were not used for the structure refinement. The atomic scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). The absorption correction was not applied ($\mu R=0{\cdot}43$).

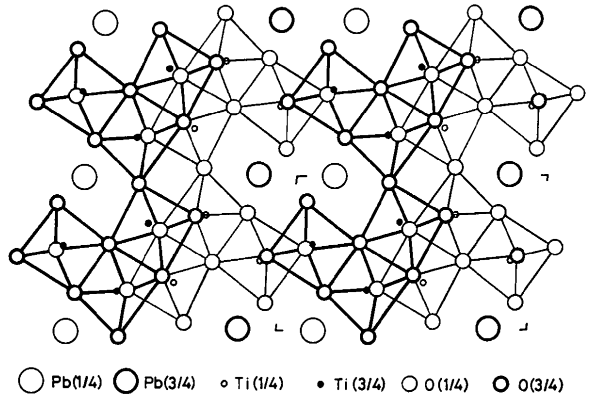

Fig. 1. The structure of $PbTi_3O_7$ projected on to (010). The fractional *y* coordinates of the atoms are given in parentheses after the chemical symbols.

Discussion. Table 1 lists the atomic coordinates and thermal parameters, Table 2 the interatomic distances. Fig. 1 depicts the way in which the TiO_6 octahedra are connected. The lead atom is surrounded by seven oxygen atoms, whereas the same atom in $PbTiO_3$ has eight oxygen nearest neighbours. The Ti_3O_7 group forms a three-dimensional network instead of a sheet as in $Na_2Ti_3O_7$ (Andersson & Wadsley, 1961).

The calculations were carried out on the FACOM 270-20 of this Institute.

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Tricarbonyl-1-*syn*-(1′,2′-dihydro-2′-oxo-1′-oxa-azulen-3′-yl)-*h*⁵-pentadienylmanganese

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Abstract. Monoclinic, $P2_1/c$, $a=13{\cdot}249(5)$, $b=7{\cdot}178(4)$, $c=15{\cdot}662(6)$ Å, $\beta=96{\cdot}66(3)°$. $C_{17}H_{11}O_5Mn$, $M=350{\cdot}2$, $Z=4$, $D_c=1{\cdot}57$ g cm^{-3}. Tropone reacts with decacarbonyldimanganese to yield a tricarbonylmanganese complex. The molecules contain an approximately planar oxa-azulenone system with an open π-pentadienyl side chain to which is bonded a tricarbonylmanganese group. Formation of the ligand has involved a hydrogen-elimination reaction between two tropone molecules.

Introduction. The preparation of the title compound has been reported earlier (Barrow, Mills, Haque & Pauson, 1971). The crystals, red monoclinic needles, were air-stable and unaffected by X-rays. Approximate cell dimensions were obtained from precession and Weissenberg photographs. The reciprocal lattice symmetry and systematic absences uniquely specified space group $P2_1/c$ (C_{2h}^5, No. 14). A crystal with dimensions $0{\cdot}39\times0{\cdot}13\times0{\cdot}15$mm, $\mu(\text{Mo } K\alpha)=9{\cdot}46$ cm^{-1}, was selected for intensity measurements.

The intensities (for $\theta<25°$) were collected on a Hilger and Watts computer-controlled single-crystal four-circle X-ray diffractometer (Edwards, Bowden, Standeven & Mills, 1966) with Zr-filtered Mo $K\alpha$ radiation and an $\omega/2\theta$ step-scanning mode. Orientation matrices were calculated by a least-squares method which utilized reflexion positions determined by a peak-finder program. Cell parameters were calculated, by the least-squares method, from the θ values of reflexions measured at both positive and negative $\omega/2\theta$ offsets. The intensities were corrected for Lorentz and polarization effects but not for absorption. 2592 independent reflexions were obtained; this analysis is based on the 1009 reflexions with $F>6\sigma(F)$, where σ(F) was derived from counting statistics. The large proportion of statistically non-significant reflexions was a consequence of an unusually large mosaic spread which gave rise to ill-defined diffracted beams of low peak height. Structure solution was by Fourier methods and refinement by least-squares methods to minimize $\sum w(F_o-k|F_c|)^2$. All hydrogen atoms were located from difference syntheses. The positional coordinates of hydrogens H(4) and Hx(4) were refined whilst the other hydrogen atoms were placed at calculated locations, [r(C–H)$=1{\cdot}09$ Å]. The temperature factors for the hydrogen atoms were set equal to the isotropic values for the carbon atoms to which they are bonded. The paucity of statistically significant reflexions produced some restriction on the number of refined variables. In the end, anisotropic thermal parameters were included for those atoms where prior refinement had shown that thermal motion was significantly anisotropic as judged by the values of the e.s.d.'s. Scattering factors were taken from Hanson, Herman, Lea & Skillman, (1964); that for manganese was corrected for the real part of the anomalous dispersion effect (Cromer, 1965) by addition of a constant, +0·36 e, over the whole range of sin θ. The final weighting scheme was $w^{-1} = 1 + 0{\cdot}0037\,(F_o - 50)^2$. The final R was 6·6%.[*] Atomic parameters are given in Table 1, and bond lengths and angles in Table 2. The labelling of the atoms is shown in Fig. 1.

