Contribution from the Department of Chemistry,
University of Nebraska, Lincoln, Nebraska 68588

Distortions of the Coordination Polyhedron in High-Spin Manganese(III) Complexes. 3. Crystal and Molecular Structure of γ-Tris(acetylacetonato)manganese(III): A Tetragonally Elongated Octahedral Form[1-4]

B. RAY STULTS, ROBERT S. MARIANELLI, and VICTOR W. DAY*[5]

Received March 16, 1977

The crystal and molecular structure of what shall be called the γ form of tris(acetylacetonato)manganese(III) has been determined by single-crystal X-ray diffraction techniques and refined (anisotropically for Mn, O, and C; isotropically for H) by full-matrix least-squares techniques to $R_1 = 0.045$ and $R_2 = 0.052$. A total of 1997 independent diffractometer-recorded (Nb-filtered Mo K$\bar{\alpha}$ radiation and θ–2θ scans) reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 60.4°$ and $I > 3\sigma(I)$ were used. The γ form of Mn(acac)$_3$ crystallizes in the uniquely determined centrosymmetric monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions $a = 7.786$ (1) Å, $b = 27.975$ (4) Å, $c = 8.020$ (1) Å, and $\beta = 100.34$ (1)° ($\rho_{\mathrm{calcd}} = 1.361$ g cm^{-3}, $\rho_{\mathrm{obsd}} = 1.366$ g cm^{-3}). The crystal contains discrete Mn(acac)$_3$ molecules in which the three bidentate acetylacetonato ligands each span an edge of a tetragonally elongated octahedron. This distortion of the coordination polyhedron is presumably the result of Jahn–Teller effects for the high-spin d^4 Mn(III) atom. Whereas the coordination polyhedron closely approximates D_{4h} symmetry, the whole molecule approximates its maximum possible symmetry of C_2. Average lengths for the four "short" and two "long" trans Mn–O bonds are 1.935 (3) and 2.111 (4) Å, respectively. The averaged length for all six Mn–O bonds is 1.994 (3) Å. Differences in Mn–O bond lengths within two of the three chelate rings are responsible for small but significant differences in the C–O and C–C bonds of these ligands. Bond lengths and angles within the third ligand are symmetrical. The ligands are planar.

Introduction

This is the third in a series of papers dealing with the coordination chemistry of high-spin manganese(III) complexes. Previous papers[1,2,6,7] described the synthesis and characterization of Mn(III) complexes having the formulations Mn(acac)$_2$(X) and Mn(acac)$_2$(X)(B) where acac is the acetylacetonato dianion, X$^-$ is a mononegative anionic ligand such as N$_3^-$, NCS$^-$, or Cl$^-$, and B is a neutral Lewis base such as methanol or pyridine. Solid-state structures have also been reported for Mn(acac)$_2$(N$_3$) and Mn(acac)$_2$(NCS).

Octahedral complexes of high-spin manganese(III) are expected to be susceptible to distortions[8] leading to deviations from idealized O_h symmetry either by a trigonal distortion or by a tetragonal elongation or compression. However, the solid-state structure reported[9] by Morosin and Brathovde in 1964 for β-Mn(acac)$_3$ revealed no such distortion. This rather surprising result led to considerable speculation[10] concerning the nature of this unusual behavior for Mn(III). When crystallographic structural analyses revealed highly distorted octahedral coordination polyhedra for Mn(acac)(pati)$_2$,[11] Mn(acac)$_2$(N$_3$),[7] Mn(trop)$_3$,[12] and Mn(acac)$_2$(NCS),[1] several groups began questioning the correctness of the reported solid-state structure for Mn(acac)$_3$. In addition to crystals for the β form of Mn(acac)$_3$, which were "reexamined" in this laboratory[13] as well as in Fackler's,[14] high-quality single crystals of a third crystalline modification—the γ form of Mn(acac)$_3$—were studied crystallographically in this laboratory. Since none of the ligands in the γ-crystalline modification are disordered or possess unusually large anisotropic thermal motion, it was possible to obtain a much more reliable characterization of the distortion in the coordination polyhedron for γ-Mn(acac)$_3$ than for β-Mn(acac)$_3$. The results reported herein for γ-Mn(acac)$_3$, when combined with those for recent structure determinations (or redeterminations) for β-Co(acac)$_3$[15] and β-Mn(acac)$_3$,[13,14] leave little doubt that the undistorted substance initially examined by Morosin and Brathovde was actually β-Co(acac)$_3$ and not β-Mn(acac)$_3$.

Experimental Section

Reagent grade tris(acetylacetonato)manganese(III), Mn(O$_2$C$_5$H$_7$)$_3$, was obtained from the J. T. Baker Chemical Co. and recrystallized from saturated (methanol or acetonitrile) solutions by slow solvent evaporation at room temperature. In addition to the predominant β-monoclinic crystalline form of Mn(acac)$_3$, both recrystallizations yielded smaller quantities of a second monoclinic form, γ-Mn(acac)$_3$.

Precession photographs used to determine the probable space group and a preliminary set of lattice constants indicated monoclinic, $2/m$, symmetry. The observed systematically absent reflections were those uniquely required by the centrosymmetric space group $P2_1/n$ (a special setting of $P2_1/c$–C_{2h}^5, No. 14).[16] This choice was fully supported by the results of sensitive tests for piezoelectricity[17] and by all stages of the subsequent structure determination and refinement.

An approximately cube-shaped crystalline specimen 0.60 mm on an edge was cut from a large single crystal and ground to a sphere 0.50 mm in diameter before being glued to the inner wall of a sealed thin-walled glass capillary. The lattice constants obtained from this specimen as previously described[6] by using 15 high-angle reflections ($2\theta_{\mathrm{MoK}\bar{\alpha}} > 20°$) and Nb-filtered Mo K$\bar{\alpha}$ radiation (λ 0.710 69 Å) on a Syntex $P\bar{1}$ Autodiffractometer at 20 ± 1 °C are $a = 7.786$ (1) Å, $b = 27.975$ (4) Å, $c = 8.020$ (1) Å, and $\beta = 100.34$ (1)°. A unit cell with these dimensions containing four Mn(O$_2$C$_5$H$_7$)$_3$ molecules has a calculated density of 1.361 g cm^{-3}, in excellent agreement with an observed density of 1.366 g cm^{-3}, measured by flotation in a ZnBr$_2$/H$_2$O solution.

