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Coordination Chemistry of Scandium. V.[1]
Crystal and Molecular Structure of Tris(acetylacetonato)scandium(III)

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The crystal and molecular structure of tris(acetylacetonato)scandium(III), $Sc(C_5H_7O_2)_3$, has been determined by single-crystal X-ray diffraction technique. The compound crystallizes in the space group *Pbca*, with cell constants $a = 15.38$ (3), $b = 13.73$ (3), $c = 16.72$ (4) Å. Least-squares refinement of the counter data give a final R factor of 0.050 for 1088 significant reflections. The structure consists of discrete $Sc(C_5H_7O_2)_3$ molecules with slight deviations from D_3 symmetry. The coordination environment about the scandium ion is a distorted octahedron with an intrachelate oxygen–oxygen separation of 2.715 Å and an interchelate separation of 2.94–3.09 Å. The scandium–oxygen bond length, 2.070 Å, suggests a radius for the scandium(III) ion of 0.68 Å.

Introduction

Many coordination compounds of scandium have been synthesized recently,[2] although at the time the work described here was initiated, only one structural characterization of a scandium complex had been reported. In scandium formate, $Sc(HCOO)_3$, the scandium(III) ions are six-coordinated in a polymeric framework with formate ions acting as bridging groups.[3] The high final R factor (0.205) for this structure was attributed to the instability of the crystals, considerable decomposition taking place in the X-ray beam.

As part of our overall investigations into the coordination chemistry of scandium, we have begun a program of structural characterization. The aims of the program are to determine the coordination environment for the scandium ion and to draw conclusions concerning the mode of bonding for each compound studied. Several factors influenced the choice of tris(acetylacetonato)scandium(III) as the first compound to be studied. First, suitable crystals which are stable to both air and X-rays could readily be obtained and, second, because of the available structural information on other tervalent 3d transition element acetylacetonates,[4,5] comparisons could readily be drawn between the determined scandium structure and those of the other complexes. Using the information obtained, it should also be possible to derive an accurate value for the effective radius of the scandium(III) ion.

Experimental Section

Scandium(III) oxide, Sc_2O_3 (99.9%), was purchased from Research Organic/Inorganic Corp. Tris(acetylacetonato)scandium(III) (abbreviated $Sc(acac)_3$), was prepared according to the procedure of Morgan and Moss.[6] Suitable crystals were obtained by recrystallization from benzene.

Measurement of Crystal and Intensity Data. Preliminary investigations were conducted using the precession technique with Mo Kα radiation. Systematic absences of $k = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$, and $h = 2n + 1$ for $hk0$ establish the space group uniquely as *Pbca* in agreement with that reported by Ivanov and Petrukin.[7] 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, with the (002) plane in diffracting position was used to obtain monochromatic Mo Kα radiation. A takeoff angle of 3° was used. The radiation was detected using a scintillation counter with pulse height discrimination. The crystal (0.3 × 0.6 × 0.08 mm) was mounted with the b axis coincident with the ϕ axis of the diffractometer. The lattice parameters were determined at room temperature from 12 hand centered reflections (Table I). Intensities were measured by an ω-scan technique with ω scanned over a width of 0.8° at a rate of 1°/min. Data were measured to a maximum $2\theta = 45°$. Backgrounds were estimated by two 4-sec counts made one at each end of the scan using stationary-crystal, stationary-counter measurements. Three standard reflections were measured every 100 reflections. No decomposition of the crystal was noted, the average deviation from the mean intensity being ±1%. A total of 2676 independent reflections were scanned of which 1088 were considered to be above background using the criterion $I/\sigma(I) > 2.5$.

Table I. Crystal Data

Molecular formula	$Sc(C_5H_7O_2)_3$
Mol wt	342.29
Crystal habit	Plate
Crystal size, mm	0.3 × 0.6 × 0.08
μ, cm^{-1}	4.40
Space group	*Pbca*
a, Å	15.38 (3)
b, Å	13.73 (3)
c, Å	16.72 (4)
Z	8
V, Å^3	3531
d_{exptl},[a] g/ml	1.26
d_{calcd}, g/ml	1.29

[a] Measured by flotation in carbon disulfide.

Solution and Refinement of Structure. All calculations were carried out using the CDC 6500 computer at the Michigan State University Computer Center.[8] Scattering factors for the neutral atoms Sc, O, and C were obtained from ref 9 and those for hydrogen from ref 10. No corrections were made for absorption.

