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Crystal and Molecular Structure of Tris(tropolonato)manganese(III), $Mn(O_2C_7H_5)_3$, a High-Spin Complex Having Structural Features Consistent with Jahn-Teller Behavior for Two Distinct MnO_6 Centers

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The crystal and molecular structure of tris(tropolonato)manganese(III), $Mn(trop)_3$, has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group $C_{2h}{}^5$-$P2_1/c$ (No. 14) with $a = 7.441$ (1) Å, $b = 25.075$ (3) Å, $c = 20.673$ (2) Å, and $\beta = 92.59$ (4)°. Least-squares refinement of 1617 reflections resulted in a final conventional R factor of 0.067. There are two crystallographically independent molecules in the unit cell ($Z = 8$). The cell also contains two disordered solvent molecules of toluene. The two asymmetric molecules of $Mn(trop)_3$ are distorted from a regular D_3 configuration. One molecule contains a tetragonally elongated MnO_6 geometry with average Mn–O bond distances of 1.94 and 2.13 Å. The other molecule shows an orthorhombic MnO_6 distortion with average Mn–O bond distances of 1.94, 1.99, and 2.05 Å. The average O· · ·O "bite" distance is 2.55 Å. The average trigonal-twist angle (from trigonal-prismatic configuration) is 49°; however, a trigonal D_3 symmetry cannot remove the orbital degeneracy of the ^5E electronic ground state. The Mn–O distortions found are expected as a consequence of the Jahn-Teller susceptible high-spin $3d^4$ configuration of manganese(III). The presence of two distinctly different molecules in the same unit cell is highly unusual. A weak intermolecular coupling through the tropolonate ligands may be the origin of this result.

Introduction

The purported structure of tris(acetylacetonato)manganese(III), $Mn(acac)_3$, by Morosin and Brathovde[1] (MB) has been a subject of controversy for several years. Six-coordinate complexes of manganese(III), a high-spin d^4 metal ion with a ^5D electronic ground state, are expected to be distorted from a regular octahedral geometry due to Jahn-Teller (JT) forces.[2] These structural changes remove the twofold degeneracy of the ^5E_g ground state. Since a regular D_3 symmetry cannot itself remove the orbital degeneracy of the ^5E state in tris chelate complexes, further reduction in symmetry is required. Before the work of MB, Forman and Orgel suggested,[3] on the basis of infrared studies of $Cr(acac)_3$, $Mn(acac)_3$, and $Fe(acac)_3$, that the MnO_6 geometry of $Mn(acac)_3$ was tetragonal (overall symmetry $\sim C_2$). The noticeably broadened Mn-O bands in $Mn(acac)_3$ were split and could be thought of as superpositions of the vibrations due to chromium and iron. It was implied that two (or four) of the Mn-O bonds are essentially equal in length to those of iron and four (or two) are equal to those of chromium. More recent ir studies of metal β-ketoenolate complexes[4-9] further supported the earlier study and refined some of the far-ir assignments. In contrast to the ir work, however, the MB structure indicated no tetragonal distortion and the average Mn-O bond distance was 1.87 Å, clearly out of the range 1.951-1.992 Å found in $Cr(acac)_3$[10] and $Fe(acac)_3$,[11] respectively.

Further evidence for a structure distorted from D_3 symmetry was obtained from electronic spectra.[12,13] Detailed studies[14-16] have been made of the uv-vis-ir spectra of a number of Mn(III) compounds (solution and solid state). This work presented substantial evidence, after considering several possibilities, that the low-energy band at 8-10 kK was due to a transition within the JT-split octahedral ^5E_g manifold such that the effective site symmetry about the metal ion was D_{4h} and the electronic ground state was either $^5A_{1g}$ (compressed structure) or $^5B_{1g}$ (elongated structure). Polarization properties of the bands in $(NH_4)_2MnF_5$ suggested[17] the assignment of the low-energy band to the $^5B_{1g} \leftrightarrow {}^5A_{1g}$ transition (Figure 1).

In spite of the large number of theoretical studies of JT distortions, the understanding of the problem is far from complete. Liehr and Ballhausen,[18] using an ionic crystal field model, predicted compressed octahedral Cu(II) structures, admittedly at odds with many observations. Lohr[19] performed an extended Huckel type of calculation on $CuCl_6{}^{4-}$ and found the elongated structure to be more stable (by 40 cm^{-1}) if the Cu 4s orbital is included in the basis set. The more rigorous CNDO/2 calculation on $CuF_6{}^{4-}$ by Allen and Clack[20] revealed a slight preference for the compressed structure.

Crystallographic evidence for the importance (or even relevance) of JT-distorted octahedral Mn(III) compounds has been scanty since most of the systems studied are composed of bridging halides, in either infinite chains or linked three-dimensional networks where the metal-ligand bonds are themselves involved in the crystal binding. Since the JT energy is expected to be of the order of 1 eV[16] and typical ionic crystal binding energies are of the order of 2-8 eV

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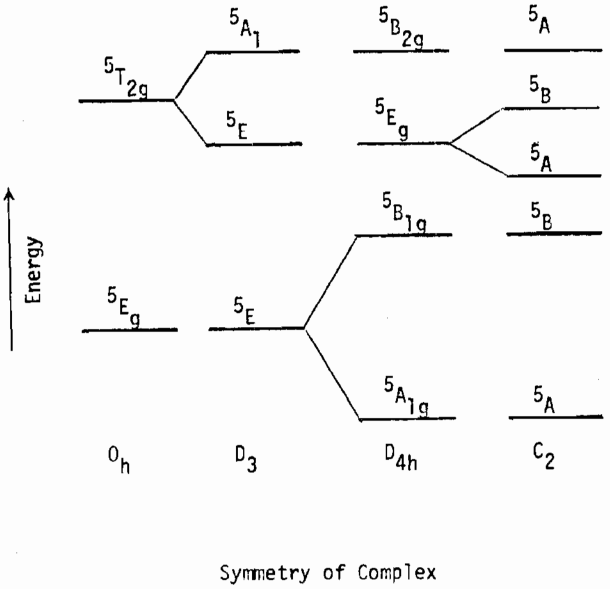

Figure 1. Schematic term diagrams for the 3d electrons in manganese(III) complexes with octahedral (O_h), trigonal (D_3), tetragonal (D_{4h}) and rhombic (C_2) geometries. (The relative ordering of some of the levels in the D_3, D_{4h}, and C_2 symmetries will depend on the specific structure present.)

Table I. Summary of Crystal Data for Mn(trop)$_3$

Molecular formula	$Mn(O_2C_7H_5)_3 \cdot {}^1/_4C_6H_5CH_3$
FW	441.32
d_{calcd}, g/cm^3	1.522
d_{obsd}, g/cm^3	1.53 (5)
Z, formula units/cell	8
Linear absorption coeff, μ, cm^{-1}	61.3
λ(Cu Kα), Å	1.5418
Crystal dimensions,^{a} mm	0.38 × 0.03 × 0.07
Systematic absences	$h0l, l = 2n + 1$ $0k0, k = 2n + 1$
Space group	$C_{2h}{}^5$-$P2_1/c$ (No. 14)
Cell constants^b	
a, Å	7.441 (1)
b, Å	25.075 (3)
c, Å	20.673 (2)
β, deg	92.59 (4)
cos β	−0.045189
U, Å^3	3852.1
F(000)^c	1812

^{a}Along a, b, and c, respectively. ^{b}At 22 (2)°; least-squares fit to diffractometer settings. ^{c}Analysis: 11% Mn, 21% O, 60% C, 8% H.

per ionic unit, packing considerations may overshadow the Jahn-Teller effect in many of the ionic crystals.

The MB structure and those of $(K_2Na)[MnF_6]$[21] (elongated), $Mn(Et_2dtc)_3$[22] (elongated), and Mn(acac)(N-phenylaminotroponiminato)$_2$[23] are the only reported structures to date of the discrete molecular type. The average Mn-O bond distance in the last compound is 2.05 Å, considerably longer than that observed by MB.