Intensities were measured by using Nb-filtered Mo K$\bar{\alpha}$ radiation and the θ–2θ scanning technique with a normal-focus X-ray tube and a 4° takeoff angle. For those reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 55.0°$ a scanning rate of 3°/min was employed for each scan between 2θ settings 0.75° above and below the calculated Kα doublet values ($\lambda_{\mathrm{K}\alpha1}$ 0.709 26 Å and $\lambda_{\mathrm{K}\alpha2}$ 0.713 54 Å). A scanning rate of 2°/min was used for the remaining reflections. Background counts, each lasting for half the total scan time, were taken at both ends of the scan range for all reflections. A total of 5126 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 60.4°$ (1.3 times the number of data in the limiting Cu K$\bar{\alpha}$ sphere) were measured in concentric shells of increasing 2θ containing approximately 2100 reflections each. Six judiciously chosen reflections, measured every 200 reflections as a monitor for possible crystal disalignment and/or deterioration, gave no indication of either.

The linear absorption coefficient[18] of the crystal for Mo K$\bar{\alpha}$ radiation is 0.83 mm^{-1}, yielding a μr of 0.21 for the spherical crystal used for intensity measurements. Since the variation of absorption for a spherical sample having $\mu r = 0.21$ is negligible,[19] absorption corrections were not made and the measured intensities were reduced to a set of relative-squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 5126 reflections examined, 3129 were eventually rejected as objectively unobserved by applying the rejection criterion $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from $\sigma^2(I) = (C_t + k^2B)$ where C_t is the total scan count, k is the ratio of scan time to total background time (in this case $k = 1$), and B is the total background count.

The atomic coordinates of the manganese atom were readily derived from a three-dimensional Patterson synthesis calculated with 1696 independent data having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > \sigma(I)$. Two cycles of

0020-1669/79/1318-1853$01.00/0

full-matrix least-squares refinement of the structural parameters for the manganese atom resulted in a conventional unweighted residual, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, of 0.485 and a set of phases sufficiently accurate to permit the location of the remaining nonhydrogen atoms of the totally general-position asymmetric unit from a single-difference Fourier synthesis. Unit-weighted full-matrix least-squares refinement of the fractional atomic coordinates and isotropic thermal parameters of the 22 crystallographically independent nonhydrogen atoms resulted in $R_1 = 0.082$ and a conventional weighted residual, $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, of 0.083. These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[20] and an anomalous dispersion correction to the scattering factor for the manganese atom.[21]

Additional cycles of unit-weighted least-squares refinement employing anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.062$ and $R_2 = 0.067$ for 1696 independent reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 43°$ and $I > \sigma(I)$.

At this point the 21 crystallographically independent hydrogen atoms were located from a single difference Fourier synthesis. Two cycles of full-matrix least-squares refinement of the atomic coordinates for the 43 crystallographically independent atoms employing anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms (as were used in all subsequent structure factor calculations) resulted in $R_1 = 0.046$ and $R_2 = 0.048$ for 1696 independent reflections.

Additional cycles of unit-weighted full-matrix least-squares minimization of the function $\sum w(|F_o| - K^{-1}|F_c|)^2$ (where K is the scale factor and w is the weight assigned each reflection) using the more complete data set with various values for the $I/\sigma(I)$ rejection criterion converged to $R_1 = 0.065$ for 3246 reflections having $I > \sigma(I)$, $R_1 = 0.060$ for 2464 reflections having $I > 2.0\sigma(I)$, and $R_1 = 0.045$ for 1997 reflections having $I > 3.0\sigma(I)$. Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n = 1.08 - 9.51 \times 10^{-3}F_o + 6.23 \times 10^{-5}F_o^{\,2} - 7.01 \times 10^{-8}F_o^{\,3}$$

with a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

where the F_c values were calculated from the fully refined model by using unit weighting and an $I > 3\sigma(I)$ rejection criterion. The final cycles of full-matrix least-squares refinement utilized these weights to give final values of 0.045 and 0.052 for R_1 and R_2, respectively, for the 1997 independent reflections[22] having $2\theta_{\text{MoK}\bar{\alpha}} < 60.4°$ and $I > 3.0\sigma(I)$. During the final cycle of refinement, no parameter (including those for the hydrogen atoms) shifted by more than $0.29\sigma_p$ with the average shift being $0.07\sigma_p$, where σ_p is the estimated standard deviation of the parameter. Since a careful examination of the final F_o and F_c values indicated the absence of extinction effects, extinction corrections were not made. Differences in structural parameters resulting from unit-weighted refinement cycles, using the various $I/\sigma(I)$ rejection criteria and those obtained from the final empirically weighted refinement with an $I > 3\sigma(I)$ rejection criteria, were insignificant.

The same computer programs as previously reported[6] were used on an IBM 360/65 computer for the work.

Results and Discussion

The results of the structural analysis show that single crystals of γ-tris(acetylacetonato)manganese(III), **1**, are composed of discrete mononuclear molecules. All atoms occupy fourfold general positions: $\pm(x, y, z)$ and $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$ of space group $P2_1/n$.

Final coordinates and anisotropic thermal parameters for all nonhydrogen atoms are listed in Tables I and II, respectively. The refined positional and isotropic thermal parameters of the hydrogen atoms are listed in Table III. A model seen in perspective of the contents of the asymmetric unit specified by the atomic coordinates given in Tables I and III is illustrated in Figure 1; all nonhydrogen atoms are represented by ellipsoids having the shape, orientation, and relative size consistent with the thermal parameters listed in Table II. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity. The numbering scheme used to designate atoms of a γ-Mn($O_2C_5H_7$)$_3$ molecule is as follows. Each symbol for a nonhydrogen atom of an acetylacetonato ligand carries a literal subscript to identify the particular ligand (a, b, or c) and a numerical subscript to distinguish between atoms of the same element within the same ligand. Each hydrogen atom carries the same two subscripts as the carbon atom to which it is covalently bonded. In addition, methyl hydrogen atoms carry a third (numerical) subscript to distinguish between hydrogens bonded to the same carbon atom. All atoms of ligands a and b are labeled in agreement with the pseudo-C_2 axis of the molecule which ideally passes through the Mn, C_{c3} and H_{c3} atoms.

