge}_2$  rhombus with a short Mn–Mn distance [Mn–Mn = 2.934(2) Å] across the ring.

**Introduction.** We have recently reported the structures of  $[\text{Mn}_2(\text{CO})_8\{\mu\text{-Sn}(X)\text{Mn}(\text{CO})_5\}_2]$  [ $X = \text{Cl}$  (Haupt, Preut & Wolfes, 1978),  $X = \text{Br}$  (Preut & Haupt, 1976)] and  $[\text{Mn}_2(\text{CO})_8\{\mu\text{-Ge}(\text{Br})\text{Mn}(\text{CO})_5\}_2]$  (Preut & Haupt, 1979a). For the first time we succeeded in preparing the iodine compound of this type and we now report on the structure of  $[\text{Mn}_2(\text{CO})_8\{\mu\text{-Ge}(\text{I})\text{Mn}(\text{CO})_5\}_2]$ .

Data were collected with a crystal  $0.79 \times 0.52 \times 0.46$  mm. Cell parameters were determined by least squares from the angles of 21 reflexions measured with a Hilger & Watts Y290 automatic four-circle diffrac-

tometer, graphite-monochromated Mo  $K\alpha$  radiation and a scintillation counter. The intensities of 2613 reflexions ( $I > 3\sigma$ ) with  $2 \leq \theta \leq 26.3^\circ$  were measured by the  $\omega/2\theta$  scan technique, with a scan width  $\Delta 2\theta = (1.374 + 0.34 \tan \theta)^\circ$  from background to background and a scan speed of  $0.02^\circ \text{ s}^{-1}$  in  $2\theta$ . Backgrounds were measured at either end of the scan range for 9 s. Five standards were measured every fifty reflexions, and showed only random deviations from their mean intensities. Lp but no absorption corrections were applied, and after the equivalent reflexions were averaged the data set contained 2279 independent reflexions.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with all atoms anisotropic, using the program *SHELX* (Sheldrick, 1976). Complex neutral-atom scattering factors were taken from Cromer & Mann (1968) and Cromer & Liberman (1970); the weighting scheme was  $w = 1/[\sigma^2(F) + 0.009|F_o|^2]$ . Refinement converged to  $R = 0.053$  with  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.055$ .\*

The data were processed on an IBM 370/158 computer. The figures were drawn with *PLUTO* written by Drs W. D. S. Motherwell and W. Clegg and *POP 1* written by B. W. van de Waal.

Table 1. Final positional parameters ( $\times 10^4$ ) with e.s.d.'s

	x	y	z
I(1)	-1887 (1)	2080 (0)	5026 (0)
Ge(1)	613 (1)	3392 (1)	4802 (0)
Mn(1)	-525 (1)	4887 (1)	6038 (1)
Mn(2)	3004 (2)	2056 (1)	4373 (1)
C(1)	4703 (14)	1044 (9)	4088 (8)
C(2)	1412 (14)	1208 (7)	5410 (8)
C(3)	3505 (12)	2762 (8)	5259 (7)
C(4)	4494 (13)	2950 (8)	3345 (8)
C(5)	2377 (13)	1411 (8)	3510 (7)
C(6)	-2711 (12)	4557 (7)	6286 (6)
C(7)	-627 (12)	3728 (8)	6787 (6)
C(8)	1629 (13)	5237 (8)	5840 (7)
C(9)	-1388 (13)	5879 (7)	7023 (6)
O(1)	5689 (12)	378 (8)	3905 (7)
O(2)	534 (12)	709 (7)	6044 (6)
O(3)	3811 (11)	3145 (7)	5807 (6)
O(4)	5433 (12)	3435 (8)	2729 (6)
O(5)	2020 (11)	1029 (6)	2958 (5)
O(6)	-4067 (10)	4370 (7)	6505 (6)
O(7)	-852 (14)	3015 (7)	7305 (6)
O(8)	2896 (11)	5444 (7)	5773 (7)
O(9)	-1977 (12)	6460 (6)	7674 (5)

