with the phosphines, triphenylarsine, and triphenylstibine are thallium(III) derivatives and thallium metal, the reaction probably involves the initial formation of the substituted thallous cobalt carbonyl followed by disproportionation as indicated in eq 7 and 8. At 0°, the reaction of $TlCo(CO)_4$

$$TlCo(CO)_4 + L \rightarrow TlCo(CO)_3L + CO \qquad (7)$$

$$3TlCo(CO)_3L \rightarrow 2Tl(s) + Tl[Co(CO)_3L]_3 \qquad (8)$$

with triphenyl phosphite proceeds only through reaction 7 giving the thallium(I) derivative. At higher temperatures some conversion to the thallium(III) derivative by reaction 8 is observed. Since thallous tetracarbonylcobaltate does not disproportionate, even at elevated temperatures,[35] the reaction of the other Lewis bases probably proceeds by the initial formation of a thallium(I) derivative followed by disproportionation. In addition, the reaction of thallous nitrate and $NaCo(CO)_3P(C_6H_5)_3$ also forms $Tl[Co(CO)_3P(C_6H_5)_3]_3$[6] and almost certainly involves the initial formation of $TlCo(CO)_3P(C_6H_5)_3$.

The weakness of the Tl-Co interaction in solutions of $TlCo(CO)_4$ in dichloromethane, benzene, and tetrahydrofuran is reflected in its reactions with covalent metal halides. Thallous tetracarbonylcobaltate is an excellent source of the $Co(CO)_4$ group.[36] It reacts with triphenyltin chloride in benzene, with bromomanganese pentacarbonyl in dichloromethane, and with indium(III) chloride in tetrahydrofuran giving high yields of $(C_6H_5)_3SnCo(CO)_4$, $(CO)_4CoMn(CO)_5$, and $In[Co(CO)_4]_3$, respectively.

Like the Hg(II),[37] In(III),[26] and Tl(III)[26] derivatives of $Co(CO)_4^-$, $TlCo(CO)_4$ will add 1 additional equiv of $Co(CO)_4^-$. A weak complex, $Tl[Co(CO)_4]_2^-$, is formed which is extensively dissociated in solution in dichloromethane. This complex is similar in its stability to the dihalothallate(I) complexes,[38] TlX_2^-, and the thallium(I) complex with pentacyanocobaltate(II),[39] $Tl[Co(CN)_5]_2^{5-}$. The complex probably contains two Tl-Co bonds rather than Tl-O coordination since no CO stretching frequencies lower than that of free $Co(CO)_4^-$ are observed in the infrared spectrum. Bonding of the oxygen of a metal carbonyl group to a second metal has been observed to reduce the stretching frequency of the CO involved.[40,41] As with the anions $Hg[Co(CO)_4]_3^-$,[37] $In[Co(CO)_4]_4^-$,[26] and $Tl[Co(CO)_4]_4^-$,[26] the CO stretching frequencies of the anion $Tl[Co(CO)_4]_2^-$ are of lower energy than respective frequencies of the neutral parent compound. This reduction in frequency from $TlCo(CO)_4$ to $Tl[Co(CO)_4]_2^-$ reflects the correspondingly greater electron density in the antibonding orbitals of the CO groups resulting from the negative charge on the anion.

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Registry No. $TlCo(CO)_4$, 38991-21-8; $Co_2(CO)_8$, 10210-68-1; $[(C_6H_5)_3(C_6H_5CH_2)P][Co(CO)_4]$, 42535-64-8; $[(C_6H_5)_3(C_6H_5CH_2)P][Tl[Co(CO)_4]_2]$, 39433-90-4; $Tl[Co(CO)_3P(C_6H_5)_3]_3$, 42535-65-9; $Tl[Co(CO)_4]_3$, 42535-66-0; $Hg[Co(CO)_4]_2$, 13964-88-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-153.

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Coordination Chemistry of Scandium. VI.[1] Crystal and Molecular Structure of Tris(tropolonato)scandium(III). Stereochemistry of Some Six-Coordinate Complexes

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The crystal and molecular structure of tris(tropolonato)scandium(III), $Sc(C_7H_5O_2)_3$, has been determined by a single-crystal X-ray diffraction technique. The compound crystallizes in the space group $R\bar{3}c$, with cell constants $a = 10.455$ (2) and $c = 32.595$ (1) Å in the hexagonal setting. Least-squares refinement of the counter data gave a final R factor of 0.033 for 783 significant reflections. The complex has D_3 imposed molecular symmetry. The coordination environment is intermediate between trigonal antiprismatic and trigonal prismatic as determined from a value of 33° for the projected twist angle Φ. The significance of Φ and its relationship to both metal ion and ligand restrictions is discussed.

