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Distortions of the Coordination Polyhedron in High-Spin Manganese(III) Complexes. 2. Crystal Structure of Thiocyanatobis(acetylacetonato)manganese(III)[1-4]

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

The crystal structure of thiocyanatobis(acetylacetonato)manganese(III), $Mn(O_2C_5H_7)_2(NCS)$, has been determined by single-crystal X-ray diffraction techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares techniques to $R_1 = 0.057$ and $R_2 = 0.061$ by using 1917 independent diffractometer-recorded reflections (Nb-filtered Mo K_α radiation and θ–2θ scans) having $2\theta_{MoK\alpha} < 55°$ and $I > 2\sigma(I)$. The compound crystallizes in the uniquely determined centrosymmetric orthorhombic space group *Pbca* with eight molecules in a unit cell of dimensions $a = 13.422$ (2) Å, $b = 14.519$ (3) Å, and $c = 13.763$ (3) Å ($\rho_{calcd} = 1.541$ g/cm³, $\rho_{obsd} = 1.540$ g/cm³). Each thiocyanato ligand bridges two adjacent quasi-planar $Mn(acac)_2^+$ groups in the three-dimensional lattice by using the glide operator perpendicular to the $\vec{c}$ axis of the unit cell to generate infinite chains of octahedral Mn(III) subunits along the $\vec{a}$ axis. The octahedral coordination polyhedron is tetragonally elongated and approximates idealized C_{4v} symmetry with the trans-coordinated thiocyanato nitrogen and sulfur atoms on the pseudo-fourfold axis. The four "short" Mn–O bonds have average lengths of 1.912 (4) Å while the two long trans Mn–N and Mn–S' bonds to the ends of bridging thiocyanato ligands have lengths of 2.189 (5) and 2.880 (2) Å, respectively. The dissimilarity of the two ends of the thiocyanato ligand has a pronounced effect on the Mn coordination geometry in this complex. The Mn atom is displaced by 0.12 Å from the mean plane of the quasi-square of four coordinated oxygen atoms toward the coordinated thiocyanato nitrogen atom.

Introduction

This is the second of three papers[1] dealing with the coordination chemistry for a series of high-spin manganese(III) acetylacetonato (acac) complexes. The first paper described the synthesis and characterization of a series of compounds having the formulations $Mn(acac)_2(X)$ and $Mn(acac)_2(X)(B)$, where X is a mononegative anionic ligand such as N_3^-, NCS^-, or Cl^- and B is a neutral Lewis base such as pyridine or methanol. These compounds serve as useful synthetic intermediates for manganese(III) porphyrins and provide a simple high-yield procedure for preparing these interesting compounds in pure form. The solid-state structure of $Mn(acac)_2(N_3)$, **1**, reported in the first paper of this series[1] revealed several interesting features of high-spin Mn(III) and azide ligand coordination chemistry. Each azide ligand in crystals of this compound symmetrically bridges (through its first and third nitrogen atoms) two adjacent $Mn(acac)_2^+$ groups in the three-dimensional lattice to produce infinite chains of octahedral Mn(III) subunits. Each of these octahedral coordination polyhedra is tetragonally elongated and approximates idealized D_{4h} symmetry with four "short" Mn–O and two "long" Mn–N bonds. Since the azide ligand produced symmetrical bridges between Mn atoms in the solid state to give regularly elongated octahedral species with identical trans Mn–N bonds, it was of interest to characterize the closely related complex $Mn(acac)_2(NCS)$ (**2**), in which the azide ligand has been replaced by the less symmetrical thiocyanate ligand. Other properties[1] also did not exclude the possibility of a five-coordinate Mn in this complex. Although each of the thiocyanate ligands in **2** also bridges adjacent $Mn(acac)_2^+$ groups in the three-dimensional lattice to produce infinite chains of octahedral Mn(III) subunits, the dissimilarity of the two ends of the thiocyanate ligand have a significant effect on the coordination geometry observed for the Mn atom.

Experimental Section

Large, well-shaped single crystals of thiocyanatobis(acetylacetonato)manganese(III), prepared as previously reported,[1,6] may be grown from a saturated solution of methanol or acetonitrile by slow solvent evaporation at 5 °C. Single crystals (as shown by X-ray photographs) grown from methanol are rapidly converted into a powder at room temperature which analyzes as $Mn(O_2C_5H_7)_2(NCS)$, **2**. These results are presumably due to the loss of (coordinated or lattice) methanol from the original crystalline material. Crystals grown from acetonitrile proved to be unsolvated and stable; they were used for subsequent crystallographic studies.

Precession photographs used to determine a preliminary set of lattice constants and the probable space group indicated orthorhombic, *mmm*, symmetry. The observed systematically absent reflections were those uniquely required by the centrosymmetric space group *Pbca* (D_{2h}^{15}, No. 61).[7] This choice was fully supported by the negative results of sensitive tests for piezoelectricity[8] and by all stages of the subsequent structure determination.

An approximately cube-shaped crystalline specimen 0.50 mm on an edge was cut from a large single crystal and ground to a sphere 0.44 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[1] by using 15 high-angle reflections ($2\theta_{MoK\alpha} > 30°$) and Nb-filtered Mo $K\alpha$ radiation (λ 0.710 69 Å) on a Syntex $P\bar{1}$ Autodiffractometer at 20 ± 1 °C are $a = 13.422$ (2), $b = 14.519$ (3), and $c = 13.763$ (3) Å. A unit cell with these dimensions containing eight $Mn(acac)_2(NCS)$ formula units has a calculated density of 1.541 g cm⁻³, which is in excellent agreement with the observed density of 1.540 g cm⁻³ measured by flotation in a carbon tetrachloride/hexane solution.