The short Mn-O distance in Mn(acac)$_3$ was not easy to reconcile with other experimental observations. However, the absence of distortion, which was of more interest, served as a basis for tenuous, unfortunately faulty, speculation:[23] "symmetrical tris-chelates may remove the degeneracy of the d_{z^2} and $d_{x^2-y^2}$ levels by an angular distortion [presumably trigonal] rather than a bond lengthening." A similar

Table II. Summary of Final Refinement Characteristics for Mn(trop)$_3$

Data used	$I/\sigma(I) \geq 2$
No. of reflections (corrected for absorption)	1617
No. of varied parameters (nonhydrogen)/half-cycle^a	253
No. of reflections/no. of varied parameters	6.4
R	0.067
R_w	0.074
Erf	0.876
Weighting scheme, Cruickshank type	$w_i = 1/(\Delta F_i)^2$
ΔF_i for $F_o \leq 30$, reduced $\chi^2 = 18.4$	$15.948 - 0.406F_o$
ΔF_i for $F_o > 30$, reduced $\chi^2 = 4.7$	$1.980 + 0.0143F_o - 3.3 \times 10^{-6}F_o{}^2$
Max.^{b} position shift/error (nonhydrogen)	0.34[y of CA15-2]^c
Max.^{b} thermal parameter shift/error (nonhydrogen)	0.53[β_{23} of C23(1)]

^{a}See text. ^{b}Excluding the carbons of the disordered toluene. ^{c}0.005-Å shift in atomic position.

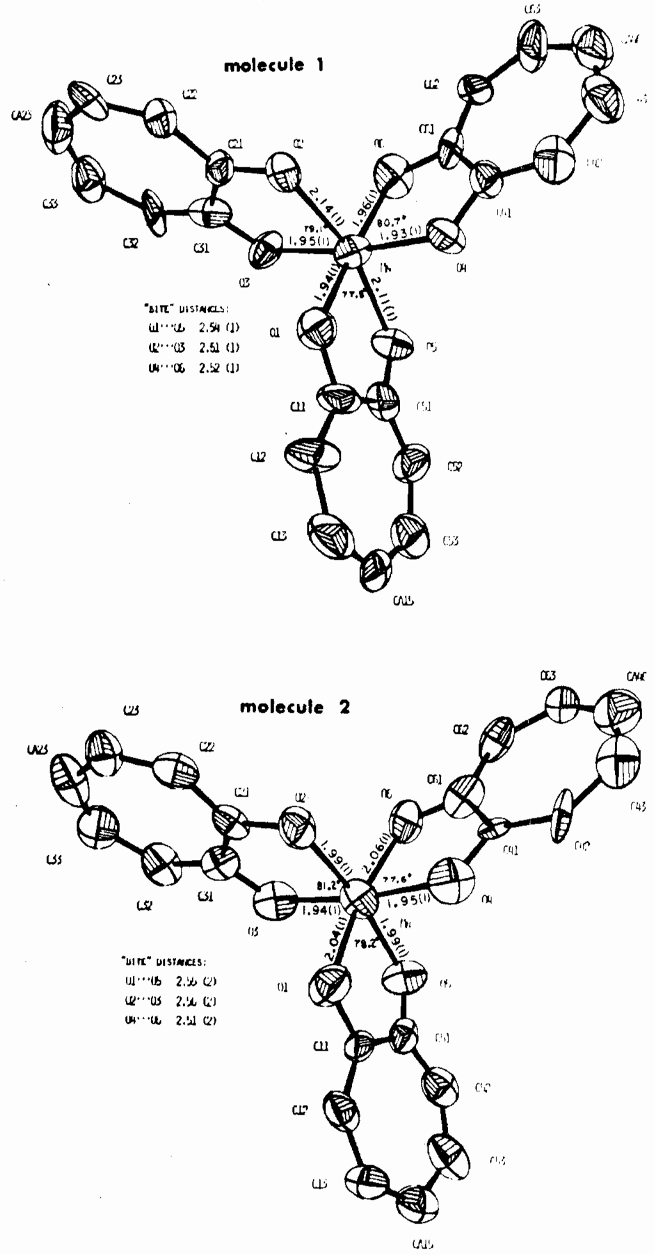

Figure 2. An ORTEP thermal ellipsoid projected view (50% probability level) of the two asymmetric molecules of Mn(trop)$_3$.

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Table III. Positional Parameters and Estimated Standard Deviations for Mn(trop)$_3$

Molecule 1				Molecule 2			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	0.4830 (3)	0.2293 (1)	0.0152 (1)	Mn(2)	0.2928 (4)	0.4797 (1)	0.2029 (1)
O1(1)	0.5556 (13)	0.2922 (3)	0.0639 (5)	O1(2)	0.2017 (16)	0.4183 (5)	0.1456 (5)
O2(1)	0.4741 (15)	0.2792 (4)	−0.0691 (4)	O2(2)	0.2890 (17)	0.5302 (4)	0.1287 (5)
O3(1)	0.2292 (12)	−0.1461 (4)	0.0091 (4)	O3(2)	0.5434 (15)	0.4735 (4)	0.1803 (5)
O4(1)	0.7270 (13)	0.2054 (0)	0.0079 (4)	O4(2)	0.0522 (14)	0.4968 (5)	0.2288 (6)
O5(1)	0.4780 (13)	0.2021 (4)	0.1117 (4)	O5(2)	0.3027 (15)	0.4188 (5)	0.2648 (5)
O6(1)	0.4379 (15)	0.1648 (4)	−0.0369 (5)	O6(2)	0.3399 (17)	0.5398 (5)	0.2697 (5)
C11(1)	0.5820 (22)	0.2886 (8)	0.1277 (8)	C11(2)	0.1824 (23)	0.3729 (6)	0.1751 (8)
C21(1)	0.3147 (23)	0.2972 (5)	−0.0788 (7)	C21(2)	0.4428 (24)	0.5322 (6)	0.1005 (8)
C31(1)	0.1718 (28)	0.2810 (6)	−0.0354 (7)	C31(2)	0.5890 (28)	0.5011 (7)	0.1295 (8)
C41(1)	0.7529 (29)	0.1653 (7)	−0.0312 (8)	C41(2)	0.0310 (30)	0.5367 (6)	0.2689 (7)
C51(1)	0.5368 (20)	0.2357 (7)	0.1524 (8)	C51(2)	0.2335 (22)	0.3758 (8)	0.2435 (8)
C61(1)	0.5845 (27)	0.1444 (7)	−0.0563 (8)	C61(2)	0.1985 (29)	0.5604 (8)	0.2914 (8)
C12(1)	0.6394 (21)	0.3340 (7)	0.1576 (8)	C12(2)	0.1183 (22)	0.3295 (8)	0.1383 (8)
C22(1)	0.2901 (25)	0.3342 (5)	−0.1309 (7)	C22(2)	0.4500 (25)	0.5658 (6)	0.0448 (8)
C32(1)	−0.0090 (23)	0.2930 (6)	−0.0388 (8)	C32(2)	0.7694 (29)	0.4977 (7)	0.1109 (9)
C42(1)	0.9281 (27)	0.1514 (7)	−0.0430 (8)	C42(2)	−0.1456 (24)	0.5472 (8)	0.2834 (7)
C52(1)	0.5541 (23)	0.2211 (7)	0.2179 (8)	C52(2)	0.2151 (25)	0.3337 (8)	0.2859 (8)
C62(1)	0.5590 (27)	0.1019 (6)	−0.1017 (7)	C62(2)	0.2073 (26)	0.6067 (8)	0.3327 (7)
C13(1)	0.6875 (25)	0.3413 (7)	0.2245 (10)	C13(2)	0.0783 (24)	0.2785 (7)	0.1577 (10)
C23(1)	0.1344 (30)	0.3584 (7)	−0.1544 (8)	C23(2)	0.6007 (28)	0.5762 (7)	0.0090 (7)
C33(1)	−0.1074 (21)	0.3255 (7)	−0.0803 (8)	C33(2)	0.8481 (27)	0.5241 (8)	0.0601 (10)
C43(1)	0.9799 (29)	0.1110 (9)	−0.0853 (11)	C43(2)	−0.2108 (26)	0.5876 (9)	0.3232 (9)
C53(1)	0.6191 (24)	0.2512 (8)	0.2721 (8)	C53(2)	0.1479 (26)	0.2825 (8)	0.2771 (10)
C63(1)	0.6811 (33)	0.0735 (7)	−0.1328 (9)	C63(2)	0.0684 (37)	0.6343 (8)	0.3626 (10)
CA15-1	0.6816 (21)	0.3050 (8)	0.2744 (8)	CA15-2	0.0855 (26)	0.2553 (7)	0.2192 (9)
CA23-1	−0.0451 (28)	0.3541 (7)	−0.1339 (9)	CA23-2	0.7713 (29)	0.5574 (8)	0.0136 (9)
CA46-1	0.8732 (35)	0.0795 (8)	−0.1254 (10)	CA46-2	−0.1174 (38)	0.6264 (8)	0.3593 (10)
H1(11)	0.655	0.364	0.130	H1(21)	0.093	0.337	0.094
H2(11)	0.725	0.376	0.236	H2(21)	0.036	0.255	0.124
H3(11)	0.720	0.318	0.316	H3(21)	0.051	0.219	0.221
H4(11)	0.627	0.233	0.312	H4(21)	0.145	0.262	0.316
H5(11)	0.519	0.186	0.227	H5(21)	0.249	0.343	0.329
H1(12)	0.395	0.342	−0.154	H1(22)	0.342	0.584	0.033
H2(12)	0.149	0.382	−0.190	H2(22)	0.580	0.600	−0.027
H3(12)	−0.133	0.375	−0.157	H3(22)	0.851	0.571	−0.017
H4(12)	−0.233	0.328	−0.075	H4(22)	0.971	0.516	0.055
H5(12)	−0.074	0.277	−0.005	H5(22)	0.849	0.477	0.138
H1(13)	0.018	0.172	−0.021	H1(23)	−0.233	0.525	0.263
H2(13)	0.106	0.107	−0.088	H2(23)	−0.338	0.588	0.327
H3(13)	0.938	0.051	−0.151	H3(23)	−0.189	0.650	0.383
H4(13)	0.636	0.047	−0.162	H4(23)	0.109	0.663	0.390
H5(13)	0.437	0.094	−0.114	H5(23)	0.326	0.620	0.342
HTOL	0.463	0.570	0.433				