The positional coordinates of the scandium and six oxygen atoms were obtained from a three-dimensional Patterson[8a] map. Structure factors were calculated based on these atomic positions and used to produce a Fourier map[8a] from which the atomic positions of the carbon atoms were obtained. Isotropic thermal parameters of 3.5 Å^2 were assigned to all atoms at this point, and after four cycles of least-squares refinement[8b] on positional and thermal parameters, a difference Fourier was generated. This yielded atomic positions for all methyl hydrogens. The coordinates of the hydrogen atoms on the γ carbons were obtained by assuming a unit vector on a line from the

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(1) Part IV: M. R. Wagner and G. A. Melson, *J. Inorg. Nucl. Chem.*, in press.

(2) G. A. Melson and R. W. Stotz, *Coord. Chem. Rev.*, 7, 133 (1971).

(3) M. K. Guseinova, A. S. Antsyshkina, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 9, 1040 (1968); *J. Struct. Chem. (USSR)*, 9, 926 (1968).

(4) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 88, 2951 (1966).

(5) B. Morosin and H. Montgomery, *Acta Crystallogr., Sect. B*, 25, 1354 (1969).

(6) G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, 189 (1914).

(7) V. I. Ivanov and O. M. Petrukin, *Sov. Phys.–Crystallogr.*, 15, 492 (1970).

(8) We list the major computer programs used in the analysis: (a) M. A. Neuman, CONNIE, a Fortran Fourier summation program; (b) WRFLS, a least-squares refinement program based on ORFLS of W. Busing, K. Martin, and H. Levy; (c) ORFFE, function and error analysis program by Busing, Martin, and Levy; (d) C. K. Johnson, ORTEP II: "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations."

(9) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

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

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

Atoms[b]	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sc	0.1434 (1)	0.2687 (1)	0.2418 (1)	0.00419 (6)	0.00474 (7)	0.00279 (5)	0.00071 (8)	0.00004 (7)	0.00001 (7)
O1(1)	0.0704 (4)	0.3526 (4)	0.3189 (3)	0.0057 (3)	0.0061 (4)	0.0038 (2)	0.0002 (3)	0.0014 (3)	−0.0012 (3)
O2(1)	0.0386 (3)	0.1749 (4)	0.2539 (4)	0.0040 (3)	0.0057 (4)	0.0057 (3)	0.0002 (3)	0.0003 (3)	−0.0013 (3)
O1(2)	0.0966 (4)	0.3367 (4)	0.1394 (3)	0.0063 (3)	0.0065 (4)	0.0034 (3)	0.0018 (3)	−0.0009 (2)	0.0000 (3)
O2(2)	0.1979 (4)	0.1760 (4)	0.1569 (3)	0.0066 (4)	0.0052 (4)	0.0037 (3)	0.0012 (3)	0.0003 (2)	−0.0005 (3)
O1(3)	0.2441 (4)	0.3671 (4)	0.2524 (4)	0.0051 (3)	0.0052 (3)	0.0056 (3)	−0.0001 (3)	−0.0001 (4)	0.0006 (3)
O2(3)	0.2125 (4)	0.1968 (4)	0.3293 (3)	0.0052 (4)	0.0056 (4)	0.0045 (3)	−0.0004 (3)	−0.0006 (3)	0.0011 (3)
C1(1)	−0.0313 (8)	0.4222 (9)	0.4052 (7)	0.0115 (9)	0.0123 (10)	0.0059 (5)	0.0039 (8)	0.0034 (6)	−0.0004 (6)
C2(1)	−0.0015 (7)	0.3396 (7)	0.3519 (5)	0.0066 (6)	0.0078 (8)	0.0036 (4)	0.0016 (6)	0.0013 (4)	0.0006 (4)
C3(1)	−0.0531 (6)	0.2589 (8)	0.3417 (6)	0.0053 (5)	0.0079 (7)	0.0062 (5)	0.0008 (6)	0.0024 (4)	0.0015 (5)
C4(1)	−0.0304 (6)	0.1796 (6)	0.2944 (6)	0.0055 (5)	0.0045 (6)	0.0066 (5)	0.0008 (5)	−0.0003 (4)	0.0019 (4)
C5(1)	−0.0906 (6)	0.0937 (8)	0.2875 (6)	0.0051 (5)	0.0085 (7)	0.0084 (6)	0.0007 (5)	0.0009 (5)	0.0003 (5)
C1(2)	0.0535 (8)	0.3832 (9)	0.0107 (6)	0.0115 (9)	0.0143 (10)	0.0051 (5)	0.0009 (9)	−0.0015 (6)	0.0027 (6)
C2(2)	0.0998 (6)	0.3137 (7)	0.0666 (5)	0.0070 (6)	0.0079 (6)	0.0031 (4)	−0.0012 (6)	−0.0012 (4)	0.0006 (4)
C3(2)	0.1424 (7)	0.2339 (8)	0.0363 (5)	0.0085 (6)	0.0104 (8)	0.0033 (3)	0.0017 (7)	0.0000 (4)	−0.0018 (5)
C4(2)	0.1887 (6)	0.1690 (6)	0.0826 (6)	0.0055 (5)	0.0061 (7)	0.0044 (4)	−0.0008 (5)	0.0008 (4)	−0.0012 (4)
C5(2)	0.2368 (8)	0.0864 (9)	0.0425 (6)	0.0101 (8)	0.0101 (9)	0.0070 (5)	−0.0007 (7)	0.0021 (6)	−0.0037 (6)
C1(3)	0.3630 (7)	0.4610 (7)	0.2932 (7)	0.0090 (7)	0.0088 (7)	0.0084 (6)	−0.0036 (7)	0.0002 (6)	−0.0017 (5)
C2(3)	0.3088 (6)	0.3716 (6)	0.2964 (6)	0.0061 (5)	0.0053 (6)	0.0050 (4)	−0.0004 (5)	0.0004 (4)	−0.0012 (4)
C3(3)	0.3330 (6)	0.2977 (8)	0.3486 (6)	0.0056 (6)	0.0093 (8)	0.0056 (5)	−0.0009 (5)	−0.0019 (4)	0.0002 (5)
C4(3)	0.2851 (7)	0.2139 (7)	0.3607 (5)	0.0064 (6)	0.0084 (8)	0.0044 (4)	0.0020 (6)	−0.0007 (4)	0.0013 (5)
C5(3)	0.3195 (7)	0.1378 (10)	0.4176 (7)	0.0083 (7)	0.0166 (12)	0.0080 (6)	0.0005 (8)	−0.0026 (6)	0.0059 (8)

