Crystal and Molecular Structure of Tricarbonyl(2-methylindolyl)manganese †

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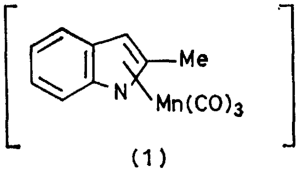
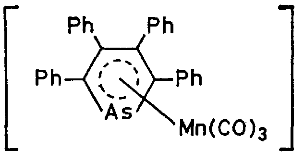
The crystal and molecular structure of the title compound have been determined by *X*-ray diffraction methods from photographic data. Crystals are monoclinic tablets, space group *C*2/*c*, with *Z* = 8 in a cell with *a* = 25.46, *b* = 11.62, *c* = 8.25 Å, and β = 109.8°. The structure has been solved by Patterson and Fourier methods, and refined by least-squares techniques to *R* 0.087 7 for 660 reflections. The manganese is bonded to the heterocyclic ring; one of the carbonyl groups is *trans* to the nitrogen atom. The root-mean-square deviation from planarity for the atoms of the heterocyclic ring is 0.04 Å.

THE tricarbonylmanganese group may be considered to have a unit positive charge, and a requirement for a ligand supplying six electrons.[1] The group forms a stable, neutral, π-bonded compound with the cyclopentadienyl anion, whose molecular structure has been determined,[2a] and with a number of substituted derivatives of this anion [2b,c] and with derivatives of the pentadienyl anion.[2c–e] The carbocyclic ring can be replaced by a pyrrolyl anion,[3a,b] although no such compound has yet had its structure determined, or by an indolyl anion to give (1), whose structure we describe. A preliminary report on the structure of the analogous derivative of 2,3,4,5-tetraphenylarsole (2) has been published.[4]



(1)



(2)

EXPERIMENTAL

Compound (1) [3b] sublimed at 60 °C (0.01 mmHg) ‡ as tablets, m.p. 91.5—92 °C, elongated along *c* with {100} prominent and {100}, {111}, and {11$\bar{3}$} developed, giving the tablets a hexagonal appearance.

Crystal Data.—$C_{12}H_8MnNO_3$, $M = 269$, Monoclinic, $a = 25.46$, $b = 11.62$, $c = 8.25$ Å, $\beta = 109.8°$, $U = 2\ 296$ Å, $D_m = 1.547 \pm 0.005$, $Z = 8$, $D_c = 1.556$ g cm^{-3} $F(000) = 1\ 088$. Space group *C*2/*c* (no. 15) from systematic absences. Cu-K_α radiation: $\lambda = 1.541\ 8$ Å, μ(Cu-K_α) 94.38 cm^{-1}. Crystal dimensions, 0.15 × 0.3 × 0.4 mm.

Crystallographic Measurements.—The symmetry and cell dimensions were obtained from rotation and Weissenberg photographs about *c* with Cu-K_α radiation, and from precession photographs with Mo-K_α (λ 0.710 7 Å) radiation. The intensity data for the layers *hk*0—6 were collected as equi-inclination multiple-film Weissenberg photographs. Initially the reflections (1 044, including 133 unobserved ones assessed at one third the locally observable minimum [5]) were estimated visually and used, uncorrected for absorption, to determine the structure. Subsequently the intensities were measured and corrected for absorption at the S.R.C. Microdensitometer Laboratory; data for 660 reflections were supplied for layers *hk*0—5. In each case these were corrected for time of exposure, polarization, and Lorentz factors.

Structure Determination.—A three-dimensional Patterson map yielded co-ordinates for the manganese atom, and successive rounds of structure-factor calculations with isotropic temperature parameters and Fourier syntheses revealed the sites of the remaining atoms other than hydrogen. Atoms at the sites for N(5) and C(11) were both weighted as carbon, others appropriately. When all the atoms had been located their positions and temperature factors were adjusted by block-diagonal least-squares refinement. After three rounds, using isotropic temperature parameters and with $w^{\frac{1}{2}} = 1.0$ for all the data, the atom entered as carbon at the site of N(5) had a lower temperature factor than any other atom, the Mn atom having the next lowest value. Later, when the data measured by the film scanner and corrected for absorption were available, the atom sites and types previously determined were used. Throughout the subsequent calculations, scattering factors for each atom type were corrected for the real and imaginary components of anomalous dispersion using values taken from ref. 6. Interlayer scaling was done by the structure-factor program, which scales the data so that for each layer $\Sigma(\text{scaled } |F_o|) = \Sigma(|F_c|)$; this program was applied after convergence of the least-squares refinement with isotropic temperature parameters for all the atoms. The parameters were optimized by block-diagonal least-squares refinement of an overall scale factor, an overall temperature factor, and positions and temperature factors for each atom; the manganese was allowed to vibrate anisotropically. The final weighting scheme used was $w^{\frac{1}{2}} = 1.0$ if $|F_o| \leqslant 70.0$, otherwise $w^{\frac{1}{2}} = |F_o|/70.0$. When refinement had converged, a Fourier map based on $(|F_o| - |F_c|)$ was computed and searched for peaks higher than 0.5 eÅ^{-3}. Two positive (0.6 and 0.6) and three negative peaks (−1.0, −0.6, and −0.6 Å^{-3}) were found; their sites were not chemically significant. The final discrepancy ratios were *R* 0.087 7 and $R'(= \Sigma w\Delta^2/\Sigma w F_o^2)$ 0.109 6. Observed and calculated structure factors, and evidence of convergence of the refinement, are listed in Supplementary publication No. SUP 22081 (9 pp.).§