Complexing bond lengths and angles are shown in Figures 2 and 3, respectively, and in addition to the polyhedral edge

Table I. Atomic Coordinates in Crystalline γ-Mn($O_2C_5H_7$)$_3$[a]

	Fractional coordinates		
Atom type[b]	10^4x	10^4y	10^4z
Mn	1701 (1)	1096 (1)	3714 (1)
O_{a1}	4319 (4)	1290 (1)	4646 (4)
O_{a2}	1010 (4)	1718 (1)	4444 (4)
O_{b1}	−957 (4)	971 (1)	2719 (4)
O_{b2}	1960 (4)	1362 (1)	1551 (4)
O_{c1}	2389 (5)	482 (1)	2945 (4)
O_{c2}	1499 (5)	828 (1)	5892 (4)
C_{a1}	6791 (9)	1793 (3)	5324 (11)
C_{a2}	4852 (7)	1711 (2)	4963 (6)
C_{a3}	3750 (7)	2104 (2)	5032 (7)
C_{a4}	1955 (7)	2090 (2)	4792 (6)
C_{a5}	926 (10)	2537 (2)	4979 (12)
C_{b1}	−3712 (7)	1056 (2)	988 (9)
C_{b2}	−1762 (6)	1130 (2)	1342 (7)
C_{b3}	−973 (7)	1373 (2)	153 (6)
C_{b4}	773 (7)	1470 (2)	298 (6)
C_{b5}	1437 (8)	1717 (2)	−1132 (7)
C_{c1}	3149 (10)	−330 (3)	2818 (10)
C_{c2}	2609 (6)	94 (2)	3772 (7)
C_{c3}	2374 (8)	44 (2)	5426 (7)
C_{c4}	1853 (6)	401 (2)	6406 (6)
C_{c5}	1714 (10)	315 (2)	8224 (8)

[a] Figures in parentheses are the estimated standard deviations.
[b] Atoms labeled in agreement with Figures 1–3.

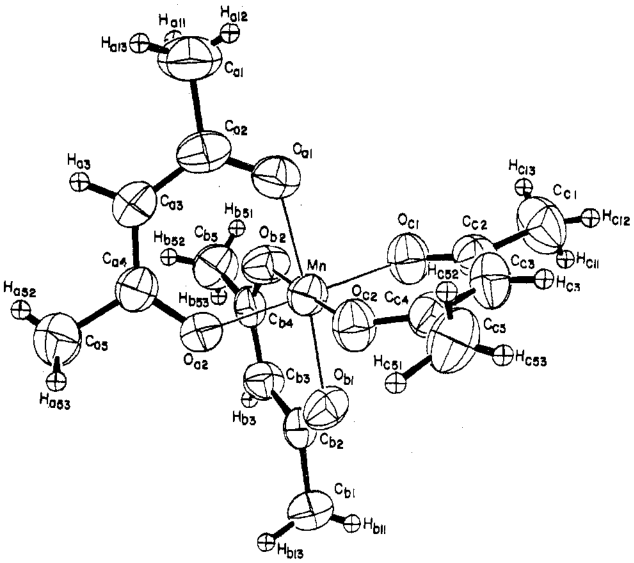

Figure 1. Model in perspective showing one γ-Mn($O_2C_5H_7$)$_3$ molecule. All nonhydrogen atoms are represented by 50% probability ellipsoids which reflect the refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres which in no way represent their true thermal motion. The pseudo-C_2 axis of the molecule ideally passes through the Mn, C_{c3}, and H_{c3} atoms.

Table II. Anisotropic Thermal Parameters in Crystalline γ-Mn$(O_2C_5H_7)_3$[a]

	Anisotropic parameters, Å^2						
Atom type[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
Mn	4.07 (3)	3.92 (3)	3.88 (3)	0.00 (3)	0.80 (2)	0.31 (3)	3.94
O_{a1}	4.0 (2)	5.4 (2)	5.1 (2)	0.3 (1)	0.5 (1)	0.2 (1)	4.8
O_{a2}	3.7 (1)	4.0 (2)	5.7 (2)	−0.1 (1)	1.3 (1)	0.3 (1)	4.3
O_{b1}	4.8 (2)	4.9 (2)	4.7 (2)	−0.8 (1)	1.1 (1)	0.8 (1)	4.7
O_{b2}	4.0 (2)	6.0 (2)	4.4 (2)	−0.3 (1)	0.9 (1)	0.9 (1)	4.6
O_{c1}	6.4 (2)	4.4 (2)	4.4 (2)	0.4 (1)	1.3 (1)	−0.3 (1)	4.9
O_{c2}	5.9 (2)	4.0 (2)	4.1 (2)	0.3 (1)	1.2 (1)	0.3 (1)	4.5
C_{a1}	3.9 (3)	8.8 (5)	8.4 (5)	−0.1 (3)	0.3 (3)	−0.2 (4)	6.7
C_{a2}	3.9 (2)	6.5 (3)	3.7 (2)	−0.7 (2)	0.6 (2)	0.5 (2)	4.5
C_{a3}	4.7 (3)	4.2 (2)	6.4 (3)	−0.8 (2)	1.2 (2)	0.2 (2)	4.9
C_{a4}	4.7 (2)	3.8 (2)	4.7 (2)	−0.1 (2)	1.3 (2)	1.2 (2)	4.2
C_{a5}	6.7 (4)	4.5 (3)	9.8 (5)	0.2 (3)	3.0 (4)	1.1 (3)	6.3
C_{b1}	3.9 (2)	5.6 (3)	7.1 (3)	−0.6 (3)	1.0 (2)	−0.3 (3)	5.3
C_{b2}	4.4 (2)	3.0 (2)	4.6 (2)	0.0 (2)	0.9 (2)	−0.8 (2)	3.8
C_{b3}	3.9 (2)	4.6 (2)	4.0 (2)	0.3 (2)	0.5 (2)	−0.8 (2)	4.2
C_{b4}	4.9 (2)	2.8 (2)	3.8 (2)	0.3 (2)	1.3 (2)	−0.2 (2)	3.7
C_{b5}	6.2 (3)	5.9 (3)	5.0 (3)	−0.1 (3)	1.9 (2)	1.2 (2)	5.4
C_{c1}	7.8 (4)	5.4 (4)	7.0 (4)	1.4 (3)	0.7 (3)	−2.1 (3)	6.3
C_{c2}	3.9 (2)	4.7 (3)	5.2 (3)	0.3 (2)	−0.1 (2)	−0.8 (2)	4.6
C_{c3}	6.6 (3)	3.7 (2)	5.2 (3)	0.6 (2)	0.4 (2)	0.7 (2)	5.0
C_{c4}	4.2 (2)	4.2 (2)	4.3 (3)	−0.5 (2)	0.4 (2)	0.5 (2)	4.2
C_{c5}	8.0 (4)	5.3 (1)	4.6 (3)	−1.1 (1)	1.1 (1)	1.0 (1)	5.6

