Iodo(η^5-methylcyclopentadienyl)nitrosyl(thiocarbonyl)manganese(II)

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Abstract. [Mn(C₆H₇)(CS)I(NO)], monoclinic, $P2_1/a$, $a = 12.811$ (9), $b = 8.078$ (8), $c = 12.435$ (18) Å, $\beta = 126.90$ (3)°, $Z = 4$, $D_o = 2.20$ (1), $D_c = 2.17$ Mg m⁻³. The structure was refined to an R_F value of 0.038 ($R_{wF} = 0.036$). It contains discrete (η^5-CH₃C₅H₄)Mn-(CS)(NO)I units with Mn coordinated to the ligands CH₃C₅H₄, CS, NO, and I; the three unidentate ligands and the center of the cyclopentadienyl ring surround the Mn atom in a distorted tetrahedral arrangement. The Mn–I distance [2.645 (2) Å] is 0.166 Å shorter than that found for the square-pyramidal Mn^II cation [MnI(OPPh₃)₄]⁺. The Mn–C(S) distance [1.803 (6) Å] is substantially longer than the Mn–N(O) distance [1.647 (6) Å] and is approximately equal to the Mn–C(O) distances reported for similar Mn complexes, suggesting that, for complexes of this type, Mn–C(S) ≃ Mn–C(O) > Mn–N(O).

Introduction. The present structural investigation was undertaken as part of a project designed to prepare and characterize novel mononuclear (cyclopentadienyl)(thiocarbonyl)manganese complexes (Efraty, Arneri & Ruda, 1977). The title complex was prepared from [(CH₃C₅H₄)Mn(CS)(CO)NO]⁺.PF₆⁻ as described previously (Efraty *et al.*, 1977), and suitable crystals were obtained at 195 K from pentane. A black plate of dimensions 0.10 × 0.17 × 0.36 mm, mounted in a sealed glass capillary under N₂, was used. Weissenberg and precession photographs indicated a monoclinic lattice and showed systematic absences consistent with space group $B2_1/c$ (*hkl*, $h + l = 2n + 1$; $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). Data were collected and cell dimensions measured using the *B*-centered lattice and an Enraf–Nonius CAD-3 automated diffractometer. The cell dimensions and data were then converted to the primitive space group $P2_1/a$. With $Z = 4$ in space group $P2_1/a$, the observed (flotation) and calculated densities agreed well.

Data were collected (θ–2θ scan, $4 < 2\theta < 55°$) at 295 ± 2 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). A total of 1411 reflections

having $F^2 \geq 3\sigma(F^2)$ were considered observed, corrected for Lp effects and used for the structure solution and refinement. Standard deviations were assigned as $\sigma(F^2) = (Lp)^{-1}[N_t + (0.03N_n)^2]^{1/2}$, where N_t is the total count and N_n is the net count. Absorption corrections were not applied ($\mu = 0.38$ mm⁻¹ for Mo $K\alpha$ radiation).

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques. Refinement was accomplished using the program *FLINUS* obtained from Brookhaven National Laboratory; the remaining programs have been described previously (Fawcett, Ou, Potenza & Schugar, 1978). Neutral-atom scattering factors and anomalous-dispersion corrections for I, Mn and S were obtained from *International Tables for X-ray Crystallography* (1974). Approximate coordinates for the I, Mn, and S atoms were determined from a normal-sharpened Patterson map. The remaining non-hydro-

Table 1. *Fractional atomic coordinates*

Estimated standard deviations are given in parentheses.

|	x	y	z
I	0.50245 (4)	0.71008 (6)	0.20531 (4)
Mn	0.63159 (8)	0.4270 (1)	0.29582 (8)
S	0.3789 (2)	0.2119 (3)	0.0490 (2)
O	0.5833 (5)	0.3685 (6)	0.4868 (5)
N	0.6007 (5)	0.3969 (6)	0.4052 (5)
C(1)	0.7500 (5)	0.2695 (8)	0.2684 (6)
C(2)	0.8154 (6)	0.3020 (9)	0.4066 (7)
C(3)	0.8389 (6)	0.4772 (9)	0.4278 (7)
C(4)	0.7889 (6)	0.5492 (8)	0.3043 (7)
C(5)	0.7316 (6)	0.4245 (9)	0.2061 (6)
C(6)	0.7190 (6)	0.1024 (8)	0.2048 (7)
C(7)	0.4919 (6)	0.3156 (7)	0.1590 (6)
H[C(2)]	0.844	0.223	0.475
H[C(3)]	0.882	0.534	0.512
H[C(4)]	0.791	0.665	0.291
H[C(5)]	0.692	0.442	0.114
H[C(6)1]	0.672	0.033	0.233
H[C(6)2]	0.658	0.121	0.099
H[C(6)3]	0.808	0.049	0.234
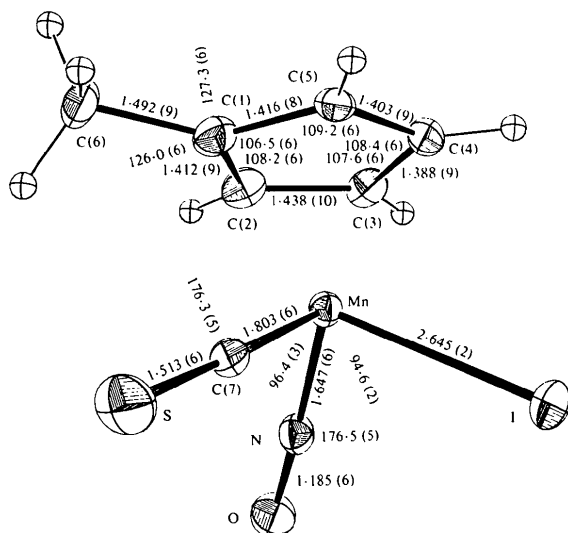
Fig. 1. View of the title complex showing the atom numbering scheme and bond distances (Å) and angles (°). Additional distances and angles are: Mn—C(1), 2·158 (6); Mn—C(2), 2·137 (6); Mn—C(3), 2·163 (6); Mn—C(4), 2·189 (6); Mn—C(5), 2·146 (6); Mn—CG, 1·794 Å; I—Mn—C(7), 91·0 (2)°. CG is the center of gravity of the cyclopentadienyl ring.