Introduction

Studies of complexes exhibiting six-coordination have recently 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, Wentworth[2] has shown that for most metal ions the ligand field stabilization energy (LFSE) of a trigonal-pris-

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matic complex is less than that of an octahedral complex. 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 the stereochemistries. The structures of several $[M(bidentate)_3]^{n+}$ complexes have recently been reported, and Kepert[3] has concluded that the stereochemistry of these complexes is mainly dependent on the "bite" of the ligand, trigonal-prismatic coordination being favored by a short ligand bite. The most widely studied complexes of this type contain the acetylacetonate and tropolonate ions. The tropolonate ion has a shorter bite and is a much more rigid ligand[4] than the acetylacetonate ion[5] and thus complexes containing the former ligand may have stereochemistries closer to trigonal prismatic than the corresponding acetylacetonate complexes. This is expected to be particularly true when these ligands are coordinated to metal ions where no stereochemical preference is predicted from LFSE considerations. The projected twist angle, Φ, for the complexes (60° for trigonal antiprismatic and 0° for trigonal prismatic) gives an indication of the extent of deviation from the two extremes and attempts have been made to relate Φ to intramolecular rearrangement processes in solution.[4,6]

Recently, as part of our program of structural characterization of scandium complexes, we[1] reported the crystal and molecular structure of tris(acetylacetonato)scandium(III). The coordination environment for the d^0 ion was found to be close to trigonal antiprismatic. In view of the considerations outlined above, it was thought possible that the tropolonato ions might induce a stereochemistry approaching trigonal prismatic in tris(tropolonato)scandium(III). Comparison of the structure of this complex with similar $[M^{III}(bidentate)_3]$ complexes containing 3d transition elements should provide information for determining the influence of the electronic configuration and size of the metal ion and ligand requirements on the ultimate stereochemistry of the complexes.

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 at room temperature for 2-3 hr 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 the crystal structure studies were readily separated from this mixture. The procedure reported by Muetterties and Wright[7] for the preparation of Sc(trop)$_3$ from HSc(trop)$_4$ did not give suitable crystals.

Measurement of Crystal and Intensity Data. Preliminary investigations were conducted using the precession technique with Mo Kα 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 a^* axis for the precession geometry which was transformed to $C2/c$ or Cc ($a = 12.36$, $b = 10.39$, $c = 18.11$ Å; $\beta = 119°$).[8] However, a more rigorous investigation on the precession camera showed that the diffraction pattern repeated for every 60° rotation of the camera's spindle axis with c^* coincident with the spindle axis and resulted in the assignment of the trigonal space group, in the hexagonal setting, $R\bar{3}c$ or $R3c$ ($hkil$, $-h + k + l = 3n$; $h\bar{h}0l$, $l = 2n$ observed.[9-11] The monoclinic to hexagonal transformations were (200) to (006), (020) to (110), and (0,0,−2) to (−1,1,−2), respectively. Our choice of the centrosymmetric space group was later verified by the refinement. Based upon this assignment, complete three-dimensional single-crystal X-ray diffraction data were obtained on a Picker four-circle automatic diffractometer controlled by a PDP-8/I computer. A graphite monochromator in perpendicular geometry with the (002) plane in diffracting position was used to obtain monochromatic Mo Kα radiation. A takeoff angle of 3.0° was used. The radiation was detected using a scintillation counter with pulse height discrimination. The crystal was mounted with the (1,−1,4) reflection approximately coincident with the ϕ axis of the diffractometer. Lattice parameters (Table I) were determined from 12 hand-centered reflections at ambient temperature (22 ± 2°). Intensities were measured by an ω-scan technique with ω scanned over a width of 0.8° at a rate of 0.5°/min. Data were measured to a maximum $2\theta = 60°$. Backgrounds were estimated by two 10-sec counts made one at each end of the scan using stationary-crystal, stationary-counter measurements. Attenuators were used for count rates >10,000 counts/sec. One monitor reflection was measured every 50 reflections. No decomposition nor motion of the crystal was noted, the average deviation from the mean raw intensity being ±1%. Two sets of data were collected, the first being a hemisphere (to $2\theta = 30°$) (h, $\pm k$, $\pm l$) to verify the systematic absences for the space group and lattice type employed. The only exception found was (0,0,13), which is probably a result of the Renninger effect, since the crystal was oriented in a manner which made this possible. The second set, used in refinement was the unique (hkl) data. A total of 1075 independent reflections were scanned of which 783 were found to be above background using the criterion $I/\sigma(I) > 3.0$.