Table 1. *Atomic parameters with estimated standard deviations in parentheses*

	x/a	y/b	z/c	B(Å^2)
Mn	0·13984 (15)	0·12358 (27)	0·16326 (13)	
C(1)	0·0092 (10)	0·1446 (22)	0·1271 (9)	
O(1)	−0·0772 (7)	0·1569 (15)	0·1053 (7)	
C(2)	0·1326 (10)	−0·1112 (21)	0·1146 (7)	
O(2)	0·1243 (9)	−0·2478 (15)	0·0833 (7)	
C(3)	0·1814 (10)	0·2475 (19)	0·0729 (9)	
O(3)	0·2084 (8)	0·3224 (12)	0·0160 (6)	
C(4)	0·1555 (12)	0·3950 (23)	0·2300 (9)	4·5 (3)
C(5)	0·1132 (9)	0·2592 (19)	0·2800 (8)	3·9 (3)
C(6)	0·1528 (9)	0·0821 (16)	0·2998 (7)	3·8 (3)
C(7)	0·2391 (9)	0·0094 (17)	0·2680 (8)	3·4 (3)
C(8)	0·3069 (8)	0·1012 (17)	0·2211 (7)	3·3 (2)
C(9)	0·3857 (9)	0·0071 (16)	0·1813 (8)	3·1 (2)
C(10)	0·3981 (9)	−0·1962 (16)	0·1797 (8)	3·5 (3)
O(4)	0·3488 (6)	−0·3255 (10)	0·1998 (5)	
O(5)	0·4881 (6)	−0·2311 (10)	0·1429 (5)	
C(11)	0·4640 (8)	0·0780 (14)	0·1420 (6)	2·5 (2)
C(12)	0·5296 (9)	−0·0683 (15)	0·1203 (7)	2·9 (2)
C(13)	0·6164 (9)	−0·0690 (15)	0·0839 (7)	3·0 (2)
C(14)	0·6693 (9)	0·0838 (17)	0·0552 (7)	3·7 (3)
C(15)	0·6429 (9)	0·2676 (18)	0·0541 (8)	3·7 (3)
C(16)	0·5577 (9)	0·3502 (17)	0·0869 (7)	3·7 (2)
C(17)	0·4822 (9)	0·2745 (16)	0·1267 (7)	3·2 (2)
H(4)	0·221 (9)	0·436 (14)	0·244 (7)	4·5
Hx(4)	0·112 (9)	0·458 (16)	0·198 (7)	4·5
H(5)	0·0427	0·2956	0·3056	3·9
H(6)	0·1141	−0·0050	0·3429	3·8
H(7)	0·2552	−0·1372	0·2818	3·4
H(8)	0·3002	0·2519	0·2139	3·3
H(13)	0·6501	−0·2053	0·0757	3·0
H(14)	0·7408	0·0514	0·0305	3·7
H(15)	0·6930	0·3624	0·0246	3·7
H(16)	0·5523	0·5008	0·0784	3·7
H(17)	0·4287	0·3721	0·1501	3·2