Intensities were measured by using Nb-filtered Mo $K\alpha$ radiation and θ–2θ scans with a 3° takeoff angle and a normal-focus X-ray tube. A scan rate of 3°/min was employed for scans between 2θ settings 1.0° above and below the calculated $K\alpha$ doublet ($\lambda_{K\alpha_1}$ 0.709 26 Å and $\lambda_{K\alpha_2}$ 0.713 54 Å) values for each reflection. Background counts, each lasting for half the total scan time, were taken at both ends of the scan range. A total of 3076 independent reflections having $2\theta_{MoK\alpha} < 55°$ (the equivalent of one limiting Cu $K\alpha$ sphere) were measured in two concentric shells of increasing 2θ containing approximately 1550 reflections each. Six standard reflections, measured every 200 reflections as a monitor for disalignment and/or deterioration of the crystal, gave no indication of either.

The linear absorption coefficient of the crystal for Mo $K\alpha$ radiation is 1.186 mm⁻¹,[9] yielding a μr of 0.26 for the spherical specimen used for intensity measurements. Since variable absorption for a spherical

sample having $\mu r = 0.26$ is negligible,[10] no absorption correction was applied and the intensity measurements were reduced to a set of relative-squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 3076 reflections examined, 1159 were eventually rejected as objectively unobserved by applying the rejection criterion $I < 2\sigma(I)$ 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 ($K = 1$ in this case), and B is the total background count.

When a three-dimensional Patterson synthesis failed to locate the manganese and sulfur atoms, the "heavy-atom" technique of structure determination was abandoned in favor of "direct" methods. The 1538 independent reflections having $2\theta_{MoK\alpha} < 43°$ were used to calculate a Wilson plot and were then reduced to a corresponding set of normalized structure factors, E_{hkl}. The various statistical indicators using these normalized structure factors were all in agreement with the choice of a centrosymmetric space group. The 170 reflections having the largest E_{hkl} values were phased by iterative use of the weighted tangent formula and used to calculate an E map which revealed the manganese and sulfur atomic positions as well as those for many of the remaining nonhydrogen atoms. The remaining nonhydrogen atoms were then located from a single-difference Fourier synthesis which used the phases calculated from the partial model derived from the E map.

Unit-weighted full-matrix least-squares refinement of the positional and isotropic thermal parameters for the 18 crystallographically independent nonhydrogen atoms resulted in a conventional unweighted residual, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, of 0.151 and a conventional weighted residual, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.130 for the 1323 reflections having $2\theta_{MoK\alpha} < 43°$ and $I > 2\sigma(I)$. The atomic form factors compiled by Cromer and Mann[11] and anomalous dispersion corrections[12] to the scattering factors of the manganese and sulfur atoms were employed in these and all subsequent structure factor calculations. Additional cycles of unit-weighted full-matrix least-squares refinement employing anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.073$ and $R_2 = 0.072$ for the 1323 reflections. Although a difference Fourier synthesis calculated at this point revealed discrete electron density maxima at chemically anticipated positions for the two methine hydrogen atoms, discrete maxima were not found for the methyl hydrogens but rather a toroid of electron density which was distributed symmetrically about the idealized threefold axis of the methyl group at a distance of ~1.0 Å from the methyl carbons. After several attempts to derive and refine individual positions for the methyl (and methine) hydrogens gave highly distorted tetrahedral methyl groups, it was decided to omit all hydrogen atoms from the final cycles of least-squares refinement.

Additional cycles of unit-weighted full-matrix anisotropic least-squares minimization of the function $\sum w(|F_o| - k|F_c|)^2$ (where k is the scale factor and w is the weight assigned each reflection) using the more complete data set converged to $R_1 = 0.058$ and $R_2 = 0.063$ for the 1917 reflections having $2\theta_{MoK\alpha} < 55°$ and $I > 2\sigma(I)$.

Empirical weights ($w = 1/\sigma^2$) were calculated from

$$\sigma = \sum_0^3 a_n |F_o|^n = 0.236 - 3.43 \times 10^{-2}F_o + 2.42 \times 10^{-4}F_o^2 -$$

$$2.59 \times 10^{-7}F_o^3$$

the 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 $I > 2\sigma(I)$ rejection criterion. The final cycles of totally anisotropic full-matrix least-squares refinement utilized these empirical weights and gave final values of 0.057 and 0.061 for R_1 and R_2, respectively, for the 1917 independent reflections.[13] During the final refinement cycle, no parameter shifted by more than $0.25\sigma_p$ with the average shift being $0.05\sigma_p$, where σ_p is the estimated standard deviation of the individual 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.

In addition to those programs previously described,[1] the following programs were used on an IBM 360/65 computer for this work: FAME,

Table I. Atomic Coordinates in Crystalline $Mn(O_2C_5H_7)_2(NCS)^a$

Atom type[b]	Fractional coordinates		
	10^4x	10^4y	10^4z
Mn	1245 (1)	1275 (1)	2021 (1)
S	-1852 (1)	1379 (1)	3939 (1)
O_{a1}	1406 (3)	-24 (2)	2173 (3)
O_{a2}	1935 (3)	1519 (2)	3203 (3)
O_{b1}	1130 (3)	2581 (2)	1845 (3)
O_{b2}	829 (3)	1049 (2)	712 (3)
N	-248 (4)	1247 (4)	2662 (4)
C	-929 (4)	1309 (4)	3180 (4)
C_{a1}	1741 (5)	-1487 (4)	2839 (5)
C_{a2}	1780 (4)	-441 (3)	2904 (4)
C_{a3}	2229 (5)	-21 (4)	3685 (5)
C_{a4}	2328 (5)	931 (4)	3768 (4)
C_{a5}	2963 (5)	1313 (5)	4578 (4)
C_{b1}	765 (6)	4043 (4)	1216 (6)
C_{b2}	819 (4)	3005 (4)	1109 (4)
C_{b3}	541 (5)	2588 (4)	236 (5)
C_{b4}	584 (4)	1648 (4)	76 (4)
C_{b5}	321 (5)	1266 (5)	-915 (4)