Table I. Crystal Data

Mol formula	$Sc(C_7H_5O_2)_3$	a, Å	10.455 (2)
Mol wt	408.31	c, Å	32.595 (1)
Crystal habit	Trigonal	V, Å^3	3085
Crystal color	Reddish brown	d_{exptl},[a] g/ml	1.33
Space group	$R\bar{3}c$	d_{calcd}, g/ml	1.318
		Z	6

[a] Measured by flotation in methylene chloride.

Solution and Refinement of the Structure. All calculations were performed using the CDC 6500 computer at the Michigan State University Computer Center.[12] Scattering factors for the neutral atoms, Sc, O, and C were obtained from ref 13 and those for H from ref 14.

The positional coordinates for the scandium atom were obtained from a three-dimensional Patterson[12a] map. The scandium was found to be located at the 32 special position.[9] Because of the complexity of the Patterson synthesis and the need for only one-sixth of the molecule to be defined, an Sc(trop)$_3$ model consisting of all nonhydrogen atoms was generated. Bond distances for the tropolonate ion were taken from ref 4, an Sc-O distance of 2.05 Å was assumed,[1] and a rotation of the tropolonato ring about its C_2 axis of 45° out of the ab plane of the crystal was introduced. The model was located with the scandium atom at the 32 position. Isotropic thermal parameters of 2.5 Å^2 were assigned to all atoms. A structure factor calculation at this stage resulted in a conventional R_1[15] = 0.46. The thermal parameters and positional coordinates were then allowed to vary for three cycles of least-squares refine-

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[3] D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

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[8] Tris(tropolonato)aluminum(III)[4] crystallizes in the space group $C2/c$ with $a = 10.855$, $b = 10.214$, $c = 17.710$ Å, and $\beta = 112.71°$.

[9] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962.

[10] Tris(tropolonato)iron(III)[11] crystallizes in the space group $R\bar{3}c$ with $a = 10.375$ and $c = 32.68$ Å.

[11] T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

[12] Computer programs used in the analysis: (a) FOURR, a Fortran Fourier summation program from X-RAY 70, J. M. Stewart, F. A. Kundell, and J. C. Baldwin; (b) WRFLS, a least-squares refinement program based on ORFLS of W. Busing, K. Martin, and H. Levy; (c) ORFEE, function and error analysis program by Busing, Martin, and Levy; (d) ORTEP II, a Fortran thermal-ellipsoid plot program for crystal structure illustrations by C. K. Johnson.

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[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3172 (1965).

Table II. Final Atomic Coordinates and Thermal Parameters[a]

Atom	x/a	y/b	z/c	β_{11} or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc[b]	0.0	0.0	0.25	0.00551 (9)		0.000428 (6)		0.0	0.0
O1	0.18920 (12)	0.05680 (13)	0.21466 (3)	0.00746 (13)	0.01094 (15)	0.00053 (9)	0.00512 (11)	0.00026 (3)	0.00075 (3)
C1	0.29064 (15)	0.03308 (15)	0.22962 (4)	0.00657 (15)	0.00719 (14)	0.00049 (1)	0.00339 (11)	0.00021 (3)	0.00033 (3)
C2	0.41776 (18)	0.07189 (20)	0.20662 (5)	0.00783 (18)	0.01135 (22)	0.00066 (1)	0.00481 (16)	0.00065 (4)	0.00077 (4)
C3	0.53915 (22)	0.05670 (28)	0.21557 (7)	0.00896 (20)	0.01713 (33)	0.00104 (2)	0.00757 (21)	0.00119 (5)	0.00119 (6)
C4[b]	0.56953 (25)	0.0	0.25	0.00961 (27)	0.02114 (56)	0.00135 (4)		0.00084 (5)	
H2	0.4252 (25)	0.1221 (25)	0.1808 (6)	2.88 (41)					
H3	0.6173 (28)	0.1077 (27)	0.1943 (7)	3.91 (49)					
H4	0.6619 (45)	0.0	0.25	5.40 (89)					

[a] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Symmetry requires [W. J. A. M. Peterse and J. H. Palm, *Acta Crystallogr.*, **20**, 147 (1966)] that for Sc, $\beta_{22} = \beta_{11}$, $\beta_{12} = 0.5\beta_{11}$, and $\beta_{13} = \beta_{23} = 0$ and for C4, $\beta_{12} = 0.5\beta_{22}$ and $\beta_{23} = 2.0\beta_{13}$.