Anisotropic temperature coefficients in the form:

$$t = \exp\left[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})\right]$$

	b_{11}	b_{22}	b_{33}
Mn	0·00457 (10)	0·0134 (3)	0·00372 (8)
C(1)	0·0068 (10)	0·025 (4)	0·0064 (8)
O(1)	0·0066 (7)	0·039 (3)	0·0078 (6)
C(2)	0·0080 (11)	0·027 (4)	0·0025 (6)
O(2)	0·0167 (12)	0·019 (2)	0·0062 (6)
C(3)	0·0068 (11)	0·018 (3)	0·0046 (8)
O(3)	0·0138 (10)	0·018 (2)	0·0057 (6)
O(4)	0·0071 (6)	0·0095 (18)	0·0057 (5)
O(5)	0·0057 (6)	0·0091 (16)	0·0049 (5)

	b_{12}	b_{13}	b_{23}
Mn	−0·00011 (28)	0·00124 (7)	0·00006 (23)
C(1)	−0·0019 (20)	0·0014 (8)	−0·0007 (17)
O(1)	−0·0003 (15)	0·0003 (6)	0·0052 (13)
C(2)	−0·0018 (21)	0·0008 (6)	0·0022 (16)
O(2)	−0·0035 (16)	0·0005 (7)	−0·0042 (10)
C(3)	−0·0001 (16)	0·0014 (8)	0·0019 (13)
O(3)	0·0014 (12)	0·0048 (6)	0·0041 (9)
O(4)	−0·0011 (9)	0·0015 (5)	0·0009 (7)
O(5)	−0·0000 (9)	0·0008 (4)	−0·0008 (7)

Discussion. This analysis continues our investigations into the structural chemistry of complexes formed by the reactions of tropone with transition-metal carbonyls (Barrow & Mills, 1971). In the present analysis, the ligand, which has clearly been formed from two tropone molecules, is bonded to a Mn(CO)$_3$ fragment by an open-chain pentadienyl system. Formation of the ligand has left one tropone molecule essentially intact whilst the other has undergone cleavage, probably to an open-chain ketene intermediate, before addition to the first molecule to yield an α,β-unsaturated γ-lactone. The reaction involves the loss of one hydrogen atom and the migration of another to what eventually becomes the terminal methylene group.

The C–C distances unambiguously locate the single and double bonds in the essentially planar oxa-azulene portion of the ligand. In the 7-membered ring, the double bonds have rotated cyclically by one atom with respect to tropone itself (Barrow, Mills & Filippini, 1973). The conformation and bond lengths in the α,β-unsaturated γ-lactone entity are similar to those reported for 1-oxa-azulan-2-one (Sasada, 1959), and unlike those in saturated γ-lactones where puckered rings

Table 2. *Molecular geometry*

(*a*) Intramolecular distances (Å) with estimated standard deviations in parentheses

Mn—C(1)	1·76 (1)	C(8)—C(9)	1·44 (1)
Mn—C(2)	1·85 (2)	C(9)—C(10)	1·47 (2)
Mn—C(3)	1·81 (1)	C(9)—C(11)	1·37 (1)
Mn—C(4)	2·21 (2)	C(10)—O(4)	1·20 (1)
Mn—C(5)	2·14 (1)	C(10)—O(5)	1·41 (1)
Mn—C(6)	2·15 (1)	O(5)—C(12)	1·36 (1)
Mn—C(7)	2·14 (1)	C(11)—C(12)	1·43 (1)
Mn—C(8)	2·30 (1)	C(12)—C(13)	1·34 (2)
Mn···H(4)	2·73 (11)	C(13)—C(14)	1·40 (1)
Mn···Hx(4)	2·50 (11)	C(14)—C(15)	1·36 (2)
Mn···H(8)	2·36	C(15)—C(16)	1·42 (2)
C(1)—O(1)	1·16 (1)	C(16)—C(17)	1·35 (1)
C(2)—O(2)	1·10 (2)	C(17)—C(11)	1·46 (2)
C(3)—O(3)	1·13 (1)	C(4)—H(4)	0·92 (12)
C(4)—C(5)	1·41 (2)	C(4)—Hx(4)	0·84 (11)
C(5)—C(6)	1·40 (2)	C(3)···H(4)	2·99 (11)
C(6)—C(7)	1·40 (2)	C(3)···Hx(4)	2·72 (11)
C(7)—C(8)	1·39 (2)	C(3)···H(8)	2·56
		H(4)···H(8)	1·78

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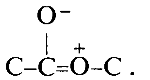
[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30368 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (*cont.*)