Disordered toluene							
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C1	0.326 (4)	0.511 (1)	0.471 (1)	C3	0.640 (6)	0.531 (1)	0.478 (1)
C1M	0.181 (14)	0.518 (3)	0.457 (4)	C3M	0.768 (12)	0.536 (3)	0.488 (3)
C2	0.480 (4)	0.539 (1)	0.459 (1)				

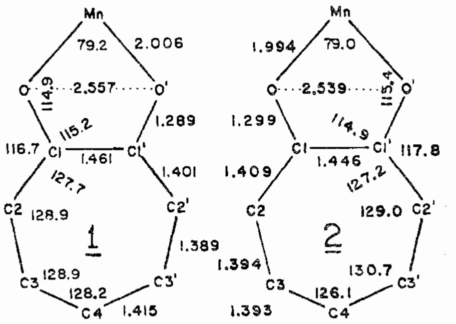

Figure 3. Summary of the weighted mean bond distances and angles of the ligands in 1 and **2** of the Mn(trop)$_3$ structure.

suggestion was proposed by Cotton and Wilkinson:[24] “the reason for this [Mn(acac)$_3$ isotropy] is not clear, but in this case the chelate rings with their π systems introduce a significant low symmetry (D_3) component into the ligand field and this may influence the operation of the Jahn–Teller effect here in a manner that remains to be investigated.”

To obtain further insight into the problem it was decided that the crystal structure of tris(tropolonato)manganese(III), Mn(trop)$_3$, should be determined. The infrared[25] and electronic[16] spectra indicated patterns similar to those exhibited by Mn(acac)$_3$, interpretable in terms of a substantial distortion from D_3 symmetry. It was expected that some of the structural questions surrounding the work of MB might be cleared up by this study. A preliminary account already has been reported.[26]

Experimental Section

Space Group and Lattice Parameters. The Mn(trop)$_3$ complex

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Table IV. Thermal Parameters[a] and Estimated Standard Deviations for Mn(trop)$_3$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			Molecule 1			
Mn(1)	0.0161 (5)	0.0017 (1)	0.0018 (1)	−0.0003 (2)	−0.0000 (2)	0.0001 (1)
O1(1)	0.0227 (31)	0.0012 (2)	0.0027 (1)	−0.0002 (6)	−0.0004 (8)	0.0001 (2)
O2(1)	0.0154 (28)	0.0022 (3)	0.0024 (3)	0.0023 (7)	0.0007 (8)	−0.0002 (2)
O3(1)	0.0125 (25)	0.0020 (2)	0.0019 (3)	0.0001 (6)	0.0005 (6)	0.0008 (2)
O4(1)	0.0175 (29)	0.0016 (2)	0.0023 (3)	0.0003 (6)	0.0011 (8)	−0.0006 (2)
O5(1)	0.0203 (29)	0.0016 (2)	0.0020 (3)	−0.0011 (6)	0.0008 (7)	−0.0004 (2)
O6(1)	0.0064 (27)	0.0023 (3)	0.0037 (4)	−0.0010 (7)	−0.0001 (8)	−0.0004 (3)
C11(1)	0.0151 (47)	0.0029 (5)	0.0023 (5)	0.0011 (12)	−0.0017 (12)	−0.0014 (4)
C21(1)	0.0197 (40)	0.0007 (3)	0.0020 (5)	0.0008 (10)	−0.0013 (13)	0.0000 (3)
C31(1)	0.0320 (63)	0.0009 (4)	0.0015 (5)	−0.0021 (12)	0.0012 (15)	0.0000 (3)
C41(1)	0.0155 (67)	0.0019 (4)	0.0022 (5)	0.0017 (13)	0.0014 (14)	0.0002 (4)
C51(1)	0.0135 (40)	0.0010 (4)	0.0031 (6)	−0.0003 (10)	−0.0008 (12)	−0.0005 (4)
C61(1)	0.0069 (45)	0.0024 (4)	0.0024 (5)	0.0021 (12)	0.0026 (12)	0.0014 (4)
C12(1)	0.0143 (44)	0.0028 (5)	0.0027 (6)	−0.0025 (12)	−0.0009 (12)	−0.0013 (4)
C22(1)	0.0264 (66)	0.0011 (3)	0.0023 (5)	0.0016 (11)	−0.0006 (13)	−0.0001 (3)
C32(1)	0.0089 (44)	0.0016 (4)	0.0045 (6)	0.0029 (10)	−0.0018 (13)	−0.0008 (4)
C42(1)	0.0185 (58)	0.0022 (4)	0.0031 (6)	0.0006 (11)	0.0031 (14)	0.0010 (4)
C52(1)	0.0237 (49)	0.0028 (5)	0.0019 (6)	0.0025 (12)	0.0006 (14)	0.0005 (5)
C62(1)	0.0454 (63)	0.0009 (3)	0.0017 (4)	0.0038 (12)	−0.0010 (14)	−0.0005 (3)
C13(1)	0.0216 (55)	0.0028 (5)	0.0036 (8)	0.0019 (12)	0.0018 (16)	−0.0011 (5)
C23(1)	0.0395 (57)	0.0013 (4)	0.0026 (6)	0.0024 (13)	0.0008 (15)	−0.0010 (4)
C33(1)	0.0152 (40)	0.0017 (4)	0.0042 (6)	0.0012 (10)	−0.0023 (12)	−0.0006 (4)
C43(1)	0.0272 (58)	0.0020 (5)	0.0034 (7)	0.0021 (15)	0.0045 (17)	0.0006 (5)
C53(1)	0.0213 (48)	0.0027 (5)	0.0031 (6)	0.0022 (12)	0.0017 (12)	−0.0001 (4)
C63(1)	0.0294 (70)	0.0015 (4)	0.0044 (7)	0.0037 (13)	0.0002 (17)	0.0006 (4)
CA15-1	0.0116 (40)	0.0035 (5)	0.0022 (6)	0.0045 (11)	0.0002 (11)	−0.0003 (4)
CA23-1	0.0241 (59)	0.0017 (4)	0.0045 (6)	0.0027 (13)	−0.0038 (16)	−0.0001 (4)
CA45-1	0.0463 (68)	0.0022 (5)	0.0031 (7)	0.0059 (15)	0.0038 (18)	0.0008 (5)
			Molecule 2			
Mn(2)	0.0200 (8)	0.0019 (1)	0.0020 (1)	0.0002 (2)	−0.0007 (2)	−0.0003 (1)
O1(2)	0.0269 (34)	0.0020 (3)	0.0024 (4)	−0.0014 (4)	0.0007 (9)	0.0004 (3)
O2(2)	0.0152 (33)	0.0020 (3)	0.0030 (4)	0.0018 (7)	0.0015 (9)	0.0002 (3)
O3(2)	0.0202 (34)	0.0019 (3)	0.0029 (4)	0.0001 (7)	−0.0016 (9)	0.0002 (3)
O4(2)	0.0134 (29)	0.0023 (3)	0.0039 (4)	0.0002 (7)	−0.0015 (8)	0.0001 (3)
O5(2)	0.0219 (32)	0.0015 (3)	0.0030 (4)	−0.0008 (8)	−0.0013 (9)	0.0002 (3)
O6(2)	0.0119 (32)	0.0023 (3)	0.0037 (4)	−0.0009 (8)	0.0021 (9)	−0.0000 (3)
C11(2)	0.0194 (50)	0.0009 (3)	0.0027 (6)	0.0014 (10)	0.0037 (13)	0.0007 (4)
C21(2)	0.0087 (44)	0.0012 (4)	0.0024 (5)	0.0005 (9)	−0.0006 (13)	−0.0005 (4)
C31(2)	0.0197 (62)	0.0015 (4)	0.0013 (5)	−0.0015 (12)	−0.0021 (13)	−0.0002 (3)
C41(2)	0.0234 (66)	0.0006 (3)	0.0019 (5)	0.0013 (11)	0.0025 (15)	0.0010 (3)
C51(2)	0.0120 (44)	0.0015 (4)	0.0024 (6)	0.0015 (11)	0.0017 (12)	0.0006 (4)
C61(2)	0.0167 (52)	0.0022 (5)	0.0015 (5)	−0.0029 (15)	−0.0022 (13)	−0.0002 (5)
C12(2)	0.0136 (44)	0.0019 (5)	0.0028 (6)	0.0001 (12)	0.0013 (12)	−0.0008 (5)
C22(2)	0.0170 (54)	0.0014 (4)	0.0027 (6)	0.0009 (10)	−0.0015 (14)	−0.0000 (4)
C32(2)	0.0124 (53)	0.0023 (5)	0.0031 (7)	0.0002 (12)	−0.0006 (15)	−0.0006 (4)
C42(2)	0.0068 (60)	0.0031 (5)	0.0019 (5)	0.0007 (12)	0.0020 (12)	0.0010 (4)
C52(2)	0.0140 (51)	0.0020 (4)	0.0029 (6)	0.0009 (13)	−0.0002 (13)	−0.0004 (4)
C62(2)	0.0217 (58)	0.0026 (5)	0.0015 (5)	−0.0019 (14)	0.0002 (13)	0.0005 (4)
C13(2)	0.0246 (51)	0.0012 (4)	0.0039 (8)	−0.0003 (11)	0.0018 (15)	−0.0003 (5)
C23(2)	0.0163 (63)	0.0021 (4)	0.0023 (5)	−0.0005 (12)	0.0005 (13)	−0.0003 (4)
C33(2)	0.0246 (59)	0.0023 (4)	0.0029 (7)	−0.0018 (13)	0.0004 (17)	−0.0004 (5)
C43(2)	0.0211 (52)	0.0031 (6)	0.0019 (6)	0.0019 (15)	−0.0009 (15)	0.0009 (5)
C53(2)	0.0267 (54)	0.0025 (5)	0.0040 (8)	0.0025 (13)	0.0020 (14)	−0.0007 (5)
C63(2)	0.0290 (71)	0.0016 (5)	0.0049 (8)	0.0012 (16)	0.0068 (21)	0.0006 (5)
CA15-2	0.0295 (60)	0.0014 (4)	0.0032 (7)	0.0006 (12)	0.0018 (16)	−0.0000 (4)
CA23-2	0.0198 (65)	0.0030 (5)	0.0020 (6)	−0.0003 (13)	0.0014 (15)	−0.0013 (5)
CA46-2	0.0296 (72)	0.0025 (5)	0.0042 (8)	0.0007 (16)	0.0015 (19)	0.0007 (5)