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34959 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

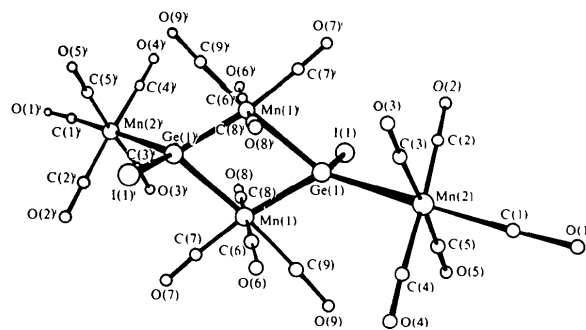


Fig. 1. Drawing of  $[\text{Mn}_2(\text{CO})_8\{\mu\text{-Ge}(\text{I})\text{Mn}(\text{CO})_5\}_2]$  and the atom numbering. Symmetry code: (i)  $\bar{x}, 1 - y, 1 - z$ .

**Discussion.** The structure of the title compound is shown in Fig. 1; a stereoview of the two molecules in the unit cell is given in Fig. 2. The positional parameters are given in Table 1, and bond lengths and angles in Table 2.

[Mn<sub>2</sub>(CO)<sub>8</sub>{GeMn(CO)<sub>5</sub>I}<sub>2</sub>] is isotopic with [Mn<sub>2</sub>(CO)<sub>8</sub>{μ-M(X)Mn(CO)<sub>5</sub>}<sub>2</sub>] [*X* = Br, *M* = Ge (Preut & Haupt, 1979*a*); *X* = Cl, Br, *M* = Sn (Preut & Haupt, 1976; Haupt, Preut & Wolfes, 1978)] whose molecules, like those of [M<sub>2</sub>'(CO)<sub>8</sub>{μ-MM'(CO)<sub>5</sub>}<sub>2</sub>] [*M* = Ga, *M*' = *M*'' = Mn; *M* = In, *M*' = *M*'' = Mn, Re (Preut & Haupt, 1974, 1975)] and [Fe<sub>2</sub>(CO)<sub>8</sub>{InMn(CO)<sub>5</sub>}<sub>2</sub>] (Preut & Haupt, 1979*b*), contain a planar four-membered metal ring.

Table 2. Bond lengths (Å) and angles (°)

