REGULAR STRUCTURAL PAPERS

Pentacarbonyliodomanganese(I)

ALEXANDER J. BLAKE,* BRIAN F. G. JOHNSON AND ANKE SIEKER

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

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Abstract

Molecules of $Mn(CO)_5I$ occupy sites of *mm* (C_{2v}) symmetry with the iodine, manganese and one carbonyl on the twofold axis. The Mn—I distance is 2.6940 (8) Å and the Mn—C distances are inequivalent, that *trans* to iodine being shorter by 0.043 (9) Å. The four equivalent carbonyl ligands are bent from coplanarity with the metal by 0.102 (4) Å in the direction of the iodine.

Comment

Co-sublimation of $NaMn(CO)_5$ with CH_3I at 333–343 K *in vacuo* yielded crystals of diffraction quality. A crystal was covered with a film of mineral oil and transferred under cold CO_2 gas into the cold stream of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) operating at 150 K. Data were acquired using the learnt-profile method (Clegg, 1981).

Structure determinations have been reported for the chloro and bromo analogues (Greene & Bryan, 1971), for $Re(CO)_5Cl$ and $Re(CO)_5I$ (Cotton &
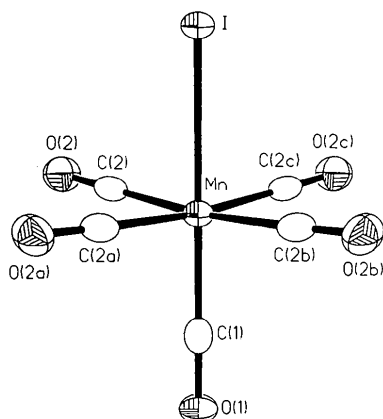
Daniels, 1983) and for $Re(CO)_5Br$ (Couldwell & Simpson, 1977) – all of which crystallize in the space group *Pnma* with the molecules having only *m* (C_s) symmetry imposed crystallographically. However, all the molecules studied show the same features: approximate non-crystallographic C_{4v} symmetry; bending of the four equatorial CO groups towards the axial halide; and, with the exception of the less-precise study of $Re(CO)_5Br$, axial *M*—C distances which are significantly shorter than equatorial *M*—C distances.

Note added in proof: a recent re-determination of the structure of $Re(CO)_5Br$ (Fackler, Porter & Reid, 1992) does in fact show an axial Re—C distance which is shorter than the Re—C equatorial distances. As with the title compound, the carbonyl ligands are bent towards the halide, in this case by 0.081 (5) Å.

Experimental

Crystal data

[Mn(CO)$_5$I]	Mo $K\alpha$
M_r = 321.9	λ = 0.71073 Å
Orthorhombic	Cell parameters from 38
Cmcm	reflections
a = 7.4783 (15) Å	θ = 12–13°
b = 10.810 (3) Å	μ = 5.058 mm^{-1}
c = 10.731 (3) Å	T = 150.0 (1) K
V = 867.5 Å^3	Column
Z = 4	0.19 × 0.12 × 0.08 mm
D_x = 2.465 Mg m^{-3}	Orange

Data collection

Stoe Stadi-4 diffractometer	R_{int} = 0.019
ω–2θ (learnt-profile) scans	θ_{max} = 22.5°
Absorption correction:	h = −8 → 8
ψ scans	k = −11 → 11
T_{min} = 0.394, T_{max} = 0.456	l = −11 → 11
1471 measured reflections	3 standard reflections
308 observed reflections	frequency: 60 min
[$F \geq 4.0\sigma(F)$]	intensity variation: <2%

Refinement

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Refinement on F	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
Final R = 0.0117	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
wR = 0.0163	Extinction correction: F^* =
S = 0.68	$F(1 + 0.002\chi F^2 / \sin 2\theta)^{0.25}$
308 reflections	χ = 9(5) × 10^{-5}
36 parameters	Atomic scattering factors
w = $1/[\sigma^2(F) + 0.00042F^2]$	from *SHELXTL-Plus*
$(\Delta/\sigma)_{max}$ = 0.034	

Fig. 1. View of the molecule showing the labelling of the atoms. I, Mn, C(1) and O(1) lie on the crystallographic twofold axis and the remaining four carbonyl groups are equivalent. Thermal ellipsoids are drawn at the 50% probability level.

