We are currently studying whether the iron and manganese nitrosyl porphyrins undergo similar reactions with oxygen.

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Registry No. $O_2N(3,5\text{-lut})CoTPP$, 51364-55-7.

Supplementary Material Available. A listing of the observed and calculated structure factor amplitudes (× 10) 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, 24× reduction, negatives) containing all of the supplementary material for the papers of 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1875.

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada

Eight-Coordination and Hydrogen Bonding in a Complex of Scandium: Crystal Structure of the Acid Dimer of Tetrakis(tropolonato)scandium(III)

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The acid dimer of tetrakis(tropolonato)scandium(III) $(HScT_4)_2$ crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 11.624$ (3) Å, $b = 11.986$ (3) Å, $c = 10.004$ (3) Å, $\alpha = 95.33$ (1)°, $\beta = 116.27$ (1)°, $\gamma = 102.32$ (1)°, and $Z = 2$. Of the 4212 reflections measured by counter methods (Mo Kα radiation λ_{α_1} 0.70926 Å), 2732 $\geqslant 2.3\sigma$ were used for structure determination. Full-matrix least-squares refinement gave a final R factor of 5.9%. The molecules exist as centrosymmetrically related hydrogen-bonded dimers (O···O separation of 2.484 (4) Å). Each scandium atom is eight-coordinate; oxygen atoms are at the vertices of a polyhedron which is best described as an irregular bicapped trigonal prism distorted toward a dodecahedron (Sc–O lengths range from 2.161 (3) to 2.310 (3) Å). The four tropolonato ligands are of three types. Two are symmetrically coordinated and show regularly decreasing C–C bond lengths with increasing distance from the oxygen atoms. The other two rings are asymmetrically coordinated and are different from each other; the differences in ring type can be attributed to the degree of hydrogen bond involvement. The hydrogen atom is asymmetrically placed (despite the short O···O contact) and this is further reflected by the different bond length alternation in these two rings.

Introduction

The many chelated species that occur in high coordination have been thoroughly reviewed,[1,2] and the delicate balance between configurational types in eight-coordination can be conveniently studied in complexes having multidentate ligands. The tropolonato ligand, $C_7H_5O_2^-$ (abbreviated to T^-), forms stable complexes with many different metals; its compact shape, skeletal rigidity, and small interoxygen atom separation make it a very suitable ligand for attempting to force a high coordination number.

The lightest covalently bonded eight-coordinate atom known to us is scandium in the form of the tetrakis(tropolonato)scandium(III) anion[3] shown originally as $M^+ScT_4^-$ where $M^+ = H^+$ or Na^+. The initial intention in studying $HScT_4$ was to determine the arrangement of the eight-coordinated oxygens about scandium and to correlate this arrangement with the existing theories of high coordination geometry due originally to Hoard and coworkers[4] and recently extended to the M(biden)$_4$ system by Kepert and Blight.[5]

Experimental Section

The species $HScT_4$ was prepared according to the method reported by Muetterties and Wright.[1] Scandium chloride (0.01 mol) was dissolved in water and added to a solution of tropolone (0.04 mol) in ethanol; crystallization was carried out by adding acetonitrile to the reaction mixture and allowing the solvent to evaporate slowly over a number of days. Small yellow crystals were obtained, and one of approximate dimensions 0.13 × 0.22 × 0.40 mm was mounted for the purpose of data collection.

Weissenberg photographs of the reciprocal lattice layers $hk0$ and $hk1$ and precession photographs of the $h0l$ and $0kl$ zones were taken using copper radiation (λ 1.5418 Å), and as a result of these, triclinic Laue symmetry was assigned.

Accurate dimensions were determined from counter measurement of 29 of the strongest reflections having $2\theta > 25°$, using a Picker FACS-1 computer-controlled four-circle diffractometer and Mo $K\alpha_1$ radiation (λ 0.70926 Å). The takeoff angle was 1.0°, and the crystal was mounted with the c axis (corresponding to the needle axis) approximately parallel to the ϕ axis.