^{a} Figures in parentheses are the estimated standard deviations. ^{b} Atoms labeled in agreement with Figures 1 and 2.

a Wilson plot and normalized structure factor program by R. Dewar and A. Stone; and MULTAN, a direct methods program by P. Main, M. M. Woolfson, and G. Germain.

Results and Discussion

The final coordinates and anisotropic thermal parameters for all nonhydrogen atoms are listed in Tables I and II, respectively. Each atom is uniquely designated according to the following scheme. A literal subscript (a or b) is used to differentiate atoms of the two crystallographically independent acetylacetonato ligands while a second (numerical) subscript is used to differentiate atoms of the same element within the same ligand. Atoms of the thiocyanato ligand are represented by the nonsubscripted symbol for the element. Atoms of the symmetry-related thiocyanato ligand which completes the octahedral coordination sphere of the manganese atom specified by the atomic coordinates of Table I are designated by a prime (').

A model seen in perspective showing the octahedral environment of the Mn atom is shown in Figure 1; all atoms are labeled in agreement with Tables I–IV and are represented by ellipsoids having the shape, orientation, and relative size consistent with the thermal parameters listed in Table II.

All atoms occupy eightfold general positions of space group *Pbca*. Each thiocyanato ligand bridges two adjacent Mn-$(acac)_2^+$ groups in the three-dimensional lattice, by using the glide operator perpendicular to the $\vec{c}$ axis of the unit cell to generate infinite chains of octahedral Mn(III) subunits along the $\vec{a}$ axis. A section of one such chain, containing two octahedral Mn(III) groupings, is shown in Figure 2.

Complexing bond lengths and angles as well as polyhedral edge lengths are given along with their estimated standard deviations in Table III. Whereas both orthorhombic and tetragonal distortions of the idealized octahedral coordination polyhedron of O_h symmetry are known for high-spin Mn(III) complexes, the majority of those studied crystallographically approximate a tetragonally elongated octahedron.[1] Such a coordination polyhedron would have four "short" and two "long" complexing bonds and would ideally possess C_{4v} symmetry for a complex containing two dissimilar trans-coordinated atoms. Departure of the coordination polyhedron in Mn(acac)_2(NCS) from idealized C_{4v} symmetry is primarily the result of slight displacements of the coordinated nitrogen and sulfur atoms off the idealized fourfold axis which is perpendicular to the least-squares mean plane (given by the equation $0.914X + 0.041Y - 0.404Z = 0.599$, where X, Y, and Z are orthogonal coordinates measured in Å along $\vec{a}$, $\vec{b}$, and

Table II. Anisotropic Thermal Parameters in Crystalline $Mn(O_2C_5H_7)_2(NCS)^a$

Atom type[b]	Anisotropic parameters, Å^2						$B,^c \text{Å}^2$
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
Mn	3.27 (3)	1.78 (3)	2.56 (3)	−0.01 (3)	−0.72 (3)	0.11 (3)	2.41
S	3.6 (1)	4.4 (1)	3.6 (1)	0.2 (1)	0.1 (1)	0.0 (1)	3.9
O_{a1}	4.1 (2)	1.9 (1)	3.5 (2)	−0.3 (1)	−1.1 (2)	0.0 (1)	2.9
O_{a2}	3.9 (2)	2.5 (1)	2.7 (2)	−0.4 (1)	−0.8 (1)	0.1 (1)	2.9
O_{b1}	4.1 (2)	1.9 (1)	3.1 (2)	0.1 (1)	−0.4 (2)	0.2 (1)	2.9
O_{b2}	3.9 (2)	2.7 (2)	2.7 (2)	0.0 (1)	−1.0 (1)	−0.1 (1)	3.0
N	3.5 (2)	3.8 (2)	5.1 (3)	−0.7 (2)	0.2 (2)	0.4 (2)	4.0
C	3.2 (2)	2.1 (2)	3.7 (3)	−0.3 (2)	−0.7 (2)	0.0 (2)	2.8
C_{a1}	4.8 (3)	2.0 (2)	6.7 (4)	0.5 (2)	−0.6 (3)	0.7 (2)	3.9
C_{a2}	2.5 (2)	2.3 (2)	3.8 (3)	0.3 (2)	0.2 (2)	0.7 (2)	2.7
C_{a3}	4.2 (3)	3.2 (2)	3.6 (3)	0.2 (2)	−0.9 (3)	0.7 (2)	3.5
C_{a4}	2.4 (2)	3.7 (2)	2.4 (2)	−0.3 (2)	0.1 (2)	0.4 (2)	2.8
C_{a5}	4.3 (3)	5.5 (3)	3.1 (3)	−1.1 (3)	−1.5 (2)	0.0 (3)	3.9
C_{b1}	6.4 (4)	1.7 (2)	6.8 (4)	0.3 (2)	0.3 (4)	0.4 (3)	4.2
C_{b2}	2.5 (2)	2.5 (2)	3.7 (2)	0.3 (2)	0.2 (2)	1.0 (2)	2.7
C_{b3}	4.3 (3)	3.2 (3)	4.1 (3)	−0.3 (3)	−1.1 (3)	0.7 (2)	3.7
C_{b4}	1.9 (2)	4.0 (3)	2.8 (2)	−0.4 (2)	−0.2 (2)	0.6 (2)	2.7
C_{b5}	5.1 (3)	5.8 (3)	2.5 (2)	−0.6 (3)	−0.7 (2)	−0.2 (3)	4.1