Disordered toluene

Atom	B, Å^2	Atom	B, Å^2
C1	10.4 (8)	C1M	13.9 (31)
C2	10.0 (7)	C3M	10.8 (25)
C3	11.8 (10)		

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

was prepared in the manner previously described.[16] The product was recrystallized from 1:1 chloroform–toluene solution, from which dark green needles were obtained. A single crystal of elongated rectangular prismatic shape was chosen for preliminary film examination and subsequently was used for the data collection. A complete set of Weissenberg photographs revealed the systematic extinctions which were uniquely consistent with the space group $P2_1/c$. The lattice parameters, obtained from a least-squares fit to the angular settings of 18 carefully centered reflections on a Picker automatic X-ray diffractometer (card controlled), are presented in Table I. By the flotation method, using bromobenzene and CCl$_4$, the measured density was 1.53 g/cm^3. Assuming eight molecules of Mn(trop)$_3$ and two toluene molecules of crystallization (*vide infra*) per cell, the calculated density is 1.522 g/cm^3. The various crystal data are summarized in Table I.

For eight molecules in the unit cell all the atoms must occupy the general position (e), with no crystallographic site symmetry. Since other observations[16] indicated the compound to be monomeric, the

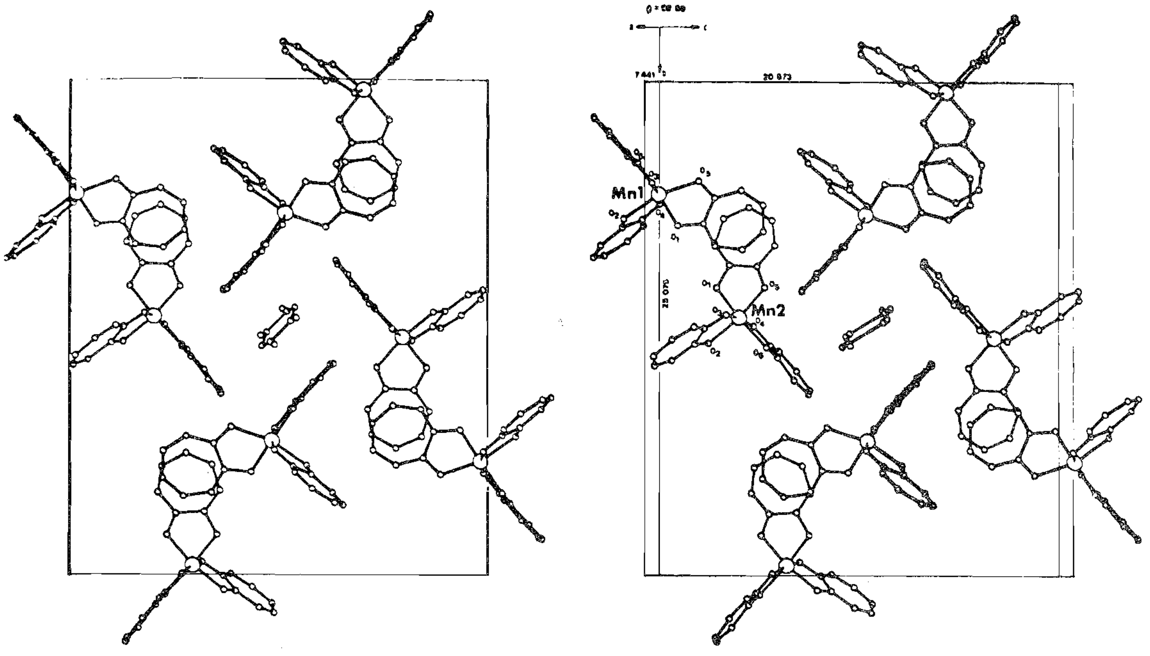

Figure 4. Stereopair view of the projection of the Mn(trop)$_3$ cell in the *bc* plane. The toluene molecules along the origin are not shown.

Table V. Root-Mean-Square Displacement of Thermal Ellipsoids (in Å) for Mn(trop)$_3$

Atom	Molecule 1			Molecule 2		
Mn	0.194	0.211	0.233	0.194	0.237	0.256
O1	0.196	0.234	0.261	0.206	0.250	0.290
O2	0.173	0.231	0.289	0.178	0.244	0.280
O3	0.168	0.188	0.275	0.210	0.246	0.277
O4	0.176	0.226	0.256	0.184	0.271	0.298
O5	0.185	0.220	0.262	0.212	0.227	0.282
O6	0.147	0.262	0.296	0.166	0.274	0.289
C11	0.158	0.207	0.344	0.138	0.173	0.299
C21	0.143	0.191	0.254	0.151	0.177	0.248
C31	0.148	0.181	0.309	0.127	0.213	0.266
C41	0.179	0.213	0.273	0.037	0.198	0.286
C51	0.161	0.197	0.272	0.156	0.184	0.272
C61	0.093	0.159	0.333	0.116	0.220	0.299
C12	0.135	0.239	0.335	0.176	0.211	0.286
C22	0.174	0.218	0.286	0.185	0.217	0.265
C32	0.089	0.226	0.339	0.183	0.236	0.293
C42	0.176	0.233	0.319	0.105	0.191	0.333
C52	0.194	0.232	0.328	0.191	0.231	0.276
C62	0.120	0.198	0.376	0.166	0.228	0.308
C13	0.188	0.275	0.339	0.191	0.251	0.301
C23	0.131	0.268	0.344	0.211	0.214	0.268
C33	0.183	0.222	0.326	0.225	0.255	0.301
C43	0.204	0.229	0.343	0.163	0.249	0.331
C53	0.205	0.268	0.311	0.205	0.305	0.323
C63	0.157	0.307	0.327	0.203	0.220	0.380
CA15	0.118	0.217	0.362	0.211	0.252	0.297
CA23	0.172	0.260	0.354	0.196	0.238	0.342
CA46	0.191	0.237	0.414	0.258	0.280	0.327

occupation of special positions was ruled out, since the tris-bidentate ligand sphere cannot possess inversion site symmetry. Thus the asymmetric unit had to be composed of two crystallographically independent molecules of Mn(trop)$_3$.