gen atoms were located on an electron density map prepared using phases derived from the I, Mn, and S coordinates.

Refinement was based on F with weights derived from standard deviations estimated from counting statistics. Following isotropic refinement of the C, N and O atoms, and anisotropic refinement of the I, Mn and S atoms, H-atom coordinates were calculated using methods described previously (Fawcett *et al.*, 1978) and confirmed with electron density maps. Isotropic thermal parameters for all H atoms were set according to $B_H = B_N + 1$ where B_N is the temperature factor of the atom bonded to H. H parameters were not refined. Several cycles of anisotropic refinement of all non-hydrogen atoms led to convergence with $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0·038$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0·036$. For the final cycle, all parameter changes were less than $0·05\sigma$, where σ is the e.s.d. obtained from the inverse matrix. A final difference map showed a general background of $\pm 0·4$ e Å^{-3} and revealed no significant features. Atom parameters* are given in Table 1, while a view of the structure, showing the atom numbering scheme as well as bond distances and angles, is given in Fig. 1.

Discussion. The structure consists of discrete units of the title complex with each Mn atom coordinated to one I, NO, CS and CH₃C₅H₄ ligand. The coordination geometry is typical of Cp*ML*₃ complexes where Cp = cyclopentadienyl and *L* is a unidentate ligand and may be described as distorted tetrahedral, ψ-octahedral (Messer, Landgraf & Behrens, 1979) or '5 and 3 eightfold coordination' depending upon whether the methylcyclopentadienyl ligand is assumed to occupy one, three, or five coordination sites, respectively.

As indicated by the Mn—C distances, the Cp group is very nearly symmetrically bound to Mn. The average Mn—C(ring) distance [2·159 (20) Å] lies within experimental error of those reported for (η^5-C₅H₅)Mn(CO)₃ [2·151 (21) Å, Berndt & Marsh, 1963] and (η^5-C₅H₅)Mn(CO)(NO)(CONH₂) [2·144 (10) Å, Messer *et al.*, 1979] and is significantly longer than that reported for (η^5-C₅H₅)Mn(CO)₂SO₂ [2·09 (2) Å, Barbeau & Dubey, 1973]. Bonding parameters of the Cp ring are typical. All five ring C atoms are planar to within $\pm 0·01$ Å while the mean C—C distance [1·411 (18) Å] and C—C—C angle [108 (1)°] lie within experimental error of those reported for the Mn complexes cited above. The C(methyl) carbon atom is *exo* to Mn, 0·16 Å from the least-squares plane of the Cp ring.

Bonding parameters of the nitrosyl group [Mn—N(O), 1·647 (6); N—O, 1·185 (6) Å; Mn—N—O, 176·5 (5)°] closely resemble those reported for 5-*exo*-CH₃C₅H₄Mn(CO)(NO)P(C₆H₅)₃ [1·674 (5); 1·200 (7) Å; 178·4 (5)°; Evrard, Thomas, Davis & Bernal, 1976] and (η^5-C₅H₅)Mn(CO)(NO)(CONH₂) [1·651 (4); 1·187 (7) Å; 179·1 (4)°]. In each of these structures, the Mn—N—O group is nearly linear, in contrast to Mn(NO)₂[P(OMe)₂Ph]₂Cl where it was found to be bent [Mn—N—O, 165 (1)°; Laing, Reimann & Singleton, 1974]. The near linearity of the Mn—N—O groups in these structures is in disagreement with the prediction of Laing *et al.* (1974) that Mn—N—O groups would be bent substantially. The Mn—I distance [2·645 (2) Å], while close to the value usually found for second- and third-row transition elements (~2·7 Å), is 0·166 Å shorter than that reported for the square-pyramidal Mn^{II} cation MnI(OPPh₃)₄⁺ [2·811 (8) Å, Ciani, Manassero & Sansoni, 1972].