^{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 and 2. ^{c} Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table III. Bond Distances, Polyhedral Edge Lengths, and Bond Angles Subtended at the Mn(III) Atom in the Coordination Group of Crystalline $Mn(O_2C_5H_7)_2(NCS)^a$

Bond Lengths

Type[b]	Length, Å	Type[b]	Length, Å
$Mn-O_{a1}$	1.910 (4) ⎫	$O_{a1}\cdots N$	2.963 (7) ⎫ 2.934 (7, 29, 29)
$Mn-O_{a2}$	1.905 (4) ⎬ 1.912 (4, 4, 7)^c	$O_{b1}\cdots N$	2.905 (6) ⎭
$Mn-O_{b1}$	1.917 (4) ⎪	$O_{a2}\cdots N$	3.049 (7) ⎫ 3.055 (7, 6, 6)
$Mn-O_{b2}$	1.914 (4) ⎭	$O_{b2}\cdots N$	3.061 (7) ⎭
$Mn-S'$	2.880 (2)	$O_{a1}\cdots S'$	3.457 (4) ⎫ 3.427 (4, 30, 30)
$Mn-N$	2.189 (5)	$O_{b1}\cdots S'$	3.397 (4) ⎭
$O_{a1}\cdots O_{a2}{}^d$	2.745 (5) ⎫ 2.745 (5, 0, 0)	$O_{a2}\cdots S'$	3.373 (4) ⎫ 3.279 (4, 94, 94)
$O_{b1}\cdots O_{b2}{}^d$	2.745 (5) ⎭	$O_{b2}\cdots S'$	3.185 (4) ⎭
$O_{a1}\cdots O_{b2}$	2.659 (5) ⎫ 2.656 (5, 4, 4)		
$O_{b1}\cdots O_{a2}$	2.652 (5) ⎭		

Bond Angles Subtended at the Mn(III) Atom

Type[b]	Angle, deg	Type[b]	Angle, deg
$O_{a1}MnO_{a2}$	92.0 (2) ⎫ 91.8 (2, 3, 3)	$O_{a2}MnN$	96.0 (2) ⎫ 96.2 (2, 1, 1)
$O_{b1}MnO_{b2}$	91.5 (2) ⎭	$O_{b2}MnN$	96.3 (2) ⎭
$O_{a1}MnO_{b2}$	88.1 (2) ⎫ 88.0 (2, 1, 1)	$O_{a1}MnS'$	90.1 (1) ⎫ 89.0 (1, 12, 12)
$O_{b1}MnO_{a2}$	87.9 (2) ⎭	$O_{b1}MnS'$	87.8 (1) ⎭
$NMnS'$	175.9 (2)	$O_{a2}MnS'$	87.2 (1) ⎫ 83.9 (1, 34, 34)
$O_{a1}MnN$	92.4 (2) ⎫ 91.1 (2, 13, 13)	$O_{b2}MnS'$	80.5 (1) ⎭
$O_{b1}MnN$	89.8 (2) ⎭		

^{a} Figures in parentheses are the estimated standard deviations of the last significant digit. ^{b} Atoms labeled in agreement with Tables I and II and Figures 1 and 2. ^{c} Average values. The first number in parentheses after 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 average value, respectively. ^{d} "Bite" of the ligand.

$\vec{c}$, respectively, of the unit cell) of the four coordinated oxygen atoms. This quasi-square of oxygen atoms is ruffled in accord with approximate S_4 symmetry; each oxygen atom is displaced by 0.084 Å from the four-atom mean plane. Oxygen atoms O_{a1} and O_{b1} are displaced toward the coordinated nitrogen atom (N) while O_{a2} and O_{b2} are displaced toward the coordinated sulfur atom (S'). The Mn atom is also displaced from this mean plane by 0.120 Å toward the coordinated nitrogen atom.

A polyhedron having an S_4-ruffled array of oxygen atoms oriented perpendicular to a linear N–Mn–S' group would ideally have O–Mn–N and O–Mn–S' bond angles and O···N and O···S' polyhedral edge lengths occurring in pairs; the members of each pair would be related by a C_2 axis collinear with the (linear) N–Mn–S' group. Averaged values for these pairs of bond angles in Mn(acac)$_2$(NCS), which has a N–Mn–S' bond angle of 175.9 (2)°,[14] are 91.1 (2, 13, 13)° [14] for $O_{a1}MnN$ and $O_{b1}MnN$, 96.2 (2, 1, 1)° for $O_{a2}MnN$ and