[a] Numbers in parentheses following each B_{ij} value are the estimated standard deviations in the last significant figure. The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Atoms labeled in agreement with Table I and Figures 1-3. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Refined Parameters for Hydrogen Atoms in Crystalline γ-Mn$(O_2C_5H_7)_3$[a]

	Fractional coordinates			
Atom type[b]	10^3x	10^3y	10^3z	B,[c] Å^2
H_{a11}	710 (11)	191 (3)	432 (11)	10 (2)
H_{a12}	733 (9)	156 (2)	553 (9)	4 (1)
H_{a13}	712 (11)	206 (3)	620 (11)	9 (2)
H_{a3}	423 (7)	242 (2)	524 (6)	3 (1)
H_{a51}	37 (10)	262 (3)	377 (10)	8 (2)
H_{a52}	156 (9)	275 (2)	515 (9)	5 (1)
H_{a53}	29 (11)	251 (3)	594 (10)	8 (2)
H_{b11}	−396 (9)	79 (2)	110 (9)	4 (2)
H_{b12}	−424 (10)	115 (3)	−8 (10)	7 (2)
H_{b13}	−426 (13)	133 (3)	158 (13)	13 (3)
H_{b3}	−166 (7)	147 (2)	−88 (7)	4 (1)
H_{b51}	234 (9)	158 (2)	−134 (10)	8 (2)
H_{b52}	170 (10)	203 (3)	−91 (10)	8 (2)
H_{b53}	55 (10)	171 (3)	−218 (10)	5 (1)
H_{c11}	230 (16)	−51 (4)	215 (15)	15 (4)
H_{c12}	342 (12)	−60 (3)	348 (11)	9 (3)
H_{c13}	389 (14)	−24 (4)	215 (13)	12 (4)
H_{c3}	251 (7)	−24 (2)	591 (6)	3 (1)
H_{c51}	100 (13)	63 (4)	874 (12)	12 (3)
H_{c52}	277 (9)	37 (2)	895 (9)	6 (2)
H_{c53}	149 (10)	5 (3)	840 (9)	6 (2)

[a] Figures in parentheses are the estimated standard deviations. [b] Atoms labeled in agreement with Figures 1-3. [c] Isotropic thermal parameter.

lengths are given along with their estimated standard deviations in Table IV. The approximate D_{4h} distortion of the octahedral coordination polyhedron in γ-Mn(acac)$_3$ is similar to that observed for Mn(acac)$_2$(N$_3$) and Mn(acac)$_2$(NCS). There are four short Mn–O bonds of average length 1.935 (3, 4, 7) Å[23] which describe a quasi-square that is oriented perpendicular to the idealized fourfold axis and two long trans Mn–O bonds (Mn–O_{a1} and Mn–O_{b1}) of average length 2.111 (4, 2, 2) Å[23] which are nearly collinear with this axis. The quasi-square of coordinated oxygen atoms (O_{a2}, O_{b2}, O_{c1}, and O_{c2}) are all coplanar with the manganese atom to within 0.01 Å. The averaged value of 1.994 (3, 78, 118) Å[23] for the six crystallographically independent Mn–O bond lengths in γ-Mn(acac)$_3$ is quite comparable to the 1.981 (8) Å averaged value for the six Mn–O bond lengths in β-Mn(acac)$_3$ determined independently by Fackler and Avdeef[14] and in this laboratory,[13] but is considerably longer than the 1.872 (8, 10, 24) Å average value originally reported by Morosin and Brathovde[9] for β-Mn(acac)$_3$.

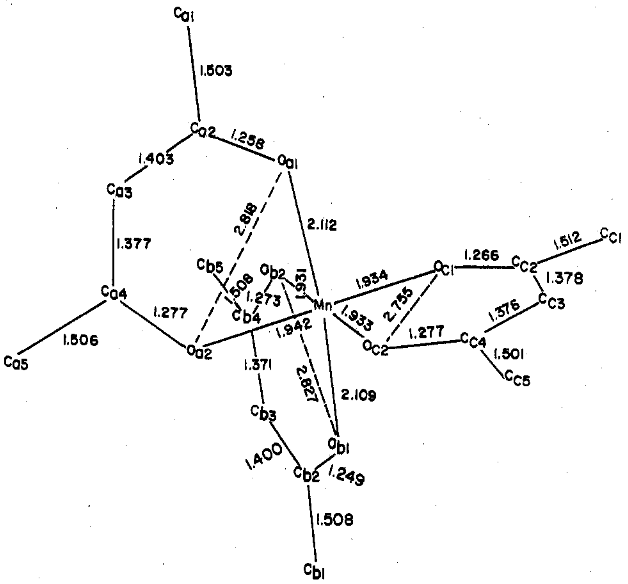

Figure 2. Diagram derived from the ORTEP drawing of Figure 1 showing selected bond lengths in the solid-state structure of γ-Mn$(O_2C_5H_7)_3$.