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
I	0.0	0.10662 (2)	0.75	0.0254 (2)
Mn	0.0	−0.14258 (7)	0.75	0.0212 (2)
C(1)	0.0	−0.3132 (5)	0.75	0.0261 (17)
O(1)	0.0	−0.4179 (3)	0.75	0.0398 (13)
C(2)	−0.1805 (3)	−0.13314 (18)	0.62744 (22)	0.0251 (7)
O(2)	−0.2904 (3)	−0.12566 (13)	0.55679 (18)	0.0346 (6)

Table 2. *Geometric parameters* (Å, °)

I—Mn	2.6940 (8)	Mn—C(1)	1.844 (5)
Mn—C(2)	1.887 (3)	C(1)—O(1)	1.133 (6)
C(2)—O(2)	1.121 (3)		
I—Mn—C(2)	86.9 (1)	C(1)—Mn—C(2)	93.1 (1)
C(2)—Mn—C(2A)	88.3 (2)	C(2)—Mn—C(2B)	173.8 (1)
C(2A)—Mn—C(2B)	91.3 (2)	Mn—C(2)—O(2)	178.1 (2)

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A New Modification of Hg[Mn(CO)5]2

Ulrich Flörke and Hans-Jürgen Haupt

Anorganische und Analytische Chemie, Universität-GH Paderborn, Warburgerstrasse 100, D-4790 Paderborn, Germany

Abstract

The molecular structure of bis(pentacarbonylmanganese)mercury shows a linear Mn—Hg—Mn bond [Mn—Hg 2.614(1) Å]. The coordination of the Mn atoms is ide-
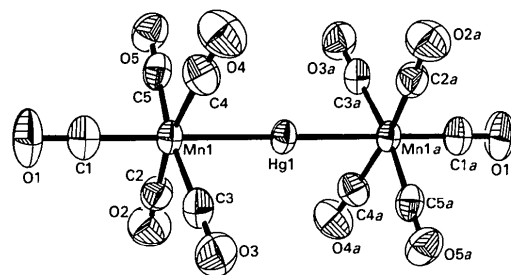
Fig. 1. Structure of Hg[Mn(CO)5]2.

alized octahedral, the CO ligands realizing an eclipsed conformation.

Comment

We have occasionally isolated crystals of Hg[Mn(CO)5]2 as a byproduct of the reaction of NaMn(CO)5 with μ-(dicyclohexylphosphanido)-dirhenium-octacarbonylmercury dichloride in THF solution at 298 K and recrystallization of the products from dichloromethane. As Guinier powder patterns of our sample proved not to be isotypic with the previously reported triclinic structure of Hg[Mn(CO)5]2 (Clegg & Wheatley, 1971; Katcher & Simon, 1972), we undertook a single-crystal structure determination. The new modification of Hg[Mn(CO)5]2 has a monoclinic structure with site symmetry $\bar{1}$ as is true for the triclinic structure. This means that the molecular geometries are the same for both structures with an eclipsed conformation of the carbonyl ligands. There is no significant difference between the measured bond lengths of the triclinic [2.610(2) Å] and the monoclinic [2.614(1) Å] structures. In the few other reported structures with Hg—Mn bonds, the bond lengths vary from 2.557(1) to 2.659(3) Å (Jaitner, Peringer, Huttner & Zolnai, 1981; Kuzmina, Ginzburg, Struchkov & Kursanov, 1983; Gäde & Weiss, 1981; Onaka, Kondo, Yamashita, Tatematsu, Kato, Goto & Ito, 1985). A comparison of the lattice energies of the two stuctures [calculated with the program *PCK*83 (Williams, 1983) and taking into account the nonbonding interactions C···C, C···O, O···O with potential parameters from Mirsky (1978)] shows a slightly increased energy (−71.40 kJ mol⁻¹) for the more dense triclinic structure relative to the monoclinic one (−70.68 kJ mol⁻¹).

Experimental

Crystal data

Hg[Mn(CO)5]2	Mo $K\alpha$ radiation
M_r = 590.6	λ = 0.71073 Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
a = 6.462 (1) Å	θ = 8–18°
b = 6.278 (1) Å	μ = 11.76 mm⁻¹
c = 18.720 (3) Å	T = 293 K
β = 95.89 (1)°	