A STRUCTURAL STUDY OF SOME COMPLEXES CONTAINING THE SCANDIUM(III) ION: SIX AND EIGHT COORDINATION

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ABSTRACT

A STRUCTURAL STUDY OF SOME COMPLEXES CONTAINING THE SCANDIUM(III) ION: SIX AND EIGHT COORDINATION

BY

Thomas John Anderson

The crystal and molecular structures of some complexes containing the scandium(III) ion and uninegative bidentate oxygen donor ligands have been determined.

Precession camera techniques have been used to determine space group information and lattice parameters and three-dimensional single-crystal intensity data have been collected by use of a four-circle, computer controlled diffractometer.

The crystal and molecular structure of tris(acetylacetonato)-scandium(III), $Sc(C_5H_7O_2)_3$, has been determined. The crystal structure belongs to the orthorhombic space group Pbca, with $\underline{a}$ = 15.38(3), $\underline{b}$ = 13.73(3) and $\underline{c}$ = 16.72(4)Å, with $\underline{Z}$ = 8. The structure has been solved by Patterson and Fourier techniques with 1088 reflections refined by full-matrix least-squares to a final reliability factor, based on F, of 0.059. The structure consists of discrete $Sc(C_5H_7O_2)_3$ molecules with the six oxygen atoms forming a distorted octahedron about the scandium(III) ion.

The compound tris(tropolonato)scandium(III), $Sc(C_7H_5O_2)_3$, crystallizes in the trigonal space group $R\bar{3}c$, with $\underline{a}$ = 10.455(2) and $\underline{c}$ = 32.595(1) in the hexagonal setting, with $\underline{Z}$ = 6. The structure was solved by Patterson and Fourier techniques and 783 reflections were refined to a final reliability factor, based on F, of 0.033.

The structure consists of discrete $Sc(C_7H_5O_2)_3$ molecules with crystallographically imposed D_3 symmetry. The coordination environment about the scandium(III) ion is intermediate between octahedral stereochemistry and trigonal prismatic stereochemistry.

The crystal and molecular structure of hydrogentetrakis(tropolonato)-scandium(III), $HSc(C_7H_5O_2)_4$, has been determined. The crystal structure belongs to the triclinic space group $P\bar{1}$, with $\underline{a}$ = 10.022(4), $\underline{b}$ = 11.515(3), $\underline{c}$ = 12.004(4)Å, α = 72.74(1), β = 84.58(1) and γ = 65.04°, with $\underline{Z}$ = 2. The molecular structure has been solved by a combination of Patterson, direct method and Fourier techniques with 2539 reflections refined to a final reliability factor, based on F, of 0.027. The structure consists of a hydrogen bonded dimer, with halves of the dimer joined across the center of inversion. The hydrogen bond is nearly linear with the O-H...O angles being 175.9°. The O-H bond length is 1.00Å, while the O...H separation is 1.49Å. Each scandium(III) ion is eight-coordinate. The stereochemistry of the scandium is intermediate between a D_{2d} dodecahedron and a C_{2v} bicapped trigonal prism.

Factors controlling the stereochemistry for six- and eight-coordinate complexes of scandium(III) are discussed.

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Preface

This thesis has been divided into four main divisions: 1)the introduction, describing the chemistry of scandium, chemical similarities to the lanthanides, and reasons for the investigation itself; 2)chapters discussing the crystal and molecular structures of tris(acetylacetonato)-scandium(III) and tris(tropolonato)scandium(III), and a chapter discussing factors controlling six-coordination and the relationships of these two structures to those factors; 3)a chapter presenting the crystal and molecular structure of hydrogentetrakis(tropolonato)-scandium(III) and eight-coordination; finally, 4)other work partially completed or work that has been attempted but was not successful.

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CHAPTER 1

INTRODUCTION

History

The discovery of scandium (Sc) in 1879 by Nilson (1) and the subsequent determination of its elemental properties established it as the first member of the 3d transition series. The discovery also helped substantiate Mendelev's Periodic Law (2) by verifying the existence of an element he had predicted, viz., "eka-boron". The chemical properties of eka-boron were predicted to be intermediate between those of aluminun and yttrium in the boron group.

The early chemical investigations of scandium dealt principally with the purification of the metal from its mineral sources, development of analytical techniques and the preparation of binary compounds (3). During the period 1879 until after World War II, only scattered reports of investigations of coordination compounds of scandium have appeared.

The Chemistry of Scandium and Its Relationship to Yttrium and the Lanthanides

The free scandium atom has an electronic configuration $[Ar]3d^1 4s^2$. Because of the similarity of their electronic configurations, the chemistry of scandium is often discussed along with that of yttrium and the lanthanides. Moeller, et al. (5), have discussed these similarities. The most common oxidation state of all these elements is +3, each with a noble gas configuration resulting in unfilled outer d orbitals. For the lanthanides, the +3 oxidation state arises because electrons occupying the 4f orbitals are screened from the environment by overlying 5s and 5p shells, thereby rendering the 4f electrons relatively inert to the chemical surroundings.

The electronegativities and other properties of these elements are listed in Table 1. The tervalent ions, in particular, exhibit the greatest affinity for ligands containing electronegative donor atoms, especially oxygen. Complexes containing chelating oxygen donor ligands may be isolated as anhydrous products of reactions that have taken place in aqueous solutions. Examples of these are β-diketonates, carboxylates and tropolonates. Complexes with neutral, unidentate oxygen donor ligands are thermodynamically unstable relative to the hydrated species. In these cases, insoluble adducts may be obtained from solutions of the hydrated metal(III) salts in organic solvents, since a reduction of water concentration would reduce the concentration of $[M(H_2O)_n]^{+3}$ species. Hydration is an ever present problem when working with any of the tervalent salts of scandium (especially the halides). The preparation of all but the anhydrous fluoride must be completed under anhydrous conditions. A method for these preparations was reported by Stotz and Melson (7).

The degree of electrostatic contribution to the metal-ligand bond increases with decreasing electronegativity of the cation in the order $La^{+3}<Y^{+3}<Sc^{+3}$ (Table 1). This behavior affects both the thermodynamic stability and the coordination number of the complexes containing the same ligand species. A comparison of the first formation

Table 1. Selected Parameters of Scandium, Yttrium and the Lanthanides[a]

	Sc	Y	La	Lu
Electronic Configuration of M^{+3}	[Ar]	[Kr]	[Xe]	$[Xe]4f^{14}$
Oxidation Potential (V) $M = M^{+3}(aq) + 3e^-$	-1.88	-2.37	-2.52	-2.25
Electronegativity (Allred-Rochow)	1.20	1.11	1.08	1.14
Pauling Radius (Å)	0.81	0.93	1.15	0.85
Effective Ionic Radius[b] (Å) (Coordination Number, CN, = 6)	0.73	0.89	1.06	0.85
Effective Ionic Radius[b] (Å) (CN = 8)	0.87	1.02	1.18	0.97

[a]See Reference 6.

[b]Based upon structural results of M-O distances; R.D. Shannon and C.T. Prewitt, Acta Crystallogr., Sect. B, 25, 925(1969).

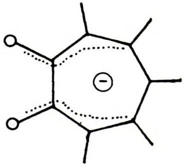
constants (K_1) for the acetylacetonates of Sc(III), Y(III) and La(III) shows a regular decrease from scandium to lanthanum (8). Scandium and yttrium form tris-chelated species with β-diketonates, while the lanthanides rarely form six-coordinate species. Usually they incorporate solvent or form tetrakis-species (9, 10). Species of the form $M[Z(hfac)_4]$, $M = K^+$, Rb^+, Cs^+; Z = Sc(III), a lanthanide(III), or $Z(tfac)_3.L$, L = bipy or phen, have been reported (8, 9, 11-13). Muetterties and Wright (14) have isolated tristropolonates for scandium, yttrium and the lanthanides, but the nature of the complexes is believed that the scandium and yttrium species are different from those of the lanthanides. The lanthanides presumably have coordination numbers greater than six by formation of a polymeric network in the solid state (14). Scandium, yttrium and the lanthanides also form a complex with the general formula, $HM(trop)_4$. These are isomorphous from X-ray powder intensity data (14), thus suggesting that $HSc(trop)_4$ exists with the scandium ion in an eight-coordinate environment as is expected for the analogous lanthanide complexes.

Complexes of Scandium

Horovitz, *et al*. (15), have reviewed the chemistry of scandium up to 1973. Melson and Stotz (16) have reviewed the coordination chemistry up to 1970.

One of the most widely studied classes of uninegative bidentate oxygen donor ligands is that of the β-diketonates. Scandium(III) forms complexes with various substituted β-diketonates (16). Like other tervalent 3d transition metal acetylacetonates, $Sc(acac)_3$, is thermally stable and sublimable. Some β-diketonates of scandium have been isolated with associated solvent molecules. Except for hexafluoroacetylacetone, all other β-diketonates form only 3:1 complexes. Several alkali metal ions have been used to isolate complexes containing the tetrakis(hexafluoroacetylacetonato)-scandate(III) ion (11). This anion is expected to contain an eight-coordinate scandium(III) ion due to the electron withdrawing power of the per-fluorinated methyl groups, lessening the negative charge on the oxygen atoms; this reduced negative charge would enable more bidentate ligands to coordinate to the central metal ion.

Another class of uninegative bidentate oxygen donor ligands is the tropolonates, the unsubstituted species being the tropolonate anion, $C_7H_5O_2^-$. The tris(tropolonate) of scandium(III) results from the dissociation of the "acid", $HSc(trop)_4$ (14). From X-ray powder data it is shown that the tetrakis-complex, $Na[Sc(trop)_4]$, is isomorphous with the lanthanide analogs, which are known to form eight-coordinate species. Eight-coordination, again, seems reasonable for the scandium(III) ion, since the tropolonate anion is capable of reducing negative charge on the oxygen atoms as in the hexafluoro-acetylacetonate ion, by delocalizing the charge into the ring, viz.:



Structural Studies of Scandium Complexes

Single crystal X-ray structural determinations of scandium compounds have been reported, however, only one structure has involved scandium in an environment of a non-ionic nature. Studies of ionic compounds of Sc^{+3} indicate the lattices are typical ionic arrays with the scandium having either a coordination number of six as found in the salts with F^- (17), Cl^- (18), OH^- (19), and the oxide, Sc_2O_3 (20) or a coordination number of eight as found in $Na_5[Sc(CO_3)_4].2H_2O$ (21), $ScPO_4$ (22), $ScVO_4$ (23), $Sc_2(C_2O_4)_3.6H_2O$ (24) and $ScAsO_4$ (25).

Scandium formate, $Sc(CHO_2)_3$, crystallizes in the monoclinic space group, $P2_1/c$, with $\underline{a}$ = 10.316, $\underline{b}$ = 6.222 and $\underline{c}$ = 8.904Å, and β = 94° (26). The structure consists of six-coordinate scandium ions with bridging formate ligands in a polymeric network (Figure 1). The formate ions in the plane are bonded in the *syn-anti* configuration and those joining the planar layers are bonded in the *anti-anti* configuration. This layering and polymeric framework is a common feature of transition metal formates. The average Sc-O bond distances are 2.03Å and 2.09Å for the two types of bridging formate bonds. The high final reliability factor (R = 0.20) was attributed to decomposition upon exposure to X-rays.

Outline of Investigation

At the time this investigation was initiated, only one structure of a covalently bonded scandium ion had been reported, *viz*., $Sc(CHO_2)_3$. By modern standards, the quality of the refinement is poor (a good refinement has a reliability factor less than 0.10). The poor

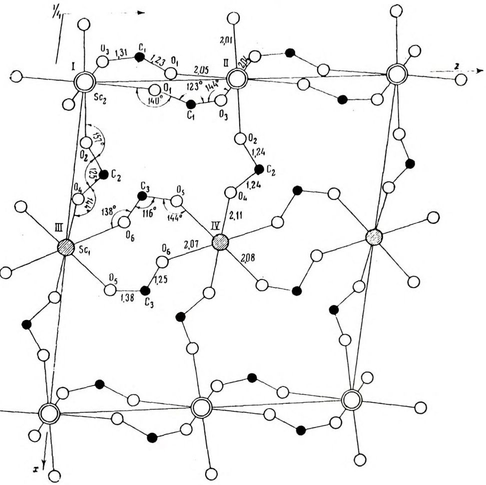


Figure 1. Structure of scandium formate, $Sc(CHO_2)_3$, projected on (010).

refinement of this structure leaves a great deal of uncertainty about atomic positions. The overall stereochemistry should not be altered, but bond distances could be in error by 0.1Å. A series of complexes containing scandium(III) and uninegative bidentate oxygen donor ligands has been studied to assess critically factors controlling stereochemistry in a d^0 system and the types of coordination involved in the complexes studied. The ligands that have been chosen are the anions of acetylacetone ($acac^-$) and tropolone ($trop^-$). Both of these ligands have been used in previous structural studies. This will provide information to aid in discussions of the results when using scandium as the central metal ion.

CHAPTER 2

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(ACETYLACETONATO)SCANDIUM(III)

Introduction

The first compound chosen for this investigation was tris(acetylacetonato)scandium(III). Two factors influenced this decision: 1) the relative stability of this compound toward exposure to X-rays and 2) the extensive data available for the tervalent *3d* transition element acetylacetonates (27, 29). Thus, comparisons with these previously determined structures would enable one to assess the quality of the structure relative to the other acetylacetonates.

Experimental Section

Scandium(III)oxide, Sc_2O_3(99.9%), was purchased from Research Organic/Inorganic Corporation. Tris(acetylacetonato)scandium(III) was prepared according to the procedure of Morgan and Moss (29). Suitable crystals were obtained by slow evaporation from benzene.

Determination of Space Group and Measurement of Intensity Data

Preliminary determination of the crystallographic space group was conducted by using precession film techniques with MoKα radiation. *mmm* orthorhombic Laue symmetry was observed. Systematic absences of $k = 2n + 1$ for $0k\ell$, $\ell = 2n + 1$ for $h0\ell$, and $h = 2n + 1$ for $hk0$ establish the space group uniquely as Pbca in agreement with the previous assignment of Ivanov and Petrukin (30). This structure is then isomorphous with $Fe(acac)_3$ (31, 32). Complete three dimensional single-crystal X-ray diffraction data were obtained by use of a Picker four-circle automatic diffractometer controlled by a PDP-8/I computer. A graphite monochromator, with the (002) plane in diffracting position was used to obtain monochromatic MoKα radiation. A takeoff angle of 3° was used. The radiation was detected by using a scintillation counter with pulse height discrimination. The crystal was mounted with the b axis coincident with the Φ axis of the diffractometer. The lattice parameters were determined at room temperature (22±2°) from 12 hand-centered reflections (Table 2). Intensities were measured by an ω-scan technique with ω being scanned over a width of 0.8° at a rate of 1°/min. Data were measured to a maximum $2\Theta = 45°$. Attenuators were automatically inserted if the count rate exceeded 10,000 counts/sec. Backgrounds were estimated by two 4 second counts made one at each end of the scan using stationary-crystal,stationary-counter measurements. Three monitor reflections were measured every 100 reflections. The average deviation from the mean intensity for each monitor was ±1%, thus suggesting no motion nor decomposition of the crystal. A total of 2676 independent reflections were scanned with 1088 being considered to be above background by using the criterion $I/\sigma(I) > 2.5$. The data were corrected for the Lorentz and polarization phenomena, but no correction for absorption was applied ($\mu = 4.40 cm^{-1}$).

Solution and Refinement of the Structure

Scattering factors for the neutral atoms, Sc, O, and C were taken

Table 2. Crystal Data

Molecular Formula	$Sc(C_5H_7O_2)_3$
Molecular Weight	342.29
Crystal Habit	Plate
Crystal Size, mm	0.3 X 0.6 X 0.08
Crystal Color	Clear
μ, cm^{-1}	4.40
Space Group	Pbca, Orthorhombic
Systematic Absences	$hk0$, $h = 2n + 1$
	$h0\ell$, $\ell = 2n + 1$
	$0k\ell$, $k = 2n + 1$
a, Å	15.38(3)
b, Å	13.73(3)
c, Å	16.72(4)
Z	8
U, Å^3	3531
D_{exp}, g/ml[a]	1.26
D_{calc}, g/ml	1.29

[a]Measured by flotation in carbon disulfide.

from Cromer and Waber (33) and those for Hydrogen from Stewart, et al. (34).