[a] The 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] The numbers in parentheses refer to the ring number.[8c]

Table III. Hydrogen Atom Positions ($B = 8.0$ Å^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
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 standard deviation ±0.006 for all values. [b] The atoms are labeled as follows: 1-3 attached to C1; 4 to C3; 5-7 to C5. The numbers in parentheses correspond to the ring number.

scandium to the γ-carbon atom. At this point the unweighted reliability factor, R_1, was 0.12 ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). Further refinement using anisotropic temperature factors for all nonhydrogen atoms was then carried out. An isotropic temperature factor of 8.0 Å^2 was assigned for the hydrogens, based on the final isotropic thermal parameters of the methyl carbons. This value was not permitted to vary. At convergence, a value of 0.050 was obtained for R_1 and of 0.067 for R_2 [$R_2 = \Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ where $w = 1/\sigma^2(F)$. [$\sigma(F) = 0.05F$ for $F > 4F_{\min}$ and $\sigma(F) = 0.20F_{\min}$ for $F < 4F_{\min}$. $F_{\min} = 9.46$.] The two strongest reflections (020 and 002) were omitted from the least-squares refinement.

The atomic positions and anisotropic thermal parameters of the nonhydrogen atoms as obtained from the final least-squares cycle are given in Table II and the refined hydrogen atom positions in Table III. In the final cycle, no parameter shift was greater than 0.2 of the associated standard deviation (esd). Observed and calculated structure factor amplitudes are available.[11]

Description of Structure and Discussion

In Sc(acac)$_3$, the *b* axis is nearly parallel with the molecular C_3 axis. A view down this C_3 axis (Figure 1) shows the numbering scheme adopted, bond lengths, and the 20% probability envelopes of the anisotropic thermal ellipsoids.[8d] Stereoscopic views of the molecule and the unit cell down the *b* axis are shown in Figures 2 and 3. Intramolecular distances and angles together with their estimated standard deviations[8c] are listed in Table V.