ment.[12b] At this point $R_1 = 0.096$. Hydrogen atoms were then placed 0.96 Å from their appropriate carbon atoms using the corresponding angle bisectors. For the next three cycles of refinement all positional and thermal parameters (anisotropic for nonhydrogen atoms and isotropic for hydrogen atoms) were varied and the refinement converged to $R_1 = 0.033$ and R_2[15] $= 0.057$. Early in the refinement it became obvious that several strong reflections were suffering from either extinction [(006) and (012)] or Renninger effects [(104) and (122)].[16] These reflections were omitted from the refinement and are indicated by an asterisk in the structure factor table.[17]

The atomic positions and anisotropic thermal parameters of all atoms as obtained from the final least-squares cycle are given in Table II along with their estimated standard deviations (esd).[12c] In the final cycle, no parameter shift was greater than one-tenth of the associated esd. A difference Fourier of the final structure showed only two peaks with density as high as 0.5 e/Å^3, these being at the origin and within 1 Å of the scandium position. Observed and calculated structure factor amplitudes are available.[17]

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

	Distances		
Sc–O1	2.102 (1)	C3–H3	1.00 (3)
O1–C1	1.299 (2)	C4–H4	0.97 (3)
C1–C2	1.398 (2)	O1–O2[b]	2.523 (2)
C2–C3	1.387 (3)	O1–O3	4.129 (2)
C3–C4	1.379 (3)	O1–O4	3.045 (2)
C1–C1′	1.457 (3)[c]	O1–O5	3.325 (2)
C2–H2	0.97 (2)	O2–O3	3.045 (2)
	Angles		
O1–Sc–O2	73.77 (6)	C1–C2–C3	130.24 (15)
O1–Sc–O3	158.32 (6)	C2–C3–C4	129.89 (18)
O1–Sc–O4	92.83 (4)	C3–C4–C3′	127.10 (24)[c]
O1–Sc–O5	104.56 (7)	C1–C2–H2	115.3 (14)
O1–Sc–O6	92.83 (4)	H2–C2–C3	114.4 (14)
O1–C1–C1′	114.23 (8)[c]	C2–C3–H3	110.2 (14)
O1–C1–C2	119.45 (12)	C4–C3–H3	119.5 (14)
C2–C1–C1′	126.32 (8)[c]	C3–C4–H4	127.10 (25)

[a] Errors referred to last significant digit are in parentheses. [b] For relations between oxygens see Figure 2. [c] Primed atom related to unprimed atom (x, y, z) by $(x - y, -y, \frac{1}{2} - z)$.

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

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

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

Description of Structure and Discussion

Tris(tropolonato)scandium(III), Sc(trop)$_3$, crystallizes from aqueous methanol solution in the space group $R\bar{3}c$ and is thus isomorphous with the corresponding iron(III) compound.[11] Final atomic coordinates and thermal parameters for all atoms are listed in Table II. A stereoscopic view of the molecule down the C_3 axis (which is parallel with the c axis), Figure 1, shows the numbering scheme adopted and the 20% probability envelopes of the thermal ellipsoids.[12d] The coordination environment is shown in Figure 2. Interatomic distances and angles are listed in Table III and also shown in Figure 3.

The structure consists of discrete Sc(trop)$_3$ molecules with the scandium atom located at the 32 special position (0, 0, $^1/_4$). Thus, the molecule has crystallographically imposed D_3 symmetry. Deviations from the ligand planes are small, Table IV, as anticipated from the symmetry of the molecule and also noted[11] in Fe(trop)$_3$. This is in contrast to the twisting and folding observed for the chelate rings in Al(trop)$_3$, where D_3 symmetry is not imposed on the molecule.[4] A stereoscopic view of the unit cell is shown in Figure 4. There are no unusually short intermolecular contacts; the shortest H- - -H is 2.48 Å, H- - -O is 2.68 Å, H- - -C is 2.97 Å, and C- - -C is 3.44 Å. The bond lengths and angles within the tropolonato ligands are similar to those found in other compounds containing this anion and the features noted by Muetterties and Guggenberger[4] are also observed in Sc(trop)$_3$. The ligand "bite" (2.523 Å) falls within the narrow range observed for compounds containing chelating tropolonato ligands. Thus the ligand behaves as a rigid, inflexible chelating agent, coordination to the scandium(III) ion causing little change in its overall structure. The scandium-oxygen bond length (2.102 Å) is close to that observed in Sc(acac)$_3$ and suggests an ionic radius for the scandium(III) ion of about 0.70 Å, a value similar to that calculated from other scandium(III) compounds where considerable covalent character is expected in the scandium-donor atom bond[1,18,19] and slightly smaller than that calculated from some "ionic" six-coordinate species.[20,21]

The coordination environment of the scandium in Sc(trop)$_3$ is best discussed by consideration of the intramolecular nonbonding O- - -O distances. There are three distinct groups which define the ScO$_6$ polyhedron (see Figure 2): first, three intrachelate distances (O1-O2, O3-O4, O5-O6), the ligand bite, 2.523 Å; second, two sets which define two

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(15) $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $R_2 = [(\Sigma w|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$, where $w = 1/\sigma^2(F)$. $\sigma(F) = 0.05F$ for $F > 4F_{\min}$ and $\sigma(F) = 0.20F_{\min}$ for $F < 4F_{\min}$; $F_{\min} = 9.90$.