The positional coordinates of the scandium and six oxygen atoms were obtained from a three-dimensional point-atom sharpened Patterson map. Structure factors calculated on the basis of these coordinates and isotropic thermal parameters of $3.5\mathring{A}^2$ were used to generate a three-dimensional heavy atom Fourier map which yielded the positions of the carbon atoms. The positional and isotropic thermal parameters associated with all nonhydrogen atoms were refined by using full-matrix least-squares on all parameters for four cycles. A difference Fourier map was calculated at this time and it yielded positions of all methyl hydrogens. The γ- carbon hydrogens were then positioned by assuming a unit vector beyond the vector from the scandium to the γ-carbon. Isotropic thermal parameters of $8.0\mathring{A}^2$ were assigned to the hydrogen atoms, based upon the thermal parameters of the methyl carbons. The coordinates of all atoms and anisotropic thermal parameters of non-hydrogen atoms were refined to convergence. The final agreement factor, R_1, was 0.05($R_1 = \Sigma||F_O-F_C||/\Sigma|F_O|$) while the weighted agreement factor, R_w, was 0.067($R_w = [\Sigma w(F_O-F_C)^2/\Sigma(F_O)^2]^{1/2}$ where $w = 1/\sigma^2(F)$. $\sigma(F) = 0.05F$ for $F > 4F_{min}$ and $(F) = 0.20F_{min}$ for $F<4F_{min}$, $F_{min} = 9.46$. (This is a modified Hughes' weighting scheme (35).)

The final atomic coordinates of all non-hydrogen atoms and the anisotropic thermal parameters with their associated estimated standard deviations, e.s.d.'s, are listed in Table 3. The final hydrogen atom positions are listed in Table 4 along with their e.s.d.'s. The largest parameter shift in the final cycle of refinement was not larger than 0.2 of its associated e.s.d. A difference Fourier map of the final structure

Table 3a. Final Atomic Coordinates

Atoms[a]	x/a	y/b	z/c
Sc	0.1434(1)	0.2687(1)	0.2418(1)
O1(1)	0.0704(4)	0.3526(4)	0.3189(3)
O2(1)	0.0386(3)	0.1749(4)	0.2539(4)
O1(2)	0.0966(4)	0.3367(4)	0.1394(3)
O2(2)	0.1979(4)	0.1760(4)	0.1569(5)
O1(3)	0.2441(4)	0.3671(4)	0.2524(4)
O2(3)	0.2125(4)	0.1968(4)	0.3293(3)
C1(1)	-0.0313(8)	0.4222(9)	0.4052(7)
C2(1)	-0.0015(7)	0.3396(7)	0.3519(5)
C3(1)	-0.0531(6)	0.2589(8)	0.3417(6)
C4(1)	-0.0304(6)	0.1796(6)	0.2944(6)
C5(1)	-0.0906(6)	0.0937(8)	0.2875(6)
C1(2)	0.0535(8)	0.3832(9)	0.0107(6)
C2(2)	0.0998(6)	0.3137(7)	0.0666(5)
C3(2)	0.1424(7)	0.2339(8)	0.0363(5)
C4(2)	0.1887(6)	0.1690(6)	0.0826(6)
C5(2)	0.2368(8)	0.0864(9)	0.0425(6)
C1(3)	0.3630(7)	0.4610(7)	0.2932(7)
C2(3)	0.3088(6)	0.3716(6)	0.2964(6)
C3(3)	0.3330(6)	0.2977(8)	0.3486(6)
C4(3)	0.2851(7)	0.2139(7)	0.3607(5)
C5(3)	0.3195(7)	0.1378(10)	0.4176(7)

[a]The numbers in parentheses refer to the ring number.

Table 3b. Final Anisotropic Thermal Parameters[b]

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc	0.00419(6)	0.00474(7)	0.00279(5)	0.00071(8)	0.00004(7)	0.00001(7)
O1(1)	0.0057(3)	0.0061(4)	0.0038(2)	0.0002(3)	0.0014(3)	-0.0012(3)
O2(1)	0.0040(3)	0.0057(4)	0.0057(3)	0.0002(3)	0.0003(3)	-0.0013(3)
O1(2)	0.0063(3)	0.0065(4)	0.0034(3)	0.0018(3)	-0.0009(2)	0.0000(3)
O2(2)	0.0066(4)	0.0052(4)	0.0037(3)	0.0012(3)	0.0003(2)	-0.0005(3)
O1(3)	0.0051(3)	0.0052(3)	0.0056(3)	-0.0001(3)	-0.0001(4)	0.0006(3)
O2(3)	0.0052(4)	0.0056(4)	0.0045(3)	-0.0004(3)	-0.0006(3)	0.0011(3)
C1(1)	0.0115(9)	0.0123(10)	0.0059(5)	0.0039(8)	0.0034(6)	-0.0004(6)
C2(1)	0.0066(6)	0.0078(8)	0.0036(4)	0.0016(6)	0.0013(4)	0.0006(4)
C3(1)	0.0053(5)	0.0079(7)	0.0062(5)	0.0008(6)	0.0024(4)	0.0015(5)
C4(1)	0.0055(5)	0.0045(6)	0.0066(5)	0.0008(5)	-0.0003(4)	0.0019(4)
C5(1)	0.0051(5)	0.0085(7)	0.0084(6)	0.0007(5)	0.0009(5)	0.0003(5)
C1(2)	0.0115(9)	0.0143(10)	0.0051(5)	0.0009(9)	-0.0015(6)	0.0027(6)
C2(2)	0.0070(6)	0.0079(6)	0.0031(4)	-0.0012(6)	-0.0012(4)	0.0006(4)
C3(2)	0.0085(6)	0.0104(8)	0.0033(3)	0.0017(7)	0.0000(4)	-0.0018(5)
C4(2)	0.0055(5)	0.0061(7)	0.0044(4)	-0.0008(5)	-0.0008(4)	-0.0012(4)

Table 3b. (Continued)

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C5(2)	0.0101(8)	0.0101(9)	0.0070(5)	-0.0007(7)	0.0021(6)	-0.0037(6)
C1(3)	0.0090(7)	0.0088(7)	0.0084(6)	-0.0036(7)	0.0002(6)	-0.0017(5)
C2(3)	0.0061(5)	0.0053(6)	0.0050(4)	-0.0004(5)	0.0004(4)	-0.0012(4)
C3(3)	0.0056(6)	0.0093(8)	0.0056(5)	-0.0009(5)	-0.0019(4)	0.0002(5)
C4(3)	0.0064(6)	0.0084(8)	0.0044(4)	0.0020(6)	-0.0007(4)	0.0013(5)
C5(3)	0.0083(7)	0.0166(12)	0.0080(6)	0.0005(8)	-0.0026(6)	0.0059(8)

[b]The anisotropic thermal parameters are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$.

Table 4. Hydrogen Atom Positions (B = 8.0 $\mathring{A}^2$)[a]

Atom[b]	x/a	y/a	z/a
H1(1)	-0.092	0.422	0.406
H2(1)	-0.007	0.400	0.449
H3(1)	-0.033	0.487	0.375
H4(1)	-0.107	0.251	0.368
H5(1)	-0.073	0.053	0.330
H6(1)	-0.079	0.064	0.234
H7(1)	-0.152	0.109	0.308
H1(2)	0.094	0.427	0.004
H2(2)	0.006	0.398	0.030
H3(2)	0.070	0.379	-0.036
H4(2)	0.147	0.216	-0.019
H5(2)	0.213	0.061	-0.009
H6(2)	0.285	0.095	0.393
H7(2)	0.215	0.034	0.064
H1(3)	0.426	0.448	0.285
H2(3)	0.373	0.483	0.347
H3(3)	0.359	0.486	0.253

Table 4. (Continued)

Atom[b]	x/a	y/a	z/a
H4(3)	0.400	0.303	0.373
H5(3)	0.281	0.134	0.465
H6(3)	0.374	0.152	0.434
H7(3)	0.292	0.091	0.405

[a]No attempt was made to idealize methyl hydrogens. Estimated deviation ± 0.006 for all values.

[b]The atoms are labelled as: 1-3 attached to C1; 4 to C3; 5-7 to C5. The numbers in parentheses correspond to the ring number.

showed no peaks larger than $0.35e^-/\AA^3$. The final calculated and observed structure factor amplitudes are listed in Table 5.

Description of the Structure

In $Sc(acac)_3$, the b axis is nearly parallel with the pseudo-C_3 axis of the molecule. A view down the pseudo-C_3 axis is shown in Figure 2. This illustrates the numbering scheme, bond lengths and 20% probability envelopes for all non-hydrogen atoms of one molecule. Stereoscopic views of the molecule and the molecular contents of the unit cell (also down the b axis) are shown in Figures 3 and 4, respectively. Intramolecular distances and angles together with their estimated standard deviations are listed in Table 6.

The structure consists of discrete $Sc(acac)_3$ molecules within the unit cell. The molecules have distorted D_3 symmetry with the chelate rings showing only small deviations from planarity (Table 7). The non-planarity may be due to intermolecular forces which cause rotations about the O1...O2 vector (folding) and rotations about the Sc...γ-carbon (C_3) of the ring. Thus, the former effect can account for the Sc atom being out of the plane for ring 2. A deviation of 0.15Å of the metal ion from the plane corresponds to a rotation of approximately 5° about the O...O vector. The latter effect may explain why C_1 and C_5 atoms are markedly out of the plane of ring 3. These effects may also explain similar deviations found in other acac complexes (36-39).

In comparison with close packed organic structures, the intermolecular contacts observed are generally long. The shortest H...H contact is 2.49Å, while for C...H approaches the shortest is 2.95Å. For O...H approaches, one value at 2.56Å is found while all others are close

Table 5. Final Calculated and Observed Structure Factor Amplitudes

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

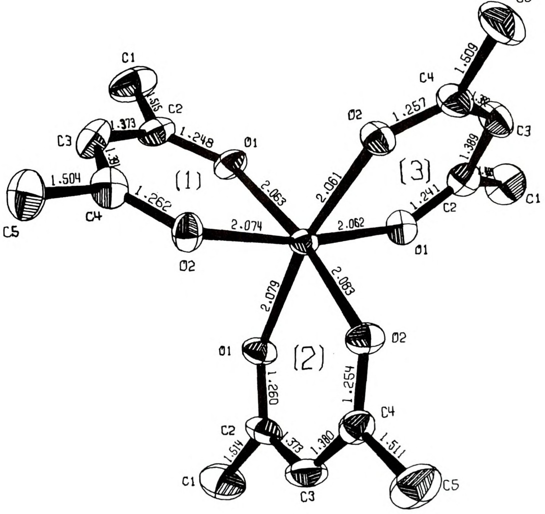


Figure 2. View of $Sc(acac)_3$ showing numbering scheme, adopted bond lengths, and the 20% probability envelopes of the anisotropic thermal ellipsoids.

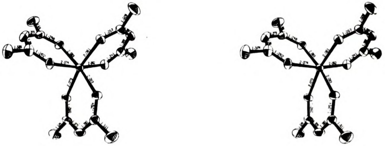


Figure 3. Stereoscopic view of $Sc(acac)_3$ down the C_3 axis of the molecule, 20% probability envelopes, hydrogens omitted for clarity.

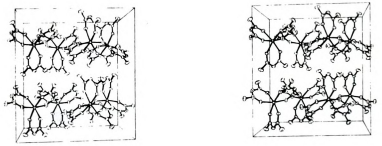


Figure 4. Stereoscopic view of the Unit Cell of $Sc(acac)_3$ down the b axis, hydrogens omitted for clarity.

Table 6. Intramolecular Interatomic Distances (Å) and Angles (deg)[a]

Distances

Sc–O		O–O "bite"	
Sc–O1(1)	2.062(6)	O1(1)–O2(1)	2.717(7)
Sc–O2(1)	2.073(5)	O1(2)–O2(2)	2.716(8)
Sc–O1(2)	2.079(6)	O1(3)–O2(3)	2.713(8)
Sc–O2(2)	2.082(6)	Average	2.715(5)[b]
Sc–O1(3)	2.062(7)	**Polyhedron Edges**	
Sc–O2(3)	2.061(6)	O1(1)–O1(2)	3.037(10)
Average	2.070(9)[b]	O1(1)–O1(3)	2.900(9)
O–C		O1(2)–O1(3)	2.981(9)
O1(1)–C2(1)	1.248(10)	O2(1)–O2(2)	2.938(9)
O2(1)–C4(1)	1.261(10)	O2(1)–O2(3)	2.972(9)
O1(2)–C2(2)	1.259(10)	O2(2)–O2(3)	2.907(10)
O2(2)–C4(2)	1.254(10)	O1(1)–O2(3)	3.063(9)
O1(3)–C2(3)	1.240(10)	O1(2)–O2(1)	3.065(9)
O2(3)–C4(3)	1.257(11)	O1(3)–O2(2)	3.152(9)
Average	1.253(11)[b]		
C–C (Methyl)		**C–C (Ring)**	
C1(1)–C2(1)	1.514(14)	C2(1)–C3(1)	1.373(13)
C4(1)–C5(1)	1.504(12)	C3(1)–C4(1)	1.390(13)
C1(2)–C2(2)	1.513(14)	C2(2)–C3(2)	1.373(13)
C4(2)–C5(2)	1.511(13)	C3(2)–C4(2)	1.379(12)
C1(3)–C2(3)	1.485(12)	C2(3)–C3(3)	1.389(13)
C4(3)–C5(3)	1.509(13)	C3(3)–C4(3)	1.382(13)
Average	1.506(14)[b]	Average	1.381(8)[b]

Table 6. (Continued)

Angles

O1(1)-Sc-O2(1)	82.1(2)	O1(1)-C2(1)-C3(1)	125.0(9)
O1(2)-Sc-O2(2)	81.5(2)	O2(1)-C4(1)-C3(1)	123.9(9)
O1(3)-Sc-O2(3)	82.3(2)	O1(2)-C2(2)-C3(2)	125.1(8)
Sc-O1(1)-C2(1)	132.7(6)	O2(2)-C4(2)-C3(2)	124.4(8)
Sc-O2(1)-C4(1)	132.4(6)	O1(3)-C2(3)-C3(3)	123.5(8)
Sc-O1(2)-C2(2)	123.1(6)	O2(3)-C4(3)-C3(3)	124.7(8)
Sc-O2(2)-C4(2)	132.6(6)	C2(1)-C3(1)-C4(1)	120.1(9)
Sc-O1(3)-C2(3)	133.3(6)	C2(2)-C3(2)-C4(2)	119.3(9)
Sc-O2(3)-C4(3)	131.7(6)	C2(3)-C3(3)-C4(3)	118.9(9)
O1(1)-C2(1)-C1(1)	114.9(9)	C1(1)-C2(1)-C3(1)	120.1(9)
O2(1)-C4(1)-C5(1)	115.9(8)	C3(1)-C4(1)-C5(1)	120.2(9)
O1(2)-C2(2)-C1(2)	114.9(9)	C1(2)-C2(2)-C3(2)	120.0(9)
O2(2)-C4(2)-C5(2)	116.2(9)	C3(2)-C4(2)-C5(2)	119.3(9)
O1(3)-C2(3)-C1(3)	118.1(9)	C1(3)-C2(3)-C3(3)	118.4(9)
O2(3)-C4(3)-C5(3)	116.4(9)	C3(3)-C4(3)-C5(3)	118.9(9)

[a]Errors referred to the last significant digit are in parentheses.

[b]Errors for averages are computed using the method of small sample statistics. (See Blaedel, W. and Meloche, V.,"Elementary Quantitative Analysis," Row, Peterson, and Co., 1957, p. 557.)

Table 7. Deviations from Ligand Planes (Å)[a]

Ring	Sc	C1	C5
1	-0.011	-0.011	+0.007
2	-0.149	+0.071	+0.051
3	+0.031	-0.164	+0.105

[a]Ligand planes defined by atoms O1, C2, C3, C4, and O2 of their respective ring. Estimated standard deviation is 0.02 Å. Equations of planes:

Ring 1 $-0.4553x + 0.4351y - 0.7768z = -2.5289$

Ring 2 $0.8212x + 0.5569y - 0.1245z = 3.5116$

Ring 3 $0.4986x - 0.4758y - 0.7246z = -3.6160$

x, y and z are coordinates (Å) in an orthogonal system relative to the crystal axes _a_, _b_ and _c_, respectively.

to 3Å.

The bond lengths and angles within the acac ligand are similar to those found for other acac complexes (27). In Table 6, the oxygen-oxygen separations are listed for the molecule. The average intrachelate separation (2.715Å) usually referred to as the "bite" of the ligand is similar to that found in other tervalent acac complexes (27). Two types of distances are found for the interchelate distances. For oxygen atoms in planes formed by the C_3 axis, the separations average to 2.956Å, while those between the planes average to 3.093Å. It is thus apparent that considerable distortion from a regular octahedral environment is observed for the coordination environment of the scandium(III) ion. In contrast, for the $Cr(acac)_3$ complex (40) a nearly regular octahedron is found with the intrachelate separations, 2.715Å. The interchelate separations in $Sc(acac)_3$, all being longer than the minimum van der Waals contact distances found in other acac complexes (27) (<u>ca.</u> 2.60Å), indicate that the rings probably behave independently within the molecule. This nonrigid stereochemistry then allows the rotations described earlier to take place.