Crystal Data. $HScT_4$, formula weight 530.42, crystallizes in the triclinic space group $P\bar{1}$: $a = 11.624$ (3) Å, $b = 11.986$ (3) Å, $c = 10.004$ (3) Å, $\alpha = 95.33$ (1)°, $\beta = 116.27$ (1)°, $\lambda = 102.32$ (1)°, $V = 1207.2$ Å^3, $d_m = 1.46$ (2) g cm^{-3} (flotation), $Z = 2$, $d_x = 1.46$ g cm^{-3}, μ(Mo Kα) = 3.69 cm^{-1}, $T = 21°$ (±1°).

Reflections for the unique set of data for $\sin\theta < 0.4226$ were collected using a scintillation detector with pulse height analysis. Measurement was made using niobium-filtered molybdenum radiation (λ(Mo Kα) 0.70926 cm^{-1}) and a takeoff angle of 3.0° with a symmetrical θ–2θ scan of 1.6° base width increased to allow for α_1–α_2 dispersion. Background counts of 10 sec were measured at both scan limits. After each 70 reflections, 2 standard reflections were measured; their variation was ±3.0% over the entire data collection. The intensities were corrected for Lorentz and polarization effects; absorption was neglected since it was estimated to introduce a maximum error of ±3.0% in I. A total of 4212 reflections were measured, of which 2732 were considered observed (*i.e.*, greater than 2.3σ, where $\sigma_I(\text{net}) = [\text{TC} + (t_st_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$ where TC is the total count, B_1 and B_2 are the background counts at each end of the scan range, t_s is the scan time, t_b is the total background-count time, k is a constant set to 0.03, and I is the net count.)

Structure Determination and Refinement. Examination of the

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(1) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967).

(2) S. J. Lippard, *Progr. Inorg. Chem.*, 8, 109 (1967).

(3) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, 87, 4706 (1965).

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

(5) D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 11, 1556 (1972).

three-dimensional Patterson function based on all data gave the position of the scandium atom and seven oxygens. Refinement of the scale and these atomic coordinates gave $R = 0.474$ where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. A Fourier synthesis revealed the other oxygen and five carbon atoms. Three cycles of refinement and subsequent electron density difference maps gave the remaining carbon atom positions. Hydrogen atom positions (except for the proton) were found after a further cycle of refinement. With the nonhydrogen atoms refined anisotropically and $R = 0.062$, the remaining proton position was found between oxygen atoms O_1 and O_3' on a centrosymmetrically related molecule. Because the O_1-O_3 separation was so short (2.48 Å), a symmetrical arrangement was assumed and the proton was placed at the midpoint of the line joining the oxygen atoms. Upon refinement, however, the shifts indicated that this was not a valid assumption, and the final position is that resulting from refinement of the original parameters obtained from the difference map.

Using an inner set of data, hydrogen atom positions and temperature factors, together with the positions of the carbon atoms and oxygen atoms O_1 and O_3, were refined. Two of the hydrogen temperature factors were not well behaved and the other values were averaged to give a final hydrogen atom temperature factor of 3.4 Å^2. The hydrogen atomic positions and isotropic temperature factor of the proton only were included along with all other coordinate and temperature factor parameters in the final two cycles of full-matrix least-squares refinement which gave an R factor of 0.059 for all the observed data. In the early refinement, constant unit weights were used; in the final stages, weights ($=1/\sigma^2(F)$) were given in terms of $\sigma(F) = \sigma_I/(Lp)(2F_o)$. Atomic scattering factors used were taken from ref 6 and included corrections for anomalous dispersion for the scandium atom ($\Delta f' = 0.2$, $\Delta f'' = 0.5$).

Crystallographic computer programs used in this determination have been cited elsewhere.[7] A table of the measured and calculated structure factors (×10) is available.[8]

Final atomic parameters and thermal parameters are listed in Table I. Interatomic distances and angles (uncorrected for thermal motion) for the "ScO_8" polyhedron are given in Table II. Least-squares planes relevant to the discussion are given in Table III and geometrical parameters for the oxygen atom configuration in Table IV. Interatomic distances and angles for the tropolonato ligands are given in Tables V and VI. A perspective view of the acid dimer (Figure 1), a diagram of the oxygen atom configuration (Figure 2), and a diagram of generalized eight-coordination (Figure 3) are also given.