Ge(1)–I(1)	2.642 (1)	Ge(1)–Mn(1)–C(9)	174.7 (3)
Ge(1)–Mn(1)	2.494 (1)	Ge(1')–Mn(1)–C(6)	89.7 (3)
Ge(1)–Mn(2)	2.519 (2)	Ge(1')–Mn(1)–C(7)	172.9 (3)
Ge(1)–Mn(1')	2.497 (2)	Ge(1')–Mn(1)–C(8)	90.7 (3)
Mn(1)–Mn(1')	2.934 (2)	Ge(1')–Mn(2)–C(9)	77.3 (3)
Mn(1)–C(6)	1.855 (12)	C(6)–Mn(1)–C(7)	88.6 (4)
Mn(1)–C(7)	1.810 (9)	C(6)–Mn(1)–C(8)	177.8 (5)
Mn(1)–C(8)	1.858 (13)	C(6)–Mn(1)–C(9)	89.3 (5)
Mn(1)–C(9)	1.816 (9)	C(7)–Mn(1)–C(8)	90.8 (5)
Mn(2)–C(1)	1.844 (13)	C(7)–Mn(1)–C(9)	95.8 (5)
Mn(2)–C(2)	1.879 (11)	C(8)–Mn(1)–C(9)	88.7 (5)
Mn(2)–C(3)	1.862 (11)	Ge(1)–Mn(2)–C(1)	178.1 (4)
Mn(2)–C(4)	1.874 (11)	Ge(1)–Mn(2)–C(2)	85.7 (4)
Mn(2)–C(5)	1.868 (12)	Ge(1)–Mn(2)–C(3)	88.9 (3)
C(1)–O(1)	1.133 (16)	Ge(1)–Mn(2)–C(4)	91.2 (4)
C(2)–O(2)	1.109 (14)	Ge(1)–Mn(2)–C(5)	87.2 (3)
C(3)–O(3)	1.122 (14)	C(1)–Mn(2)–C(2)	92.4 (5)
C(4)–O(4)	1.102 (14)	C(1)–Mn(2)–C(3)	91.2 (5)
C(5)–O(5)	1.154 (15)	C(1)–Mn(2)–C(4)	90.7 (5)
C(6)–O(6)	1.120 (15)	C(1)–Mn(2)–C(5)	92.6 (5)
C(7)–O(7)	1.140 (12)	C(2)–Mn(2)–C(3)	88.0 (5)
C(8)–O(8)	1.121 (17)	C(2)–Mn(2)–C(4)	176.9 (5)
C(9)–O(9)	1.142 (11)	C(2)–Mn(2)–C(5)	91.5 (5)
		C(3)–Mn(2)–C(4)	92.5 (5)
		C(3)–Mn(2)–C(5)	176.1 (5)
Mn(1)–Ge(1)–Mn(1')	72.0 (0)	C(4)–Mn(2)–C(5)	87.8 (5)
Mn(1)–Ge(1)–Mn(2)	131.4 (1)	Mn(2)–C(1)–O(1)	175.9 (11)
Mn(1')–Ge(1)–Mn(2)	129.9 (1)	Mn(2)–C(2)–O(2)	176.0 (11)
Ge(1)–Mn(1)–Ge(1')	108.0 (1)	Mn(2)–C(3)–O(3)	177.1 (10)
Ge(1)–Mn(1)–C(6)	90.2 (3)	Mn(2)–C(4)–O(4)	176.4 (11)
Ge(1)–Mn(1)–C(7)	78.9 (3)	Mn(2)–C(5)–O(5)	178.3 (10)
Ge(1)–Mn(1)–C(8)	91.7 (3)	Mn(1)–C(6)–O(6)	174.9 (10)
Mn(1)–Ge(1)–I(1)	109.4 (0)	Mn(1)–C(7)–O(7)	173.5 (10)
Mn(1')–Ge(1)–I(1)	109.9 (0)	Mn(1)–C(8)–O(8)	176.2 (10)
Mn(2)–Ge(1)–I(1)	101.9 (0)	Mn(1)–C(9)–O(9)	176.5 (9)

The geometry of the metal rings is given in Table 3. The change of halide atoms has no perceptible influence on the geometry of the metal ring, as is shown by the results (I) to (IV).

The exchange of Ge for Sn, or Ga for In, with the composition of the ring unchanged otherwise, does not lead to an obvious change of the ring angles, as is shown by the results (I) to (VI). The angle *M*–*M*''–*M* seems, in the case of *M*'' = Mn for the elements Ge and Sn, to have the value of 107.9 (3)° (mean value), characteristic of Group IV elements of the periodic table, while this angle is about 4.5° smaller for the Group III elements Ga and In. If, however, Mn is replaced by Re in [In<sub>2</sub>Mn<sub>4</sub>(CO)<sub>18</sub>], a marked widening of *M*–*M*''–*M* results.