CHAPTER 3

THE CRYSTAL AND MOLECULAR STRUCTURE OF TRIS(TROPOLONATO)SCANDIUM(III)

Introduction

The tropolonate ion has a shorter "bite" and the ligand itself is not easily distorted as the acetylacetonate ion. These two factors may influence the overall stereochemistry of a complex involving this ligand and scandium(III). For these reasons the second compound of scandium used for structural investigation was the tris-tropolonate of scandium, $Sc(C_7H_5O_2)_3$.

Experimental Section

Scandium(III) oxide, Sc_2O_3 (99.9%), was purchased from Research Organic/Inorganic Corp. Tropolone, $C_7H_6O_2$ (98%), was purchased from Aldrich Chemical Co., Inc., and was used without further purification.

Tris(tropolonato)scandium(III), $Sc(trop)_3$. Hydrated scandium nitrate (0.34 g), prepared by evaporation of a solution of Sc_2O_3 and dilute nitric acid, was dissolved in water (30 ml) and added to a solution of tropolone (0.46 g) in methanol (5 ml). The solution was stirred for 2-3 hours at room temperature and then filtered. The residue was dried under vacuum over P_4O_{10} at room temperature and consisted of pale-yellow $HSc(trop)_4$ and red-brown $Sc(trop)_3$ crystals. Crystals of $Sc(trop)_3$ suitable for crystal structure studies were readily separated from the mixture. The procedure reported by Muetterties and Wright (14) for the preparation of $Sc(trop)_3$ from $HSc(trop)_4$ did not yield acceptable crystals.

Measurement of Crystal and Intensity Data

Preliminary symmetry and space group determination was conducted by using the precession film technique and MoKα radiation. On the basis of systematic absences, the crystal was initially assigned to the space group I2/a or Ia with the spindle axis coincident with the $\underline{a}^*$ axis for the precession geometry. This was transformed to the equivalent C2/c or Cc space groups (correct orientation for monoclinic space) ($\underline{a}$ = 12.36, $\underline{b}$ = 10.39, $\underline{c}$ = 18.11Å; β = 119°). It was suspected then that $Sc(trop)_3$ could be isomorphic with $Al(trop)_3$ (41). However, further investigation of reciprocal space revealed six-fold symmetry with $\underline{c}^*$ coincident to the spindle axis of the camera. Dr. L. J. Guggenberger was kind enough to send the precession pictures of $Al(trop)_3$ (43), which also encouraged further inspection of the symmetry involved as the intensity patterns were not similar.) As a result the crystal is assigned to the trigonal space group, in the hexagonal setting, R3c or $R\bar{3}c$ ($hki\ell$, $-h + k + \ell = 3n$; $h\bar{h}0\ell$, $\ell = 2n$, observed). The monoclinic to hexagonal transformation was as follows: The (200) reflection became the (006), the (020) relection became the (110), and the $(00\bar{2})$ reflection became the $(\bar{1}1\bar{2})$. The choice of the centrosymmetric space group, $R\bar{3}c$, was later justified by the refinement. Based upon this assignment, complete three-dimensional X-ray diffraction data were again measured by use of a Picker Four-circle computer controlled diffractometer. Conditions were the same as discussed in Chapter 2. The crystal was mounted with the $(1\bar{1}4)$ reflection approximately coincident with the Φ-axis of the diffractometer. Lattice parameters (Table 8) were determined from twelve hand-centered reflections at ambient temperature (24 ± 2°).

Table 8. Crystal Data

Molecular Formula	$Sc(C_7H_5O_2)_3$
Molecular Weight	408.31
Crystal Habit	Trigonal
Crystal Color	Reddish-Brown
Crystal Dimensions, mm	0.31 X 0.31 X 0.42
μ, cm^{-1}	4.00
Space Group	$\underline{R\bar{3}c}$, Trigonal, Hexagonal Setting
Systematic Absences	$\underline{hki\ell}^{b}$, $-\underline{h} + \underline{k} + \underline{\ell} = 3\underline{n} + 1$
	$\underline{h\bar{h}0\ell}$, $\underline{\ell} = 2\underline{n} + 1$
$\underline{a}$, Å	10.455(2)
$\underline{c}$, Å	32.595(1)
$\underline{U}$, $Å^3$	3085
D_{exp}, g/ml[a]	1.33
D_{calc}, g/ml	1.318
$\underline{Z}$	6

[a]Measured by flotation in methylene chloride.

[b]In hexagonal setting, $\underline{i} = -(\underline{h} + \underline{k})$.

Intensities were determined from ω-scans over a width of 0.8° at a rate of 0.5°/min. Data were collected over the range $2.5° < 2\theta < 60°$. Backgrounds were measured by two 10 second counts, one at each end of the scan. Attenuators were automatically inserted when the count rate exceeded 10,000 counts per second. One monitor reflection was measured every 50 reflections. No decomposition nor motion of the crystal was observed, the average deviation being $\pm 1\%$. An initial set of data was collected (to $2\theta = 30°$) ($\underline{h}$, $\underline{+k}$, $\underline{+\ell}$) to verify the systematic absences for the space group and lattice type employed (Table 8). The only exception was the (0, 0, 13) reflection, this may be explained as a result of the Renninger effect (44), since the crystal was oriented in a manner to allow multiple reflections. The second data set, which was used in the refinement of the structure, was the unique ($\underline{h}$, $\underline{k}$, $\underline{\ell}$) set. A total of 1075 independent relections were scanned of which 783 were found to be above background using the criterion $I/\sigma(I) \geq 3.0$.

Solution and Refinement of the Structure

The positional coordinates for the scandium were obtained from a three-dimensional Patterson map. The scandium is located at the $\underline{32}$ special position (0, 0, 1/4). Because of the complexity of a Patterson map in high symmetry space groups and the need to determine only one sixth of the molecule, a model was generated with Sc-O distances within the ligand and bond angles were used as found by Muetterties and Guggenberger (42). A rotation of 45° out of the $\underline{ab}$ plane was assumed for the ligand (about the Sc-C(4) line). The coordinates of all non-hydrogen atoms were placed relative to the $\underline{32}$

position. Isotropic thermal parameters of 2.5Å^2 were initially assigned to all atoms. A structure factor calculation at this stage resulted in R_1 = 0.46. The positional and istropic thermal parameters of those atoms allowed to vary were refined for three cycles of full-matrix least-squares. At this point, R_1 = 0.096. Hydrogen atoms were then placed 0.96Å from their bonded carbon atoms by assuming the corresponding angle bisector. Further refinement of the positional parameters, anisotropic thermal parameters for the hydrogen atoms resulted in a converged R_1 = 0.033 and R_w = 0.057 (45). Early in the refinement, it became obvious several strong reflections were suffering from either extinction [(006) and (012)] or Renninger effects [(104) and (122)]. As a complete hemisphere of data had been taken, the inconsistencies of intensities could be verified easily. These reflections were omitted from refinement and are indicated by an asterisk in the final listing of calculated and observed strucutre factor amplitudes (XIO) (Table 9). No correction for absorption (μ = 4.00 cm^{-1}) was made. The error of a measurement of unit weight was 1.14 ($S^2 = w(|F_0| - |F_C|)^2/(m - n)$, m = the number of observations, n = the number of variables and w = weight applied to each reflection (see footnote 45). The error suggests that the weighting scheme employed was not incorrect, but could have been improved.

The atomic positions and anisotropic thermal parameters of all non-hydrogen atoms and isotropic thermal parameters of the hydrogen atoms obtained from the final cycle of least-squares refinement are listed in Table 10 along with their estimated standard deviations, e. s. d.'s. A difference Fourier map of the final structure showed

Table 9. Final Calculated and Observed Structure Factor Amplitudes (X 10)

K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL	K	L	FOBS	FCAL

Table 10a. Final Atomic Coordinates

Atom	x/a	y/b	z/c
Sc	0.00	0.00	0.25
O1	0.18920(12)	0.05680(13)	0.21466(3)
C1	0.29064(15)	0.03308(15)	0.22962(4)
C2	0.41776(18)	0.07189(20)	0.20662(5)
C3	0.53915(22)	0.05670(28)	0.21557(7)
C4	0.56953(25)	0.00	0.25
H2	0.4252(25)	0.1221(25)	0.1808(6)
H3	0.6173(28)	0.1077(27)	0.1943(7)
H4	0.6619(45)	0.00	0.25

Table 10b. Final Thermal Parameters[a]

Atom	β_{11} or B, $\AA^2$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc[b]	0.00551(9)	-----------	0.000428(6)	-----------	0.0	0.0
O1	0.00746(13)	0.01094(15)	0.00053(9)	0.00512(11)	0.00026(3)	0.00075(3)
C1	0.00657(15)	0.00719(14)	0.00049(1)	0.00339(11)	0.00021(3)	0.00033(3)
C2	0.00783(18)	0.1135(22)	0.00066(1)	0.00481(16)	0.00065(4)	0.00077(4)
C3	0.00896(20)	0.01713(33)	0.00104(2)	0.00757(21)	0100119(5)	0.00119(6)
C4[b]	0.00961(27)	0.02114(56)	0.00135(4)	-----------	0.00084(5)	-----------
H2	2.88(41)					
H3	3.91(49)					
H4	5.40(89)					

[a]Anisotropic thermal parameters are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$.

[b]Symmetry requires [W.J.A.M. Peterse and J.H. Palm, Acta Crystallogr., **20**, 147(1966)] that for Sc: $\beta_{22} = \beta_{11}$, $\beta_{12} = 0.5*\beta_{11}$, $\beta_{13} = \beta_{23} = 0$ and for C4, $\beta_{12} = 0.5*\beta_{22}$, $\beta_{23} = 2.0*\beta_{13}$.

only two peaks with a density as high as $0.5e^-/\mathring{A}^3$, these being at the origin and within $1\mathring{A}$ of the scandium position, thus indicating no other species (solvent or associated molecules) present.

Description of the Structure and Discussion

Tris(tropolonato)scandium(III), $Sc(trop)_3$, crystallizes from aqueous methanol solution in the space group $\underline{R\bar{3}c}$ and is thus isomorphous with the corresponding iron(III) compound (46). A stereoscopic view down the crystallographic C_3 axis (parallel with $\underline{c}$ in this space group), Figure 5, shows the numbering scheme adopted and the 20% probability envelopes of the thermal ellipsoids. The coordination environment; relating those coordinates found in Table 10 to the coordinates of the whole molecule is shown in Figure 6. Interatomic distances and angles are listed in Table 11 and also are shown in Figure 7. A stereoscopic view of the molecular contents of the unit cell is shown in Figure 8.

The structure consists of discrete $Sc(trop)_3$ molecules with crystallographically imposed D_3 symmetry. Deviations from the ligand planes are small, Table 12, as would be expected from the molecular symmetry and noted (46) in $Fe(trop)_3$. $Fe(trop)_3$ crystallizes in the space group $\underline{R\bar{3}c}$ with $\underline{a}$ = 10.375 and $\underline{c}$ = 32.68$\mathring{A}$ and is isomorphic to $Sc(trop)_3$. The small deviations from planarity may be contrasted with the deviations found in $Al(trop)_3$ (42), where the rings are either twisted or folded. A stereoscopic view of the molecular contents of the unit cell (hydrogens omitted) is shown in Figure 8. There are no short intermolecular contacts; The shortest H...H is 2.48$\mathring{A}$, H...O is 2.68$\mathring{A}$, H...C is 2.97$\mathring{A}$, and C...C is 3.44$\mathring{A}$; these

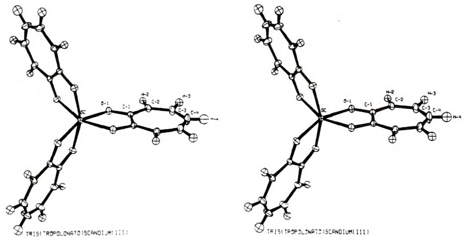
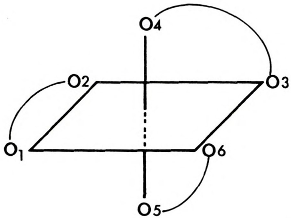


Figure 5. Stereoscopic view of tris(tropolonato)dcandium(III) down the C_3 axis showing the numbering scheme adopted.



$O1 = (X, Y, Z)$
$O2 = (X-Y, -Y, \frac{1}{2}-Z)$
$O3 = (-X, Y-X, \frac{1}{2}-Z)$
$O4 = (-Y, X-Y, Z)$
$O5 = (Y, X, \frac{1}{2}-Z)$
$O6 = (Y-X, X, Z)$

Figure 6. Coordination environment of $Sc(trop)_3$.

Table 11. Interatomic Distances (Å) and Angles (deg)[a]

Distances

Sc-O1	2.102(1)	O1-O2[b]	2.523(2)
O1-C1	1.299(2)	O1-O3	4.129(2)
C1-C2	1.398(2)	O1-O4	3.045(2)
C2-C3	1.387(3)	O1-O5	3.325(2)
C3-C4	1.379(3)	O2-O3	3.045(2)
C1-C1'	1.457(3)[c]		
C2-H2	0.97(2)		
C3-H3	1.00(3)		
C4-H4	0.97(3)		

Angles

O1-Sc-O2	73.77(6)	C2-C1-C1'	126.32(8)[c]
O1-Sc-O3	158.32(6)	C1-C2-C3	130.24(15)
O1-Sc-O4	92.83(4)	C2-C3-C4	129.89(18)
O1-Sc-O5	104.56(7)	C3-C4-C3'	127.10(24)[c]
O1-Sc-O6	92.83(4)	C1-C2-H2	115.3(14)
O1-C1-C1'	114.23(8)[c]	H2-C2-C3	114.4(14)
O1-C1-C2	119.45(12)	C2-C3-H3	110.2(14)

[a]Errors referred to last significant digit are in parentheses.

[b]For relations between oxygens, see Figure 6.

[c]Primed atom related to unprimed atom (x,y,z) by (x-y, -y, 1/2-z).

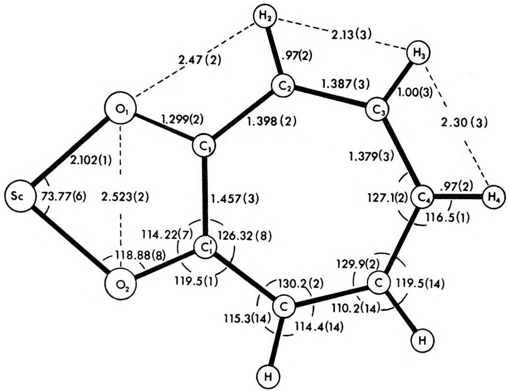


Figure 7. Interatomic distances and angles.

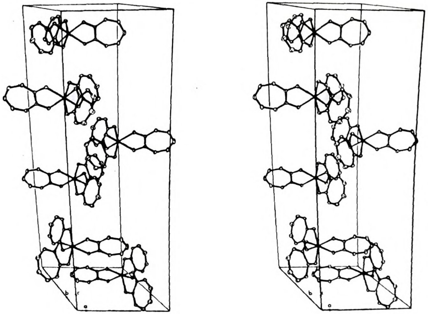


Figure 8. Stereoscopic view of the molecular contents of the Unit Cell, 20% probability envelopes, hydrogens omitted for clarity.

Table 12. Deviations from Ligand Plane (Å)[a]

Atom	Deviation
Sc	0.0000
O1	0.0060(9)
C1	0.0008(11)
C2	-0.0102(14)
C3	-0.0048(20)
C4	0.0000
H2	-0.0672(172)
H3	-0.1250(192)
H4	0.0000

[a]Ligand plane defined by all non-hydrogen atoms. Equation of plane: $-0.4553\ x - 0.7891\ y - 0.4119\ z = -3.3567$. x, y and z are coordinates (Å) in an orthogonal system defined by $\underline{b \times c}$, $\underline{b}$, $\underline{c}^*$, respectively.

contacts are in the ab plane with no short contacts in the c direction. The bond lengths and angles within the tropolonato ligand conform well with those found by Muetterties and Guggenberger (42) for other structures containing the tropolonato ligand. The ligand "bite" (2.523Å) falls within the narrow range observed for compounds containing chelating tropolonato ligands. Thus, the planarity and apparent rigidity of the chelating agent indicate little change in overall structure of the ligand upon coordination to the scandium(III) ion.

The coordination environment of the scandium in $Sc(trop)_3$ is best discussed by consideration of the intermolecular non-bonding O...O distances. There are three distinct groups which define two planes normal to the C_3 axis, viz., O1-O6, O1-O4, O4-O6, and O2-O3, O2-O5, O3-O5, separations being 3.045Å; third, a group of distances between the two planes defined above, O1-O5, O2-O4, and O3-O6, each having a value of 3.325Å. These distances correspond to a trigonal distortion (elongation along the C_3 axis) of the six donor oxygen atoms about the scandium(III) ion. This distortion may be due to two factors: first, the restrictions placed on the molecule due to a short bite distance and the inflexible nature of the ligand and second, packing within the unit cell such that contacts have been increased in the ab plane but not along directions in c thus, solid state energies may play an important role.

