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Redetermination of di-μ-bromo-bis[tetracarbonylmanganese(I)] at low temperature

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(O–C) = 0.003 Å
R factor = 0.036
wR factor = 0.091
Data-to-parameter ratio = 20.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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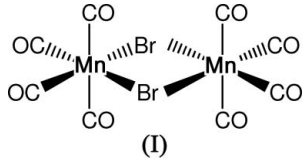
The structure of the title compound, $[Mn_2Br_2(CO)_8]$, has previously been determined at room temperature using film data [Dahl & Wei (1963). *Acta Cryst*. **16**, 611–616]. The 100 K structure reported here is in good agreement with the previous study but of significantly higher precision.

Comment

Following the first synthesis of a transition metal carbonyl complex, considerable progress has been made towards extending this area of chemistry (Holleman-Wiberg, 1995). Earlier studies have shown that the carbonyl halides of manganese $[Mn(CO)_5X]$ (X = Cl, Br, I) undergo thermal dissociation of coordinated carbon monoxide to give bis[halotetracarbonylmanganese(I)] (Brimm *et al.*, 1954). We now have found that storing manganese pentacarbonyl bromide $[Mn(CO)_5Br]$ dissolved in CD_2Cl_2 *in vacuo* leads also to the formation of the the title dimeric manganese complex, $[Mn(CO)_4Br]_2$, (I), (Fig. 1).



(I)

The structure of (I) was first determined at room temperature using film data from Weissenberg exposures (Dahl & Wei, 1963). The present low-temperature determination yielded results of significantly improved precision (*e.g.*: the s.u.'s for the Mn—Br bonds decrease from 0.009 and 0.010 to 0.0005 Å, the s.u.'s for the Mn—C bonds decrease from 0.04

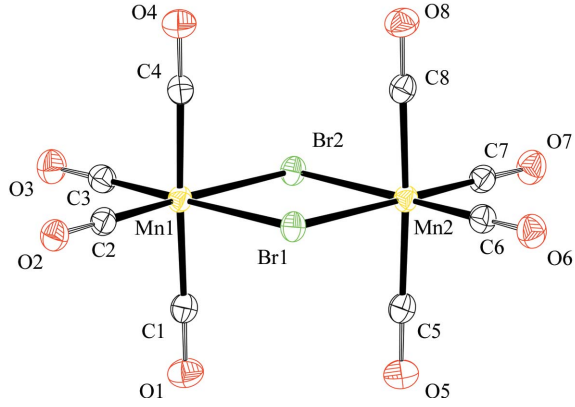


Figure 1
View of (I), showing 50% displacement ellipsoids.

and 0.05 to 0.003 Å). The improved precision helps to emphasize the difference between the Mn—C bond length *trans* to Br (mean value 1.887 Å) and *trans* to C (mean value 1.814 Å) (Table 1). The C—O bonds, on the other hand, show an inverse behaviour: those *trans* to Br (mean value 1.144 Å) are longer that those *trans* to C (mean value 1.134 Å). Both Mn atoms are octahedrally coordinated by four CO groups and two Br atoms bridging two Mn atoms. The molecule has chemical but not crystallographic D_{2h} symmetry.

Experimental

$[Mn(CO)_5Br]$ (0.036 g, 0.13 mmol) and 1 ml CD_2Cl_2 were stored in a sealed and evacuated NMR tube for several days at rom temperature. Orange crystals of (I) suitable for X-ray diffraction were grown from this solution.

Crystal data

$[Mn_2Br_2(CO)_8]_2$
M_r = 493.78
Monoclinic, $P2_1/c$
a = 9.4545 (7) Å
b = 11.5713 (8) Å
c = 12.6818 (9) Å
β = 109.148 (6)°
V = 1310.64 (16) Å^3
Z = 4
D_x = 2.502 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20694 reflections
θ = 3.6–29.5°
μ = 8.06 mm^{-1}
T = 100 (2) K
Block, orange
0.36 × 0.20 × 0.18 mm

Data collection

STOE IPDS II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.160, T_{max} = 0.225
20694 measured reflections
3694 independent reflections
3267 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 29.7°
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.091
S = 1.04
3694 reflections
181 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2 + 0.3697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.16 e Å^{-3}
$\Delta\rho_{min}$ = −1.38 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—C3	1.807 (3)	Mn2—C6	1.813 (3)
Mn1—C2	1.820 (3)	Mn2—C7	1.815 (3)
Mn1—C4	1.884 (3)	Mn2—C5	1.878 (3)
Mn1—C1	1.892 (3)	Mn2—C8	1.895 (3)
Mn1—Br2	2.5296 (5)	Mn2—Br1	2.5215 (5)
Mn1—Br1	2.5315 (5)	Mn2—Br2	2.5230 (5)
Mn2—Br1—Mn1	95.533 (16)	Mn2—Br2—Mn1	95.543 (17)

The highest peak and deepest hole in the final difference map are located 0.80 and 0.78 Å, respectively, from atom Br2.
Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PLATON*.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Brimm, L., Lynch, M. A. & Sesny J. (1954). *J. Am. Chem. Soc.* **76**, 3831–3835.
Dahl, L. F. & Wei, C.-H. (1963). *Acta Cryst.* **16**, 611–616.
Holleman-Wiberg (1995). *Lehrbuch der Anorganischen Chemie*, pp. 1629–1655. 101. Aufl. Berlin: de Gruyter.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.