(16) As we had taken multiple data sets, the variation in intensity of equivalent reflections in different orientations is consistent with the presence of a Renninger effect.

(17) See paragraph at end of paper regarding supplementary material.

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(19) J. L. Atwood and K. D. Smith, *J. Amer. Chem. Soc.*, **95**, 1488 (1973).

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(21) C. Frondell, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **127**, 121 (1968).

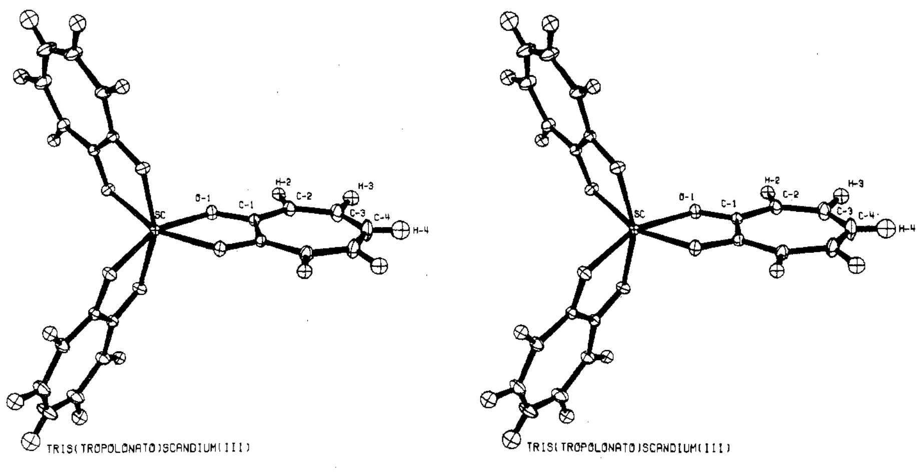

Figure 1. Stereoscopic view of tris(tropolonato)scandium(III) down the C_3 axis.

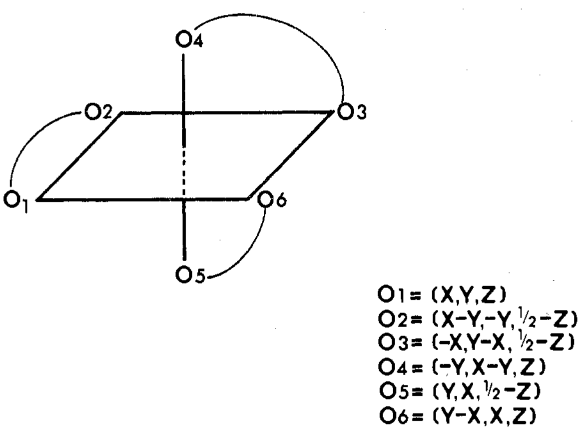

Figure 2. Coordination environment of tris(tropolonato)scandium(III).

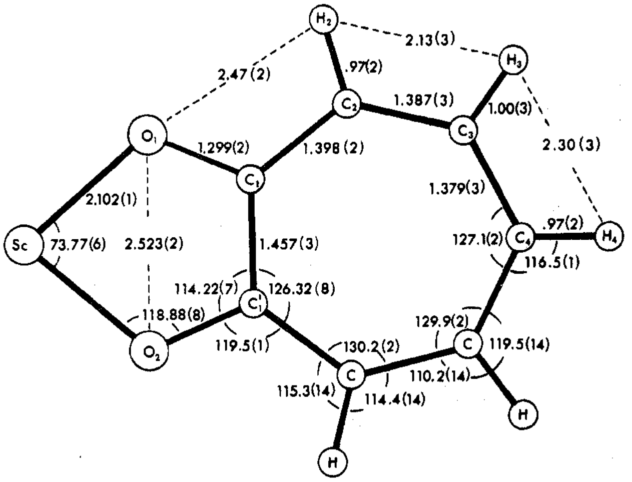

Figure 3. Interatomic distances and angles.