CHAPTER 4

DISCUSSION OF SIX COORDINATION

Introduction

Studies of complexes exhibiting six-coordination have attracted considerable attention because of the characterization of octahedral (or trigonal-antiprismatic (TAP)), trigonal-prismatic (TP), and intermediate stereochemistries. For complexes where the ligands do not control stereochemistry ("innocent ligands"), Wentworth (47) has shown that for most metal ions the ligand field stabilization energy (LFSE) of a trigonal-prismatic complex is less than that for an octahedral complex (see Figure 9). Exceptions to this are predicted for ions with d^0, d^1, low spin d^2, high spin d^5 and d^{10} configurations where there is no preference between stereochemistries. A discussion of the structures of several $[M(bidentate)_3]^{+n}$ complexes by Kepert (48) concludes that the stereochemistry of these complexes is principally dependent upon the ligand "bite", with trigonal-prismatic coordination being favored by a short ligand bite distance. The most widely studied complexes of this type contain either the acetylacetonate ion or the tropolonate ion. The tropolonate ion has a shorter bite and is a much more rigid ligand (42 and Chapter 3) than the acetylacetonate ion (27 and Chapter 2) and thus complexes containing the former ligand may have stereochemistries closer to trigonal-prismatic than the corresponding acetylacetonate complexes. This should be more the case when these ligands are coordinated to metal ions where no stereochemical preference is predicted from

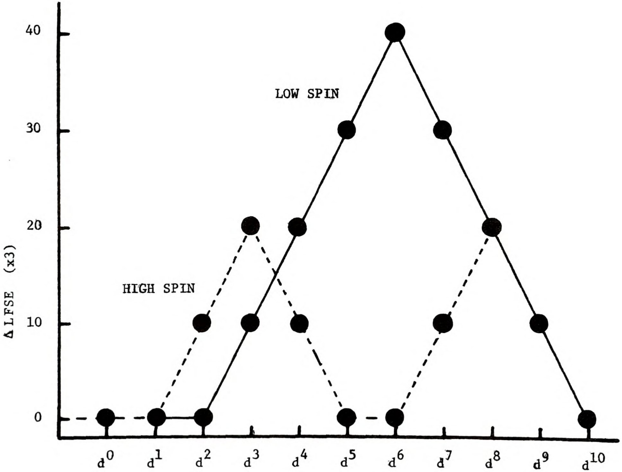
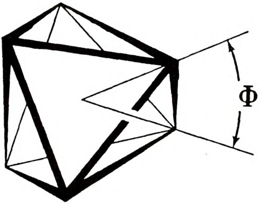


Figure 9. Variation of ΔLFSE with the d orbital occupation number, where ΔLFSE = LFSE(TAP) - LFSE(TP) (from Wentworth (47)).

LFSE considerations.

There have been several reports discussing a convenient way to differentiate between trigonal-prismatic and trigonal-antiprismatic stereochemistries, and ways to describe intermediate geometries (47-50). The simplest to use is the projected twist angle, Φ. This angle is defined as that made by projecting the two chelated donor atoms and the metal atom onto the same plane which is normal to the C_3 axis of the molecule, viz.:



with the metal atom as the vertex and the two donor atom projections at the ends. Thus, the projected twist angle for an octahedron would be 60°, while that for a trigonal-prism would be 0°, since both threefold faces would be eclipsed and the donor atoms would be projected onto the same point. Φ may then be used to indicate the degree of distortion from octahedral geometry.

Discussion of [M(bidentate)$_3$] Complexes

Structural details for some M(acac)$_3$ and M(trop)$_3$ complexes are listed in Table 13. First, note that for complexes where data

Table 13. Structural Details of Some $M(acac)_3$ and $M(trop)_3$ Complexes

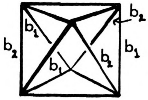
		ACAC					TROP				
Metal	d^n	M–O (Å)	Bite (Å)	OMO (Deg)	Φ (Deg)	Ref	M–O (Å)	Bite (Å)	OMO (Deg)	Φ (Deg)	Ref
Sc	d^0	2.07	2.72	82	47	Chapt. 1	2.10	2.52	74	33	Chapt. 3
V	d^2	1.98	2.75	88	56	51					
Cr	d^3	1.95	2.79	91	61	40					
Mn	d^4	1.99	2.79	90	~60	52	2.00	2.55	79	49	53
Fe	d^5	1.99	2.74	87	55	32	2.01	2.52	78	~40	46
Co	d^6	1.90	2.85	97	~60	27				~55	14
Al	d^0	1.89	2.73	92	60	27	1.89	2.49	82	48	14

are available for the acetylacetonate and the tropolonate ligands, the values of Φ are smaller for the tropolonato complexes. As Kepert (48) has pointed out, a shorter ligand bite should generate a smaller Φ. Obviously, the more flexible $acac^-$ ligand, behaving in a non-rigid manner, is able to undergo rotations and folding with changes in ligand bite distances and O-M-O angles to reduce interactions between ligands to a minimum. These processes take place in preference to the twisting of the molecule from trigonal-antiprismatic toward trigonal-prismatic stereochemistry, as should be expected with the tropolonato ligand. Second, for the series of 3d transition metal complexes containing $trop^-$ for which structural details are available, the Φ value decreases in the order $Co(trop)_3 > Mn(trop)_3 > Fe(trop)_3 >$ $Sc(trop)_3$. Co(III) and Mn(III), with electronic configurations, d^6 and d^4, respectively, have a preference toward trigonal-antiprismatic stereochemistry by consideration of ΔLFSE with the larger ΔLFSE being predicted for the Co(III) ion (47) (see Figure 9). $Co(trop)_3$ (with a value of Φ = 55°) has a stereochemistry close to octahedral, showing that in this case, the electronic preference almost completely overcomes the limitation placed on it by the ligand. For $Fe(trop)_3$ and $Sc(trop)_3$, with d^5 and d^0 configurations, respectively, there is no preference toward either stereochemistry from LFSE considerations. In these cases, restrictions placed on the molecule by the ligand bite distance are the important factors and considerable distortion toward trigonal-prismatic stereochemistry results. For $Mn(trop)_3$ where there is a small ΔLFSE in favor of TAP stereochemistry, both the ligand restrictions and electronic considerations are important in determining the resultant stereochemistry.

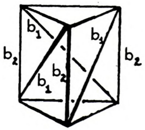
The value of Φ for $Sc(trop)_3$ is the smallest observed for any $M(trop)_3$ complex. The $Al(trop)_3$ complex, also a d^0 system, has Φ = 48°, with an Al-O bond length of 1.89Å. (In $Sc(trop)_3$, this distance is 2.10Å.)

The observed crystal and molecular structures for $Al(trop)_3$ and $Sc(trop)_3$ result from a combination of inter- and intra-molecular contacts. In $Al(trop)_3$, with a twist angle of 48°, the intra-molecular O...O nearest neighbor contacts are almost equal at 2.7Å. If a twist angle of 33° is introduced (as found in $Sc(trop)_3$) two sets of O...O contacts are predicted, those within the plane normal to the C_3 axis at 2.56Å and those between the planes at 3.15Å. Correspondingly, the contacts in $Sc(trop)_3$ are 3.05 and 3.25Å, respectively. Thus as Φ decreases, i.e., the molecule is distorted toward trigonal-prismatic stereochemistry, the "in-plane" O...O separations decrease while the "between plane" separations (b_1 and b_2) increase, viz.:

Octahedron



Trigonal Prism



In Table 14, predicted O...O contacts for trigonal-prismatic stereochemistry are listed for some $M(acac)_3$ and $M(trop)_3$ complexes. (For $acac^-$, the bite is assumed to be 2.8Å, while for $trop^-$, the value of 2.5Å was used.) If one assumes a van der Waals separation for O...O contacts of 2.70Å (effective ionic radius of O^{-2} = 1.35Å (54, 55)), it can be seen that for $acac^-$ complexes, the O...O van der Waals contact is not attained until M-O bond lengths of ca. 2.10Å are reached for TP stereochemistry while for $trop^-$ complexes the value is reached for M-O bond lengths of ca. 2.0Å. Further, the structure of $Al(trop)_3$ may be considered as a deviation from TP stereochemistry due to the need for the molecule to increase intramolecular O...O contacts from the calculated 2.42Å to the observed values, which are close to the van der Waals contacts, viz., ~2.73Å. However, the distortion of $Sc(trop)_3$ from TP sterochemistry appears to be the result of a different reason. The in-plane O...O separations already exceed the van der Waals values. Thus, although a TP stereochemistry could be stable for $Sc(trop)_3$ on a geometric basis, in the crystalline lattice a distortion toward TAP geometry is observed. The conclusion is that the molecular structure in the crystal is the result of intermolecular compressive forces which tend to reduce the volume of the molecule.

The Ionic Radius of Sc(III)

The average Sc-O distances found in $Sc(acac)_3$ and $Sc(trop)_3$ are 2.070 and 2.102Å, respectively. By using the assumed effective ionic radius of oxygen as 1.40Å (51), one calculates a radius of 0.67 and 0.70Å for the scandium(III) in these structures. This is

Table 14. Predicted O...O Contacts for Some $M(acac)_3$ and $M(trop)_3$ with Trigonal Prismatic Stereochemistry

M (+3 ionic radius Å)	M-O (Å)	In Plane (Å) ACAC	In Plane (Å) TROP	Out of Plane (Å) TROP
Al (0.5)	1.90	2.22	2.48	3.52
Fe (0.6)	2.00	2.47	2.70	3.68
Sc (0.7)	2.10	2.71	2.92	3.85
M (0.8)	2.20	2.94	3.14	4.01

in contrast to the Pauling value of 0.81Å (4). This value is similar to that found in structures that have appeared since completion of this work where considerable covalent character in the Sc-O bond is expected (56-61) and is somewhat smaller than that determined for "ionic" six-coordinate species (54, 55).

The Reaction Path Model for Six-Coordination

Muetterties and Guggenberger (42) have developed another set of criteria to describe the coordination polyhedron. The criteria are based upon the dihedral angles formed by the intersection of adjacent planes formed by the donor atoms. There are eight faces and twelve edges determined by either an octahedron or trigonal prism; thus, there are twelve dihedral angles present in either of these polyhedra. The calculated values for $Sc(acac)_3$ and $Sc(trop)_3$ are listed in Table 15 along with the theoretical values for an ideal octahedron and a trigonal prism. For $Sc(acac)_3$ with a Φ of 47°, indicative of distorted octahedron, the dihedral angles do not differ greatly from the ideal octahedron dihedral angles. However, for $Sc(trop)_3$ the dihedral angles indicate considerable distortion toward trigonal-prismatic stereochemistry, as does a Φ value of 33°. Thus, both structures are indicated to be intermediate between TAP stereochemistry and TP stereochemistry.

Conclusions for Six-Coordination

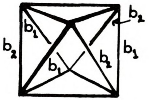
In predicting the stereochemistry of $M(bidentate)_3^{+n}$ complexes both the size and electronic configuration of the metal ion, the nature of the bidentate ligands, and the interactions between these

Table 15. Dihedral Angles for $Sc(acac)_3$ and $Sc(trop)_3$ (deg.)[a]

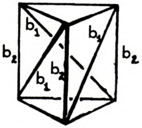
	b_1 edges	b_2 edges	Other edges
$Sc(acac)_3$	60.2, 62.3, 58.1	81.3, 79.7, 81.5	68.2, 68.5, 73.1
			70.1, 72.2, 73.2
$Sc(trop)_3$	3 at 57.5	3 at 156.5	6 at 66.5
Octahedron	3 at 70.5	3 at 70.5	6 at 70.5
Trigonal Prism	3 at 0.0	3 at 120.0	6 at 90.0

[a]The dihedral angles are defined as the angle between the normals of two adjacent planes.

Octahedron



Trigonal Prism



ligands must be considered since it is apparent that all these factors play important roles in determining the ultimate stereochemistry.

If one can correlate twist angles as determined in the solid state with reaction pathways in solution, as suggested by Muetterties and coworkers (42, 59), $Sc(trop)_3$ and its derivatives should undergo rapid intramolecular rearrangements due to an anticipated low barrier to rotations about the C_3 axis of the molecule, or more precisely, concerted rotations of the ligands about the C_2 axes.

CHAPTER 5

THE CRYSTAL AND MOLECULAR STRUCTURE OF HYDROGEN TETRAKIS(TROPOLONATO)SCANDIUM(III)

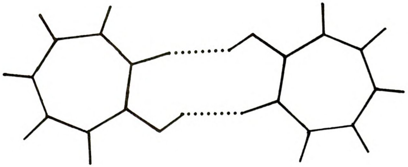
Introduction

Muetterties and Wright (14) reported the synthesis of metal complexes with the tropolonate anion as the ligand. Among these complexes was the "acid", $HSc(trop)_4$. With only a few physical measurements being made, it was proposed that the scandium ion was in an eight-coordinate environment, surrounded by eight oxygen atoms from four tropolone ligands. Isomorphism was indicated with $NaSc(trop)_4$ and the corresponding lanthanide complexes, which are known to exhibit high coordination. There is however, the possibility that $HSc(trop)_4$ may instead be of the form $Sc(trop)_3.Htrop$, that is, a tropolone adduct to the tris-complex. This possibility arises because the tris-chelated complex may be obtained from the "acid" complex in solution (14). The species $ScQ_3.HQ$ has been isolated (60) from the reaction of scandium(III) and 8-hydroxyquinoline, HQ. This species dissociates readily in solution to form ScQ_3 and HQ (61). The scandium(III) ion is much smaller than any of the lanthanides (see Table 1) which usually have high coordination numbers, thus making it difficult for a large number of ligands to coordinate to the scandium(III) ion. However, an example of a complex of scandium(III) in an eight-coordinate environment has recently been reported by Hansson (62).

The absorptions associated with ν(C=O) and ν(O-H) in the infrared spectra of $HSc(trop)_3$, $Sc(trop)_3$ and Htrop are shown in Table 16. The absence of any absorption at 1606 or 3500cm^{-1} in the spectrum of $HSc(trop)_4$ suggests that no uncoordinated Htrop is present in this compound.

X-ray photoelectron spectroscopy can be a useful tool for determining chemical differences of atoms in a compound. The X-ray photoelectron spectra of several scandium compounds have been determined (63) in order to ascertain differences in chemical environment between oxygen atoms of these complexes.

Table 17 lists the results of X-ray photoelectron spectra obtained in the oxygen (1s) region for Htrop, $Sc(trop)_3$ and $HSc(trop)_3$. For Htrop, a broad spectrum with a width at half height of 2.7 eV is observed, suggesting two types of oxygen atoms present in this compound. The crystal structure of tropolone (64) verifies the conclusion that there are two types of oxygen atoms present. The molecule is a hydrogen bonded dimer, viz.;



X-ray photoelectron spectroscopy is thus sensitive to small differences in the chemical environment of several oxygen atoms in the same molecule. For $Sc(trop)_3$, the symmetrical peak with a width at half height of 2.0 eV suggests all six oxygen atoms are equivalent. The

Table 16. Infrared Spectra (nujol mull)[a]

Compound	$\nu(C{=}O)$, cm^{-1}	$\nu(O{-}H)$, cm^{-1}
$HSc(trop)_4$	1593	not seen
$Sc(trop)_3$	1593	----
Htrop	1606	~3500

[a]Obtained on a Perkin-Elmer 457 grating infrared spectrophotometer.

Table 17. X-ray Photoelectron Spectra in the Oxygen (1s) Region for Several Compounds

Compound	Width of Peak at Half-Height (eV)	Comment
Htrop	2.7	Unsymmetrical
$Sc(trop)_3$	2.0	Symmetrical
1:1 Composite	2.3	Unsymmetrical
$HSc(trop)_4$	2.1	Symmetrical

crystal structure of $Sc(trop)_3$ verifies the equivalence. The spectrum of $HSc(trop)_4$ is also symmetrical with a half height of 2.1 eV, suggesting that the eight oxygen atoms are equivalent. In order to simulate a mixture of Htrop and $Sc(trop)_3$, a composite spectrum was constructed with the components of the spectra from each compound. This resulted in an unsymmetrical, broad spectrum (a width at half height of 2.3 eV), very unlike the observed spectrum for $HSc(trop)_4$. Thus, the X-ray photoelectron data suggest $HSc(trop)_4$ does not exist as an adduct, viz., $Sc(trop)_3$.Htrop.