Collection and Reduction of Intensity Data. Cu Kα radiation (λ(K$\bar{\alpha}$) 1.5418 Å), filtered by a nickel foil, was used. The crystal was mounted on a eucentric goniometer head such that the *a* axis (needle direction) was collinear with the ϕ axis of the four-circle diffractometer. Data were collected by the moving-crystal, moving-counter θ-2θ scan technique at a rate of 2°/min out to $(\sin\theta)/\lambda = 0.27$ ($2\theta = 50°$) and from there to $(\sin\theta)/\lambda = 0.59$ ($2\theta = 130°$) at the slower rate of 1°/min. Each stationary-background count at the limits of the scan was taken for 30 sec. Approximately 7000 symmetry-independent reflections were collected.

The intensity of one strong reflection was monitored as a standard every 100 reflections. During the period of the data collection there was no significant reduction in the intensity of the standard. Of the collected reflections only 2382 had scan counts at least 1% above the properly scaled background counts. Absorption corrections were applied to the latter group of reflections (calculated transmission coefficients range from 66 to 83%).

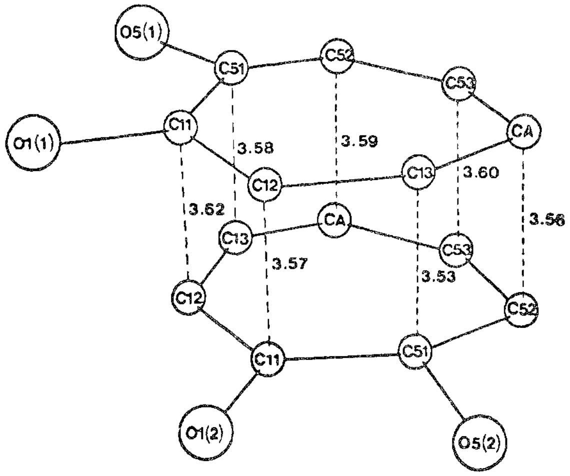

Figure 5. The contact distances in the stacking of tropolonates along the *a* axis. The average interplanar distance is 3.58 Å and the interplanar dihedral angle is 2.6°.

The intensities and associated errors were defined as before.[27] The reflections chosen for the structure solution were those which had $I/\sigma(I) \geqslant 2$. The number of such reflections, 1617, was somewhat modest. (Larger crystals were examined by photographic methods but proved to be multicrystalline.)

Solution and Refinement of the Structure. Examination of the Harker section and line in a Patterson synthesis suggested the positions for the two independent manganese atoms. An initial structure factor calculation using the coordinates of the metal atoms yielded $R = 0.43$ and $R_w = 0.55$, using unit weights.[28] The positions of the oxygens and some of the carbons were located in a three-dimensional Fourier map. The successive application of Fourier syntheses along with placement of initially unobserved carbon atoms into chemically

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(27) J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Amer. Chem. Soc.*, **95**, 774 (1973).

(28) $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1$ or is as given in Table II. $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively.

Table VI. Intramolecular Distances and Estimated Standard Deviations for Mn(trop)$_3$ (Å)

	Molecule 1			Molecule 2	
Mn–O1	1.936 (10)[a]		Mn–O3	1.949 (12)	
Mn–O3	1.945 (10)		Mn–O4	1.939 (12)	
Mn–O4	1.925 (10)		Mean	1.944 (8)	
Mn–O6	1.963 (12)			[0.35, 55.6%]	
Mean	1.941 (16)[b]				
	[2.11, 9.7%][c]	Mean 2.006 (99) [92.65, 0.00%]	Mn–O2	1.987 (12)	
			Mn–O5	1.993 (13)	
Mn–O2	2.144 (10)		Mean	1.990 (5)	Mean 1.994 (49) [15.78, 0.00%]
Mn–O5	2.110 (10)			[0.12, 73.5%]	
Mean	2.127 (25)		Mn–O1	2.041 (12)	
	[5.78, 1.6%]		Mn–O6	2.063 (13)	
			Mean	2.051 (16)	
				[1.55, 21.4%]	
		Mean 2.007 (79) [49.62, 0.00%]			

	Molecule 1	Molecule 2
O1–O5[d]	2.543 (14)	2.545 (16)
O2–O3	2.609 (14)	2.561 (17)
O4–O6	2.518 (14)	2.510 (17)
Mean	2.557 (48)	2.539 (26)
	[11.28, 0.00%]	[2.36, 9.4%]
	Mean 2.549 (37) [5.86, 0.00%]	
O1–O2	2.808 (15)	2.905 (17)
O1–O3	2.856 (14)	2.956 (17)
O1–O4	2.800 (12)	2.872 (18)
O2–O4	3.037 (13)	2.901 (17)
O2–O6	2.958 (16)	2.933 (17)
O3–O5	2.984 (13)	2.903 (17)
O3–O6	2.975 (15)	2.953 (18)
O4–O5	2.899 (14)	2.780 (17)
O5–O6	3.213 (14)	3.047 (18)
Mean	2.945 (131)	2.915 (72)
	[88.85, 0.00%]	[16.93, 0.00%]
	Mean 2.934 (110) [50.77, 0.00%]	
O1–C11	1.327 (26)	1.303 (22)
O2–C21	1.277 (20)	1.309 (22)
O3–C31	1.292 (19)	1.316 (22)
O4–C41	1.309 (20)	1.315 (21)
O5–C51	1.255 (10)	1.267 (24)
O6–C61	1.286 (23)	1.272 (25)
Mean	1.289 (24)	1.299 (22)
	[1.29, 26.7%]	[0.87, 49.9%]
	Mean 1.293 (23) [1.05, 40.3%]	

	Molecule 1	Molecule 2
C11–C51	1.466 (27)	1.450 (25)
C21–C31	1.479 (26)	1.447 (26)
C41–C61	1.434 (29)	1.438 (30)
Mean	1.461 (23)	1.446 (6)
	[0.69, 50.2%]	[0.05, 95.2%]
	Mean 1.453 (17) [0.40, 65.2%]	
C11–C12	1.356 (26)	1.397 (27)
C21–C22	1.428 (21)	1.429 (25)
C31–C32	1.378 (28)	1.415 (30)
C41–C42	1.382 (30)	1.386 (29)
C51–C52	1.404 (26)	1.383 (28)
C61–C62	1.428 (24)	1.442 (28)
Mean	1.401 (30)	1.409 (25)
	[1.40, 22.1%]	[0.75, 58.5%]
	Mean 1.405 (27) [1.01, 43.5%]	
C12–C13	1.425 (27)	1.378 (29)
C22–C23	1.377 (28)	1.395 (28)
C32–C33	1.371 (24)	1.392 (30)
C42–C43	1.403 (30)	1.405 (29)
C52–C53	1.417 (26)	1.387 (30)
C62–C63	1.341 (29)	1.410 (32)
Mean	1.339 (32)	1.394 (12)
	[1.33, 24.9%]	[0.15, 98.0%]
	Mean 1.392 (24) [0.68, 75.9%]	
C13–CA15	1.378 (28)	1.397 (29)
C53–CA15	1.427 (30)	1.435 (28)
C23–CA23	1.424 (31)	1.353 (30)
C33–CA23	1.415 (26)	1.379 (29)
C43–CA46	1.426 (32)	1.392 (32)
C63–CA46	1.432 (37)	1.396 (40)
Mean	1.415 (21)	1.393 (29)
	[0.46, 80.3%]	[0.86, 50.9%]
	Mean 1.404 (27) [0.74, 69.6%]	
	Disordered Toluene	
C1–C2		1.37 (5)
C2–C3		1.25 (6)
C3–C1′		1.50 (6)
Mean		1.37 (12)
		[4.34, 1.3%]