The 0.176-Å difference between the averaged values for the two "long" and four "short" Mn–O bonds in γ-Mn(acac)$_3$ agrees well with the tetragonal elongations of 0.19, 0.148, and 0.20 Å observed for Mn–O or Mn–S bonds in tris(tropolonato)manganese(III),[12] tris(dithiocarbamato)manganese(III),[24] and (acetylacetonato)bis(N-phenylaminotroponiminato)manganese(III),[11] respectively.

Although one cannot consider **1** as having rigorous Jahn–Teller distortion since the molecule cannot possess full O_h symmetry, the observed tetragonal elongation is consistent with the presence of this effect for a high-spin d^4 metal ion with one 3d electron occupying each of the three σ-nonbonding (d$_{xy}$, d$_{xz}$, and d$_{yz}$) metal orbitals and the fourth 3d electron oc-

Table IV. Bond Distances, Polyhedral Edge Lengths, and Bond Angles Subtended at the Mn(III) Atom in the Coordination Group of Crystalline γ-$Mn(O_2C_5H_7)_3$[a]

Type[b]	Length, Å		Type[b]	Length, Å	
$Mn-O_{a1}$	2.112 (4)	2.111 (4, 2, 2)[c]	$O_{b1}-O_{a2}$	2.803 (5)	2.817 (5, 7, 14)
$Mn-O_{b1}$	2.109 (3)		$O_{a1}-O_{b2}$[d]	2.818 (5)	
$Mn-O_{a2}$	1.942 (3)	1.935 (3, 4, 7)	$O_{a1}-O_{a2}$[d]	2.818 (5)	
$Mn-O_{b2}$	1.931 (3)		$O_{b1}-O_{b2}$[d]	2.827 (5)	
$Mn-O_{c1}$	1.934 (4)		$O_{c1}-O_{c2}$[d]	2.755 (5)	2.737 (5, 18, 36)
$Mn-O_{c2}$	1.933 (3)		$O_{c1}-O_{b2}$	2.701 (5)	
$O_{a1}-O_{c1}$	2.916 (5)	2.909 (5, 16, 32)	$O_{a2}-O_{c2}$	2.745 (5)	
$O_{a1}-O_{c2}$	2.877 (5)		$O_{a2}-O_{b2}$	2.746 (5)	
$O_{b1}-O_{c1}$	2.921 (5)				
$O_{b1}-O_{c2}$	2.923 (5)				
Type[b]	**Angle, deg**		**Type[b]**	**Angle, deg**	
$O_{a1}MnO_{a2}$	88.0 (1)	88.1 (1, 4, 6)	$O_{b2}MnO_{c1}$	87.7 (1)	89.8 (1, 10, 21)
$O_{a1}MnO_{b2}$	88.2 (1)		$O_{a2}MnO_{c2}$	90.2 (1)	
$O_{b1}MnO_{b2}$	88.7 (1)		$O_{c1}MnO_{c2}$	90.9 (1)	
$O_{b1}MnO_{a2}$	87.5 (1)		$O_{b2}MnO_{a2}$	90.3 (1)	
$O_{a1}MnO_{c1}$	92.1 (1)	91.9 (1, 7, 13)			
$O_{a1}MnO_{c2}$	90.6 (1)				
$O_{b1}MnO_{c1}$	92.4 (1)				
$O_{b1}MnO_{c2}$	92.5 (1)				

[a] Figures in parentheses are the estimated standard deviations. Entries in the table are grouped according to the idealized D_{4h} tetragonally elongated octahedral geometry of the coordination polyhedron with O_{a1}, Mn, and O_{b1} lying on the fourfold axis or according to the pseudo-C_2 symmetry for the entire molecule with Mn, C_{c3} and H_{c3} lying on the twofold axis. [b] Atoms labeled in agreement with Tables I–II and Figures 1–3. [c] Average values. The first number in parentheses following each averaged value is the rms value of the estimated standard deviation for an individual datum. The second and third numbers are the mean and maximum deviations from the averaged value, respectively. [d] The "bite" of the ligand.

Table V. Bond Lengths within the Acetylacetonato Ligands in Crystalline γ-$Mn(O_2C_5H_7)_3$[a]

Type[b]	Length, Å		Type[b]	Length, Å	
$O_{a1}-C_{a2}$	1.258 (6)	1.254 (6, 5, 5)[c]	$H_{a11}-C_{a1}$	0.94 (8)	0.92 (8, 8, 23)
$O_{b1}-C_{b2}$	1.249 (6)		$H_{a12}-C_{a1}$	0.77 (6)	
$O_{a2}-C_{a4}$	1.277 (6)	1.273 (6, 4, 7)	$H_{a13}-C_{a1}$	1.02 (8)	
$O_{b2}-C_{b4}$	1.273 (5)		$H_{a51}-C_{a5}$	1.02 (8)	
$O_{c1}-C_{c2}$	1.266 (6)		$H_{a52}-C_{a5}$	0.76 (7)	
$O_{c2}-C_{c4}$	1.277 (5)		$H_{a53}-C_{a5}$	0.99 (8)	
$C_{a2}-C_{a3}$	1.403 (7)	1.402 (7, 2, 2)	$H_{b11}-C_{b1}$	0.78 (7)	
$C_{b2}-C_{b3}$	1.400 (7)		$H_{b12}-C_{b1}$	0.92 (8)	
$C_{a3}-C_{a4}$	1.377 (7)	1.374 (7, 3, 3)	$H_{b13}-C_{b1}$	1.04 (10)	
$C_{b3}-C_{b4}$	1.371 (7)		$H_{b51}-C_{b5}$	0.85 (6)	
$C_{c2}-C_{c3}$	1.378 (7)	1.377 (7, 1, 1)	$H_{b52}-C_{b5}$	0.90 (7)	
$C_{c4}-C_{c3}$	1.376 (7)		$H_{b53}-C_{b5}$	0.99 (6)	
$C_{a1}-C_{a2}$	1.503 (8)	1.506 (8, 3, 6)	$H_{c11}-C_{c1}$	0.92 (11)	
$C_{b1}-C_{b2}$	1.508 (7)		$H_{c12}-C_{c1}$	0.93 (8)	
$C_{c1}-C_{c2}$	1.512 (8)		$H_{c13}-C_{c1}$	0.89 (10)	
$C_{a5}-C_{a4}$	1.506 (8)		$H_{c51}-C_{c5}$	1.15 (10)	
$C_{b5}-C_{b4}$	1.508 (7)		$H_{c52}-C_{c5}$	0.93 (7)	
$C_{c5}-C_{c4}$	1.501 (8)		$H_{c53}-C_{c5}$	0.77 (7)	
			$H_{a3}-C_{a3}$	0.95 (5)	0.93 (5, 2, 4)
			$H_{b3}-C_{b3}$	0.94 (5)	
			$H_{c3}-C_{c3}$	0.89 (5)	