Hamer, Tisley and Walton (65) have recently reported the X-ray photoelectron spectra in the Sc ($2p_{1/2}$) and Sc ($2p_{3/2}$) regions and in the O (1s), N (1s) and C (1s) regions for ten compounds of scandium. For $HSc(trop)_4$ and $Sc(trop)_3$ similar O (1s) spectra were obtained. Also, the Sc ($2p_{1/2}$) and Sc ($2p_{3/2}$) spectra were uninformative about the environment of the scandium ion. Presumably an increase in the number of metal-ligand bonds in $HSc(trop)_4$ compensates for the increased binding energy expected for Sc 2p electrons by increasing the Sc-O bond distance, also expected for higher coordination.

In order to ascertain the nature of the solid state environment of $HSc(trop)_4$ a complete single crystal structural determination has been completed.

Experimental Section

Hydrogentetrakis(tropolonato)scandium(III). The synthesis of $HSc(trop)_4$ is described in the experimental section of Chapter 3. In this case, the method described by Muetterties and Wright (14) also produced suitable crystals for X-ray studies.

Infrared Spectra. The infrared spectra were obtained from nujol mulls of the compounds on a Perkin-Elmer 457 Grating Spectrophotometer.

X-ray Photoelectron Spectra. Dr. D. M. Hercules (63) provided the X-ray photoelectron spectra of the compounds. The spectra were obtained in the oxygen (1s) region (KE = 716.4 $\pm$ 0.2 eV; BE = 532.0 $\pm$ 0.2 eV) by irradiating the samples with MgKα radiation.

Measurement of Cell Dimensions and Intensity Data

Preliminary investigations were conducted by using the precession technique with MoKα radiation. The highest Laue Class symmetry found was $P\bar{1}$; thus the space group is either $P1$ or $P\bar{1}$. Three-dimensional intensity data were collected by use of Picker Four-circle diffractometer controlled by a PDP-8/I computer. Monochromatic radiation (MoKα_1 = 0.70926Å) was obtained by initial diffraction of MoKα radiation by a graphite crystal with the (002) plane in diffracting orientation. Other parameters have been previously discussed (Chapters 2 and 3). The crystal (0.4 X 0.25 X 0.18 mm) was mounted with the $\underline{a}^*$ axis approximately coincident with the Φ axis of the diffractometer. Lattice parameters (Table 18) were determined from 12 hand centered reflections at room temperature (22 $\pm$ 1°). The intensities were measured by using the ω-scan technique with ω being scanned over 0.8° at a rate of 0.5°/min. Data for the hemisphere ($\underline{h}$, $+\underline{k}$, $+\underline{\ell}$) were collected between 2.8 and 45° for 2θ. Backgrounds were measured at each end of the scan for a total of 10 seconds each. The monitor reflections [(111), (014) and (2$\bar{1}$3)] were measured every 100 reflections and showed a mean variation of $\pm$1%, thus suggesting that no decomposition nor movement had taken

Table 18. Crystal Data

Molecular Formula	$HSc(C_7H_5O_2)_4$
Molecular Weight	530.43
Crystal Habit	Triclinic
Crystal Color	Pale Yellow
Crystal Size, mm	0.4 X 0.25 X 0.18
μ, cm^{-1}	4.40
Space Group	$P\bar{1}$, Triclinic
Systematic Absences	None
$\underline{a}$, Å	10.022(4) [11.647][b]
$\underline{b}$, Å	11.515(3) [12.004]
$\underline{c}$, Å	12.004(4) [10.022]
α, deg.	72.74(1) [95.42]
β, deg.	84.58(1) [116.32]
γ, deg.	65.04(1) [102.25]
$\underline{U}$, $Å^3$	1198.6(1)
D_{exp}, g/ml[a]	1.47
D_{calc}, g/ml	1.47
$\underline{Z}$	2

[a]Measured by flotation in chloroform.

[b]Lattice parameters in brackets correspond to the conventional orientation.

place during data collection. A total of 3144 independent reflections were measured of which 2539 were found to be above background using the criterion $I/\sigma(I) \geq 3.0$.

Solution and Refinement of the Structure

Scattering factor amplitudes for the neutral Sc, O and C were obtained from Cromer and Waber (33), and those for H from Stewart, et al., (34). The normal Lorentz and polarization corrections were made to the raw data, but no corrections were made for absorption nor anomalous dispersion.

After data correction, the unscaled $|F|$ values were used to calculate a three-dimensional Patterson map. Due to possible vector overlap, it was not obvious where the scandium atom was situated. For this reason, direct methods (symbolic phase addition) were used for at least a partial solution of the structure. A set of 275 $|E|$ values was calculated by using the program FAME (66). After assignment of seven symbols, the programs MAGIC, LINK and SYMPL (66) failed to yield a non-trivial solution. At this time, MULTAN (67) became available. By using the $|E|$'s calculated by FAME, a Σ_2 listing was determined from which an initial set of three origin reflections and three symbols were determined by hand for a total of 29 reflections. The program then calculated eight sets of phases. The third set of phases (Table 19) yielded an E-map which gave atomic positions for the scandium and six oxygen atoms. A reinspection of the Patterson map verified peaks corresponding to the scandium and oxygens and also revealed coordinates for the other two oxygen atoms.

Calculations of structure factor amplitudes and subsequent

Table 19. Starting Phases from MULTAN

Reflection			$\|E\|$	Symbol[a]	Phase (deg.)
h	k	ℓ			
1	-1	2	3.36	+	0
2	-1	3	2.68	+	0
6	-2	-1	3.37	+	0
1	3	12	2.48	A	0
2	-3	-4	2.87	B	0
4	3	-1	2.56	C	180

[a]+ is an origin reflection

least-squares refinement were based upon the cell being centrosymmetric, i.e., the space group is $P\bar{1}$. This conclusion arose from the statistics obtained from FAME (Table 20). A structure factor calculation based on the determined atomic coordinates and isotropic thermal parameters were used to obtain a Fourier map from which some of the carbon positions were located. It was necessary to repeat this process twice more before all non-hydrogen atom positions were defined. By using these initial coordinates and isotropic thermal parameters of 2.5Å^2 for all atoms, four cycles of full matrix least-squares refinement of coordinates and thermal parameters lowered R_1 from 0.467 to 0.096. At this time a difference Fourier map was calculated and the positions of all the ring hydrogen atoms were determined. To avoid errors in coordinates, they were placed 0.97Å (68) from their bonded carbon atoms along the line of the appropriate angle bisector. The "acid" hydrogen was placed between O1(1) and O1(3). It was thought that the hydrogen might be bridging between these oxygen atoms because there were short contacts between them (~2.5Å) and the Sc-O bond distances were longer than those for the other oxygen atoms. Further refinement of all coordinates and isotropic thermal parameters continued to a converged R = 0.064. At this time the acid hydrogen had moved ~1Å. A difference Fourier map at final convergence (Figure 10) further suggested the new hydrogen position between O1(1) and O1(4) across the center of inversion (see the hydrogen bonding discussion). Further refinement of coordinates and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms was conducted in two parts. There appeared to be two mutually perpendicular

Table 20. Statistical Analysis of $|E|$ Values from FAME

($\langle|E|^2\rangle$ rescaled to 1.00)

	Theoretical Values		Calculated Values
	Centric	Acentric	
Average Magnitude of E's	0.798	0.886	0.806
$\langle\lvert E^2 - 1\rvert\rangle$	0.968	0.736	0.950
Percentage of $\lvert E\rvert$'s>1	32.00	37.00	32.49
Percentage of $\lvert E\rvert$'s>2	5.00	1.80	3.99
Percentage of $\lvert E\rvert$'s>3	0.33	0.01	0.26

Figure 10. Difference Fourier map showing hydrogen (H) position, X, located between oxygen atoms O1(4) and O1(1). Section of map at $\underline{b}$ = 0.45. Atomic coordinates are related to those in Tables 22 and 23 by 1-x, 1-y, 1-z.

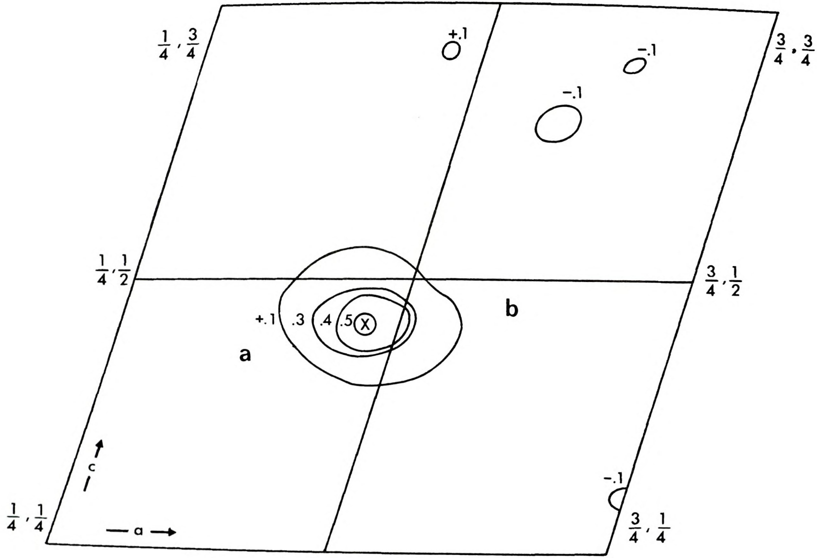


Figure 10.

quasi-mirror planes in the molecule, and atoms in each quasi-mirror plane were refined separately (due to core storage limitations of the computer for full-matrix refinement). To check on correlations between parameters, the tropolone ligands were refined in pairs not contained in a quasi-mirror plane for one cycle and did not correlate significantly. Consequently, the final cycles were not overlapped and the final reliability factor was 0.027 while $R_w = 0.029$ ($w = 1$). The final refinement obviously justified the choice of $P\bar{1}$ as the space group. The final observed and calculated structure factor amplitudes are listed in Table 21.

No parameter shift in the final two cycles was greater than 0.08 of its estimated standard deviation. A final difference Fourier map showed no peaks greater than $0.2e^{-}\mathring{A}^{3}$.

Description of the Structure and Discussion

Hydrogentetrakis(tropolonato)scandium(III) crystallizes from aqueous methanol solution in the space group $P\bar{1}$. The final atomic coordinates and thermal parameters for scandium, oxygen and carbon atoms are listed in Table 22. Those for the hydrogen atoms are listed in Table 23. The compound exists as a hydrogen-bonded dimer located about the center of inversion of the cell. A stereoscopic view of one half of the dimer, excluding ring hydrogen atoms, is shown in Figure 11. The shortest non-bonding separations are listed in Table 24. These are classified as intramolecular (within the dimer) or intermolecular (between dimers). For the intramolecular separations, the shortest O...O distances (2.49Å) involves the acid hydrogen (H) of the hydrogen bond, with the shortest separation not involving

Table 21. Final Calculated and Observed Structure Factor Amplitudes (X 10)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 21. (Continued)

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
7	5	72	71	-1	9	117	117	-1	1	45	41
8	5	21	24	1	9	17	16	1	-1	72	74
8	-5	71	75	-2	9	71	74	1	1	67	64
9	5	55	58	2	9	75	77	4	-1	93	95
10	5	67	61	3	9	32	34	4	1	91	91
-8	-6	66	38	-3	9	35	33	-4	1	22	22
0	6	37	36	5	9	125	126	5	-1	112	111
1	6	63	39	6	9	126	130	6	-1	38	38
-1	-6	99	108	8	9	70	69	7	-1	60	59
2	6	70	64	0	10	162	162	7	1	95	97
-2	-6	50	52	1	10	38	37	8	-1	21	21
3	-6	35	34	-2	10	58	57	10	-1	28	26
3	6	54	55	3	10	24	31	10	1	49	51
-3	6	71	67	4	10	66	67	-0	-2	67	65
4	6	89	90	6	10	101	98	-0	2	130	130
4	-6	67	64	0	11	99	100	-1	2	111	111
-4	6	86	83	1	11	56	53	1	2	21	22
5	6	112	115	-1	11	70	75	-1	-2	64	66
5	-6	52	51	2	11	46	44	1	-2	88	89
-5	6	68	68	3	11	36	31	2	-2	34	35
6	-6	24	28	4	11	56	58	-2	-2	91	89
6	6	59	61	6	11	40	40	2	2	52	52
7	6	42	42	1	12	55	55	-2	2	32	33
1	-7	159	111	2	12	43	45	-3	2	54	55
1	7	95	96					-3	-2	26	23
-1	7	92	94	** K = 8 **				3	2	139	138
2	7	83	83					3	-2	90	90
-2	7	116	117	-0	-0	36	39	4	2	60	61
3	-7	22	23	-1	-0	62	60	-4	2	118	119
-3	7	29	33	1	0	73	71	4	-2	142	142
-4	7	31	32	2	0	45	46	5	2	50	49
4	7	70	72	-3	-0	117	118	6	2	93	92
4	-7	75	76	4	0	119	117	6	-2	26	20
5	7	65	66	-4	-0	24	25	7	2	99	102
6	-7	10	26	5	0	97	97	7	-2	40	38
6	7	33	36	6	0	31	29	8	2	59	57
8	7	22	17	7	0	66	67	10	2	64	64
-8	8	64	63	8	0	52	56	0	3	67	69
-1	8	22	21	9	0	117	116	-0	-3	61	62
1	8	26	26	-1	-1	180	182	1	3	42	44
2	8	155	155	1	-1	51	52	1	-3	81	83
3	-8	17	19	1	1	30	32	-2	3	124	129
3	8	94	95	-1	1	35	33	2	-3	17	19
4	8	131	123	-2	-1	115	118	2	3	108	106
-4	8	92	82	2	-1	29	27	-2	-3	31	31
5	8	64	65	-2	1	97	94	3	-3	76	76
8	8	66	66	2	1	49	51	-3	-3	59	62
-8	9	67	61	-3	-1	60	57	3	3	39	42

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
4	-3	34	38	1	6	52	48	0	11	33	28
5	-3	52	51	1	-6	33	37	1	11	71	67
5	3	156	155	-1	6	79	81	3	11	49	49
6	3	71	70	2	-6	25	30	4	11	63	66
7	3	92	93	2	6	68	66	5	11	67	67
7	-3	79	79	-2	6	54	55				
8	-3	109	106	3	6	31	30	** K = 9 **			
8	3	113	115	-3	6	68	65				
10	3	22	19	3	-6	26	28	-0	-0	85	82
-0	4	45	43	5	6	37	33	-1	-0	33	36
0	-4	79	80	5	-6	47	45	2	0	76	78
1	4	118	119	6	6	41	39	-2	-0	40	42
-1	-4	100	101	6	-6	38	25	3	0	63	62
1	-4	51	51	8	6	42	41	-3	-0	55	56
-1	4	60	59	9	6	107	107	4	0	64	63
2	-4	34	32	1	7	165	171	5	0	69	69
-2	-4	30	30	-2	7	147	147	6	0	153	154
-2	4	60	61	2	7	21	24	8	0	29	29
3	4	89	89	-3	7	27	25	9	0	58	56
4	-4	72	69	3	7	40	43	-0	-1	45	44
4	4	83	81	4	7	192	193	-1	1	120	122
-4	4	46	46	5	7	79	82	-1	-1	118	123
5	4	102	104	6	7	135	134	1	-1	73	72
6	4	68	66	-0	8	35	35	2	-1	63	64
7	4	41	40	1	8	83	83	-2	1	87	89
7	-4	36	37	-1	8	37	36	2	1	124	128
8	4	29	27	2	8	24	21	-2	-1	46	50
8	-4	86	83	3	8	66	68	-3	1	23	26
9	4	97	97	-3	8	75	76	3	1	21	23
0	5	128	129	4	8	168	167	3	-1	24	17
-0	-5	22	19	5	8	150	147	4	1	106	106
-1	5	163	162	7	8	35	35	5	-1	59	59
1	-5	32	27	8	8	68	67	6	1	25	24
-1	-5	49	67	0	9	93	94	7	1	52	51
1	5	62	62	1	9	60	61	7	-1	96	96
-2	5	101	99	-2	9	88	85	8	-1	88	81
3	5	76	78	2	9	30	28	8	1	22	18
-1	5	46	43	3	9	123	126	-0	2	42	40
3	-5	47	68	4	9	67	70	-0	-2	32	33
-4	5	74	72	5	9	74	75	-1	-2	67	66
4	5	104	109	6	9	83	80	1	-2	101	109
5	5	65	53	-0	10	103	102	-1	2	65	78
5	-5	43	40	1	10	141	143	-2	-2	33	34
6	5	39	40	2	10	42	39	-2	2	63	63
7	-5	98	97	3	10	32	30	2	-2	66	69
8	5	143	141	4	10	45	46	2	2	59	59
0	6	41	40	6	10	28	30	-3	2	80	83
-0	-6	53	49	7	10	47	54	3	-2	18	9