Thermal Motion. Rigid-body analysis[9] shows that the ScT_4^- anion is not well described in terms of rigid-body motion; however, each of the four ligands gives good agreement (rings 1 and 2 give the best fit consistent with their reduced thermal motion which we attribute to their hydrogen bond participation and "internal" position in the dimer). An alternative model where each oxygen atom is assumed to ride independently on the Sc atom lengthens the Sc-O bond lengths by 0.002-0.006 Å for O_1-O_4 and 0.006 Å for O_5-O_8. If the Sc and coordinated oxygen atoms "kernel" were assumed to form a rigid body, then the corrections would be 0.001-0.004 Å. Our view of the motion is that the "ScO_8" riding model gives too large a correction (the oxygen atom motion not being independent) while the "ScO_8" rigid-body model is probably an underestimate. In any event the uncorrected Sc-O distances are too short by *at least* one standard error.

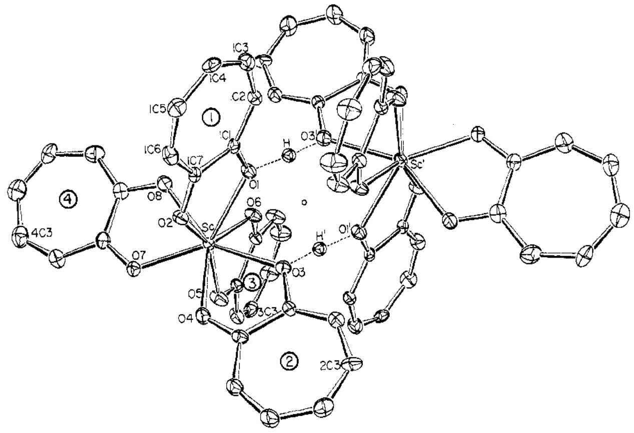

Figure 1. Perspective view of the acid dimer of tetrakis(tropolonato)scandium, illustrating the thermal motion ellipsoids (50%) and labeling.

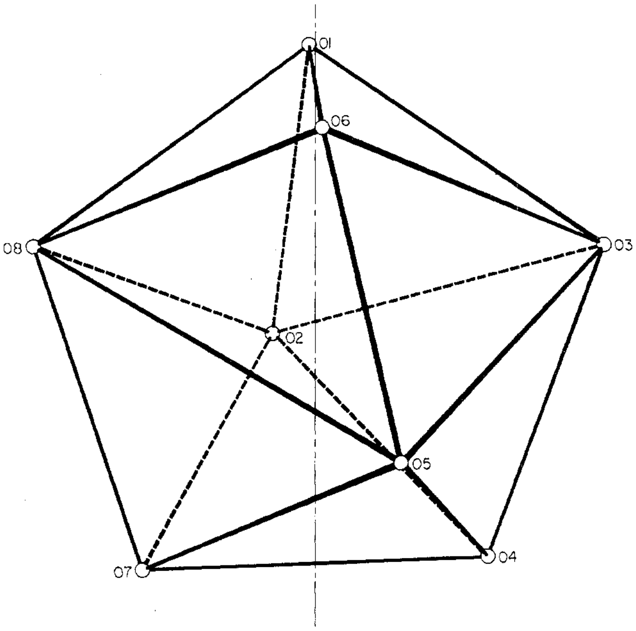

Figure 2. Perspective view of the irregular bicapped trigonal prism as observed in the $HScT_4$ dimer. The distortion toward a dodecahedron is illustrated by the vertical broken line which indicates the direction of the approximate $\bar{4}$ axis.