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† No reprints available.

‡ Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

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[4] E. W. Abel, I. W. Nowell, A. G. J. Mondinos, and C. Towers, *J.C.S. Chem. Comm.*, 1973, 258.

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[6] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 73, 77, and 149.

DISCUSSION

Table 1 gives the final co-ordinates of the atoms, their temperature factors, and standard deviations derived from the final least-squares matrix. Figure (1*a*) shows the molecule displayed and the crystallographic numbering system used, and Figure 1(*b*) is a stereopair of drawings showing the molecule viewed down the *c* axis. Table 2 lists interatomic distances, valency angles, and some non-bonded interactions, Table 3 the mean values of the parameters for selected types of bond, together with the means of some previously measured values, and the mean estimated standard deviations for bond lengths and angles.

TABLE 1

Final co-ordinates ($\times 10^4$) and isotropic temperature parameters ($\times 10^3$) and, in parentheses, their standard deviations

Atom	x/a	y/b	z/c	$U_{\text{iso.}}$
Mn(1)	1 058(1)	2 208(2)	834(4)	*
O(2)	607(7)	−84(15)	158(22)	112
O(3)	1 332(6)	2 089(13)	4 568(19)	93
O(4)	−42(6)	3 204(12)	347(18)	84
N(5)	1 626(5)	3 609(11)	957(17)	47
C(6)	786(8)	886(18)	416(27)	72
C(7)	1 188(6)	2 111(15)	3 090(21)	48
C(8)	413(7)	2 803(17)	551(23)	60
C(9)	880(9)	4 662(18)	−1 415(26)	72
C(10)	1 238(7)	3 594(16)	−657(24)	58
C(11)	1 197(6)	2 462(13)	−1 511(21)	46
C(12)	1 683(7)	1 879(14)	−391(22)	47
C(13)	1 933(8)	775(17)	−534(25)	64
C(14)	2 404(8)	458(16)	843(26)	65
C(15)	2 631(8)	1 165(17)	2 315(26)	65
C(16)	2 397(7)	2 224(18)	2 432(25)	64
C(17)	1 918(6)	2 555(13)	1 100(21)	43

* The anisotropic temperature factor was of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^3c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Final values for the components of the tensor:

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Mn(1)	29(11)	26(12)	37(16)	−2(35)	43(22)	−1(36)

TABLE 2

Selected valency parameters

(*a*) Bond lengths (Å)

Mn–C(6)	1.67	N(5)–C(10)	1.36
Mn–C(7)	1.78	N(5)–C(17)	1.42
Mn–C(8)	1.72	C(9)–C(10)	1.54
C(6)–O(2)	1.21	C(10)–C(11)	1.48
C(7)–O(3)	1.15	C(11)–C(12)	1.44
C(8)–O(4)	1.21	C(12)–C(13)	1.45
Mn–N(5)	2.16	C(12)–C(17)	1.41
Mn–C(10)	2.17	C(13)–C(14)	1.39
Mn–C(11)	2.10	C(14)–C(15)	1.42
Mn–C(12)	2.19	C(15)–C(16)	1.38
Mn–C(17)	2.16	C(16)–C(17)	1.39

(*b*) Valency angles (°)