planes normal to the C_3 axis, *viz.*, O1-O6, O1-O4, O4-O6 and O2-O3, O2-O5, O3-O5, these separations being 3.045 Å; third, a group of distances between the two planes defined above, O1-O5, O2-O4, and O3-O6, each with a value of 3.325 Å. These distances correspond to a trigonal distortion (an elongation along the C_3 axis) of the six donor oxygen atoms about the scandium(III) ion. This distortion is associated with restrictions placed on the molecule due to the short fixed ligand bite and the inflexible nature of the ligand. Perhaps the most interesting and significant feature of the coordination environment is the value of the projected twist angle, Φ, of 33°. (Φ is defined by projection of the metal-donor atom vectors within a chelate onto a plane normal to the C_3 axis.) The stereochemistry of Sc(trop)$_3$ is thus between trigonal antiprismatic ($\Phi = 60°$) and trigonal prismatic ($\Phi = 0°$). In Table V we list the structural details of some M(acac)$_3$ and M(trop)$_3$ complexes. First, note that for complexes with the tropolonato anion, the values of Φ are all smaller than those for the corresponding complexes with the acetylacetonato ligand. Obviously, the more flexible acac$^-$ ligands, behaving in a nonrigid manner, are able to undergo rotations and folding processes[1,22] and changes in ligand bite distance and O-M-O angle to reduce interactions between ligands to a minimum. These processes take place in preference to twisting of the molecule from trigonal-antiprismatic toward trigonal-prismatic stereochemistry. The tropolonato ligands however appear to cause distortions toward trigonal-prismatic stereochemistry since the ligand is rigid and the bite remains almost fixed and is less than that in the acac$^-$ ligand. Kepert[3] has previously suggested that the stereochemistry of six-coordinated complexes will be influenced by the bite of the ligand. Second, for the series of 3d transition metal complexes containing trop$^-$ for which structural details are available, the value of Φ decreases in the order Co(trop)$_3$ > Mn(trop)$_3$ > Fe(trop)$_3$ > Sc(trop)$_3$. The cobalt(III) and manganese(III) ions, with electronic configurations d^6 and d^4, respectively, both have a preference toward trigonal-antiprismatic stereochemistry by consideration of ΔLFSE (TAP-TP) with the larger ΔLFSE being predicted for the cobalt(III) ion.[2] Co(trop)$_3$, with a value of $\Phi = 55°$, has a stereochemistry close to trigonal antiprismatic showing that in this case, the electronic preference almost completely overcomes the limitations due to 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 due to the ligand are the important factors and considerable distortion toward trigonal-prismatic stereochemistry is observed. For Mn(trop)$_3$ where there is a small ΔLFSE in favor of trigonal-antiprismatic stereochemistry, this factor and the opposing steric requirements of the ligand are both important in determining the stereochemistry adopted.

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

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(22) B. Morosin, *Acta Crystallogr.*, 22, 315 (1967).

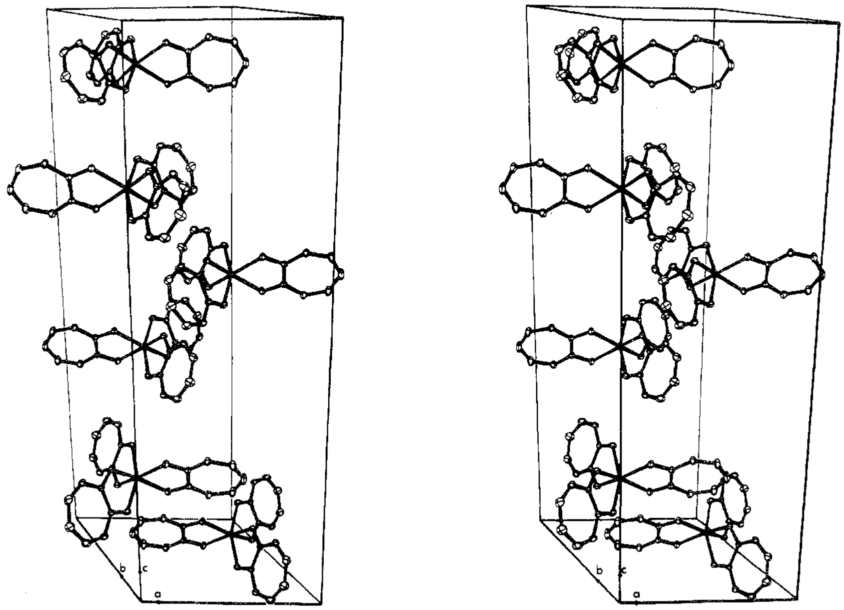

Figure 4. Stereoscopic view of tris(tropolonato)scandium(III); hydrogen atoms omitted for clarity.