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
1	2	29	34	1	-5	34	32	4	10	75	71
4	2	35	36	-2	5	33	32	5	10	45	48
5	-2	82	77	2	-5	58	61	6	10	44	44
7	2	31	36	2	5	28	25	2	11	74	69
7	-2	41	42	-1	5	46	46				
8	2	95	96	3	5	151	149	** K = 10 **			
8	-2	103	102	4	5	27	26				
9	2	78	78	4	-5	45	43	-0	-0	124	124
10	2	24	19	5	5	98	98	-1	-0	21	15
0	-3	29	23	6	-5	45	48	1	0	121	122
-0	3	28	27	6	5	47	51	2	0	58	62
-1	3	154	155	8	5	61	65	3	0	51	56
1	-3	55	55	0	6	20	19	7	0	78	76
1	3	36	35	1	6	56	55	8	0	31	31
2	3	22	16	-2	6	67	61	0	-1	95	95
-2	3	55	57	2	6	55	56	-1	1	31	34
3	3	110	108	-3	6	26	19	-1	-1	50	49
3	-3	122	121	3	6	40	58	2	1	53	57
-3	3	102	99	5	6	41	42	2	-1	64	62
4	3	37	37	6	6	66	68	3	-1	52	50
4	-3	30	30	7	6	77	76	3	1	78	75
6	-3	45	43	8	6	23	21	4	-1	55	53
6	3	24	24	-0	7	17	15	4	1	49	50
7	-3	40	40	-1	7	179	184	6	1	155	159
7	3	158	162	1	7	79	83	6	-1	157	106
8	3	22	17	2	7	17	15	8	-1	49	48
9	3	89	89	-2	7	105	104	0	-2	74	69
10	3	38	38	3	7	38	41	-1	2	21	17
0	-4	55	56	4	7	116	116	1	2	86	85
0	4	40	35	5	7	145	144	-2	2	38	44
1	4	127	131	7	7	56	56	2	-2	173	124
-1	4	53	51	8	7	68	62	2	2	26	25
1	-4	22	17	-0	8	37	37	3	-2	57	59
-2	4	87	89	1	8	66	69	4	2	44	45
2	4	149	149	-1	8	106	110	5	2	77	77
3	-4	80	79	2	8	44	48	6	2	103	105
3	4	66	62	-2	8	45	46	7	-2	33	33
-3	4	52	56	3	8	50	49	7	2	133	138
4	4	31	26	5	8	115	112	8	2	36	40
4	-4	27	26	6	8	36	33	8	-2	60	57
5	-4	34	34	7	8	67	58	9	2	63	62
6	4	88	91	8	8	51	51	0	3	47	48
6	-4	28	28	-1	9	58	58	-1	3	25	26
7	-4	37	36	2	9	59	60	1	-3	27	24
7	4	162	168	3	9	104	105	1	3	92	94
9	4	169	171	4	9	119	119	2	3	184	186
0	5	41	39	7	9	24	22	2	-3	94	94
-1	5	33	28	2	10	60	60	-2	3	51	51

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
3	-3	47	47	1	8	27	22	5	4	52	53
4	-3	134	135	1	9	100	96	6	4	57	64
4	3	182	192	2	9	41	37	7	4	34	34
7	-3	38	39	4	9	149	151	0	5	30	27
7	3	74	75	5	9	116	115	3	5	37	35
8	3	52	51	2	10	61	61	4	5	102	102
9	3	91	89	3	10	54	54	4	5	34	39
8	4	21	18	4	10	76	78	0	6	31	27
1	4	30	32	5	10	73	71	2	6	152	152
2	4	198	198					3	6	115	113
3	4	155	157	** K = 11 **				7	6	40	42
3	-4	35	32					1	7	49	49
4	-4	56	56	1	0	22	16	2	7	22	17
4	4	46	47	2	0	62	63	3	7	68	78
5	4	68	66	5	0	63	66	4	7	93	98
5	-4	23	19	6	0	88	88	5	7	46	47
6	4	37	37	7	0	62	62	6	7	35	33
7	4	32	37	8	-1	70	71	7	7	43	43
8	4	40	44	1	1	45	39	2	8	35	37
9	4	29	27	3	-1	86	85	3	8	46	50
-0	5	29	31	3	1	41	38	4	8	116	113
1	5	38	35	4	-1	65	64	5	8	66	61
2	5	76	76	5	-1	113	114	3	9	23	21
3	5	169	169	5	1	62	65	4	9	26	27
4	5	61	57	6	1	54	57				
5	5	85	84	7	1	69	68	** K = 12 **			
6	5	44	47	7	-1	50	54				
9	5	73	70	0	2	93	93	4	1	33	36
0	6	77	74	1	2	82	82	5	1	65	63
1	6	92	91	2	2	124	124	3	2	45	46
2	6	84	85	3	-2	59	63	4	2	90	96
3	6	54	51	4	2	46	45	5	2	45	44
6	6	64	67	5	-2	31	33	6	2	49	46
7	6	79	79	6	2	25	27	3	3	59	59
8	6	147	148	7	2	79	78	5	3	65	61
-0	7	56	59	8	2	58	57	6	3	66	68
1	7	20	35	1	3	60	63	2	4	25	25
-1	7	100	103	2	3	150	152	3	4	27	25
3	7	44	43	3	3	24	27	4	4	60	68
4	7	81	86	4	3	74	75	6	4	24	21
6	7	48	53	5	3	100	99	3	5	41	51
8	7	103	102	6	3	107	106	4	5	48	45
-0	8	36	33	7	3	81	86	5	5	121	127
2	8	80	84	8	3	74	69	6	5	20	8
3	8	57	59	0	4	37	39	3	6	121	129
4	8	64	64	2	4	69	67	4	6	30	37
5	8	36	36	3	4	104	103				
6	8	133	134	4	4	69	67				

Table 22a. Final Atomic Coordinates

Atom	x/a	y/b	z/c
Sc	0.32858(5)[a]	0.62313(4)	0.66803(4)
O1(1)[b]	0.3071(2)	0.5869(1)	0.4923(1)
O2(1)	0.1914(2)	0.8086(2)	0.5363(1)
C1(1)	0.2161(2)	0.6843(2)	0.4092(2)
C2(1)	0.1906(3)	0.6597(3)	0.3092(2)
C3(1)	0.1016(3)	0.7458(3)	0.2102(2)
C4(1)	0.0139(3)	0.8797(3)	0.1844(2)
C5(1)	-0.0069(3)	0.9623(3)	0.2544(2)
C6(1)	0.0538(3)	0.9336(3)	0.3621(2)
C7(1)	0.1531(3)	0.8112(2)	0.4377(2)
O1(2)	0.1389(2)	0.5736(2)	0.6861(2)
O2(2)	0.1841(2)	0.7091(2)	0.7953(1)
C1(2)	0.0427(3)	0.6087(2)	0.7610(2)
C2(2)	-0.0784(3)	0.5739(3)	0.7743(3)
C3(2)	-0.1904(4)	0.5942(3)	0.8507(3)
C4(2)	-0.2163(4)	0.6548(3)	0.9391(3)
C5(2)	-0.1371(4)	0.7146(3)	0.9675(3)
C6(2)	-0.0131(3)	0.7301(3)	0.9180(2)
C7(2)	0.0710(3)	0.6852(2)	0.8271(2)
O1(3)	0.4299(2)	0.4098(2)	0.6853(1)
O2(3)	0.4703(2)	0.5152(2)	0.8256(1)
C1(3)	0.4947(3)	0.3265(2)	0.7810(2)
C2(3)	0.5352(3)	0.1895(3)	0.7997(3)

Table 22a. (Continued)

Atom	x/a	y/b	z/c
C3(3)	0.6035(4)	0.0821(3)	0.8953(3)
C4(3)	0.6520(4)	0.0792(3)	1.0004(3)
C5(3)	0.6461(3)	0.1860(3)	1.0337(3)
C6(3)	0.5909(3)	0.3195(3)	0.9744(2)
C7(3)	0.5200(3)	0.3876(2)	0.8636(2)
O1(4)	0.5342(2)	0.6160(2)	0.5693(1)
O2(4)	0.4013(2)	0.7742(2)	0.6878(1)
C1(2)	0.5890(3)	0.7043(2)	0.5625(2)
C2(4)	0.7036(3)	0.7073(3)	0.4912(2)
C3(4)	0.7779(3)	0.7900(3)	0.4729(3)
C4(4)	0.7586(4)	0.8874(3)	0.5230(3)
C5(4)	0.6591(3)	0.9276(3)	0.6078(3)
C6(4)	0.5521(3)	0.8875(3)	0.6556(3)
C7(4)	0.5103(3)	0.7906(2)	0.6371(2)

[a]Numbers in parentheses refer to the estimated standard deviations (esd) of the last decimal place.

[b]The numbering system given refers first to the atom of a given ring, then to the ring, eg., O1(1) is the first oxygen on ring 1. O1 is bonded to C1 and O2 is bonded to C7.

Table 22b. Final Anisotropic Thermal Parameters[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc	0.00704(6)	0.00456(5)	0.00386(4)	-0.00215(5)	0.00061(4)	-0.00196(3)
O1(1)	0.0081(2)	0.0050(2)	0.0040(1)	-0.0015(2)	-0.0005(1)	-0.0018(1)
O2(1)	0.0110(3)	0.0059(2)	0.0052(2)	-0.0023(2)	-0.0066(2)	-0.0026(1)
C1(1)	0.0059(3)	0.0058(3)	0.0043(2)	-0.0024(2)	0.0009(2)	-0.0017(2)
C2(1)	0.0085(3)	0.0065(3)	0.0055(2)	-0.0023(3)	0.0000(2)	-0.0028(2)
C3(1)	0.0111(4)	0.0097(3)	0.0053(2)	-0.0029(3)	-0.0011(2)	-0.0034(2)
C4(1)	0.0118(4)	0.0092(4)	0.0052(2)	-0.0021(3)	-0.0024(3)	-0.0013(2)
C5(1)	0.0108(4)	0.0060(3)	0.0060(3)	-0.0015(3)	-0.0011(3)	-0.0005(2)
C6(1)	0.0102(4)	0.0056(3)	0.0059(2)	-0.0027(3)	0.0007(2)	-0.0021(2)
C7(1)	0.0073(3)	0.0057(3)	0.0047(2)	-0.0031(2)	0.0008(2)	-0.0017(2)
O1(2)	0.0114(3)	0.0114(2)	0.0082(2)	-0.0069(2)	0.0033(2)	-0.0058(2)
O2(2)	0.0091(3)	0.0090(2)	0.0060(2)	-0.0048(2)	0.0020(2)	-0.0039(1)
C1(2)	0.0084(4)	0.0066(3)	0.0055(2)	-0.0028(3)	0.0004(2)	-0.0012(2)
C2(2)	0.0115(5)	0.0116(4)	0.0089(3)	-0.0068(3)	0.0012(3)	-0.0034(3)

Table 22b. (Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C3(2)	0.0106(5)	0.0131(4)	0.0109(4)	-0.0071(4)	0.0019(3)	-0.0026(3)
C4(2)	0.0098(5)	0.0137(4)	0.0096(3)	-0.0049(4)	0.0039(3)	-0.0017(3)
C5(2)	0.0130(5)	0.0124(4)	0.0069(3)	-0.0045(4)	0.0034(3)	-0.0031(3)
C6(2)	0.0159(4)	0.0101(3)	0.0057(2)	-0.0043(3)	0.0016(3)	-0.0029(2)
C7(2)	0.0077(4)	0.0057(3)	0.0041(2)	-0.0019(3)	0.0001(2)	-0.0010(2)
O1(3)	0.0128(3)	0.0055(2)	0.0046(1)	-0.0027(2)	-0.0018(2)	-0.0014(1)
O2(3)	0.0128(3)	0.0060(2)	0.0061(2)	-0.0021(2)	-0.0019(2)	-0.0026(1)
C1(3)	0.0077(3)	0.0062(3)	0.0053(2)	-0.0030(3)	0.0007(2)	-0.0021(2)
C2(3)	0,0142(5)	0.0067(3)	0.0069(3)	-0.0040(3)	-0.0023(3)	-0.0018(2)
C3(3)	0.0168(5)	0.0063(3)	0.0100(3)	-0.0042(3)	-0.0038(3)	-0.0007(3)
C4(3)	0.0150(5)	0.0082(4)	0.0075(3)	-0.0040(3)	-0.0032(3)	0.0010(3)
C5(3)	0.0099(4)	0.0109(4)	0.0050(3)	-0.0027(3)	-0.0013(3)	-0.0013(3)
C6(3)	0.0090(4)	0.0086(3)	0.0054(2)	-0.0019(3)	-0.0004(2)	-0.0029(2)
C7(3)	0.0067(3)	0.0072(3)	0.0046(2)	-0.0022(3)	0.0009(2)	-0.0026(2)
O1(4)	0.0078(2)	0.0057(2)	0.0060(1)	-0.0030(2)	0.0013(1)	-0.0033(1)

Table 22b. (Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O2(4)	0.0094(2)	0.0072(2)	0.0063(2)	-0.0044(2)	0.0022(2)	-0.0037(1)
C1(4)	0.0073(3)	0.0056(3)	0.0049(2)	-0.0027(2)	-0.0003(2)	-0.0018(2)
C2(4)	0.0097(4)	0.0087(3)	0.0073(3)	-0.0047(3)	0.0027(3)	-0.0045(2)
C3(4)	0.0114(5)	0.0128(4)	0.0105(3)	-0.0078(4)	0.0053(3)	-0.0064(3)
C4(4)	0.0145(5)	0.0135(4)	0.0138(4)	-0.0109(4)	0.0059(4)	-0.0074(4)
C5(4)	0.0145(5)	0.0110(4)	0.0119(4)	-0.0086(4)	0.0042(3)	-0.0071(3)
C6(4)	0.0117(4)	0.0089(3)	0.0084(3)	-0.0055(3)	0.0026(3)	-0.0053(3)
C7(4)	0.0076(3)	0.0057(3)	0.0049(3)	-0.0026(2)	0.0002(2)	-0.0020(2)

[a]The thermal parameters are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)]$

Table 23. Final Hydrogen Atom Coordinates and Isotropic Thermal Parameters

Atom	x/a	y/b	z/c	B, $\mathring{A}^2$
H[a]	0.595(4)	0.536(4)	0.542(3)	7.30(3)
H2(1)[b]	0.240(3)	0.570(2)	0.309(2)	2.41(52)
H3(1)	0.101(3)	0.704(3)	0.149(2)	3.63(60)
H4(1)	-0.040(3)	0.922(3)	0.110(2)	3.78(62)
H5(1)	-0.068(3)	1.051(3)	0.225(2)	3.22(59)
H6(1)	0.027(3)	1.009(3)	0.391(2)	2.82(55)
H2(2)	-0.081(3)	0.533(3)	0.715(3)	4.87(74)
H3(2)	-0.264(4)	0.564(3)	0.838(3)	5.38(78)
H4(2)	-0.303(4)	0.661(3)	0.979(3)	5.49(79)
H5(2)	-0.162(4)	0.748(3)	1.034(3)	6.19(88)
H6(2)	0.030(3)	0.774(3)	0.954(2)	3.83(64)
H2(3)	0.507(3)	0.170(3)	0.732(2)	3.85(62)
H3(3)	0.613(3)	-0.004(3)	0.981(3)	5.99(82)
H4(3)	0.687(3)	-0.006(3)	1.061(3)	5.46(77)
H5(3)	0.677(3)	0.169(3)	1.108(2)	3.39(61)
H6(3)	0.601(3)	0.374(3)	1.018(2)	3.96(65)
H2(4)	0.737(3)	0.645(2)	0.449(2)	2.43(52)
H3(4)	0.852(3)	0.771(3)	0.419(2)	3.88(65)
H4(4)	0.817(3)	0.934(3)	0.499(3)	5.07(75)

Table 23. (Continued)

Atom	x/a	y/b	z/c	B, $\AA^2$
H5(4)	0.665(3)	1.000(3)	0.634(2)	4.49(67)
H6(4)	0.494(3)	0.927(3)	0.713(3)	4.42(69)

[a]Hydrogen attached to O1(4)

[b]First number refers to the carbon atom to which the hydrogen is attached, the second to the ring.

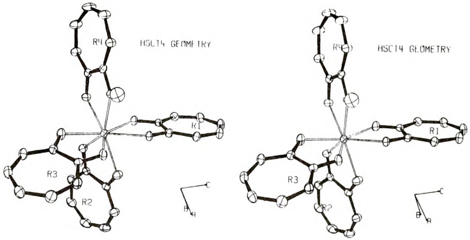


Figure 11. Stereoscopic view of half of the $HSc(trop)_4$ dimer, 25% probability envelopes, ring hydrogens omitted for clarity.

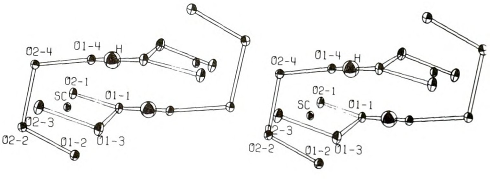


Figure 12. Interpenetrating trapezoids and hydrogen bonding in $HSc(trop)_4$.