[a] The individual esd values are based on the diagonal values of the least-squares symmetric matrix. Correlation terms have not been included. [b] Weighted mean, $\bar{l}$, and esd, s, are defined as[33] $\bar{l} = \Sigma w_i l_i / \Sigma w_i$; $s = \{[N \Sigma w_i (l_i - \bar{l})^2] / [(N-1)\Sigma w_i]\}^{1/2}$; $w_i = 1/\sigma_i^2$. [c] The first value in the brackets refers to reduced χ^2: $\chi_r^2 = (s^2/N)\Sigma w_i$. The second value refers to the probability that a random distribution of equal bonds would give a value of χ_r^2 as large as that calculated. See ref 34. [d] The "bite" distances.

reasonable positions revealed with certainty the positions of all the nonhydrogen atoms and gave values of $R = 0.23$ and $R_w = 0.27$. More rigorous refinement was initiated, using a full-matrix least-squares procedure with isotropic temperature factors. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Unit weights were used during all stages of isotropic refinement. After several least-squares cycles the agreement indices converged to $R = 0.13$ and $R_w = 0.16$. At this point a careful examination of a difference Fourier map revealed that two solvent molecules of toluene were contained in the unit cell. These molecules had to be disordered with respect to the methyl carbons since the molecules are located about centers of inversion at ($^1/_2$, $^1/_2$, $^1/_2$) and at ($^1/_2$, 0, 0). An examination of the plane formed by the benzene skeleton in a difference Fourier map suggested that the methyl carbon could be ascribed to four of the six possible positions, giving the disordered molecule the appearance of durene.

Although only minor changes in the two MnO$_6$ geometries followed, refinement was continued with anisotropic thermal parameters for all nonhydrogen atoms with the exception of the solvent atoms. The neutral atomic scattering factors for the nonhydrogen atoms were taken from Cromer and Waber.[29] Those used later for the hydrogens were taken from Stewart, *et al.*[30] Cromer's values[31]

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(29) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(30) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(31) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

Table VII. Intramolecular Angles and Estimated Standard Deviations for Mn(trop)$_3$ (deg)[a]

	Molecule 1	Molecule 2
O1-Mn-O5[b]	77.8 (6)	78.2 (6)
O2-Mn-O3	79.1 (6)	81.2 (6)
O4-Mn-O6	80.7 (6)	77.6 (8)
Mean	79.2 (15) [8.44, 0.02%]	79.0 (20) [10.33, 0.00%]
	Mean 79.1 (15) [7.55, 0.00%]	
O1-Mn-O3	94.8 (6)	95.6 (6)
O2-Mn-O6	92.1 (6)	92.8 (6)
O4-Mn-O5	91.8 (4)	90.0 (6)
O1-Mn-O2	86.8 (6)	92.3 (6)
O1-Mn-O4	93.0 (6)	92.3 (6)
O2-Mn-O4	96.4 (6)	95.2 (6)
O3-Mn-O5	94.7 (6)	94.8 (6)
O3-Mn-O6	91.3 (6)	94.7 (6)
O5-Mn-O6	104.1 (6)	97.4 (6)
Mean	93.8 (46) [89.84, 0.00%]	93.9 (23) [13.83, 0.00%]
	Mean 93.8 (38) [48.80, 0.00%]	
O1-Mn-O6	173.5 (6)	169.1 (6)
O2-Mn-O5	162.9 (6)	169.4 (6)
O3-Mn-O4	170.8 (6)	171.4 (6)
Mean	169.1 (56) [>100, 0.00%]	170.0 (13) [4.34, 1.3%]
	Mean 169.4 (39) [51.08, 0.00%]	
Mn-O1-C11	119.1 (11)	115.4 (11)
Mn-O2-C21	109.2 (9)	112.7 (11)
Mn-O3-C31	119.3 (9)	115.7 (11)
Mn-O4-C41	117.0 (19)	118.8 (11)
Mn-O5-C51	113.3 (9)	115.3 (11)
Mn-O6-C61	111.9 (11)	114.4 (11)
Mean	114.9 (42) [19.85, 0.00%]	115.4 (21) [3.95, 0.07%]
	Mean 115.1 (33) [10.86, 0.00%]	
O1-C11-C51	112.5 (12)	112.5 (12)
O2-C21-C31	119.7 (8)	116.8 (12)
O3-C31-C21	112.5 (12)	113.5 (13)
C4-C41-C61	110.7 (12)	113.0 (13)
O5-C51-C11	116.7 (12)	117.8 (13)
O6-C61-C41	118.8 (13)	116.0 (14)
Mean	115.2 (39) [115.12, 0.00%]	114.9 (23) [3.08, 0.87%]
	Mean 115.1 (31) [6.02, 0.00%]	

	Molecule 1	Molecule 2
O1-C11-C12	115.2 (12)	117.9 (12)
O2-C21-C22	115.8 (11)	116.6 (12)
O3-C31-C32	117.8 (12)	117.9 (13)
O4-C41-C42	118.0 (13)	115.1 (13)
O5-C51-C52	119.1 (12)	113.7 (13)
O6-C61-C62	114.4 (12)	121.3 (14)
Mean	116.7 (19) [2.35, 3.9%]	117.8 (20) [2.41, 3.4%]
	Mean 117.2 (20) [2.40, 0.00%]	
O11-C51-C52	124.0 (13)	123.4 (14)
O21-C31-C32	129.5 (13)	128.7 (14)
C31-C21-C22	124.4 (12)	126.6 (13)
C41-C61-C62	126.3 (14)	122.6 (16)
C51-C11-C12	132.3 (14)	129.6 (14)
C61-C41-C42	131.3 (16)	131.9 (14)
Mean	127.7 (36) [6.91, 0.00%]	127.2 (36) [6.47, 0.00%]
	Mean 127.5 (34) [6.12, 0.00%]	
C11-C12-C13	127.6 (14)	129.6 (14)
C21-C22-C23	129.0 (13)	126.7 (14)
C31-C32-C33	131.0 (13)	127.7 (16)
C41-C42-C43	125.4 (16)	128.3 (14)
C51-C52-C53	129.7 (14)	132.0 (16)
C61-C62-C63	129.7 (14)	129.9 (16)
Mean	128.9 (20) [1.91, 8.3%]	129.0 (19) [1.65, 14.3%]
	Mean 128.7 (18) [1.62, 8.7%]	
C12-C13-CA15	128.9 (16)	130.6 (16)
C22-C23-CA23	130.4 (16)	132.2 (14)
C32-C33-CA23	127.3 (13)	129.7 (16)
C42-C43-CA46	130.3 (17)	129.8 (16)
C52-C53-CA15	128.9 (14)	130.5 (16)
C62-C63-CA46	128.4 (16)	130.8 (18)
Mean	128.9 (13) [0.66, 65.5%]	130.7 (10) [0.38, 86.6%]
	Mean 129.7 (14) [0.84, 60.1%]	
C13-CA15-C53	128.4 (14)	124.0 (16)
C23-CA23-C33	128.1 (16)	128.1 (16)
C43-CA46-C63	128.0 (17)	126.5 (18)
Mean	128.2 (3) [0.02, 98.1%]	126.1 (22) [1.78, 16.8%]
	Mean 127.2 (18) [1.27, 27.5%]	

[a] See footnotes in Table VI. [b] The "bite" angles.

for real and imaginary components of the anomalous dispersion correction to the scattering factors of manganese were incorporated. An empirical weighting scheme of the Cruickshank type was used with little improvement in the result.

Due to computer storage limitations, full-matrix least-squares refinement in the anisotropic mode (62 nonhydrogen atoms) was carried out with each cycle chosen to cover only the parameters of one of the two asymmetric molecules. The standard deviations in the parameters, based on the inverse matrix, are assumed to be valid, since the average intermolecular correlation is not expected to be large. Indeed, the largest value appears to be 0.16, occurring between the y's of C53(2) and C52(1). In each of the anisotropic cycles the ratio of the number of reflections to the number of varied parameters was about 7. After two "half-cycles" of refinement R dropped to 0.095 and R_w to 0.11, with the error in an observation of unit weight at 1.24.