(*b*) Intramolecular angles with estimated standard deviations in parentheses

C(1)–Mn—C(2)	86·8 (6)°	C(10)–C(9)—C(11)	105·7 (11)°
C(1)–Mn—C(3)	94·8 (6)	C(9)—C(10)–O(4)	134·4 (12)
C(2)–Mn—C(3)	97·6 (6)	C(9)—C(10)–O(5)	106·6 (10)
C(4)–Mn—C(5)	37·7 (5)	O(4)—C(10)–O(5)	119·0 (10)
C(5)–Mn—C(6)	38·1 (4)	C(10)–O(5)—C(12)	110·0 (9)
C(6)–Mn—C(7)	38·1 (4)	C(9)—C(11)–C(12)	110·4 (10)
C(7)–Mn—C(8)	36·3 (4)	C(9)—C(11)–C(17)	125·8 (10)
C(4)–Mn—C(6)	70·0 (5)	C(17)–C(11)–C(12)	123·8 (10)
C(4)–Mn—C(7)	87·7 (5)	C(11)–C(12)–O(5)	107·2 (9)
C(4)–Mn—C(8)	80·9 (5)	O(5)—C(12)–C(13)	120·1 (10)
Mn—C(1)–O(1)	178·3 (13)	C(11)–C(12)–C(13)	132·7 (11)
Mn—C(2)–O(2)	176·6 (13)	C(12)–C(13)–C(14)	125·2 (11)
Mn—C(3)–O(3)	178·8 (12)	C(13)–C(14)–C(15)	128·5 (11)
C(4)–C(5)–C(6)	126·2 (12)	C(14)–C(15)–C(16)	127·7 (12)
C(5)–C(6)–C(7)	124·2 (11)	C(15)–C(16)–C(17)	131·2 (12)
C(6)–C(7)–C(8)	128·0 (12)	C(17)–C(16)–C(11)	127·7 (11)
C(7)–C(8)–C(9)	123·4 (11)	H(4)—C(4)—C(5)	121 (7)
C(8)–C(9)–C(10)	124·0 (12)	Hx(4)–C(4)—C(5)	114 (8)
C(8)–C(9)–C(11)	130·2 (11)	H(4)—C(4)—Hx(4)	121 (11)

are found and where the bond lengths suggest contributions from valence-bond resonance hybrids such as



$$\mathrm{C{-}\overset{O^-}{\overset{|}{C}}{=}\overset{+}{O}{-}C}\,.$$

This analysis represents the first X-ray determination of an open-chain π-pentadienyl complex of manganese. The pentadienyl system is approximately planar, the whole being slightly twisted with respect to the remainder of the ligand; the C–C lengths, mean 1·40 Å, are equal within experimental error. The manganese to carbon contacts vary systematically: the three central carbon atoms are equidistant (2·14 Å) from the metal whilst the terminal carbon atoms make longer contacts, 2·21 and 2·30 Å. Untoward intramolecular H···H interactions are alleviated through a twisting of the terminal CH_2 group out of the plane of the pentadienyl system by approximately 48°. The $Mn(CO)_3$ group takes the same orientation with respect to the pentadienyl group as it does in the cyclic pentadienyl complexes tricarbonyl-π-cyclohexadienylmanganese (Churchill & Scholer, 1969) and hexacarbonyl-*trans*-azulenedimanganese (Churchill & Bird, 1968).

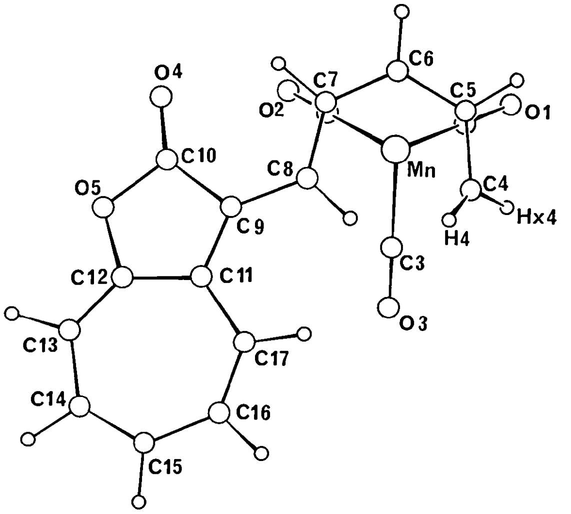


Fig. 1. Projection of the structure onto the least-squares plane through the ligand.

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