Discussion

The "ScO_8" Configuration. In order to establish a useful description of the polyhedron defined by the eight oxygen atoms, we have used two approaches. The first is based on criteria established by Porai-Koshits and Aslanov[10a] who, in treating polyhedra of the dodecahedron class (the regular dodecahedron, bicapped trigonal prism, and square antiprism), defined the set of dihedral angles, δ, between pairs of faces which intersect along the "type b" edges of a dodecahedron. These "type b" edges can be seen from Figure 2 as those which connect vertices at which five edges are joined (*i.e.*, O_2, O_3, O_5, and O_8 in this case). An additional criterion given by Porai-Koshits and Aslanov is the degree of nonplanarity of the diagonal trapezoids which characterize the dodecahedral shape. Distortions from the regular dodecahedron lead to a twisting of these trapezoids, and the corresponding parameter, ϕ, has been calculated for the trapezoids (defined by $O_1O_6O_5O_2$ and $O_3O_4O_7O_8$) according to Porai-Koshits and Aslanov's method, and is listed together with δ values for $HScT_4$ and the three regular polyhedra of this class in Table IVa. It is clear from a comparison of these results that the "ScO_8" polyhedron is best described[10] as an irregular bicapped trigonal prism distorted toward a dodecahedron.

Blight and Kepert[5] have produced a description of the effect of bidentate ligands on eight-coordination. They showed that potential energy surfaces produced by ligand-ligand repulsion are critically dependent on the parameter b (the ratio of the donor atom separation to the metal-donor atom distance). For various values of b, they gave the di-

(6) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(7) F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, 11, 395 (1972).

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

(9) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 24, 63 (1968).

(10) (a) M. A. Porai-Koshits and Aslanov, *Zh. Strukt. Khim.*, 13, 266 (1972); (b) E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 96, 1748 (1974).

Table I.

a. Fractional Atomic Coordinates in Crystalline $HScT_4$ ($\times 10^4$; $\times 10^3$ for H)[a]

Atom type	x	y	z	Atom type	x	y	z
Sc	1231 (1)	−1682 (1)	−484 (1)	3C$_7$	−1725 (4)	−2811 (4)	−1785 (5)
O$_1$	866 (3)	74 (2)	−1063 (3)	4C$_1$	1851 (4)	−3263 (4)	−2442 (5)
O$_2$	3089 (3)	−362 (2)	0 (3)	4C$_2$	2296 (5)	−4180 (4)	−2841 (6)
O$_3$	1157 (3)	−695 (2)	1500 (3)	4C$_3$	2146 (6)	−4677 (5)	−4226 (7)
O$_4$	2736 (3)	−1879 (2)	1744 (3)	4C$_4$	1543 (6)	−4395 (5)	−5615 (7)
O$_5$	157 (3)	−3255 (2)	−146 (4)	4C$_5$	947 (6)	−3516 (5)	−5962 (6)
O$_6$	−901 (3)	−1850 (2)	−1604 (3)	4C$_6$	731 (5)	−2746 (5)	−5042 (6)
O$_7$	2096 (3)	−2951 (2)	−1062 (3)	4C$_7$	1081 (4)	−2616 (4)	−3486 (6)
O$_8$	735 (3)	−1863 (3)	−2872 (3)	1H$_2$	72 (4)	193 (4)	−187 (5)
1C$_1$	1832 (4)	901 (3)	−1006 (4)	1H$_3$	204 (4)	352 (4)	−195 (5)
1C$_2$	1604 (5)	1915 (4)	−1497 (5)	1H$_4$	414 (4)	394 (4)	−122 (5)
1C$_3$	2455 (5)	2896 (4)	−1530 (6)	1H$_5$	559 (4)	275 (4)	−19 (5)
1C$_4$	3806 (5)	3155 (4)	−1057 (6)	1H$_6$	503 (4)	104 (4)	25 (5)
1C$_5$	4626 (5)	2465 (4)	−441 (6)	2H$_2$	148 (4)	55 (4)	384 (5)
1C$_6$	4338 (4)	1390 (4)	−131 (5)	2H$_3$	270 (4)	81 (4)	624 (5)
1C$_7$	3115 (4)	627 (4)	−357 (5)	2H$_4$	428 (4)	−7 (4)	748 (5)
2C$_1$	2043 (4)	−630 (4)	2939 (5)	2H$_5$	498 (4)	−128 (4)	662 (5)
2C$_2$	2070 (5)	83 (4)	4100 (5)	2H$_6$	434 (4)	−212 (4)	421 (5)
2C$_3$	2904 (5)	270 (5)	5677 (5)	3H$_2$	−123 (4)	−516 (4)	−26 (5)
2C$_4$	3866 (6)	−232 (5)	6450 (6)	3H$_3$	−330 (4)	−612 (4)	−145 (5)
2C$_5$	4274 (5)	−1084 (5)	5861 (6)	3H$_4$	−503 (4)	−556 (4)	−311 (5)
2C$_6$	3871 (1)	−1560 (5)	4385 (5)	3H$_5$	−505 (4)	−386 (4)	−387 (5)
2C$_7$	2906 (4)	−1373 (4)	2998 (5)	3H$_6$	−326 (5)	−233 (4)	−321 (5)
3C$_1$	−1121 (4)	−3641 (4)	−927 (5)	4H$_2$	279 (4)	−438 (4)	−200 (5)
3C$_2$	−1796 (5)	−4737 (4)	−891 (6)	4H$_3$	253 (4)	−532 (4)	−419 (5)
3C$_3$	−3145 (5)	−5337 (4)	−1677 (6)	4H$_4$	165 (4)	−481 (4)	−632 (5)
3C$_4$	−4211 (5)	−5003 (5)	−2690 (6)	4H$_5$	80 (4)	−338 (4)	−704 (5)
3C$_5$	−4175 (5)	−3951 (5)	−3139 (6)	4H$_6$	31 (4)	−217 (4)	−546 (5)
3C$_6$	−3106 (5)	−2994 (4)	−2748 (6)	H	−27 (5)	31 (5)	−127 (6)