$O_{b2}MnN$, 89.0 (1, 12, 12)° for $O_{a1}MnS'$ and $O_{b1}MnS'$, and 83.9 (1, 34, 34)° for $O_{a2}MnS'$ and $O_{b2}MnS'$. Averaged values for the pairs of O···N and O···S' polyhedral edge lengths are as follows: 2.934 (7, 29, 29) Å for $O_{a1}\cdots N$ and $O_{b1}\cdots N$; 3.055 (7, 6, 6) Å for $O_{a2}\cdots N$ and $O_{b2}\cdots N$; 3.427 (4, 30, 30) Å for $O_{a1}\cdots S'$ and $O_{b1}\cdots S'$; 3.279 (4, 94, 94) Å for $O_{a2}\cdots S'$ and $O_{b2}\cdots S'$. While none of the O···N contacts and only one of the O···S' contacts ($O_{b2}\cdots S'$) in the coordination polyhedron are less than the respective van der Waals distances,[15] all O···O contacts are less than the 2.80-Å van der Waals diameter of oxygen.[15] The two distinct classes of O···O distances in the coordination polyhedron ("bite" at 2.745 (5, 0, 0) Å and "nonbite" at 2.656 (5, 4, 4) Å) appear to be the result of ligand constraints and are very similar to the corresponding distances observed in Mn(acac)$_2$N$_3$.[1]

Bond lengths and angles within the acetylacetonato and thiocyanato ligands are given with their estimated standard deviations in Table IV. Chemically equivalent bond lengths

Table IV. Bond Lengths and Angles for the Acetylacetonate and Thiocyanate Ligands in Crystalline $Mn(O_2C_5H_7)_2(NCS)^a$

Type[b]	Length, Å		Type[b]	Length, Å	
N–C	1.163 (7)		C_{a1}–C_{a2}	1.523 (7)	
S–C	1.624 (6)		C_{a5}–C_{a4}	1.509 (8)	1.516 (8, 4, 7)
O_{a1}–C_{a2}	1.277 (6)		C_{b1}–C_{b2}	1.518 (8)	
O_{a2}–C_{a4}	1.270 (6)	1.270 (6, 7, 14)[c]	C_{b5}–C_{b4}	1.514 (8)	
O_{b1}–C_{b2}	1.256 (6)		C_{a2}–C_{a3}	1.374 (8)	
O_{b2}–C_{b4}	1.277 (6)		C_{a4}–C_{a3}	1.392 (8)	1.386 (8, 8, 12)
			C_{b2}–C_{b3}	1.396 (8)	
			C_{b4}–C_{b3}	1.383 (8)	

Type[b]	Angle, deg		Type[b]	Angle, deg	
MnNC	164.8 (5)		$O_{a1}C_{a2}C_{a1}$	114.4 (5)	
MnS'C'	112.2 (2)		$O_{a2}C_{a4}C_{a5}$	116.0 (5)	115.2 (5, 5, 8)
NCS	177.6 (7)		$O_{b1}C_{b2}C_{b1}$	115.1 (5)	
$MnO_{a1}C_{a2}$	126.8 (3)		$O_{b2}C_{b4}C_{b5}$	115.4 (5)	
$MnO_{a2}C_{a4}$	126.8 (4)	127.2 (4, 3, 6)	$O_{a1}C_{a2}C_{a3}$	125.2 (5)	
$MnO_{b1}C_{b2}$	127.8 (4)		$O_{a2}C_{a4}C_{a3}$	125.3 (5)	125.0 (5, 3, 3)
$MnO_{b2}C_{b4}$	127.2 (4)		$O_{b1}C_{b2}C_{b3}$	124.7 (5)	
$C_{a2}C_{a3}C_{a4}$	123.2 (5)	123.5 (5, 2, 3)	$O_{b2}C_{b4}C_{b3}$	124.9 (5)	
$C_{b2}C_{b3}C_{b4}$	123.7 (5)		$C_{a1}C_{a2}C_{a3}$	120.3 (5)	
			$C_{a5}C_{a4}C_{a3}$	118.7 (5)	119.7 (5, 5, 10)
			$C_{b1}C_{b2}C_{b3}$	120.2 (5)	
			$C_{b5}C_{b4}C_{b3}$	119.7 (5)	

[a] Figures in parentheses are the estimated standard deviations of the individual measurements. [b] Atoms labeled in agreement with Tables I and II and Figures 1 and 2. [c] Average values. The first number in parentheses after 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 average value, respectively.

Table V. Comparison of Bond Lengths and Angles for Coordinated Thiocyanate Ligands[a]

$$\text{M}\overset{a}{\diagup}\underset{e}{\overset{N}{\diagdown}}\overset{b}{-}\underset{f}{\overset{C}{\diagup\diagdown}}\overset{c}{-}\underset{g}{\overset{S}{\diagup\diagdown}}\overset{d}{\diagdown}\text{M}$$