The present structure permits a direct comparison of the structural parameters for Mn-coordinated thiocarbonyl and nitrosyl ligands, and an indirect comparison with carbonyl ligands. The Mn—C(S) distance [1·803 (6) Å] is approximately equal to the values of 1·795 (5) and 1·771 (7) Å reported for the Mn—C(O) bonds in the structurally similar complexes (η^5-C₅H₅)Mn(CO)(NO)(CONH₂) and 5-*exo*-CH₃C₅H₄-Mn(CO)(NO)P(C₆H₅)₃, respectively. The Mn—N(O) distances in these three complexes are nearly equal [1·647 (6), 1·651 (4) and 1·674 (5) Å, respectively]

and are 0·10–0·16 Å shorter than the Mn–C(S) or Mn–C(O) distances given above, suggesting that, for complexes of this type, Mn–C(S) ≃ MnC(O) > Mn–N(O).

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Strontium Bis[tris(monochloroacetato)stannate(II)]

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Abstract. Sr[Sn(CH₂ClCO₂)₃]₂, C₁₂H₁₂Cl₆O₁₂Sn₂Sr, triclinic, $P\bar{1}$, $a = 10·283$ (1), $b = 14·878$ (1), $c = 9·710$ (1) Å, $\alpha = 100·196$ (8), $\beta = 115·663$ (8), $\gamma = 99·234$ (7)°, $M_r = 885·94$, $V = 1269·9$ Å³, $Z = 2$, $D_m = 2·313$ (flotation, CHBr₃/CHCl₃), $D_c = 2·317$ Mg m⁻³, $F(000) = 840$. Each asymmetric unit consists of one Sr²⁺ cation and two [Sn(CH₂ClCO₂)₃]⁻ complex anions. Both trigonal-pyramidal Sn^II atoms are co-ordinated by three O atoms from three different unidentate chloroacetate ligands. The second O atom of each chloroacetate ligand, not bound to Sn, is involved in one contact to a Sr²⁺ cation, giving distorted octahedral coordination to Sr where the Sr–O distances range from 2·498 (7) to 2·611 (5) Å. The final R was 0·037.

Introduction. The number of crystal structures of Sn^II carboxylate compounds that are now known has grown considerably and among these are included K[Sn(HCO₂)₃] (Jelen & Lindqvist, 1969), Ca[Sn(CH₃CO₂)₃]₂ (Dewan, Silver, Donaldson & Thomas, 1977), K[Sn(CH₂ClCO₂)₃] (Clark, Donaldson, Dewan & Silver, 1979), Na₂[Sn(C₂O₄)₂] (Donaldson, Donoghue & Smith, 1976), Sn(O₂CCHCHCO₂).H₂O (Dewan, Silver, Andrews, Donaldson & Laughlin, 1977), K₂[Sn(C₂O₄)₂].H₂O (Dewan, Silver, Henrick & Donaldson, 1976; Christie, Howie & Moser, 1979), and Sn(C₂O₄) (Christie, Howie & Moser, 1979). Detailed reviews, concerned

entirely or in part with the structure and chemistry of Sn^II, are available (Donaldson, 1967; Harrison, 1976), the most recent and comprehensive of which is that by Zubieta & Zuckerman (1978). Donaldson & Jelen (1968a) have previously described the preparation of the title compound, and its structure is reported here.

The colourless crystal used in the diffraction study was bounded by ten faces: (11$\bar{1}$) and ($\bar{1}\bar{1}$1), 0·134 mm apart; (01$\bar{1}$) and (0$\bar{1}$1), 0·166 mm apart; and the three pairs (10$\bar{1}$), ($\bar{1}$01) and ($\bar{2}$10), (2$\bar{1}$0) and (010), (0$\bar{1}$0), each 0·20 mm apart. The quality of the data crystal was examined on the diffractometer, by taking ω scans of several strong low-angle reflections, and judged to be acceptable. The average width of the peaks at half-height was 0·13°. Intensity data, in the range $3 \leq 2\theta \leq 55°$, were collected at 298 K with the ω–2θ scan technique on an Enraf–Nonius CAD-4F κ-geometry diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda\alpha_1 = 0·70926$ Å). Scan rates were automatically selected to make $I/\sigma(I) = 100$, and varied from 1 to 20° min⁻¹ in ω, with a maximum scan time of 50 s. Prescans were made at 20° min⁻¹ and reflections having $I/\sigma(I) < 1$ were considered weak and were not remeasured. Scan ranges were computed according to $\Delta\omega = (0·6 + 0·35 \tan \theta)°$ and were extended 25% on either side for the measurement of backgrounds. Three standard reflections, 36$\bar{4}$, 60$\bar{3}$, and 046, measured after each 3600 s of X-ray exposure time (approximately after each 90 reflections), were