The obtuse angle *M*–*M*''–*M* in (I) to (VII) has been interpreted by us as an indication of a bond relation *M*''–*M*'' with a bond distance whose length is determined by steric hindrance. The number of valence electrons which are in Mn and Re free for a bond requires this seventh bond, whereas in the case of Fe this bond across the ring is no longer possible. This interpretation is confirmed by a marked moving apart of the Fe atoms in the inner metal ring of [In<sub>2</sub>Fe<sub>2</sub>Mn<sub>2</sub>(CO)<sub>18</sub>]. The fact that in this ring the In atoms reach a distance of 3.250 (1) Å, which deviates less from twice the covalent radius of In (2.88 Å) than is the case with the corresponding distances Mn–Mn or Re–Re in (I) to (VII), can be explained by the absence of the bulky and mutually obstructive ligands at the In

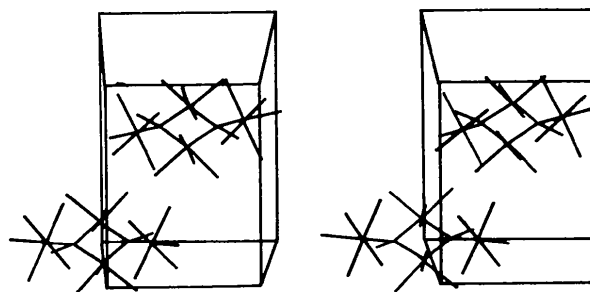


Fig. 2. Stereoscopic view of the molecules in the unit cell.

Table 3. Shape of the metal ring in the compounds [M<sub>2</sub>'(CO)<sub>8</sub>{μ-M(X)M'(CO)<sub>5</sub>}<sub>2</sub>] (*M* = Ge, *X* = Br, I, *M*' = *M*'' = Mn; *M* = Sn, *X* = Cl, Br, *M*' = *M*'' = Mn), [M<sub>2</sub>'(CO)<sub>8</sub>{μ-MM'(CO)<sub>5</sub>}<sub>2</sub>] (*M* = Ga, *M*' = *M*'' = Mn; *M* = In, *M*' = *M*'' = Mn, Re) and [M<sub>2</sub>'(CO)<sub>8</sub>{MM'(CO)<sub>5</sub>}<sub>2</sub>] (*M* = In, *M*' = Mn, *M*'' = Fe)

		<i>M</i> ''– <i>M</i> '' (Å)	<i>M</i> – <i>M</i> (Å)	<i>M</i> – <i>M</i> ''– <i>M</i> (°)	Reference
(I)	[Ge <sub>2</sub> Mn <sub>4</sub> Br <sub>2</sub> (CO) <sub>18</sub> ]	2.923 (2)	4.008 (2)	107.80 (6)	Preut & Haupt (1979 <i>a</i> )
(II)	[Ge <sub>2</sub> Mn <sub>4</sub> I <sub>2</sub> (CO) <sub>18</sub> ]	2.934 (2)	4.038 (2)	108.00 (6)	Present work
(III)	[Sn <sub>2</sub> Mn <sub>4</sub> Cl <sub>2</sub> (CO) <sub>18</sub> ]	3.091 (1)	4.241 (1)	107.83 (2)	Haupt, Preut & Wolfes (1978)
(IV)	[Sn <sub>2</sub> Mn <sub>4</sub> Br <sub>2</sub> (CO) <sub>18</sub> ]	3.086 (1)	4.330 (1)	108.09 (3)	Preut & Haupt (1976)
(V)	[Ga <sub>2</sub> Mn <sub>4</sub> (CO) <sub>18</sub> ]	3.052 (1)	3.600 (1)	103.14 (2)	Preut & Haupt (1974)
(VI)	[In <sub>2</sub> Mn <sub>4</sub> (CO) <sub>18</sub> ]	3.227 (1)	4.284 (1)	103.64 (2)	Preut & Haupt (1974)
(VII)	[In <sub>2</sub> Re <sub>4</sub> (CO) <sub>18</sub> ]	3.232 (1)	4.525 (2)	108.93 (4)	Preut & Haupt (1975)
(VIII)	[In <sub>2</sub> Mn <sub>2</sub> Fe <sub>2</sub> (CO) <sub>18</sub> ]	4.218 (1)	3.250 (1)	75.2 (0)	Preut & Haupt (1979 <i>b</i> )

atom. This means that in (I) to (VII) a shorter Mn—Mn or Re—Re distance is prevented by the repulsion of the apical CO groups. A visible proof of this explanation is each apical CO group, bent towards the molecular centre in [In<sub>2</sub>Fe<sub>2</sub>Mn<sub>2</sub>(CO)<sub>18</sub>].