[a] Figures in parentheses are the estimated standard deviations of the individual measurements. Entries in the table are grouped according to the idealized D_{4h} tetragonally elongated octahedral geometry of the coordination polyhedron with O_{a1}, Mn, and O_{b1} lying on the fourfold axis or according to the pseudo-C_2 symmetry for the entire molecule with Mn, C_{c3}, and H_{c3} lying on the twofold axis. [b] Atoms labeled in agreement with Tables I–III and Figures 1–3. [c] Average values. The first number in parentheses following each averaged value is the rms value of the estimated standard deviation for an individual datum. The second and third numbers are the mean and maximum deviations from the averaged value, respectively.

cupying the σ-antibonding d_{z^2} orbital (the z axis is collinear with the idealized fourfold axis of the coordination polyhedron).

Whereas the coordination polyhedron of γ-Mn(acac)$_3$ closely approximates D_{4h} symmetry, the whole molecule closely approximates its maximum possible symmetry of C_2 with the twofold axis ideally passing through Mn, C_{c3}, and H_{c3}. Major departures of the coordination polyhedron of **1** from D_{4h} symmetry are primarily the result of constraints imposed by the acac ligand "bite". Although the "bites" for ligands a and b are opened by 0.068 Å relative to ligand c, they would need to expand by yet another 0.041 Å to a value of 2.864 Å in order to properly span the vertical edges of a D_{4h} tetragonally elongated octahedral coordination polyhedron having lengths of 1.935 and 2.111 Å for the four "short" and two "long" metal–ligand bonds, respectively. Oxygen atoms O_{a1} and O_{b1} are translated off the idealized fourfold axis in a direction parallel to the approximate C_2 axis of the molecule toward the $O_{a2}\cdots O_{b2}$ polyhedral edge. Even with this distortion, all bond angles subtended at the Mn atom are within 2.5° of the idealized 90° value and they are grouped into pairs related by the pseudo-C_2 axis. The short Mn–O bonds for oxygen atoms O_{a2}, O_{b2}, O_{c1}, and O_{c2} relative to those for O_{a1} and O_{b1} are responsible for the four short [average value of 2.737 (5, 18, 36) Å] O⋯O contacts within the quasi-square they determine; all other O⋯O contacts within the coordination polyhedron are greater than the 2.80-Å van der Waals diameter of oxygen.[25]

Table VI. Bond Angles within the Acetylacetonato Ligands in Crystalline γ-$Mn(O_2C_5H_7)_3$[a]