(*i*) Round Mn

C(6)–Mn–C(7)	94	C(11)–Mn–C(6)	97
C(6)–Mn–C(8)	92	C(11)–Mn–C(7)	160
C(7)–Mn–C(8)	90	C(11)–Mn–C(8)	106
N(5)–Mn–C(6)	158	C(12)–Mn–C(6)	93
N(5)–Mn–C(7)	97	C(12)–Mn–C(7)	124
N(5)–Mn–C(8)	107	C(12)–Mn–C(8)	145
C(10)–Mn–C(6)	136	C(17)–Mn–C(6)	122
C(10)–Mn–C(7)	130	C(17)–Mn–C(7)	95
C(10)–Mn–C(8)	90	C(17)–Mn–C(8)	146

(*ii*) Carbonyl groups

Mn–C(6)–O(2)	178	Mn–C(8)–O(4)	179
Mn–C(7)–O(3)	172		

(*iii*) In the heterocyclic ring

N(5)	105	C(12)	108
C(10)	113	C(17)	111
C(11)	102		

(*iv*) In the benzene ring

C(12)	120	C(15)	121
C(13)	117	C(16)	118
C(14)	122	C(17)	122

(*v*) Others

C(9)–C(10)–N(5)	121	C(9)–C(10)–C(11)	126

TABLE 2 (*Continued*)

(*c*) Intermolecular contacts <3.6 Å

$O(2) \cdots O(2^{I})$	3.02	$C(9) \cdots O(4^{II})$	3.57
$O(2) \cdots O(3^{III})$	3.11	$C(10) \cdots C(15^{V})$	3.59
$O(2) \cdots C(6^{I})$	3.54	$C(11) \cdots O(3^{IV})$	3.39
$O(2) \cdots C(7^{III})$	3.52	$C(12) \cdots C(15^{V})$	3.55
$O(3) \cdots O(2^{VIII})$	3.11	$C(12) \cdots C(16^{V})$	3.48
$O(3) \cdots O(4^{VI})$	3.55	$C(13) \cdots C(16^{V})$	3.55
$O(3) \cdots C(11^{XI})$	3.39	$C(14) \cdots O(5^{V})$	3.46
$O(3) \cdots C(16^{X})$	3.44	$C(14) \cdots C(17^{V})$	3.57
$O(4) \cdots O(3^{VI})$	3.55	$C(15) \cdots O(5^{VII})$	3.55
$O(4) \cdots O(4^{VI})$	3.49	$C(15) \cdots C(10^{V})$	3.59
$O(4) \cdots C(9^{II})$	3.57	$C(15) \cdots C(12^{V})$	3.55
$N(5) \cdots C(14^{V})$	3.46	$C(16) \cdots O(3^{X})$	3.44
$N(5) \cdots C(15^{IX})$	3.55	$C(16) \cdots C(12^{V})$	3.48
$C(6) \cdots O(2^{I})$	3.54	$C(16) \cdots C(13^{V})$	3.55
$C(7) \cdots O(2^{VIII})$	3.52	$C(17) \cdots C(14^{V})$	3.57

The Roman numerals as superscripts refer to the following equivalent positions:

I	$-x, -y, -z$	VII	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
II	$-x, 1 - y, -z$	VIII	$x, -y, \frac{1}{2} + z$
III	$x, -y, -\frac{1}{2} + z$	IX	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
IV	$x, -y, -1 + z$	X	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
V	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	XI	$x, y, 1 + z$
VI	$-x, y, \frac{1}{2} - z$		

TABLE 3

Means of selected valency parameters. Values in parentheses are the means of previously measured values

(*a*) Bond lengths (Å)

Mn–C (carbonyl)	1.72	(1.78) [a]	(1.80) [b]
C–O (carbonyl)	1.19		
Mn–C (ligand)	2.16	(2.16) [a]	
C(ar)–C(ar)	1.41		

(*b*) Bond angles (°) involving the carbonyl group

C–Mn–C	92	(92) [a,b]
Mn–C–O	176	

(*c*) Mean estimated standard deviations over all the values

(*i*) Bond lengths (Å)

Mn–N 0.01; Mn–C, C–O, C–N, 0.02; C–C 0.03

(*ii*) Bond angles (°)

Centred on Mn	1.5
Carbonyl	2.4
Heterocyclic ring	2.0
Carbocyclic ring	2.4

[a] Ref. 2*a*, *b*, and *c* (cyclopentadienyl ligand). [b] Ref. 2*c* (pentadienyl ligand), *d*, and *e*.

The mean Mn–C(carbonyl) bond length (1.72 Å) is shorter than the average distance of those given in ref. 2*a*—*c*; the mean C–O distance (1.19 Å) is slightly longer. Empirically, the sums of the two distances [at C(6), 2.88; at C(7), 2.93; at C(8), 2.93 Å] do not differ significantly from their mean (2.91 Å), which is close to that in related compounds. The bond angle at C(7) (172°) departs from 180° by more than three standard deviations; the other two carbonyl groups are not significantly bent. The mean C(carbonyl)–Mn–C(carbonyl) angle (92°) is unexceptional.