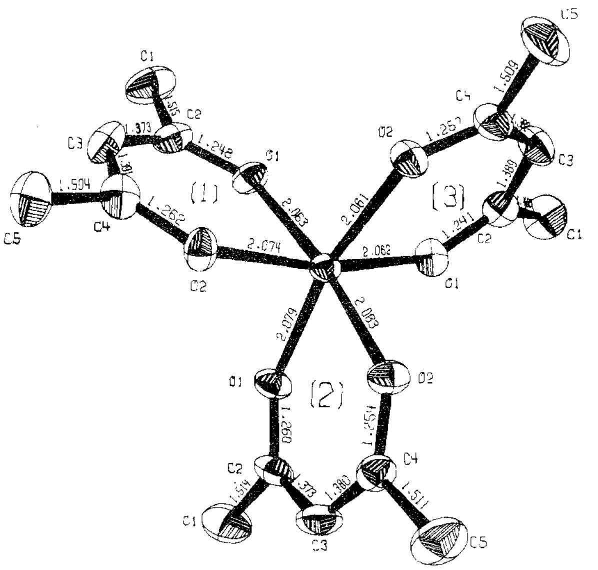

Figure 1. ORTEP view of Sc(acac)$_3$ showing numbering scheme, adopted bond lengths, and the 20% probability envelopes of the anisotropic thermal ellipsoids.

The structure consists of discrete Sc(acac)$_3$ molecules within the unit cell. The molecules have virtual D_3 symmetry, with the chelate rings showing only slight deviations from planarity (Table VI). These deviations are probably the result of intermolecular forces which cause rotations about the O1 · · · O2 vector and about the Sc γ carbon (C3) of the ring. Thus the former effect can account for the Sc atom being

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(11) Table IV, a listing of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth 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-73-927.

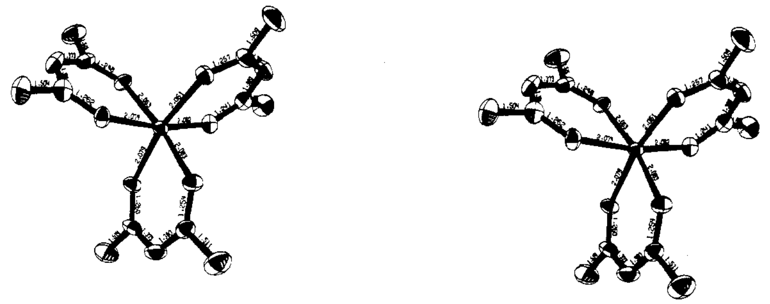

Figure 2. Stereoscopic view of Sc(acac)$_3$ down the C_3 axis of the molecule.

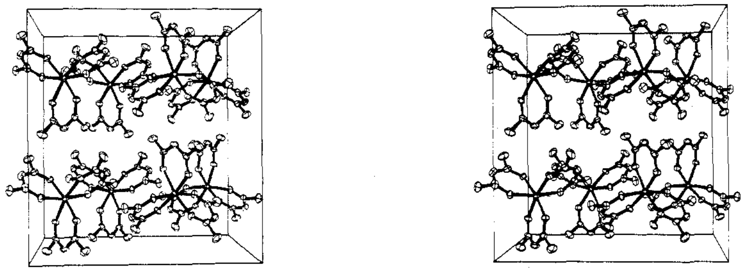

Figure 3. Stereoscopic view of the unit cell of Sc(acac)$_3$ down the *b* axis.