Some of the anisotropic thermal parameters of the carbon atoms were not positive-definite. With all the parameters other than these fixed, several cycles of isotropic refinement were performed, after which the thermal parameters of the troublesome carbons were converted back to anisotropic forms. Four more half-cycles of anisotropic refinement were performed. Each of the four locations of the methyl carbons in toluene was assigned quarter weights. The agreement indices at this point were $R = 0.069$ and $R_w = 0.075$. Further refinement was not attempted. The positions of all the hydrogen atoms were calculated, assuming the C-H bond to be 0.95 Å. The inclusion of hydrogens in a structure factor calculation (B's set at 6 Å^2) lowered R to 0.067 and R_w to 0.074. No refinement of the hydrogen parameters was attempted. The error in an observation of unit weight in the final cycle was 0.876. There were no intramolecular correlation elements greater than 0.40 in the final least-squares cycle. The final difference Fourier revealed peaks with densities as high as 0.6 e/Å^3. Most of these were randomly distributed with the exception of those in the vicinity of the dis-

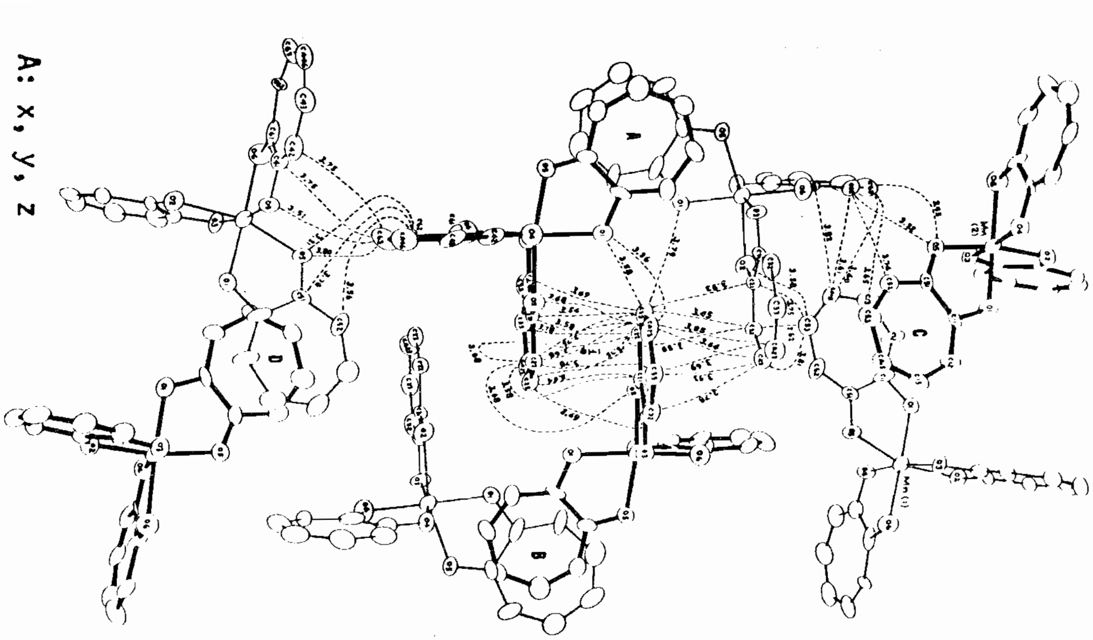

Figure 6. ORTEP/II-drawn view of the packing (30% probability ellipsoids) in Mn(trop)$_3$ along with the contact distances (<3.87 Å). Some of the distances related by symmetry are not shown.

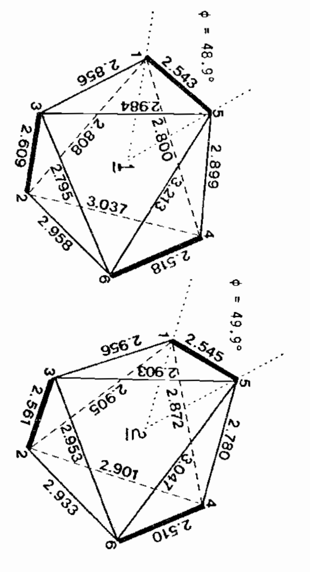

Figure 7. Polyhedra edge lengths in the two MnO$_6$ groups in Mn-(trop)$_3$. The dihedral angles between the top and the bottom trigonal faces are 5.7 and 4.2° in 1 and 2, respectively. The thick edges refer to the "bite" distances. The average "twist" angle is labeled as ϕ.

ordered toluenes. It was not possible to refine the solvent molecules to reasonable C–C distances. However, a good semblance of the benzene skeleton was obtained.

The various final refinement characteristics are summarized in

Table VIII. Structural Details of Compounds Containing the Tropolonate Ligand[a]

Compd	M-O	O···O′	O-C$_1$	C$_1$-C$_1$′	C$_1$-C$_2$	C$_2$-C$_3$	C$_3$-C$_4$	O-M-O′	M-O-C$_1$	O-C$_1$-C$_2$	O-C$_1$-C$_1$′	C$_1$-C$_1$′-C$_2$′	C$_1$-C$_2$-C$_3$	C$_2$-C$_3$-C$_4$	C$_3$-C$_4$-C$_3$′	Ref
Tropolone			1.261	1.454	1.410	1.373	1.410			120.4	115.4	128.8	130.6	129.4	127.5	*b*
			1.333		1.379	1.393	1.341			116.5	114.7	124.2	129.4	129.9		
NaT		2.650	1.284	1.490	1.423	1.383	1.393			118.1	117.2	125.0	131.8	130.1	127.3	*c*
AlT$_3$	1.888	2.490	1.291	1.450	1.397	1.384	1.371	82.6	115.1	119.8	113.7	126.6	129.9	129.9	127.2	*d*
MnT$_3$	2.001	2.549	1.293	1.453	1.405	1.392	1.404	79.1	115.1	117.2	115.1	127.5	128.9	129.7	127.2	This work
FeT$_3$	2.008	2.522	1.294	1.463	1.397	1.385	1.379	77.8	116.9		114.2	126.1	130.4	130.1	126.7	35
CuT$_2$	1.91	2.58	1.28	1.44	1.43	1.38	1.43	85	112	116	116	129	130	129	126	*e*
			1.32		1.38	1.43	1.37		112	116	116	128	126	133		
SnT$_3$Cl	2.129	2.548	1.287	1.453	1.412	1.392	1.393	72.8	117.7		115.6	127.0	129.4	129.5	127.9	*f*
SnT$_3$OH	2.146	2.538	1.285	1.458	1.396	1.377	1.380	71.6	119.0		115.3	126.0	130.9	129.8	126.7	*f*
ThT$_4$DMF	2.457	2.541	1.277	1.471	1.408	1.385	1.383	62.5	122.9	119.8	114.7	125.4	131.0	129.6	127.0	*g*
[(H$_2$O)NiT$_2$]$_2$	2.024	2.583	1.279	1.486	1.412	1.407	1.375	79.3	113.9	118.8	115.4	125.8	129.9	130.7	126.8	*h*
Averages		2.556	1.290	1.462	1.404	1.390	1.386			118.1	115.3	126.6	129.9	130.1	127.0	

[a] T = tropolonate. The atoms are designated in the same manner as in Figure 2. Distances are in angstroms; angles are in degrees. [b] H. Shimanouchi and Y. Sada, *Acta Crystallogr., Sect. B*, 29, 81 (1973). [c] R. Shiono, *Acta Crystallogr.*, 14, 42 (1961). [d] E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 94, 8046 (1972). [e] W. M. Macintire, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc., Ser. A*, 289, 161 (1966). [f] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 92, 3636 (1970). [g] V. W. Day and J. L. Hoard, *ibid.*, 92, 3626 (1970). [h] R. J. Irving, M. L. Post, and D. C. Povey, *J. Chem. Soc., Dalton Trans.*, 697 (1973).

Table IX. Least-Squares Fitted Planes for Mn(trop)$_3$

I. Deviations from the Mean Planes (in Å)

		A(1)[a]	A(2)	B(1)	B(2)	C(1)	C(2)	D(1)	D(2)	E(1)	E(2)	F(1)	F(2)	G
trop A	Mn							−0.046	0.003	0.004	0.043	0.065	−0.016	
	O1	0.035	−0.077					−0.009	−0.061	0.130	−0.143			
	O11	0.009	−0.010											
	C12	−0.044	0.037											
	C13	−0.012	0.050											
	CA15	0.033	−0.014											
	C53	0.009	−0.051											
	C52	−0.018	−0.006											
	C51	−0.003	0.005											
	O5	−0.010	0.067							−0.115	0.117	−0.213	0.144	
trop B	O2			0.042	−0.032					−0.113	0.104	−0.229	0.156	
	C21			0.011	0.009									
	C22			−0.036	0.018									
	C23			−0.022	−0.006									
	CA23			0.054	0.015									
	C33			0.007	−0.031									
	C32			0.005	0.000									
	C31			−0.031	0.015									
	O3			−0.012	0.012			0.033	0.057			0.204	−0.148	
trop C	O4					0.036	0.031	0.035	0.070			0.173	−0.136	
	C41					−0.013	0.011							
	C42					−0.014	−0.013							
	C43					−0.011	−0.010							
	CA46					0.005	−0.010							
	C63					0.030	0.014							
	C62					−0.013	0.051							
	C61					−0.010	−0.023							
	O5					−0.010	−0.030	−0.013	−0.069	0.094	−0.122			
Toluene	C1													0.026
	C1M													−0.034
	C2													0.017
	C3													0.028
	C3M													−0.037
Rms dev		0.023	0.044	0.026	0.018	0.019	0.021	0.031	0.057	0.102	0.111	0.186	0.131	0.029
(esd)		(15)	(17)	(16)	(18)	(18)	(18)	(9)	(11)	(9)	(11)	(8)	(11)	(60)