Complex	a,[b] Å	b,[b] Å	c,[b] Å	d,[b] Å	e,[b] deg	f,[b] deg	g,[b] deg	Ref
			Bridging SCN⁻ Groups					
$Mn(acac)_2(SCN)^c$	2.189 (5)	1.163 (6)	1.624 (6)	2.880 (2)	164.8 (5)	177.6 (7)	112.2 (2)	h
$[Cu(SCN)(PCH_3(C_6H_5)_2)_2]_2$	2.02 (2)	1.14 (2)	1.64 (2)	2.46 (1)	158 (2)	177 (2)	99.1 (6)	i
α-$[Pt(SCN)Cl(P(C_3H_7)_3)]_2$	2.05 (28)	1.31 (39)	1.66 (28)	2.44 (6)	147 (22)	167 (24)	100 (10)	j
$(CH_3)_2Sn(SCN)_2$	2.10 (2)	1.15 (5)	1.60 (4)	3.21 (1)	168 (3)	179 (3)	91 (1)	k
$(CH_3)_3Sn(SCN)$	2.15 (6)	1.15 (7)	1.64 (7)	3.13 (2)	173 (5)	175 (6)	97 (2)	l
$[Cu(den)(SCN)][ClO_4]_2^c$	1.95 (1)	1.16 (2)	1.62 (1)	2.76 (1)	164.9 (8)	177.7 (8)	95.1 (4)	m
$Pd_2(SCN)_2[((C_6H_5)_2PO)_2H]_2$	2.078 (7)			2.453 (2)				n
$[Cu(en)_2(SCN)][ClO_4]^c$	2.73 (1)	1.13 (2)	1.62 (2)			97.2 (5)	179.8 (8)	o
$Cu_2(SCN)_3(NH_3)_3$ { $Cu(I)^d$	2.00 (3)	1.13 (4)	1.67 (3)	2.42 (1)	165 (2)	176 (3)	97.7 (9)	p
{ $Cu(II)$	1.99 (2)	1.13 (4)	1.67 (3)	3.11 (1)	172 (2)	179 (3)		
			Nonbridging SCN⁻ Groups					
$Fe(py)_4(NCS)_2^c$	2.088 (4)	1.140 (5)	1.604 (4)		155.3 (4)	179.0 (4)		q
$[Cu(tren)(NCS)](SCN)^{c,e}$	1.959 (5)	1.142 (8)	1.612 (5)		163.3 (3)	177.4 (5)		r
$(CH_3)_2Sn(NCS)_2(terpy)^c$	2.283 (4)	1.153 (6)	1.609 (4)		177.3 (5)	177.6 (4)		s
					155.1 (4)			
$Hg(SCN)_2(P(C_6H_5)_3)_2$		1.14 (2)	1.67 (2)	2.571 (4)		177 (2)	99.2 (5)	t
$[Cu(tn)_2(SCN)][ClO_4]^c$	2.11 (1)	1.17 (3)	1.61 (3)		173.8 (7)	178 (2)		u
$Cu(den)(SCN)_2^c$	2.26 (1)	1.14 (3)	1.62 (3)		167 (2)	178 (2)		v
$Pd(dppn)(SCN)(NCS)^{c,g}$	2.063 (7)	1.14 (1)	1.611 (8)		177.6 (5)	178.6 (8)		w
		1.15 (1)	1.658 (8)	2.295 (2)		173.0 (8)	107.3 (3)	
$Pd(dpe)(SCN)(NCS)^{c,g}$	2.00 (2)			2.364 (5)				x
$Pd(dpm)(SCN)_2^c$				2.365				y
$Pd(dpp)(NCS)_2^c$	2.051							y

[a] Numbers in parentheses following each entry in the table are the estimated standard deviations of the last significant digit for that bond length or angle. [b] The parameters being compared are shown in the accompanying drawing. [c] See ref 22. [d] Structure is polymeric and consists of sheets of Cu(I) tetrahedra cross-linked by pairs of Cu(II) octahedra. [e] The complex also contains a noncomplexed thiocyanate anion having an N–C distance of 1.168 (7) Å and an S–C distance of 1.624 (5) Å, with an SCN angle of 178.6 (5)°. [f] The complex consists of two crystallographically unique SCN ligands, one occupying a position in the square-pyramidal base and the other the apical position of the pyramid having the longer Cu–N bond distance. [g] Complex contains both N- and S-bonded thiocyanate groups. [h] This work. [i] A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, 4, 640 (1970). [j] P. G. Owston and J. M. Rowe, *Acta Crystallogr.*, 13, 253 (1960). [k] Y. M. Chow, *Inorg. Chem.*, 9, 794 (1970). [l] R. A. Forder and G. M. Sheldrick, *J. Organomet. Chem.*, 21, 115 (1970). [m] M. Cannas, G. Carta, and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 556 (1974). [n] D. V. Naik, G. J. Palenik, S. Jacobson and A. J. Carty, *J. Am. Chem. Soc.*, 96, 2286 (1974). [o] M. Cannas, G. Carta, and G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 251 (1973). [p] J. Garaj, *Inorg. Chem.* 8, 304 (1969). [q] I. Sotofte and S. E. Rasmussen, *Acta Chem. Scand.*, 21, 2028 (1967). [r] P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, 89, 6131 (1967). [s] S. V. Naik and W. R. Scheidt, *Inorg. Chem.*, 12, 272 (1973). [t] R. C. Makhija, A. L. Beauchamp, and R. Rivest, *J. Chem. Soc., Dalton Trans.*, 2447 (1973). [u] M. Cannas, G. Carta, G. Marongiu, *J. Chem. Soc., Dalton Trans.*, 550 (1973). [v] Reference *u*, p 553. [w] G. R. Clark and G. J. Palenik, *Inorg. Chem.*, 9, 2754 (1970). [x] G. Beran and G. J. Palenik, *Chem. Commun.*, 1354 (1970). [y] G. J. Palenik, W. L. Steffen, M. Mathew, and D. W. Meek, *Inorg. Nucl. Chem. Lett.*, 10, 125 (1974).