Table 24. Shortest Non-bonding Separations

Intramolecular[a]

Type	Distance Å
H - H	2.73
H1(1) - H	2.24
O1(3) - H	2.62
O1(3) - O1(4)	3.13
C2(1) - O1(4)	3.23
C1(1) - C1(3)	3.29
O1(1) - O1(4)[b]	2.49

Intermolecular

Type	Distance Å	Atoms related by
H2(1) - H5(2)	2.31	(x, y, z-1)
H1(1) - H1(2)	2.43	(-x, 1-y, 1-z)
H1(3) - H4(4)	2.48	(x, y-1, z)

[a]Atoms are from opposite halves of the dimer.

[b]Hydrogen H is located between these atoms.

H being 3.13Å (O1(3)-O1(4)). (The shortest O...O distance within one $HSc(trop)_4$ unit is the ligand "bite" distance, the average value being 2.505Å). For separations involving other atoms, no unusually short distances are found. The closest intermolecular contacts involve the tropolonate ring hydrogen atoms, the shortest distance being 2.13Å, (H2(1)-H5(2)).

Coordination Polyhedron

Each of the scandium(III) ions in the dimer is surrounded by four bidentate ligands. Interatomic distances and angles within the coordination polyhedron are listed in Table 25. The average Sc-O distance calculated from bond lengths involving oxygen atoms of ligands 2 and 3, which are not part of the hydrogen bonding system is 2.18Å from which an ionic radius for eight-coordinated scandium(III) of approximately 0.78Å is estimated. This value is similar to that obtained from the Sc-O distance in $ScPO_4$ (22), $Na_5[Sc(CO_3)_4].2H_2O$ (21), $Sc_2(CO_3)_3.6H_2O$ (24). For a coordination number of eight, there are two important idealized coordination polyhedra, the dodecahedron and the square antiprism, although the polyhedron found in a structure is often distorted from one of these types (69, 70). The intermediate polyhedron between these two extremes is the bicapped trigonal prism (42, 71). If the method of Lippard and Russ (70) is employed to distinguish between the two extremes, several parameters must be defined. The determination of the best trapezoidal planes for a dodecahedron and the calculation of the angle of intersection between these planes is necessary. Table 26 and Figure 12 identify the planes T_1 and T_2. The angle between them, $\alpha_{T_1T_2}$, is 89.5°. For an idealized dodecahedron, this value should be 90° whereas for a square antiprism this value should be 77.4°. The values θ_A and θ_B are close to those expected for dodecahedral stereochemistry.

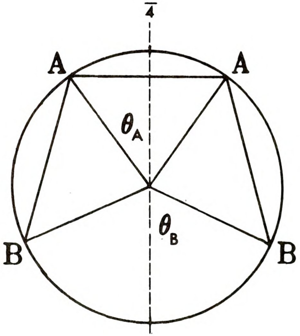


Table 25 lists the O...O separations for the polyhedron edges and Figure 13 shows the polyhedron with edges a, b, m, and g (as defined by Hoard and Silverton (69) for a dodecahedron. Table 27 lists the normalized values for these edges (the length of the edge divided by the average Sc-O distance). The bidentate ligands span equivalent m edges of the polyhedron and thus the dodecahedron has approximate D_{2d} symmetry. This mode of chelation is quite common for bidentate ligands (72, 73), although in $Sc_2(C_2O_4)_3 \cdot 2H_2O$ the three oxalato ligands span two m edges and one a edge of the dodecahedron (62) and in $Cs[Y(hfac)_4]$, $hfac^-$ = hexafluoroacetonate ion, the diketonate ligands span g edges resulting in D_2 symmetry (74). In an idealized D_{2d} dodecahedron, there may be a difference in the bond lengths between the A and B type Sc-O bonds as defined by Hoard and Silverton (69).

Table 25. Interatomic Distances (Å) and Angles (deg) within the Coordination Polyhedron[a]

Distances

Sc - O1(1)	2.314(2)	O1(1) - O1(2)	2.747(3)
Sc - O2(1)	2.209(2)	O1(1) - O1(3)	2.518(3)
Sc - O1(2)	2.180(2)	O1(1) - O1(4)	2.715(3)
Sc - O2(2)	2.164(2)	O2(1) - O1(2)	2.995(3)
Sc - O1(3)	2.178(2)	O2(1) - O1(4)	3.192(3)
Sc - O2(3)	2.183(2)	O2(1) - O2(2)	2.983(3)
Sc - O1(4)	2.260(2)	O2(1) - O2(4)	2.736(3)
Sc - O2(4)	2.228(2)	O1(2) - O1(3)	2.726(4)
Average	2.215(5)[b]	O1(2) - O2(3)	3.577(4)
		O2(2) - O2(3)	2.767(4)
O1(1) - O2(1)	2.516(2)[c]	O2(2) - O2(4)	2.768(4)
O1(2) - O2(2)	2.496(2)[c]	O1(3) - O1(4)	2.920(4)
O1(3) - O2(3)	2.507(2)[c]	O2(3) - O1(4)	3.059(4)
O1(4) - O2(4)	2.500(2)[c]	O2(3) - O2(4)	2.691(4)
Average	2.505(5)[b]		
		H - O1(4)	1.00(4)
		H...O1(1)	1.49(4)

Angles

O1(1) - Sc - O2(1)	67.53(6)	O1(3) - Sc - O2(3)	69.84(7)
Sc - O1(1) - C1(1)	119.9(1)	Sc - O1(3) - C1(3)	120.2(1)
Sc - O2(1) - C7(1)	123.6(1)	Sc - O2(3) - C7(3)	120.3(1)
O1(2) - Sc - O2(2)	70.50(7)	O1(4) - Sc - O2(4)	67.69(6)
Sc - O1(2) - C1(2)	120.2(2)	Sc - O1(4) - C1(4)	121.8(1)

Table 25. (Continued)

Sc - O2(2) - C7(2)	120.9(1)	Sc - O2(4) - C7(4)	122.9(1)
O1(1) - H - O1(4)	175.9(33)		
H - O1(1) - Sc	137.5(21)		
H - O1(4) - Sc	119.0(2)		

[a]Errors referred to last significant digit are in parentheses.

[b]Errors for averages are computed using the method of small sample statistics: See W. Blaedel and V. Meloche, "Elementary Quantitative Analysis", Row, Peterson and Co., Evanston, Ill., 1957, p. 557.

[c]Ligand "bite".

Table 26. Least Squares Planes[a]

Trapezoids

Plane	a	b	c	d	Atom	Dev. from Plane Å
T_1	0.8337	0.3754	-0.4050	-3.4044	O1(1)[b]	0.154(2)
					O2(1)[b]	-0.109(2)
					O1(3)[b]	-0.190(2)
					O2(3)[b]	0.125(2)
					Sc	-0.133(1)
T_2	-0.5291	0.3826	-0.7574	2.9261	O1(2)[b]	0.141(2)
					O2(2)[b]	-0.182(2)
					O1(4)[b]	-0.105(2)
					O2(4)[b]	0.175(2)
					Sc	-0.118(1)

Tropolonato Rings[a]

	a	b	c	d
Ring 1	0.7828	0.4542	-0.4253	-4.0678
Ring 2	-0.5389	0.5289	-0.6557	0.4985
Ring 3	0.9040	0.1692	-0.3926	-1.7281
Ring 4	-0.6187	0.2501	-0.7448	4.7944

Deviations from Planes Å

Atom	Ring 1	Ring 2	Ring 3	Ring 4
O1	0.174(2)	-0.089(2)	-0.012(2)	-0.077(2)
O2	-0.026(2)	0.026(2)	-0.044(2)	0.110(2)

Table 26. (Continued)

Atom	Ring 1	Ring 2	Ring 3	Ring 4
C1[b]	0.002(3)	-0.024(3)	-0.004(2)	-0.022(3)
C2[b]	0.000(3)	0.015(4)	0.011(3)	-0.010(3)
C3[b]	0.000(3)	0.023(5)	0.005(3)	0.024(4)
C4[b]	0.001(3)	-0.018(5)	-0.016(3)	0.023(4)
C5[b]	-0.006(3)	-0.018(4)	-0.002(3)	-0.034(4)
C6[b]	0.008(3)	-0.015(4)	0.018(3)	-0.014(3)
C7[b]	-0.005(3)	0.009(3)	-0.010(3)	0.035(3)
Sc	-0.227(1)	-0.194(1)	-0.428(1)	0.153(1)

[a]General equation for planes: $ax + by + cz + d = 0$.

x, y, and z are coordinates (Å) in an orthogonal system defined by $\underline{b} \times \underline{c}$, $\underline{b}$, $\underline{c}^*$, respectively.

[b]Atoms defining planes.

Figure 13. Coordination polyhedron for the scandium(III) ion in $HSc(trop)_4$.

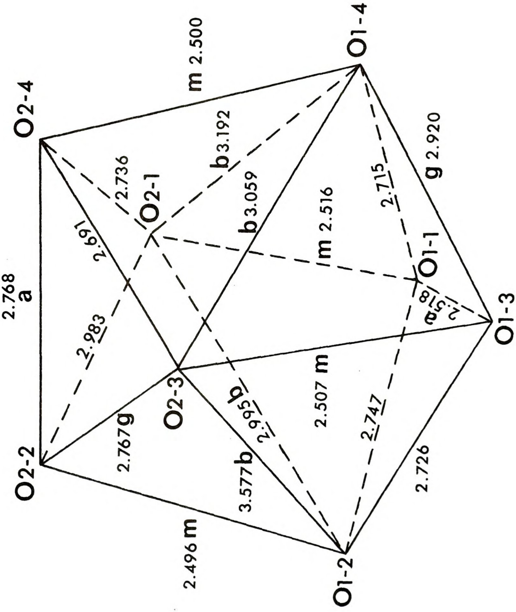

O2-4
O2-2
O2-1
O2-3
O1-4
O1-1
O1-2
O1-3
m 2.500
b3.192
2.736
b3.059
m 2.516
2.715
g 2.920
2.768
a
2.691
2.983
2.518
a
2.507 m
2.747
2.767g
2.995
b
3.577b
2.496 m
2.726

Figure 13.

Table 27. Shape Parameters[a] for $HSc(trop)_4$

Parameter[b]	$HSc(trop)_4$	Dodecahedron
a	1.19	1.17
m[c]	1.13	1.17
b	1.45	1.49
g	1.26	1.24
Θ_A, deg.	36.4	35.2
Θ_B, deg.	74.7	73.5
$\alpha_{T_1T_2}$[d]	89.5	90.0
d_{T_1}[e]	0.005	0.0
d_{T_2}[e]	0.007	0.0

[a]See references 17 and 18 for definition of shape parameters.

[b]Polyhedron edges normalized by dividing by the average Sc-O bond distance (2.215Å).

[c]m is the normalized ligand "bite" distance.

[d]$\alpha_{T_1T_2}$ is the angle between the best trapezoidal planes T_1 and T_2.

[e]d_{T_1} and d_{T_2} are mean displacements of ligand atoms from best trapezoidal planes T_1 and T_2.

However, for $HSc(trop)_4$, no significant differences are apparent.

Another method used to describe eight-coordinate polyhedra was first proposed by Porai-Koshits and Aslanov (71) and expanded by Muetterties and Guggenberger (50). This again is based upon dihedral angles of the edges in the polyhedron as in six-coordination. The non-planarity of the trapezoids distorts the polyhedron from D_{2d} symmetry through the bicapped trigonal prism of C_{2v} symmetry until the limit of a D_{4d} square antiprism is reached. The pertinent structural parameters are listed in Table 28. The dihedral angles, δ', are defined as the angle made by the normals of the planes adjacent to the edges defined by double lines in Figure 14. From this comparison, $HSc(trop)_4$ does not belong with the dodecahedral class nor with the bicapped trigonal prism class, but is intermediate. It is preferred, however, to consider the coordination polyhedron to be distorted D_{2d} dodecahedron as the C_{2V} bicapped trigonal prism should be more regular in shape than a dodecahedron.

Hydrogen Bonding and Ligands

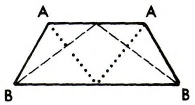
In the crystal, the two polyhedra are held together about the center of inversion by two almost linear hydrogen atoms attached to the O1(4) oxygen atom (O-H bond length is 1.00(3)Å) are hydrogen bonded to the O1(1) oxygen atoms across the center. The hydrogen bonded O...H distance is 1.49(3)Å and the O-H...O angle is 175.9°. The atoms, Sc, O1(1) and H and the related atoms across the center form a chair-shaped arrangement with O1(4), H and O1(1) atoms almost planar. The scandium atoms are located such that they make an angle of 132° with this plane.

Table 28. Dihedral Angles for $HSc(trop)_4$ and Ideal Polyhedra (deg.)

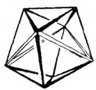
Complex	δ' Angles[a]	Φ's[b]
Ideal Dodecahedron	29.5, 29.5	0.0
	29.5, 29.5	
Ideal Bicapped	0.0, 21.8	14.1
Trigonal Prism	48.2, 48.2	
Ideal Square	0.0, 0.0	24.5
Antiprism	52.4, 52.4	
$HSc(trop)_4$	13.2, 28.7	9.7
	42.4, 42.9	

[a]For definition of δ, see text.

[b]Φ is defined as the dihedral angle between the dotted and dashed triangles for the trapezoidal atoms, BAAB.

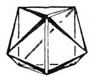


$\underline{D_{2d}}$



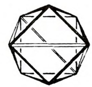
δ's $\begin{cases} 29.5, & 29.5° \\ 29.5, & 29.5 \end{cases}$

$\underline{C_{2v}}$



δ's $\begin{cases} 0.0, & 21.8° \\ 48.2, & 48.2 \end{cases}$

$\underline{D_{4d}}$



δ's $\begin{cases} 0.0, & 0.0° \\ 52.4, & 52.4 \end{cases}$

Figure 14. Polyhedron edges defining the dihedral angles indicated by double lines.

During the refinement of the strucutre, the hydrogen was placed initially between O1(1) and O1(3) of one polyhedron, because of the short O...O separation between these atoms (2.518Å). However, after refinement, the hydrogen was located in the position described above, with H...O1(3) across the center equal to 2.62(4)Å. The position of O1(3) is probably influenced by the hydrogen, but the hydrogen bond is not bifurcated as in tropolone itself (64). Any effect that the hydrogen produces on ring 3 is of much smaller magnitude than that produced in rings 1 and 4.

Further information concerning the hydrogen bonding is obtained by considering the nature of the ligands coordinated to the scandium(III) ion. Table 29 records the interatomic distances and angles for these ligands. The C_7H_5 rings are nearly planar with only small deviations of the carbon atoms from the planes defined by C1-C7. Table 26 lists the deviations and equations of the planes. However, O1 and O2 for the four rings show a complex pattern of distortions from the ring planes. Rings 2 and 3 show much smaller deviations than do rings 1 and 4, with a total out of plane distance being 0.20Å for ring 1, 0.11A for ring 2, 0.03Å for ring 3 and 0.19Å for ring 4. The twisting of rings 1 and 4 may be related to the nature of these ligands.