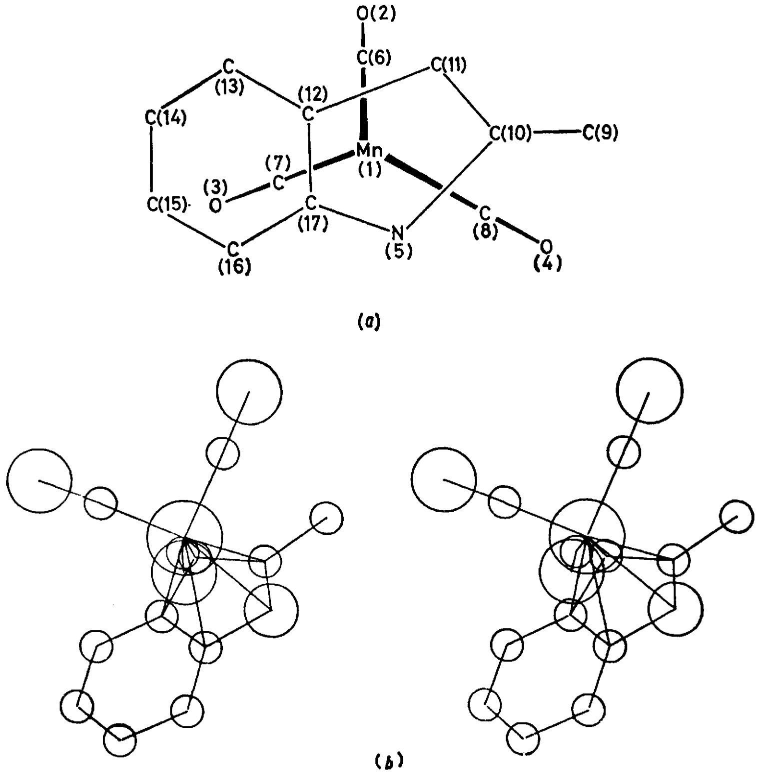

Figure 1(*a*) The molecule displayed, showing the crystallographic numbering; π-bonds involving Mn have been omitted. (*b*) The molecule viewed down the *c* axis

The manganese atom is almost but not quite symmetrically situated with respect to the carbon atoms of the heteroring, and the mean Mn–C distance (2.16 Å) is the same as that for other compounds containing a tricarbonyl(cyclopentadienyl)manganese group; it is somewhat shorter than that (2.19 Å) in the corresponding tetraphenylarsole compound (2).[4] The manganese–nitrogen distance (2.16 Å) is close to the sum (2.12 Å) of the covalent radii of manganese in the group $[Mn(CO)_3]^+$ (1.38 Å), and of nitrogen (0.74 Å);[7] the non-polar radius for nitrogen has been quoted since the radius for carbon in the cyclopentadienyl anion is that for σ-bonded carbon.[1] Table 4 gives the data for a stereographic projection of the bond vectors about the manganese atom, with the north pole at the geometrical centre of the heteroring. This reveals C(6) as *trans* to N(5).

Table 4

Stereographic projection of the bond vectors about Mn. The limiting radius = 100; vectors ending in the northern hemisphere or on the equator are labelled Dot, those ending in the southern hemisphere, Ring

Vector to	Radius	Azimuth	
Centroid of ring	0	0	Dot
N(5)	31	0	Dot
C(10)	29	−69	Dot
C(11)	33	−144	Dot
C(12)	30	145	Dot
C(17)	30	72	Dot
C(6)	52	168	Ring
C(7)	53	42	Ring
C(8)	55	−73	Ring

The indole system is not planar, although the benzene ring is. If the benzene ring is used as a reference plane, then the distortion of the system can be described as the resultant of three operations: a fold, approximately along the line C(12)—C(17), bringing N(5), C(11), and, by implication, C(9) and C(10), towards the manganese; a sharper fold, approximately along the line N(5)–C(11), moving C(9) and C(10) away from the metal atom and the carbonyl group involving C(8); and a twist, approximately about the line C(9)–C(10), moving N(5) away

Table 5

Mean planes and departures (Å) of atoms from mean planes (in square brackets). Italicized atoms were not used to locate the mean plane

Plane (1): N(5), C(10)—(17)