Type[b]	Angle, deg		Type[b]	Angle, deg	
$MnO_{a1}C_{a2}$	125.1 (3)	125.3 (3, 2, 2)[c]	$C_{a2}C_{a1}H_{a11}$	107 (5)	111 (6, 3, 9)
$MnO_{b1}C_{b2}$	125.4 (3)		$C_{a2}C_{a1}H_{a12}$	114 (5)	
$MnO_{a2}C_{a4}$	128.1 (3)	128.3 (3, 2, 2)	$C_{a2}C_{a1}H_{a13}$	111 (5)	
$MnO_{b2}C_{b4}$	128.5 (3)		$C_{a4}C_{a5}H_{a51}$	103 (5)	
$MnO_{c1}C_{c2}$	127.8 (3)	127.6 (3, 2, 2)	$C_{a4}C_{a5}H_{a52}$	108 (6)	
$MnO_{c2}C_{c4}$	127.4 (3)		$C_{a4}C_{a5}H_{a53}$	111 (5)	
$O_{a1}C_{a2}C_{a1}$	117.7 (6)	117.1 (6, 6, 6)	$C_{b2}C_{b1}H_{b11}$	112 (5)	
$O_{b1}C_{b2}C_{b1}$	116.5 (5)		$C_{b2}C_{b1}H_{b12}$	114 (5)	
$O_{a2}C_{a4}C_{a5}$	113.8 (5)	114.0 (5, 2, 2)	$C_{b2}C_{b1}H_{b13}$	107 (6)	
$O_{b2}C_{b4}C_{b5}$	114.2 (5)		$C_{b4}C_{b5}H_{b51}$	112 (5)	
$O_{c1}C_{c2}C_{c1}$	115.5 (5)	115.0 (5, 5, 5)	$C_{b4}C_{b5}H_{b52}$	113 (5)	
$O_{c2}C_{c4}C_{c5}$	114.5 (5)		$C_{b4}C_{b5}H_{b53}$	110 (6)	
$O_{a1}C_{a2}C_{a3}$	124.1 (5)	124.2 (5, 1, 1)	$C_{c1}C_{c2}H_{c11}$	120 (8)	
$O_{b1}C_{b2}C_{b3}$	124.2 (5)		$C_{c1}C_{c2}H_{c12}$	114 (6)	
$O_{a2}C_{a4}C_{a3}$	125.7 (5)	125.9 (5, 2, 2)	$C_{c1}C_{c2}H_{c13}$	111 (7)	
$O_{b2}C_{b4}C_{b3}$	126.1 (4)		$C_{c4}C_{c5}H_{c51}$	111 (5)	
$O_{c1}C_{c2}C_{c3}$	124.3 (5)	124.3 (5, 1, 1)	$C_{c4}C_{c5}H_{c52}$	112 (5)	
$O_{c2}C_{c4}C_{c3}$	124.2 (5)		$C_{c4}C_{c5}H_{c53}$	113 (6)	
$C_{a1}C_{a2}C_{a3}$	118.3 (6)	118.8 (6, 5, 5)	$C_{a2}C_{a3}H_{a3}$	120 (3)	117 (3, 2, 3)
$C_{b1}C_{b2}C_{b3}$	119.2 (5)		$C_{a4}C_{a3}H_{a3}$	114 (3)	
$C_{a3}C_{a4}C_{a5}$	120.5 (5)	120.2 (5, 4, 4)	$C_{b2}C_{b3}H_{b3}$	119 (3)	
$C_{b3}C_{b4}C_{b5}$	119.8 (5)		$C_{b4}C_{b3}H_{b3}$	115 (3)	
$C_{c1}C_{c2}C_{c3}$	120.3 (5)	120.8 (5, 5, 5)	$C_{c2}C_{c3}H_{c3}$	119 (3)	
$C_{c3}C_{c4}C_{c5}$	121.3 (5)		$C_{c4}C_{c3}H_{c3}$	116 (3)	
$C_{a2}C_{a3}C_{a4}$	125.8 (5)	125.7 (5, 2, 3)	$H_{a11}C_{a1}H_{a12}$	104 (8)	107 (7, 7, 19)
$C_{b2}C_{b3}C_{b4}$	126.0 (5)		$H_{a11}C_{a1}H_{a13}$	106 (6)	
$C_{c2}C_{c3}C_{c4}$	125.4 (5)		$H_{a12}C_{a1}H_{a13}$	113 (8)	
			$H_{a51}C_{a5}H_{a52}$	99 (7)	
			$H_{a51}C_{a5}H_{a53}$	125 (7)	
			$H_{a52}C_{a5}H_{a53}$	109 (7)	
			$H_{b11}C_{b1}H_{b12}$	108 (7)	
			$H_{b11}C_{b1}H_{b13}$	122 (8)	
			$H_{b12}C_{b1}H_{b13}$	93 (6)	
			$H_{b51}C_{b5}H_{b52}$	108 (5)	
			$H_{b51}C_{b5}H_{b53}$	106 (6)	
			$H_{b52}C_{b5}H_{b53}$	107 (6)	
			$H_{c11}C_{c1}H_{c12}$	88 (8)	
			$H_{c11}C_{c1}H_{c13}$	106 (9)	
			$H_{c12}C_{c1}H_{c13}$	118 (9)	
			$H_{c51}C_{c5}H_{c52}$	95 (6)	
			$H_{c51}C_{c5}H_{c53}$	121 (8)	
			$H_{c52}C_{c5}H_{c53}$	104 (7)	

[a] Figures in parentheses are the estimated standard deviations of the individual measurements. Entries in the table are grouped according to the idealized D_{4h} tetragonally elongated octahedral geometry of the coordination polyhedron with O_{a1}, Mn, and O_{b1} lying on the fourfold axis or according to the pseudo-C_2 symmetry for the entire molecule with Mn, C_{c3}, and H_{c3} lying on the twofold axis. [b] Atoms labeled in agreement with Tables I–V and Figures 1–3. [c] Average values. The first number in parentheses following each averaged value is the rms value of the estimated standard deviation for an individual datum. The second and third numbers are the mean and maximum deviations from the averaged value, respectively.

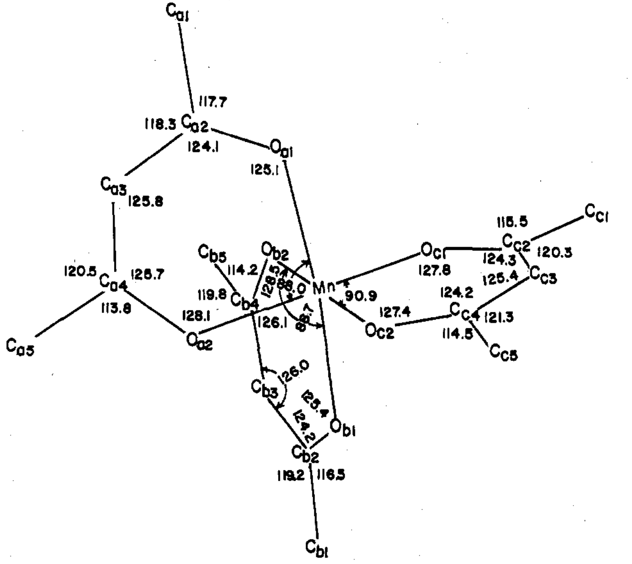

Figure 3. Diagram derived from the ORTEP drawing of Figure 1 showing selected bond angles in the solid-state structure of γ-$Mn(O_2C_5H_7)_3$.