Table V. 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	~60	*a*	2.10	2.52	74	33	*g*
V	d^2	1.98	2.75	88	56	*b*					
Cr	d^3	1.95	2.79	91	61	*c*					
Mn	d^4	1.93–2.0			~60	*d*	1.90–2.0	2.54	77–81	49	*d, h*
Fe	d^5	1.99	2.74	87	55	*e*	2.01	2.52	78	~40	*i*
Co	d^6	1.90	2.85	97	~60	*f*				~55	*j*
Al	d^0	1.89	2.73	92	60	*f*	1.89	2.49	82	48	*j*

[a] Reference 1. [b] B. Morosin and H. Montgomery, *Acta Crystallogr., Sect. B*, **25**, 1354 (1969). [c] B. Morosin, *Acta Crystallogr.*, 19, 131 (1965). [d] J. P. Fackler, Jr., private communication. [e] J. Iball and C. H. Morgan, *Acta Crystallogr.*, **23**, 239 (1967). [f] Reference 5. [g] This work. [h] J. P. Fackler, Jr., *Proc. Int. Conf. Coord. Chem.*, 14, 589 (1972). [i] Reference 11. [j] Reference 4.

The observed crystal and molecular structures for $Al(trop)_3$ and $Sc(trop)_3$ result from a combination of inter- and intramolecular contacts. In $Al(trop)_3$, with a twist angle of 48°, the intramolecular O· · ·O nearest neighbor contacts are almost equal at 2.7 Å. If a twist angle of 33° is introduced (as observed in $Sc(trop)_3$) two sets of O· · ·O contacts are predicted, those within the plane normal to the C_3 axis at 2.56 Å and those between the planes at 3.15 Å. (The corresponding contacts in $Sc(trop)_3$ are 3.05 and 3.25 Å, respectively.) Thus, as the twist angle decreases, *i.e.*, the stereochemistry approaches trigonal prismatic, the in-plane O· · ·O separations decrease while those between the planes increase. In Table VI, we have listed the predicted O· · ·O contacts for trigonal-prismatic stereochemistry for some $M(acac)_3$ and $M(trop)_3$ complexes. (For $acac^-$ the bite is assumed to be 2.8 Å, whereas for $trop^-$ the value is 2.5 Å.) It can be seen that for $acac^-$ complexes the O· · ·O van der Waals contact is not attained for TP stereochemistry until M–O bond lengths of ~2.10 Å are reached whereas for $trop^-$ complexes the value is reached for M–O bond lengths of ~2.0 Å. Further, we may consider the structure of $Al(trop)_3$ to be a deviation from TP stereochemistry due to the necessity of the molecule to increase the intramolecular O· · ·O contacts from 2.42 Å to the observed values, which are close to the van der Waals contacts. However, the distortion of $Sc(trop)_3$ from TP stereochemistry appears to arise for a different reason. The in-plane O· · ·O separations already exceed the van der Waals values. Therefore, although a TP stereochemistry could be stable for $Sc(trop)_3$ on a geometric basis, in the crystalline lattice a distortion toward trigonal-antiprismatic geometry is observed. We conclude that the molecular structure in the crystal is the result of intermolecular compressive forces which tend to reduce the volume of the molecule.

Table VI. 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 O· · ·O, Å acac	In-plane O· · ·O, Å trop	Out-of-plane O· · ·O, trop, Å
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
	2.20	2.94	3.14	4.01

Thus in predicting or discussing 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 interactions between these ligands must be considered since it is apparent that all these factors play important roles in the determination of the ultimate stereochemistry.

Finally, if the predictions of Muetterties and coworkers[4,6] are correct and one can correlate twist angles determined in the solid state with rearrangement pathways in solution, $Sc(trop)_3$ and its derivatives should undergo rapid intramolecular rearrangements due to the 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.

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Registry No. $Sc(C_7H_5O_2)_3$, 15388-96-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-158.

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Oxidation of Substituted Borane Anions to Coupled Polyhedral Ions[1]

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Electrochemical oxidations of both apical and equatorial isomers of $B_{10}H_9I^{2-}$ and $B_{10}H_9L^-$ (L = NH_3, $N(CH_3)_3$, $S(CH_3)_2$) ions have been studied in acetonitrile. Their behavior is analogous to that of the unsubstituted $B_{10}H_{10}{}^{2-}$ ion described in eq 1-3. The chemistry of the resulting $B_{20}H_{17}L_2{}^-$ and $B_{20}H_{16}L_2{}^{2-}$ ions and $B_{20}H_{16}L_2$ compounds parallels that of the unsubstituted $B_{20}H_{19}{}^{3-}$, $B_{20}H_{18}{}^{4-}$, and $B_{20}H_{18}{}^{2-}$ ions. The rates of reaction 2 for equatorial isomers show an increase with electron withdrawal as indicated by substituent σ_m values, which indicates that equatorial substituents have a primarily inductive effect on this reaction. Apical substituents have a more pronounced effect on the rates of reaction 2; an inversion of substituent effect is indicative of a change in the rate-limiting step under conditions of strong electron withdrawal.