Table VI. Comparison of Structural Parameters for Coordination Polyhedra of Several Tetragonally Elongated Octahedral High-Spin Mn(III) Complexes[a]

Compd	Equatorial ligands	Equatorial metal–ligand bond length, Å	Axial ligand[b]	Axial metal–ligand bond length, Å	Metal displacement from equatorial mean plane, Å[b,c]	Ref
Complexes Containing Similar Trans Axial Ligands						
γ-Mn(acac)₃[d,e]	O	1.935 (3, 4, 7)	O	2.111 (4, 2, 2)	0.009	h
Mn(trop)₃[d,e]	O	1.94 (1, 1, 2)	O	2.13 (1, 2, 2)	0.010	i
Mn(acac)₂(N₃)	O	1.910 (1, 0, 0)	N	2.245 (2)	0.000[g]	j
Mn(salen)(AcO)[e]	O	1.888 (4)	O	2.201 (5)	0.000[g]	k
	N	1.989 (5)				
Complexes Containing Dissimilar Trans Axial Ligands						
Mn(acac)₂(NCS)	O	1.912 (4, 4, 7)	N	2.189 (5)	0.120	l
			S	2.880 (2)		
Mn(TPP)(NCS)(py)·2C₆H₆[e]	N	1.998 (4, 6, 11)	Nₜ[f]	2.193 (5)	0.080	m
			Nₚ[f]	2.442 (4)		
Mn(TPP)(N₃)(CH₃OH)·CH₃OH[e]	N	2.018 (5, 3, 7)	N	2.187 (7)	0.083	n
			O	2.302 (5)		
Mn(acetpn)(N₃)·(CH₃OH)[e]	O	1.850 (4, 8, 8)	N	2.114 (7)	0.135	o
	N	1.972 (5, 9, 9)	O	2.390 (5)		
Mn(TPP)(Cl)(py)[e]	N	2.009 (4, 6, 13)	Cl	2.467 (1)	0.120	p
			N	2.444 (4)		

[a] The first number in parentheses following each entry for an averaged bond length in the table is the rms value of the estimated standard deviation of a single value. The second and third numbers, when given, represent the mean and maximum deviations from the averaged value, respectively. [b] For complexes containing dissimilar trans axial ligands, the manganese atom is displaced from the equatorial mean plane toward the axial ligand listed first. [c] Each of these least-squares mean planes were calculated for the four "equatorially" coordinated atoms. [d] The crystal contains two crystallographically independent Mn(O₂C₇H₅)₃ molecules. Values in the table are for the molecule having a tetragonally elongated coordination polyhedron; the coordination polyhedron of the second molecule exhibits an orthorhombic distortion. [e] See ref 22 for ligand names. [f] Nₜ and Nₚ are the nitrogen atoms of the thiocyanato and pyridine ligands, respectively. [g] These displacements are required crystallographically to be 0.000 Å. [h] See ref 2 and 20. [i] A. Avdeef, J. A. Costamagna, and J. P. Fackler, Jr., *Inorg. Chem.*, 13, 1854 (1974). [j] See ref 1 and 2. [k] J. E. Davies, B. M. Gatehouse, and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2523 (1973). [l] This work. [m] See ref 24. [n] See ref 2 and 23. [o] R. F. Stewart, private communication. [p] J. F. Kirner and W. R. Scheidt, *Inorg. Chem.*, 14, 2081 (1975).
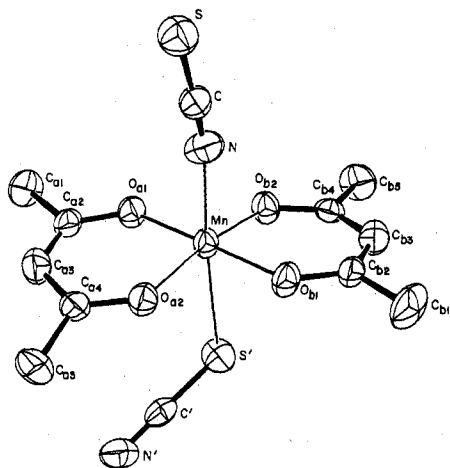

Figure 1. Model in perspective of one octahedral Mn(III) subunit of the infinite chains generated along the *ā* axis of the unit cell by the bridging thiocyanato ligands in Mn(O₂C₅H₇)₂(NCS). The drawing contains one formula unit plus an additional coordinated thiocyanato ligand. All atoms are represented by 50% probability ellipsoids which reflect the refined anisotropic thermal parameters given in Table II.

Figure 2. ORTEP drawing showing a segment of one infinite chain along the *ā* axis which illustrates the linking together of Mn(acac)₂⁺ groups by bridging thiocyanato ligands in Mn(acac)₂(NCS). Atoms shown with double primes (″) are from a symmetry-related thiocyanato ligand which completes the octahedral coordination sphere of Mn′.

and angles within the acac ligands differ by less than 2.5 standard deviations. The averaged values given in Table IV for the chemically distinct acac bond lengths and angles are in good agreement with corresponding values obtained in other accurate structural studies of compounds containing non-bridging bidentate acetylacetonato ligands.[16–18]

Although the atoms comprising both five-atom (O₁, O₂, C₂, C₃, and C₄) chelate rings are individually coplanar to within 0.05 Å, the methyl carbon atoms of each acac ligand have an average displacement of 0.10 Å from their respective five-atom least-squares mean planes (the maximum methyl carbon displacement is 0.25 Å for C₍ₐ₅₎). The manganese atom is displaced by 0.06 Å from each of these five-atom mean planes
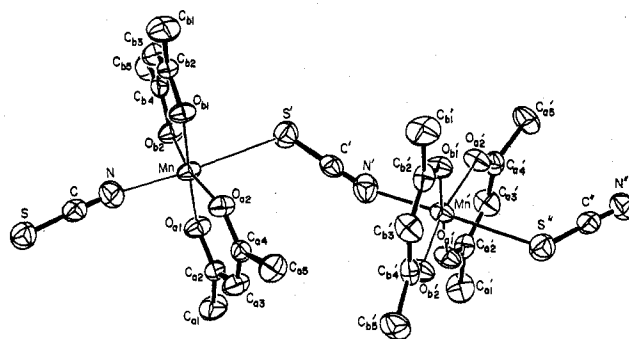
toward the coordinated nitrogen atom, thereby producing angles of fold along the O₁···O₂ polyhedral edges of 2.66 and 2.39° for ligands a and b, respectively.