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## Structure d'un Décavanadate d'Hexasodium Hydraté

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**Abstract.** Na<sub>6</sub>V<sub>10</sub>O<sub>28</sub>·18H<sub>2</sub>O,  $P\bar{1}$ ,  $a = 11.65$  (5),  $b = 10.85$  (5),  $c = 8.56$  (1) Å,  $\alpha = 101.23$  (5),  $\beta = 99.44$  (5),  $\gamma = 105.48$  (5)°,  $Z = 1$ ; 2800 independent reflexions;  $R = 0.03$ . The centrosymmetric V<sub>10</sub>O<sub>28</sub> decavanadate anion is quite similar to those already described in Ca<sub>3</sub>V<sub>10</sub>O<sub>28</sub>·17H<sub>2</sub>O and K<sub>2</sub>Zn<sub>2</sub>V<sub>10</sub>O<sub>28</sub>·16H<sub>2</sub>O.

**Introduction.** Les cristaux du décavanadate de sodium se préparent facilement en partant d'une solution concentrée de pyrophosphate de sodium dans laquelle on ajoute, à l'ébullition, du pentoxyde de vanadium en quantité suffisante pour amener le pH de cette solution à une valeur de 7. La liqueur ainsi obtenue, abandonnée à température ambiante, laisse déposer au bout de quelques jours des cristaux orangés de décavanadate de sodium octodécahydraté: Na<sub>3</sub>V<sub>10</sub>O<sub>28</sub>·18H<sub>2</sub>O. Un fragment de cristal approximativement cubique, d'arête  $\frac{16}{100}$  mm, a été utilisé pour les mesures. Ces dernières ont été effectuées à l'aide d'un diffractomètre automatique Philips PW 1100 utilisant la longueur d'onde de l'argent  $K\alpha_1\alpha_2$  monochromatisée par une lame de graphite. Chaque réflexion était mesurée dans un domaine de 1,2° à une vitesse de 0,02° s<sup>-1</sup>, en balayage  $\omega$  seul. A chaque extrémité du domaine de balayage le fond continu était mesuré durant 10 s.

Les deux réflexions de référence utilisées (370 et  $\bar{3}\bar{7}\bar{0}$ ) n'ont pas varié durant les mesures qui ont été effectuées dans un domaine angulaire s'étendant de 3 à 26° ( $\theta$ ).

Dans ces conditions 7953 réflexions ont été explorées. De cet ensemble, 4888 réflexions utilisables ou non nulles ont été utilisées pour la détermination de la structure. L'utilisation du programme *MULTAN* (Main, Woolfson & Germain, 1971) permet de localiser rapidement les cinq sites de vanadium. Des synthèses de Fourier successives révèlent ensuite l'ensemble de l'arrangement atomique. Les derniers cycles d'affinement mettant en jeu les facteurs thermiques anisotropes et qui conduisent à un facteur de véricité final de 0,031 ont été effectués en utilisant un fichier réduit de 2800 données ( $F > 20$  dans une échelle s'étendant de 0 à 235).\* Le même facteur de véricité est 0,048 pour l'ensemble des données (sans affinement).

**Discussion.** Le Tableau 1 donne les coordonnées atomiques et les facteurs thermiques  $B_{eq}$ . Les groupements V<sub>10</sub>O<sub>28</sub> centrosymétriques occupent les sommets de la maille, la cohésion entre ces groupements étant assurée par les atomes de sodium et les molécules d'eau. Une représentation perspective très schématique

\* Les listes des facteurs de structure, des paramètres thermiques anisotropes et des longueurs des axes principaux des ellipsoïdes de vibration thermique et leur orientation par rapport aux axes cristallographiques ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 34962: 34 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.