[N(5) 0.02, C(10) −0.10, C(11) 0.07, C(12) 0.01, C(13) −0.02, C(14) −0.03, C(15) 0.00, C(16) 0.00, C(17) 0.04]

Plane (2): N(5), C(10)—C(12), C(17)

[N(5) 0.04, C(10) −0.06, C(11) 0.06, C(12) −0.04, C(17) 0.00, *Mn*(*1*) 1.78, *C*(*9*) −0.25]

Plane (3): C(12)—C(17)

[C(12) 0.00, C(13) 0.00, C(14) 0.00, C(15) 0.01, C(16) −0.02, C(17) 0.01, N(5) −0.04, C(11) 0.03, C(10) −0.17]

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[7] R. T. Sanderson, 'Chemical Bonds and Bond Energy,' Academic Press, New York, 1971, p. 7.

from the manganese atom and C(11) towards it. Table 5 lists departures of atoms from selected mean planes. Within the benzene ring, the mean bond length (1.41 Å) is unexceptional, and the internal angles [$<120°$ at C(13) and C(16), $>120°$ elsewhere] are normal for a benzene ring fused to a five-membered ring.[8,9a] If the five-membered ring were an aza-analogue of a cyclopentadienyl anion, one could expect the three carbon-carbon bonds to have the same length, and analogously for the two carbon-nitrogen bonds. This symmetry is absent, and the structure is consistent with the π electrons of the benzene ring being less polarizable than those of the heteroring, so that the manganese atom bonds preferentially to the atoms outside the benzene ring. Compared with a simple indole, the bonds C(11)–C(12) and C(12)–C(17) are unexceptional; N(5)–C(17) is longer than usual, N(5)–C(10) shorter, and C(10)–C(11) very much longer than usual. The changes in the lengths of the last two bonds are those expected of electron delocalization towards a π-aza-allyl system for N(5)–C(10)–C(11). Further, the bonding between the metal atom and the ring system can be compared with that in bis(indenyl)ruthenium,[9a] duroquinone(indenyl)rhodium,[9b] tris(indenyl)uranium chloride,[9c] tricarbonyl(indenyl)iodomolybdenum,[9d] and tris(indenyl)samarium.[9e] With the exception of the last, these compounds have a planar ring system, unlike (1). The metal atom is sited so that the bonds to the carbon atoms of the benzene ring are longer than those to the other three atoms; the differences in length are sometimes small, but the pattern is consistent and holds too for compound (1). In the samarium compound the five-membered rings are all planar, but two of the benzene rings are not flat, and the samarium–carbon bond lengths show no dependence on the location of the carbon atoms.

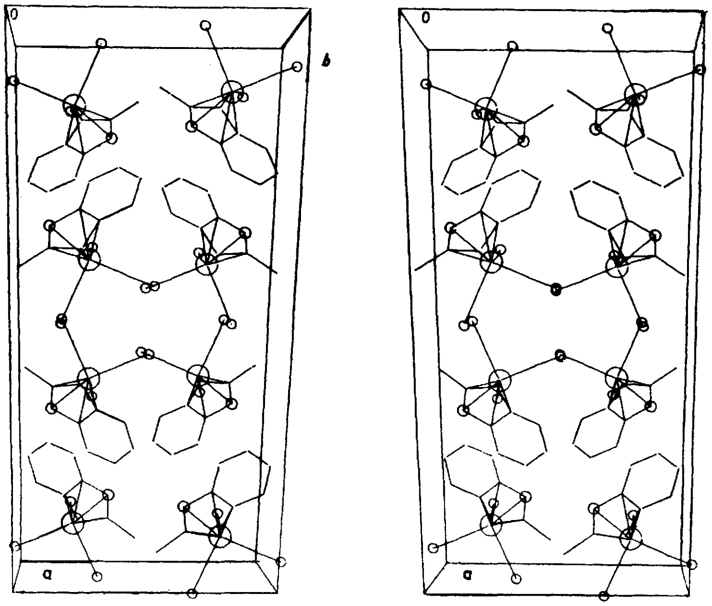

FIGURE 2 The crystal packing viewed down the c axis

Figure 2 is a stereopair of drawings showing the packing viewed down the c axis. Intermolecular contacts $\leqslant 3.6$ Å are listed in Table 2(c). As usual for this type of compound, the molecules pack with carbonyl groups opposed and, so far as possible, interleaved. The mean planes of the ring systems of adjacent molecules are approximately parallel with the heteroring of one molecule facing the carbocyclic ring of another. There are no unusually close contacts, and the distortion from planarity of the heteroring seems to be due to bonding rather than non-bonding interactions.

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