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

	Distances		
Sc-O1(1)	2.062 (6)	C2(1)-C3(1)	1.373 (13)
Sc-O2(1)	2.073 (5)	C3(1)-C4(1)	1.390 (13)
Sc-O1(2)	2.079 (6)	C2(2)-C3(2)	1.373 (13)
Sc-O2(2)	2.082 (6)	C3(2)-C4(2)	1.379 (12)
Sc-O1(3)	2.062 (7)	C2(3)-C3(3)	1.389 (13)
Sc-O2(3)	2.061 (6)	C3(3)-C4(3)	1.382 (13)
Av	2.070 (9)[b]	Av	1.381 (8)[b]
O1(1)-C2(1)	1.248 (10)	O1(1)-O2(1)	2.717 (7)
O2(1)-C4(1)	1.261 (10)	O1(2)-O2(2)	2.716 (8)
O1(2)-C2(2)	1.259 (10)	O1(3)-O2(3)	2.713 (8)
O2(2)-C4(2)	1.254 (10)	Av	2.715 (5)[b]
O1(3)-C2(3)	1.240 (10)		
O2(3)-C4(3)	1.257 (11)	O1(1)-O1(2)	3.037 (10)
Av	1.253 (11)[b]	O1(1)-O1(3)	2.900 (9)
		O1(2)-O1(3)	2.981 (9)
C1(1)-C2(1)	1.514 (14)	O2(1)-O2(2)	2.938 (9)
C4(1)-C5(1)	1.504 (12)	O2(1)-O2(3)	2.972 (9)
C1(2)-C2(2)	1.513 (14)	O2(2)-O2(3)	2.907 (10)
C4(2)-C5(2)	1.511 (13)	O1(1)-O2(3)	3.063 (9)
C1(3)-C2(3)	1.485 (12)	O1(2)-O2(1)	3.065 (9)
C4(3)-C5(3)	1.509 (13)	O1(3)-O2(2)	3.152 (9)
Av	1.506 (14)[b]		
	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)	132.1 (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 W. Blaedel and V. Meloche, "Elementary Quantitative Analysis," Row, Peterson, and Co., Evanston, Ill., 1957, p 557.

Table VI. 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. 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.

out of the plane for ring 2. A deviation of 0.15 Å 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 C1 and C5 atoms are appreciably out of the plane for ring 3. These effects may also be invoked to explain the deviations from ideal ligand planes also observed in other acac complexes.[12,13]

The intermolecular contacts observed are, in general, long as compared to close-packed organic structures. The shortest H···H contact is 2.49 Å, while for C···H approaches the shortest is 2.95 Å. For O···H approaches one value at 2.56 Å is obtained while all others are close to 3 Å.

The bond lengths and angles within the acac ligands are similar to those reported for other complexes.[4] In Table V we list the oxygen-oxygen separations for the molecule. The average intrachelate separation (2.715 Å) usually referred to as the "bite" of the ligand is similar to that found in other tervalent acac complexes.[4] For the interchelate separations, two types differing in distance are found. For the oxygens in planes and related by the C_3 axis, the separations average 2.956 Å, whereas those between these planes average 3.093 Å. It is thus clear that considerable distortion from a regular octahedral environment is observed for the coordination of the scandium(III) ion. In contrast, for the Cr(acac)$_3$ complex[14] a nearly regular octahedron is found, with the intrachelate oxygen-oxygen separations averaging 2.786 Å and the interchelate separations 2.751 Å. The interchelate separations in Sc(acac)$_3$, all of which are larger than the minimum

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

(13) Although deviations of the metal and methyl carbon atoms are quoted in Morosin's paper,[12] no directions relative to the plane are mentioned.

(14) B. Morosin, *Acta Crystallogr.*, 19, 131 (1965).

van der Waals contact distance found in other acac complexes[4] (*ca.* 2.6 Å), indicate that the rings may behave independently within the molecule. This nonrigid stereochemistry then allows the rotations described earlier to take place.

The determination of the scandium-oxygen bond length, 2.070 Å, in Sc(acac)$_3$ enables a value for the scandium(III) radius to be obtained. Using the relationship of Lingafelter and Braun[4] between the metal-oxygen bond length and the ionic radius of metal ions with rare gas configurations in acetylacetonate complexes, a value of 0.68 Å is obtained for the radius of the scandium(III) ion. The same authors also found for these complexes that the metal-oxygen bond length is in good agreement with the sum of the Pauling radii.[15] However, the use of the Pauling radius for the scandium(III) ion, 0.81 Å, predicts an Sc-O bond length of 2.20 Å, considerably longer than that observed. Since the crystals used to establish Pauling's radii for scandium(III) were ionic in nature, our determined value of 0.68 Å is a more acceptable one for use in coordination compounds of scandium where covalent character is expected to be present in the scandium-donor atom bond.[16]

Registry No. Sc($C_5H_7O_2$)$_3$, 14284-94-7.

Acknowledgment. We wish to thank the National Science Foundation (Grant GP-28235) for financial assistance.

[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 514.