$$B_{10}H_{10}{}^{2-} \rightleftarrows B_{10}H_{10}{}^{\cdot -} + e^- \qquad (1)$$

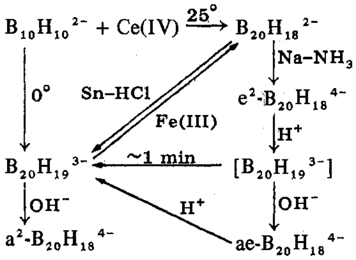
$$2B_{10}H_{10}{}^{\cdot -} \rightarrow B_{20}H_{19}{}^{3-} + H^+ \qquad (2)$$

$$B_{20}H_{19}{}^{3-} \rightarrow B_{20}H_{18}{}^{2-} + H^+ + 2e^- \qquad (3)$$

Introduction

Aqueous chemical oxidation of $B_{10}H_{10}{}^{2-}$ ion provided access to the interesting isomerism and redox chemistry of the $B_{20}H_{19}{}^{3-}$, $B_{20}H_{18}{}^{4-}$, and $B_{20}H_{18}{}^{2-}$ ions summarized in Scheme I. For the isomeric $B_{20}H_{18}{}^{4-}$ ions, the prefixes denote the linkages between B_{10} polyhedra shown in Figure 1, with a^2 indicating a B-B bond between apex boron atoms of the two B_{10} units, etc. The structure of the stable isomer of $B_{20}H_{19}{}^{3-}$ is apparently similar to that of ae-$B_{20}H_{18}{}^{4-}$, but with the B-B bond between B_{10} units protonated to form a BHB three-center bridge bond.[2] The structure of the unstable isomer of $B_{20}H_{19}{}^{3-}$ enclosed in brackets in Scheme I is not known, as it rapidly isomerizes in solution to the stable form.[2] Electrochemical oxidation of $B_{10}H_{10}{}^{2-}$ ion in acetonitrile parallels the aqueous chemical oxidation and is summarized by eq 1-3.[3]

Scheme I



$$B_{10}H_{10}{}^{2-} \rightleftarrows B_{10}H_{10}{}^{\cdot -} + e^- \qquad (1)$$

$$2B_{10}H_{10}{}^{\cdot -} \rightarrow B_{20}H_{19}{}^{3-} + H^+ \qquad (2)$$

$$B_{20}H_{19}{}^{3-} \rightleftarrows B_{20}H_{18}{}^{2-} + H^+ + 2e^- \qquad (3)$$

Relatively little is known about the reactions in Scheme I for substituted derivatives of $B_{10}H_{10}{}^{2-}$. The $B_{20}H_{18}{}^{2-}$ ion is subject to attack by hydroxide and methoxide ions, which leads to the chemistry of the B_{20} derivative ions $B_{20}H_{18}OR^{3-}$, $B_{20}H_{17}OR^{4-}$, and $B_{20}H_{17}OR^{2-}$.[4] Aqueous chemical oxidations of $B_{10}H_9L^-$ ions (L = $(CH_3)_2S$, tetramethylene sulfone, C_6H_5I, or $C_6H_5NO_2$) yield $B_{20}H_{16}L_2$ compounds which are derivatives of the $B_{20}H_{18}{}^{2-}$ ion (difference in overall charge can be viewed as resulting from substitution of a neutral Lewis base L for hydride ion as a "ligand" to boron). These $B_{20}H_{16}L_2$ compounds undergo the same reaction with base as does the $B_{20}H_{18}{}^{2-}$ ion.[5]

Electrochemical techniques can often be used to measure relatively rapid chemical reactions that follow electron transfers, such as reaction 2, and often provide clean and well-controlled conditions under which to carry out redox reactions on a preparative scale. We have examined the electrochemical oxidation of both apex and equatorial isomers of some derivatives of $B_{10}H_{10}{}^{2-}$ to determine their behavior in the context of Scheme I and the effect of substituents on reactions 1-3.

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(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of Kansas General Research Fund, for partial support of this research. (b) Taken in part from the Ph.D. thesis of A. P. Schmitt, University of Kansas, 1970.

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(5) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, 3, 1450 (1964).