Table V gives a comparison of the bonding parameters involving the coordinated thiocyanato ligand in Mn(acac)₂-(NCS) with those determined for coordinated thiocyanato ligands in several other compounds. The Mn–N–C bond angle of 164.8 (5)° falls within the range of 147–179° for similar entries of molecular complexes in Table V while the Mn–S′–C′ angle of 112.2 (2)° is the most obtuse of those listed.

A comparison of certain structural parameters that partially characterize the tetragonally elongated octahedral coordination polyhedra of several high-spin Mn(III) complexes is given in Table VI. With the exception of the four "equatorial" Mn–O bonds with an average length of 1.910 (1, 1, 1) Å in **1**,[1,2,6] the Mn–O bonds in Mn(acac)₂(NCS) with an average length of 1.912 (4, 4, 7) Å are shorter by ~0.023 Å than those observed for "short" Mn–O bonds in other tetragonally distorted acac

complexes of Mn(III). Values of 1.943 (9, 13, 13), 1.935 (3, 4, 7), and 1.959 (5) Å have been determined for such bonds in β-Mn(acac)$_3$,[19] γ-Mn(acac)$_3$,[20] and Mn(acac)(pati)$_2$,[21,22] respectively. Preference of the metal for the acetylacetonate ligands, with their "normal" distribution of negative charge and π-bonding capabilities, over the bridging anionic X ligands which must share their net charge (however unequally) with two metals is probably responsible for the shortening of the four equatorial Mn–O bonds in **1** and **2** relative to the equatorial Mn–O bonds in other tetragonally elongated acetylacetonato complexes of manganese(III). The presence of a relatively strong bonding interaction between the metal and the acac ligands is also indicated by the short "nonbite" O···O polyhedral edges in these two compounds.

The Mn–N bond length of 2.189 (5) Å in **2** is ~0.19 Å longer than the "normal" Mn–N bonds observed in other compounds and comparable to the "Jahn–Teller elongated" Mn–N bonds involving anionic ligands in Mn(acac)$_2$(N$_3$),[1,2,6] Mn(acac)(pati)$_2$,[21,22] Mn(TPP)(N$_3$)(CH$_3$OH)·CH$_3$OH,[2,22,23] and Mn(TPP)(NCS)(py)·2C$_6$H$_6$.[22,24] As one might anticipate, the differences between the Mn–N bond length in **2** and those bond lengths which involve monodentate anionic ligands in Mn(TPP)(N$_3$)(CH$_3$OH)·CH$_3$OH[2,22,23] and Mn(TPP)-(NCS)(py)·2C$_6$H$_6$[22,24] are insignificant (~0.006 Å). The small but statistically significant 0.056-Å elongation of the Mn–N bond in **1** relative to **2** is also expected, since the azide ligand in **1** symmetrically bridges and shares its single negative charge equally with two octahedral Mn(III) polyhedra.

Although a formal bonding interaction almost certainly exists between the Mn and S' atoms in **2**, the data in Table VI indicate that it is somewhat weaker than the axial Mn–ligand bonds observed in other compounds. Even after the 0.29-Å difference in covalent radii for sulfur and oxygen[25] has been taken into account, the Mn–S' bond in **2** is ~0.26 Å longer than the axial Mn–O(methanol) bond in Mn(TP-P)(N$_3$)(CH$_3$OH)·CH$_3$OH.[2,22,23] Unfavorable ligand–ligand contacts can hardly be responsible for this additional bond elongation since three of the four O···S polyhedral contacts in **2** are greater than the 3.25-Å sum of van der Waals radii for sulfur and oxygen.[15] The Mn–S' bond length of 2.880 (2) Å in **2** is also 0.479 Å longer than the average value of 2.401 (8, 21, 28) Å observed for the four "short" and 0.331 Å longer than the average value of 2.549 (7, 8, 8) Å for the two "long" Mn–S bonds in the tetragonally elongated octahedral coordination polyhedron of tris(N,N'-diethyldithiocarbamato)-manganese(III).[26]

The data presented in Table VI illustrate several interesting features of Mn(III) coordination chemistry and serve as a basis for the following predictions concerning the coordination geometries of tetragonally elongated octahedral complexes of high-spin Mn(III). For complexes in which all six coordinated atoms have identical donor ability and charge, a D_{4h} tetragonally elongated octahedral coordination polyhedron with the Mn atom in the plane of the four "equatorial" atoms will result. If the coordinated atoms have sufficiently different donor abilities and/or charges, those ligands which are capable of forming the strongest metal–ligand bonds will generally be preferred for "equatorial" coordination sites and the Mn atom will be in the plane of the four equatorial atoms only if the two trans axial atoms have identical donor abilities and charges. In complexes with dissimilar axial ligands, the metal atom will be displaced (by ~0.10 Å) from the equatorial plane toward the ligand which is capable of forming the stronger metal–ligand bond. As we have previously noted,[23] the complete removal of one of the trans axial ligands from the octahedral coordination polyhedron to give a five-coordinate

square-pyramidal Mn(III) species will result in an additional displacement (0.15–0.25 Å) of the metal atom from the quasi-square of "equatorial" atoms toward the remaining axial ligand. Although the stereochemical requirements of the ligands comprising the quasi-square have a significant effect (~0.10 Å) on the magnitude of the Mn(III) atom displacement from the "equatorial (basal)" plane in these five-coordinate species,[23] any similar effects in tetragonally elongated octahedral complexes appear to be minor.

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