[16] Since this work was completed, Smith and Atwood[17] have reported the crystal and molecular structure of $[(C_5H_5)_2ScCl]_2$. A similar value of 0.68 Å was obtained for the scandium(III) radius from the Sc–C bond distance.

[17] K. D. Smith and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 593 (1972).

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Crystal Structure of Stannic Phthalocyanine, an Eight-Coordinated Tin Complex

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The molecular configuration of stannic phthalocyanine, $Sn(C_{32}H_{16}N_8)_2$, has been determined by three-dimensional X-ray analysis. The orthorhombic cell dimensions (at 22°) and space group are $a = 10.547 \pm 0.001$, $b = 50.743 \pm 0.004$, and $c = 8.9046 \pm 0.0009$ Å; $Z = 4$; $d_c = 1.59$, $d_m = 1.60 \pm 0.01$ g/cm^3; and $P2_12_12_1$. The final parameters were determined from 2168 independent reflections measured by counter methods. The least-squares fitting of the data refined to $R_1 = 6.8\%$. The two phthalocyanine ring systems form a sandwich-type compound with the tin atom in the center. The cores of the phthalocyanine moieties are separated from each other by 2.70 ± 0.04 Å and are rotated 42° with respect to each other. The eight isoindole nitrogen atoms form an antiprism about the tin atom with Sn–N distances (individually ±0.02 Å) ranging from 2.32 to 2.37 Å and the average Sn–N distance being 2.347 ± 0.007 Å.

Introduction

Recently, there has been a great deal of interest in compounds which show a coordination number of 8 for a metal atom.[1,2] Several crystal structures of eight-coordinated metal complexes have been reported in which the configuration around the metal atom is either an antiprism or a dodecahedron. The coordination groups of the $Mo(CN)_8{}^{4-}$ ion[3] and the tetrakis(oxalato)zirconate(IV) ion[4] are dodecahedral. The fluoride ions in $TaF_8{}^{3-}$ form a square antiprism around the tantalum atom.[5] All of these eight-coordinated complexes involve a transition metal atom.

A series of tin(IV) complexes has been prepared in which the tin atom seems to be eight-coordinated. The first of these to be prepared was the potassium tin(IV) oxalate[6] in which four oxalate anions appear to coordinate as bidentate ligands to the tin atom. More recently, tin(IV) nitrate[7] was shown by infrared evidence to contain four nitrate groups which also coordinate as bidentate ligands. Ramaiah and Martin found that a tin-phenyl cleavage of diphenylbis(8-quinolinato)tin(IV), using 8-quinolinol at 300°, yielded tetrakis(8-quinolinato)tin(IV) which appears to be eight-coordinated.[2]

Probably the best known of the postulated eight-coordinated tin compounds is stannic phthalocyanine. The phthalocyanine molecule is a rigid, macrocyclic compound which behaves as a dinegative anion. In 1936 Linstead prepared the tin(IV) phthalocyanine[8] which had a stoichiometry corresponding to two phthalocyanine groups per tin atom. It was believed that the two phthalocyanine rings formed a sandwich-type compound with a tin atom in the center. Only configurations ranging between the cubic or square-antiprismatic extremes are possible because of the rigidity of the phthalocyanine rings. The Mossbauer spectrum[9] is consistent with the symmetrical configuration of eight isoindole nitrogen atoms around the tin atom, but it does not distinguish between the cubic and antiprismatic arrangements.

The X-ray crystallographic study was carried out to determine the actual configuration of the nitrogen atoms around the tin atom and to determine whether the phthalocyanine rings retain the same structure as in other metal phthalocyanine compounds in which the metal atom is found in the

[1] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963).

[2] K. Ramaiah and D. F. Martin, *Chem. Commun.*, 130 (1965).

[3] J. L. Hoard and H. H. Nordsieck, *J. Amer. Chem. Soc.*, 61, 2853 (1939).

[4] G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 2, 250 (1963).

[5] J. L. Hoard, W. J. Martin, M. E. Smith, and J. E. Whitney, *J. Amer. Chem. Soc.*, 76, 3820 (1954).

[6] H. Lienau, K. Bierbrauer, and M. Platsch, *Z. Anorg. Chem.*, 20, 281 (1899).

[7] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

[8] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1719 (1965).

[9] M. C. O'Rourke and C. Curran, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11-16, 1966, No. V-180.