Bond lengths within the acetylacetonato ligands are shown in Figure 2 and given with their estimated standard deviations in Table V. Ligand bond angles are shown in Figure 3 and given with their estimated standard deviations in Table VI. The structural parameters of the ligands appear to be significantly affected by the differences in Mn–O bond lengths. The bond lengths and angles of the six-membered ($-Mn-O_1-C_2-C_3-C_4-O_2-$) chelate ring and the seven-atom (excluding hydrogen atoms) acetylacetonato skeleton of ligand c are seen to be symmetrically related by the pseudo-C_2 axis of the ligand (and the molecule) whereas bond lengths and angles within the six-membered chelate rings and the seven-atom acetylacetonato skeletons of ligands a and b are not symmetrical within the same ligand but are related in pairs between the two ligands by the pseudo-C_2 molecular axis. The differences between Mn–O bond lengths seem to be propagated in the entire six-membered chelate ring for ligands a and b with C_2–O_1 being shorter than C_4–O_2 by 0.019–0.024 Å (3–4σ) and C_3–C_4 being shorter than C_2–C_3 by 0.026–0.029 Å (4σ). As expected the shorter C–O bonds are adjacent to the longer Mn–O bonds and the longer C–C bonds are adjacent to the shorter C–O bonds within the chelate ring. Similar effects on the geometry of the acac ligand have been observed for the precise structural analyses of Zr(acac)$_3$(NO$_3$)[26] and Zr(acac)$_2$(NO$_3$)$_2$.[27] The pairs of C–C and C–O bonds have nearly equal values for the chelate ring of ligand c where the two Mn–O bonds have nearly equal lengths. The bond lengths and angles for ligand c are significantly different from those for ligands a and b and are in accord with the values found in other acetylacetonate structures[28] and virtually the same as those determined for crystals of Mn(acac)$_2$(N$_3$)[6] and Mn(acac)$_2$(NCS)[1]—two other high-spin Mn(III) complexes with tetragonally elongated octahedral coordination polyhedra where the acetylacetonato oxygen atoms determine a quasi-square which is oriented perpendicular to the pseudo-fourfold axis.

While the entire seven-atom (excluding hydrogen atoms) ligand skeletons are somewhat nonplanar for the acetylacetonato ligands, the five-atom (O_1, O_2, C_2, C_3, and C_4) chelate rings are quite planar (maximum displacement of any atom from its least-squares mean plane is 0.01 Å). Directional displacements of the manganese atom from the least-squares mean planes of these five-atom chelate rings are 0.371 Å toward O_{b2}, 0.222 Å toward O_{a2}, and 0.051 Å toward O_{a1} for ligands a, b, and c, respectively. The angles of folding thus produced along the appropriate O···O polyhedral edge are 14.7, 8.8, and 2.2° for ligands a, b, and c, respectively. Although the folding of the acetylacetonate ligands is presumably the result of packing forces, there are no intermolecular contacts less than the sum of the respective van der Waals radii.[25]

In conclusion, the results reported herein for γ-Mn(acac)$_3$ and those obtained for recent studies of β-Mn(acac)$_3$[13,14] all reveal distorted octahedral coordination polyhedra. Whereas the coordination polyhedron for β-Mn(acac)$_3$ has either a rhombic octahedral distortion[13] or a tetragonal compression,[14] that for γ-Mn(acac)$_3$ clearly possesses a tetragonal elongation. These results, together with the nearly identical crystallographic structures for a recent study of β-Co(acac)$_3$[15] and the original study of β-Mn(acac)$_3$,[9] provide conclusive evidence for the (initial) mislabeling of β-Co(acac)$_3$ crystals as β-Mn(acac)$_3$ by Morosin and Brathhovde.[9]

Acknowledgment. Support of this research by the University of Nebraska Research Council and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank the University of Nebraska Computing Center for a generous grant of computer time.

Registry No. Mn(O$_2$C$_5$H$_7$)$_3$, 14284-89-0.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes from the final cycle of least-squares refinement for γ-Mn(O$_2$C$_5$H$_7$)$_3$ (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 2: B. R. Stults, R. O. Day, R. S. Marianelli and V. W. Day, *Inorg. Chem.*, preceding paper in this issue.

(2) A preliminary report of this work has appeared: V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Am. Chem. Soc.*, **96**, 2650 (1974).

(3) Presented before the Division of Inorganic Chemistry, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974.

(4) Presented before the American Crystallographic Association, Spring Meeting, Berkeley, Calif., March 1974.

(5) Camille and Henry Dreyfus Teacher–Scholar.

(6) B. R. Stults, R. S. Marianelli, and V. W. Day, *Inorg. Chem.*, **14**, 722 (1975).

(7) B. R. Stults, V. W. Day, E. L. Tasset, and R. S. Marianelli, *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).

(8) (a) H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A*, **161**, 220 (1937); (b) H. A. Jahn, *ibid.*, **164**, 117 (1938); (c) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); (d) J. K. Burdett, *ibid.*, **14**, 375 (1975).

(9) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, **17**, 705 (1964).

(10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 851.

(11) M. Bartlett and G. J. Palinek, *Chem. Commun.*, 416 (1970).

(12) J. P. Fackler, Jr., A. Avdeef, and J. A. Costamagna, *Inorg. Chem.*, **13**, 1854 (1974).

(13) V. W. Day, unpublished results. The results of this study for β-Mn(acac)$_3$ indicate the possibility of a rhombic octahedral distortion of the coordination polyhedron with three pairs of Mn–O bonds averaging 1.943 (5, 7, 7), 1.985 (5, 2, 2), and 2.016 (5, 2, 2) Å, respectively. Whereas the numerical values for the Mn–O bond lengths obtained by Fackler and Avdeef[14] are nearly identical with these with corresponding values of 1.944 (9, 13, 13), 1.988 (8, 4, 4), and 2.012 (8, 9, 9) Å, their precision was somewhat lower. The higher precision of our study indicates the possibility of making additional subtle distinctions among the Mn–O bond lengths.

(14) J. P. Fackler, Jr., and A. Avdeef, *Inorg. Chem.*, **13**, 1864 (1974).

(15) P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, **3**, 67 (1973).

(16) International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969, p 99.

(17) The results of tests for piezoelectricity, made with a Geibe-Schiebe detector, were kindly supplied by Professor J. L. Hoard of Cornell University.

(18) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, p 166.

(19) "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1967, p 302.

(20) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(21) D. T. Cromer, *Acta Crystallogr., Sect. A*, **18**, 17 (1965).

(22) Supplementary material.

(23) The first number in parentheses following an averaged value is the root-mean-square value of the estimated standard deviation of a single datum. The second and third numbers, when given, represent the mean and maximum deviations from the averaged value, respectively.

(24) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972).

(25) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

(26) E. G. Muller, V. W. Day, and R. C. Fay, *J. Am. Chem. Soc.*, **98**, 2165 (1976).

(27) V. W. Day and R. C. Fay, *J. Am. Chem. Soc.*, **97**, 5136 (1975).

(28) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 295 (1966).