b. Thermal Motion Parameters in Crystalline $HScT_4$ ($\times 10^3$ Å^2; $\times 10^4$ Å^2 for Sc)[b]

Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}	Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Sc	261 (5)	275 (5)	293 (5)	126 (4)	109 (4)	73 (4)	2C$_4$	70 (4)	99 (5)	20 (3)	44 (4)	6 (3)	6 (3)
O$_1$	25 (2)	28 (2)	44 (2)	10 (1)	17 (1)	12 (1)	2C$_5$	54 (3)	86 (4)	31 (3)	41 (3)	5 (3)	13 (3)
O$_2$	35 (2)	34 (2)	49 (2)	16 (1)	18 (2)	18 (2)	2C$_6$	44 (3)	60 (3)	33 (3)	30 (3)	10 (2)	9 (2)
O$_3$	30 (2)	37 (2)	27 (2)	14 (1)	9 (1)	8 (1)	2C$_7$	26 (2)	35 (2)	31 (3)	10 (2)	10 (2)	10 (2)
O$_4$	40 (2)	47 (2)	27 (2)	24 (1)	13 (1)	5 (1)	3C$_1$	37 (3)	29 (3)	40 (3)	14 (2)	25 (2)	9 (2)
O$_5$	29 (2)	37 (2)	69 (2)	15 (1)	18 (1)	23 (2)	3C$_2$	39 (3)	36 (3)	64 (4)	15 (2)	30 (3)	17 (3)
O$_6$	29 (2)	28 (2)	51 (2)	56 (1)	13 (2)	16 (1)	3C$_3$	57 (4)	38 (3)	61 (4)	11 (3)	36 (3)	13 (3)
O$_7$	48 (2)	44 (2)	32 (2)	23 (2)	19 (2)	10 (1)	3C$_4$	45 (3)	48 (3)	64 (4)	−8 (3)	24 (3)	11 (3)
O$_8$	59 (2)	55 (2)	35 (2)	36 (2)	20 (2)	12 (2)	3C$_5$	33 (3)	68 (4)	62 (4)	8 (3)	11 (3)	25 (3)
1C$_1$	33 (2)	25 (2)	25 (2)	9 (2)	18 (2)	1 (2)	3C$_6$	39 (3)	43 (3)	54 (3)	13 (3)	12 (3)	23 (3)
1C$_2$	39 (3)	37 (3)	40 (3)	18 (2)	23 (2)	15 (2)	3C$_7$	35 (3)	35 (3)	31 (2)	18 (2)	16 (2)	7 (2)
1C$_3$	49 (3)	33 (3)	60 (3)	18 (2)	34 (3)	16 (2)	4C$_1$	27 (2)	34 (3)	34 (3)	6 (2)	16 (2)	3 (2)
1C$_4$	56 (3)	36 (3)	67 (4)	14 (3)	37 (3)	21 (3)	4C$_2$	47 (3)	46 (3)	55 (4)	18 (3)	24 (3)	8 (3)
1C$_5$	36 (3)	40 (3)	55 (3)	5 (2)	23 (3)	11 (4)	4C$_3$	61 (4)	49 (4)	66 (4)	18 (3)	37 (3)	−4 (3)
1C$_6$	27 (3)	40 (3)	38 (3)	11 (2)	10 (2)	2 (2)	4C$_4$	70 (4)	71 (4)	54 (4)	15 (3)	34 (3)	−15 (3)
1C$_7$	29 (2)	31 (2)	26 (2)	8 (2)	12 (2)	2 (2)	4C$_5$	66 (4)	77 (4)	39 (3)	13 (3)	30 (3)	−1 (3)
2C$_1$	29 (2)	53 (2)	33 (3)	12 (2)	14 (2)	8 (2)	4C$_6$	50 (3)	62 (4)	38 (3)	20 (3)	12 (3)	9 (3)
2C$_2$	43 (3)	45 (3)	36 (3)	23 (2)	20 (2)	12 (2)	4C$_7$	32 (3)	37 (3)	39 (3)	6 (2)	14 (2)	4 (2)
2C$_3$	65 (4)	69 (4)	31 (3)	35 (3)	20 (3)	3 (3)							