The bond lengths and angles within the four rings all show systematic variations (see Table 29). Rings 2 and 3 conform to patterns observed in $Sc(trop)_3$ and $Al(trop)_3$ (42). These complexes each contain coordinated tropolonato ligands with the C-C bond lengths decreasing as one proceeds from the carbon atoms attached to the oxygens to the C4 ring atom. Rings 1 and 4 do not exhibit this

Table 29 . Interatomic Distances (Å) and Angles (deg.) for the Tropolonato Ligands[a]

Atoms	Ring 1	Ring 2	Ring 3	Ring 4
		Distances		
O1-C1	1.315(3)	1.275(3)	1.274(3)	1.324(3)
O2-C7	1.267(3)	1.276(3)	1.281(3)	1.257(3)
C1-C7	1.459(3)	1.467(4)	1.468(3)	1.465(3)
C1-C2	1.381(3)	1.413(4)	1.403(4)	1.373(3)
C2-C3	1.395(4)	1.366(4)	1.381(4)	1.398(4)
C3-C4	1.368(4)	1.384(5)	1.380(4)	1.360(4)
C4-C5	1.389(4)	1.369(5)	1.379(4)	1.394(4)
C5-C6	1.370(4)	1.383(4)	1.373(4)	1.355(4)
C6-C7	1.424(4)	1.400(4)	1.407(4)	1.425(4)
C2-H2	0.94(2)	0.97(3)	1.00(3)	0.93(2)
C3-H3	0.99(3)	0.97(3)	0.97(3)	0.93(3)
C4-H4	0.96(3)	0.94(3)	0.98(3)	0.93(3)
C5-H5	0.92(3)	0.95(3)	0.91(3)	1.00(3)
C6-H6	0.96(3)	0.98(3)	0.97(3)	0.95(3)
		Angles		
O1-C1-C2	120.2(2)	120.2(2)	120.0(2)	120.6(2)
O1-C1-C7	112.1(2)	114.3(2)	114.1(2)	111.0(2)
C7-C1-C2	127.7(2)	125.7(2)	125.9(2)	128.5(2)
C1-C2-C3	130.5(2)	130.9(3)	130.5(3)	129.5(3)
C1-C2-H2	114.5(14)	111.5(18)	112.3(15)	115.4(15)
H2-C2-C3	115.1(14)	117.5(18)	117.2(15)	115.1(15)
C2-C3-C4	129.9(3)	129.4(3)	129.7(3)	129.5(3)

Table 29. (Continued)

Atoms	Ring 1	Ring 2	Ring 3	Ring 4
		Angles		
C2-C3-H3	115.5(15)	114.2(19)	115.4(19)	112.1(17)
H3-C3-C4	114.6(15)	116.4(18)	114.7(19)	118.4(17)
C3-C4-C5	126.7(13)	127.5(3)	127.4(3)	127.7(3)
C3-C4-H4	117.6(16)	115.0(20)	117.2(18)	118.0(19)
H4-C4-C5	115.7(16)	117.3(19)	115.2(18)	114.2(19)
C4-C5-C6	130.0(3)	130.1(3)	130.1(3)	129.7(3)
C4-C5-H5	116.8(16)	119.3(20)	117.0(17)	114.9(16)
H5-C5-C6	113.1(16)	110.4(20)	112.8(17)	115.3(16)
C5-C6-C7	131.3(3)	130.4(3)	130.2(3)	130.9(3)
C5-C6-H6	114.5(15)	117.5(16)	113.5(16)	117.6(17)
H6-C6-C7	114.1(15)	112.0(16)	116.2(16)	111.5(17)
C6-C7-C1	123.9(2)	125.8(2)	126.2(2)	123.9(2)
C6-C7-O2	119.9(2)	120.4(2)	120.5(2)	119.8(2)
O2-C7-C1	116.2(2)	113.8(2)	113.3(2)	116.3(2)

[a]Errors referred to last significant digit are in parentheses.

pattern. The bonding pattern in ring 4 is quite similar to that found in tropolone (64) where a more localized positioning of double bonds than in tropolonato ions is expected. The placement of the hydrogen atom on O1(4) is consistent with an increased C1-O1 bond length and the corresponding decrease in C7-O2 bond length (1.324 vs. 1.257Å, respectively). Ring 4 is thus more of a "tropolone" ligand than a "tropolonato" ligand. Ring 1 also is affected by the hydrogen atom placement since the C-C bond length pattern is similar to that observed in ring 4, and C-O distances for ring 1 are unequal at 1.315 and 1.267Å. Thus, the hydrogen influences electronic distributions with rings 1 and 4, such that they appear similar to tropolone molecules. However, the difference Fourier map (Figure 10) does not indicate any "averaging" of the hydrogen position.

The hydrogen bonding in $HSc(trop)_4$ also affects the Sc-O bond lengths (2.314, 2.209, 2.260 and 2.228Å). The differences are considerably greater than the errors expected in the observed values. However, although the hydrogen bond has weakened the bond between the scandium and the oxygens of ligands 1 and 4, these ligands are still considered to be coordinated in a bidentate manner.

The carbon-hydrogen distances in the ligands average to 0.95Å, very close to the optimal C-H distances as discussed by Churchill (68). These distances are shorter than the true C-H distances (expected to be ~1.10Å) because the scattering factor curve for hydrogen devised by Stewart, et al. (34), assumes a spherical shape for the hydrogen atom instead of some polarized shape. The average ligand "bite" distance (O1...O2, Table 25), 2.505Å. falls within the narrow range observed for other compounds containing chelating tropolonato

ligands (42). The average O1-Sc-O2 angle is 69.9, smaller than 73.8° found in $Sc(trop)_3$. Thus, the change in effective ionic radius of the scandium(III) ion on increasing coordination number 6 to 8 results in a closing of the O-Sc-O angle rather than an increase in the ligand bite distance.

The thermal amplitudes of the ligand groups may be interpreted in terms of rigid body motions. The root mean square (rms) deviations of the observed $\underline{U}_{ij}$ from that for a rigid body corrected for the total number of degrees of freedom, $[\Sigma \underline{U}_{ij}^{2}/(n - s)]^{1/2}$ ($\underline{U}_{ij} = \beta_{ij}/2^{2}\underline{a}_i^{*}\underline{a}_j^{*}$, $\underline{a}_i^{*}$ and $\underline{a}_j^{*}$ are the two reciprocal lattices in $\mathring{A}^{-1}$; $\Delta\underline{U}_{ij} = \underline{U}_{ij}$(found) - $\underline{U}_{ij}$(rigid body)), of the four ligands range from 0.0016 to 0.0019$\mathring{A}^2$ and $\sigma(\underline{U}_{ij}) \sim 0.0020\mathring{A}^2$ (75). The analysis of the librational motion of the ligands, although the motions are independent, indicates each has an angular movement of approximately equal magnitude.

CHAPTER 6

DISCUSSION OF EIGHT COORDINATION AND FURTHER WORK

Hydrogentetrakis(tropolonato)scandium(III) has been shown to exist as a hydrogen bonded dimer with the coordination environment intermediate between a D_{2d} dodecahedron and a C_{4v} bicapped trigonal-prism. Thus, the prediction of Muetterties and Wright (14) that the tropolone system may be used to form complexes of high coordination numbers has been confirmed for the scandium(III) ion. Blight and Kepert (76) have discussed the effect of bidentate ligands on the stereochemistry of eight-coordination. For the M(bidentate) case, these authors conclude that as the normalized ligand bite distance increases, there is a change in preferred stereochemistry from the D_{2d} dodecahedron to the D_2 square antiprism. For $HSc(trop)_4$ the normalized ligand bite is 1.13 ($O...O_{bite}/M\text{-}O_{avg}$), which is in the region where an intermediate stereochemistry may arise. Presumably, the steric requirements of the tropolonate ligands are an important factor in the determination ot the stereochemistry adopted. It is interesting to speculate at this point, the stereochemistry of the species, $Cs(trop)_4$, where hydrogen bonding should not be of concern. It would also be educational to speculate about the stereochemistry that would result for the system $M[Sc(hfac)_4]$, M = Na^+, K^+, Rb^+, or Cs^+, reported by Gurevich, et al. (11, 77). If the ligand bite

distance obtained by Bennet, _et al_. (74), in the complex $Cs[Y(hfac)_4].2H_2O$ is assumed (2.77Å) and an eight-coordinate Sc-O distance of 2.20Å, a normalized ligand bite of approximately 1.25 is calculated. Blight and Kepert (76) suggested that there are three stereochemistries possible for values of this magnitude, _viz_., the D_2 square antiprism, the D_4 square antiprism, and the D_2 dodecahedron. Values for a few complexes are listed in Table 30 together with the stereochemistry adopted for the complex. There is little difference between these stereochemistries and it is impossible to predict which one will be preferred. It should be anticipated, however, that the stereochemistry for the $[Sc(hfac)_4]^-$ ion are presumed to be something other than the distorted D_{2d}/C_{4V} polyhedron found for $HSc(trop)_4$.

The determination of the crystal and molecular structures of $CsSc(trop)_4$ and $Cs[Sc(hfac)_4]$ would verify the comments just presented. Attempts have been made to determine these structures without success. For various reasons, $CsSc(trop)_4$ crystals are twinned and are poor X-ray scatterers. Attempts to recrystallize this compound from solvent mixtures has only resulted in the isolation of $Sc(trop)_3$ or poor quality $CsSc(trop)_4$ crystals. The problem of recrystallization has been noted by Hoard (79), also. The structure determination of $Cs[Sc(hfac)_4]$ has been attempted with difficulties arising. First, the crystals are not well formed, with a broad mosaic spread usually being observed. Second, a reasonable crystal was found, but the space group determination was initially incorrect. This was discovered after a data set had been collected based upon assignment to an orthorhombic space group, which later was found to not satisfy the diffraction pattern. Further study revealed the space group to be

Table 30. Normalized Ligand Bite Distances for Several Eight-Coordinate Complexes

Complex	N.L.B.	Stereochemistry	Reference
$HSc(trop)_4$	1.13	D_{2d} Dodecahedron	Chapt. 5
$Sc_2(C_2O_4)_3 \cdot 6H_2O$	1.18	D_{2d} Dodecahedron	62
$Cs[Y(hfac)_4]$	1.19	D_2 Dodecahedron	74
$M[Sc(hfac)_4]$	1.26	D_2 Sq. Antiprism D_4 Sq. Antiprism D_{2d} Dodecahedron	
$Nb(dpm)_4$	1.29	D_2 Sq. Antiprism	78

consistent with the monoclinic space group, $\underline{P2_1/c}$. The lattice parameters are listed in Table 31. The crystal was lost, unfortunately, before a complete data set could be collected. (Monoclinic space groups require a quadrant of data to be collected.) Attempts to recrystallize more of the material have met with difficulty. The only reasonable solvent mixture the author has found is ethanol/water. However, hexafluoroacetylacetone dissociates if the concentration of water exceeds 40%(V/V).

Table 31. Crystal Data

Molecular Formula	$Cs[Sc(C_5HO_2F_6)_4]$
Molecular Weight	1006.07
Crystal Habit	Plate
Crystal Size	Undetermined
Crystal Color	Clear
μ, cm^{-1}	15.44
Space Group	$\underline{P2_1/n}$, monoclinic
Systematic Absences	$\underline{h}0\underline{\ell}$, $\underline{h} + \underline{\ell} = 2\underline{n} + 1$
	$0\underline{k}0$, $\underline{k} = 2\underline{n} + 1$
$\underline{a}$, Å	8.195(2)
$\underline{b}$, Å	20.871(6)
$\underline{c}$, Å	18.408(5)
γ, deg.	90.15
$\underline{U}$, $Å^3$	3148.5
D_{exp}, deg.[a]	2.013
D_{calc}, deg.	2.052
$\underline{Z}$	4

[a]Measured by flotation in chloroform/bromoform.

APPENDICES

APPENDIX I

ESCA Spectrum in the O 1s Region for Htrop

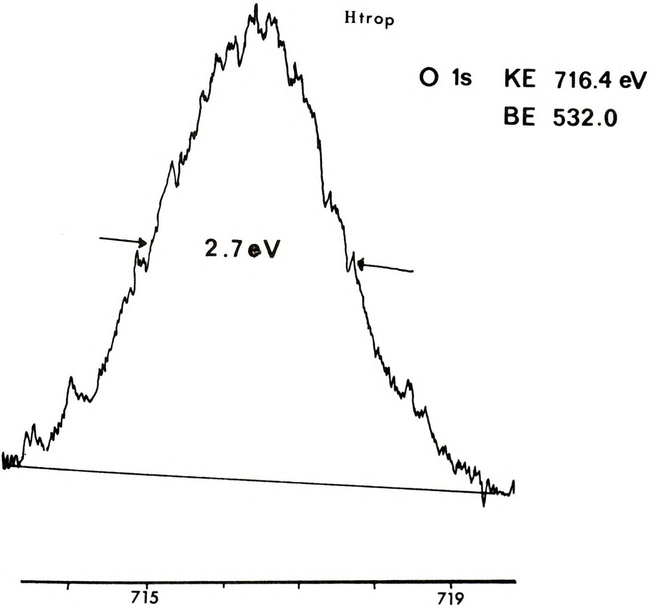


Figure A1. ESCA spectrum in the O 1s region for Htrop.

APPENDIX II

ESCA Spectrum in the O 1s Region for $Sc(trop)_3$

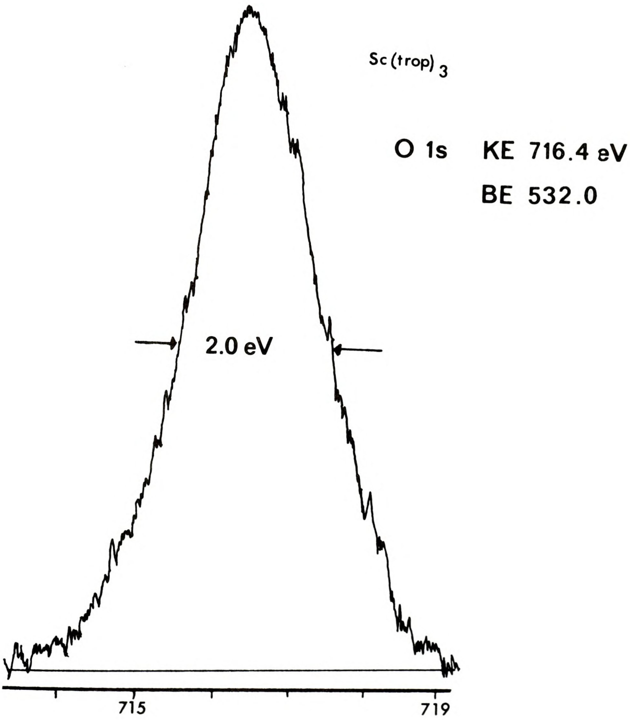


Figure A2. ESCA spectrum in the O 1s region for Sc(trop)$_3$.

APPENDIX III

ESCA Spectrum in the O 1s Region for $HSc(trop)_4$

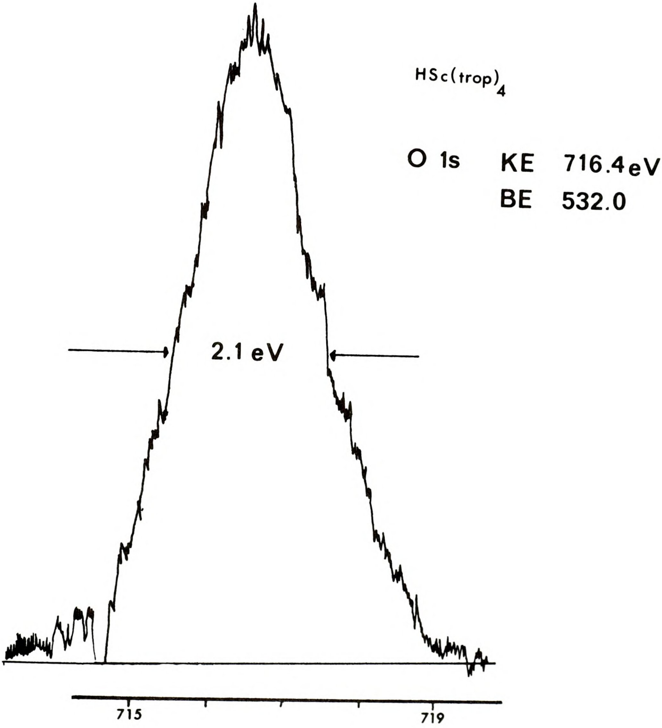


Figure A3. ESCA spectrum in the O 1s region for $HSc(trop)_4$.

APPENDIX IV

ESCA Spectrum in the O 1s Region for $Cs[Sc(trop)_4]$

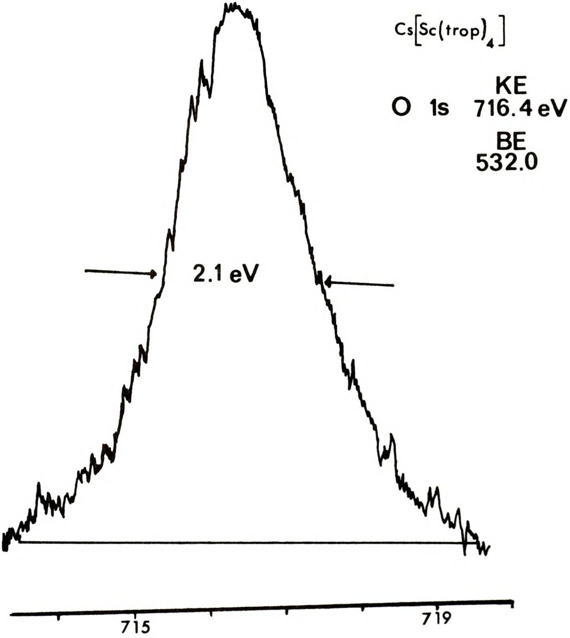


Figure A4. ESCA spectrum in the O 1s region for $Cs[Sc(trop)_4]$.

APPENDIX V

Analytical Data for the Compounds Studied

Table A1. Analytical Data for the Compounds Studied

Compound	Theoretical %Sc	Theoretical %C	Theoretical %H	Found %Sc	Found %C	Found %H
$Sc(trop)_3$	11.01	61.77	3.70	10.69	60.51	3.99
$HSc(trop)_4$	8.49	63.40	3.99	8.71	62.88	4.18

$Sc(acac)_3$ Mass spectral data indicate the parent ion peak at 342 M/e. Theoretical value is 342 M/e.

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