II. Equations of the Mean Planes

A(1): $0.9435x - 0.3008y - 0.1389z = 1.4228$
A(2): $0.9369x - 0.2978y - 0.1832z = -2.3185$
B(1): $0.1688x + 0.7771y + 0.6063z = 5.2234$
B(2): $0.2266x + 0.7717y + 0.5942z = 12.2663$
C(1): $0.0337x + 0.6594y - 0.7510z = 3.4191$
C(2): $-0.0335x + 0.6220y - 0.7923z = 4.0159$
D(1): $0.1443x + 0.5164y - 0.8441z = 3.2659$
D(2): $-0.1020x + 0.6564y - 0.7475z = 4.5590$
E(1): $0.930x - 0.1887y - 0.0613z = 2.4005$
E(2): $0.9759x - 0.1615y - 0.1470z = -0.6613$
F(1): $0.2590x + 0.8556y + 0.4482z = 6.0512$
F(2): $0.2928x + 0.6753y + 0.6770z = 11.5255$
G: $0.1792x - 0.5966y - 0.7823z = -14.9262$

III. Dihedral Angles between Some of the Planes (in deg)

	A(1)	A(2)	B(1)	B(2)	C(1)	C(2)	G
A(1)	0						
A(2)	2.6	0					
B(1)	80.9	79.4	0				
B(2)	84.2	82.7	3.4	0			
C(1)	93.6	91.6	93.6	94.0	0		
C(2)	96.3	94.2	90.2	90.4	4.8	0	
G	62.8	60.1	24.8	27.8	78.5	76.4	0

[a] The number in a parentheses designates the asymmetric molecule.

Table II. The final coordinates and thermal parameters are presented in Tables III and IV, respectively. Table V contains the dimensions of the thermal ellipsoids. The numbering scheme used in Tables III–V is shown in Figure 2. Computer programs used throughout this work have been listed.[27]

Discussion of the Structure of Mn(trop)$_3$

Metal–Oxygen Bonds. There appears to be no doubt that Mn(trop)$_3$ is distorted substantially from a trigonal symmetry in the solid state. A very unusual feature of the structure is that the asymmetric molecules **1** and **2** are both distorted differently from the regular trigonal (D_3) arrangement. We are aware of one other similar occurrence, involving $[Cu(H_2O)_6][SiF_6]$,[32] where one Cu(II) molecule has $\bar{3}$ (S_6) symmetry while three other molecules in the cell are tetragonally elongated.

The various significant intramolecular distances and angles are presented in Tables VI and VII and the weighted mean dimensions of the tropolonate are shown in Figure 3.

Molecule **1** clearly shows *tetragonal elongation*, having approximately a C_2 symmetry with the axial Mn–O bonds being about 0.19 Å longer than the equatorial ones. A χ^2 distribution test[33] indicates that it is more probable that **1** is composed of four "equivalent" bonds measuring 1.94

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(32) D. H. Templeton, S. Ray, and A. Zalkin, private communication, as quoted in P. T. Miller, P. G. Lenhert, and M. D. Joesten, *Inorg. Chem.*, 12, 218 (1973).

(33) P. R. Bevington, "Data Reduction and Error Analysis for Physical Sciences," McGraw-Hill, New York, N. Y., 1969, Chapters 2, 5, and 10; G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1969, Section 18.6.

Å and two "equivalent" ones measuring 2.13 Å, rather than of six isometric bonds. The structure is similar[34] to that of tris(1,10-phenanthroline)copper(II). The elongated axis in **1** is bent by 17° from 180°, which is a consequence of the rigid nature of the ligand. In contrast to **1**, **2** is *orthorhombically distorted*, with C_1 overall symmetry. The most probable[33] description of **2** is that there are three pairs of different Mn-O trans distances. The longest bonds (2.051 Å) are about 0.06 Å longer than the intermediate bonds (1.990 Å), which in turn are about 0.05 Å longer than the shortest set (1.944 Å).

The overall average M-O bond distance in Mn(trop)$_3$, 2.001 Å, is just slightly less than that found in Fe(trop)$_3$,[35] a value consistent with the interpretations of the ir spectra.[25] The MB value of Mn-O bond distance is considerably smaller.

Molecular Packing. The cell, shown in Figure 4, is typified by two kinds of stacking of the tropolonate rings. The two independent molecules are joined loosely through the tropolonate planes containing oxygens 1 and 5 (Figure 5) and are approximately related to each other by a pseudo-twofold axis. This stacking of rings is along the *a* axis.

The other type of stacking, involving four rings (containing oxygens 2 and 3), is shown in Figure 6. Along the center and the origin of the cell, the tropolonate planes associated with oxygen atoms 4 and 6 form the boundaries of tunnels (~7 × 9 Å^2 cross section) which contain the solvent molecules and are aligned essentially parallel to the *a* axis.

In both **1** and **2** the O_3-Mn-O_4 trans bonds align approximately with the *a* axis. These bonds are about equal at 1.942 Å. The differences in the bonds between **1** and **2** occur in the other two trans directions. The bonds in O_2-Mn-O_5 in **1** are 0.14 Å longer than in **2**, while the bonds in the trans O_1-Mn-O_6 set are 0.11 Å shorter in **1** than in **2**. This pattern of packing is vaguely similar to the in-plane alternating bond distance packing in MnF$_3$.[36]

The presence of two distinct Mn(trop)$_3$ geometries may arise from either of two effects (there may be others that we have not thought of). Since toluene is not spherically symmetric, it may perturb one molecule differently from the other. However, the magnitude of the differential perturbation required is difficult to determine. Alternatively, the tropolonate rings stacked parallel to *a* (Figure 5) may couple the molecules in such a way as to lower the overall energy of the system by destroying the structural (and electronic) degeneracy of the isolated molecules. Since the Jahn-Teller effect is vibronic in origin, coupling of the molecules through ligand vibrations certainly seems plausible, although the magnitude of the coupling constants required cannot be readily estimated. This latter explanation, perhaps subject to test by a structural investigation of a tropolonate derivative, qualitatively is more appealing than the explanation based on the presence of toluene.

Trigonal Twist. The average trigonal twists (from the trigonal prism) in **1** and **2** are 48.9 and 49.9°, respectively, while the average trigonal compression ratios, *s*/*h*, are 1.398 and 1.386, respectively. Figure 7 shows the two MnO$_6$ units along with the O· · ·O distances.

For most tris-acetylacetonate, -tropolonate, and -1,1-dithiolate complexes of first-row transition metals, there is a very high correlation between the twist angle ϕ and the ratio of the bite distance to the metal-ligand distance.[37] Barring effects other than ligand-ligand repulsions, this trend can be explained qualitatively as follows. If ϕ and r_{ML} are held constant and the bite distance becomes smaller gradually, the ML$_6$ octahedron would become increasingly compressed along the threefold axis. Accompanying this effect, the electron-electron repulsion between adjacent ligand atoms would increase. However, if ϕ were allowed to decrease from 60°, the repulsion would decrease as the ML$_6$ unit correspondingly elongates. For molecules with comparable r_{ML}, the degree to which ϕ departs from 60° directly depends on the bite distance: the shorter the distance, the smaller the angle.

The Tropolonate Ligands. The various reported structures containing tropolonate ligands are shown in Table VIII. A common feature to all the structures is the short and essentially constant bite distance. In general the conjugation in the ligand is best described as being around the periphery of the tropolone ring, including the oxygen atoms. The C-C bond between the oxygen atoms is significantly and consistently longer than any of the other C-C bonds and is not thought to be a major part of the conjugation. The planarity of the ligands in Mn(trop)$_3$ is confirmed by the small atomic deviations from the least-squares-fitted mean planes, as is shown in Table IX.

Acknowledgments. The National Science Foundation (Grant GP-40689X) is gratefully recognized for its continuing support of our studies of Jahn-Teller systems. We also thank Professor R. H. Holm of Massachusetts Institute of Technology for a sample of Mn(trop)$_3$.

Registry No. Mn(trop)$_3$, 21757-62-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1854.

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