[a] Least-squares-estimated errors are in parentheses. [b] Isotropic temperature factor for tropolonato hydrogen atoms is $U = 0.043$ Å^2; refined isotropic temperature factor for H is $U = 0.094$ (18) Å^2.

mensions of a generalized eight-coordinate stereochemistry which are predicted to have the most stable configuration. Despite the complication of hydrogen bonding, it was felt useful to compare our parameters with the predicted dimensions for a value b which was obtained by averaging over all four ligands.

The generalized sphere is shown in Figure 3, and the observed parameters and those calculated for the most stable polyhedron where $b = 1.10$ are given in Table IV. The calculated parameters correspond to a structure which is intermediate between D_{2d} (dodecahedral) and D_2 (square antiprismatic); considering the perturbing effect of the hydrogen bond, the agreement between the observed and calculated values is satisfactory.

The Tropolonato Ligands. Earlier crystal structures involving the tropolonato anion have been reviewed recently.[11] For the scandium anion presented here, the parameters for ligands 3 and 4 (*i.e.*, those not involved with the hydrogen bond) can be compared to the general results of this review. The C rings in both ligands are nonplanar, the oxygen atoms showing larger deviations from the C_7 plane than the carbon atoms (Table III). Day and Hoard have noted[12] that because the bite of the tropolonato ligand is small and therefore contributes to the loose packing of the ligand, the molecular arrangement is susceptible to distortion in the solid state as a result of packing forces. The dihedral angles be-

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(11) L. J. Guggenberger and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 8046 (1972).

(12) V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3626 (1970).

Table II. Interatomic Distances (Å) and Angles (deg) in the "ScO_8" Polyhedron

Distances

Sc–O_1	2.310 (3)	O_4–O_6	2.495 (4)	O_3–O_5	3.054 (4)
Sc–O_2	2.209 (3)	O_7–O_8	2.504 (4)	O_3–O_6	2.914 (4)
Sc–O_3	2.259 (3)	O_1–O_3	2.710 (4)	O_4–O_5	2.753 (4)
Sc–O_4	2.215 (3)	O_1–O_6	2.568 (4)	O_4–O_7	2.696 (4)
Sc–O_5	2.172 (3)	O_1–O_8	2.741 (4)	O_5–O_7	2.756 (4)
Sc–O_6	2.173 (3)	O_2–O_3	3.189 (4)	O_5–O_8	3.558 (4)
Sc–O_7	2.161 (3)	O_2–O_4	2.725 (4)	O_6–O_8	2.715 (4)
Sc–O_8	2.173 (3)	O_2–O_7	2.978 (4)	O_1–H	1.34 (6)
O_1–O_2	2.517 (4)	O_2–O_8	2.993 (4)	O_3–H	1.17 (6)
O_3–O_4	2.495 (4)				

Angles

O_1ScO_2	67.6 (1)	O_2ScO_3	91.0 (1)	O_4ScO_5	77.7 (1)
O_3ScO_4	67.7 (1)	O_2ScO_4	76.0 (1)	O_4ScO_7	75.3 (1)
O_5ScO_6	70.1 (1)	O_2ScO_7	85.9 (1)	O_5ScO_7	78.9 (1)
O_7ScO_8	70.5 (1)	O_2ScO_8	86.1 (1)	O_5ScO_8	109.9 (1)
O_1ScO_3	72.7 (1)	O_3ScO_5	87.1 (1)	O_6ScO_8	77.3 (1)
O_1ScO_6	69.8 (1)	O_3ScO_6	82.2 (1)	O_1HO_3	167 (2)
O_1ScO_8	75.3 (1)				

Table III. Atomic Displacements from the Least-Squares (L-S) Planes[a] Relevant to the Discussion of the Structure in the Acid Dimer of Tetrakis(tropolonato)scandium

Equations of the L-S planes	χ^2 [b]
P: $0.3288X - 0.2320Y - 0.9155Z - 1.2880 = 0$	3.2
Q: $0.6391X + 0.7686Y - 0.0286Z + 0.2568 = 0$	133.7
R: $0.5973X - 0.2335Y - 0.7673Z - 1.5874 = 0$	32.9
S: $-0.7502X - 0.6265Y - 0.2115Z + 0.4834 = 0$	60.3

Displacements, Å

Ligand 1 L-S plane P		Ligand 2 L-S plane Q		Ligand 3 L-S plane R		Ligand 4 L-S plane S	
O_1	−0.023	O_3	−0.078	O_5	0.040	O_7	−0.030
O_2	0.022	O_4	0.111	O_6	0.006	O_8	0.085
$1C_1$	0	$2C_1$	−0.028	$3C_1$	0.012	$4C_1$	−0.014
$1C_2$	−0.004	$2C_2$	−0.011	$2C_2$	−0.022	$4C_2$	−0.012
$1C_3$	0.003	$2C_3$	0.028	$3C_3$	0	$4C_3$	0.018
$1C_4$	0	$2C_4$	0.020	$3C_4$	0.020	$4C_4$	0.021
$1C_5$	0.003	$2C_5$	−0.035	$3C_5$	−0.003	$4C_5$	−0.028
$1C_6$	−0.006	$2C_6$	−0.014	$3C_6$	−0.016	$4C_6$	−0.012
$1C_7$	0.004	$2C_7$	0.039	$3C_7$	0.006	$4C_7$	0.028
Sc	0.217	Sc	0.152	Sc	0.415	Sc	0.193

[a] The orthogongal system of axes (X, Y, Z) has X along the a axis, Y in the ab plane, and Z along the c^* axis. The weights used in the calculation of L-S planes are given by $W_i = W_{i_1}/\sigma_i^2 = 3/[\sigma^2(X_i) + \sigma^2(Y_i) + \sigma^2(Z_i)]$. [b] χ^2 for a plane $lX + mY + nZ - p = 0$ for the N atom is given $\Sigma_{i=1}{}^{i=N}(P_i^2/\sigma^2(P_i))$, where $\sigma^2(P_i) = l^2\sigma^2(X_i) + n^2\sigma^2(Y_i) + n^2\sigma^2(Z_i)$ and P_i is the distance of atoms i from the plane.

Table IV

(a) Values of δ and ϕ (as defined in ref 10) for Regular Polyhedra of the Dodecahedra Class and for $HScT_4$

	δ, deg				ϕ, deg	
Dodecahedron	29.5	29.5	29.5	29.5	0	0
Bicapped trigonal prism	0	21.7	48.2	48.2	16.1	16.1
Square antiprism	0	0	52.5	52.5	24.5	24.5
$HScT_4$	13.4	29.0	43.0	42.3	10.8	10.8

(b) Angular Parameters (deg) for $M(biden)_4$ of Intermediate Stereochemistry[5]

	Predicted values $b = 1.10$	Values for $HScT_4$ $b = 1.13$
ϕ_A	31–43	37.8
ψ_A	50.9–51.4	55
ϕ_B	48.5–50.6	48.26
ψ_B	14.8–15.6	15.5

Table V. Bond Lengths (Å) in the Tropolonato Ligands (1-4) of $HScT_4$

Bond type	$1(O_1, O_2)$	$2(O_3, O_4)$	$3(O_5, O_6)$	$4(O_7, O_8)$
O_1–C_1	1.306 (5)	1.332 (5)	1.283 (5)	1.280 (5)
O_2–C_7	1.261 (5)	1.253 (5)	1.270 (5)	1.274 (5)
C_1–C_7	1.468 (5)	1.463 (5)	1.464 (5)	1.454 (6)
C_1–C_2	1.386 (6)	1.361 (6)	1.391 (6)	1.406 (6)
C_2–C_3	1.379 (6)	1.403 (6)	1.384 (7)	1.376 (7)
C_3–C_4	1.376 (7)	1.349 (7)	1.377 (7)	1.364 (8)
C_4–C_5	1.375 (6)	1.398 (7)	1.376 (7)	1.370 (8)
C_5–C_6	1.357 (6)	1.357 (7)	1.376 (7)	1.381 (7)
C_6–C_7	1.429 (6)	1.421 (6)	1.412 (6)	1.407 (6)

Table VI. Bond Angles (deg) in Tropolonato Ligands (1–4) of $HScT_4$

Angle type	$1(O_1, O_2)$	$2(O_3, O_4)$	$3(O_5, O_6)$	$4(O_7, O_8)$
$C_7C_1C_2$	126.7 (0.4)	129.4 (0.4)	126.6 (0.4)	125.6 (0.4)
$C_1C_2C_3$	131.3 (0.4)	129.2 (0.4)	130.2 (0.5)	130.9 (0.5)
$C_2C_3C_4$	129.6 (0.5)	129.4 (0.3)	129.9 (0.5)	129.6 (0.5)
$C_3C_4C_5$	126.9 (0.5)	128.1 (0.5)	127.2 (0.5)	127.8 (0.5)
$C_4C_5C_6$	130.0 (0.5)	129.3 (0.5)	130.1 (0.5)	129.4 (0.6)
$C_5C_6C_7$	131.9 (0.4)	131.2 (0.5)	130.2 (0.5)	130.6 (0.5)
$C_6C_7C_1$	123.6 (0.4)	123.1 (0.4)	125.6 (0.4)	125.8 (0.4)
$O_1C_1C_7$	112.3 (0.4)	110.5 (0.3)	112.8 (0.4)	114.3 (0.4)
$O_2C_7C_1$	116.0 (0.4)	116.7 (0.3)	114.9 (0.3)	114.2 (0.4)
$O_1C_1C_2$	121.0 (0.4)	120.2 (0.4)	120.7 (0.4)	120.0 (0.4)
$O_2C_7C_6$	120.0 (0.4)	120.2 (0.4)	119.5 (0.4)	120.0 (0.4)

tween the least-squares plane for the C_7 ring and the plane containing the ScO_2 atoms in the same ligand are 12.8° for ligand 3 and 6.0° for ligand 4. Bond lengths in the C_7 rings of these ligands follow those reported for other structures with a steady decrease in the C-C length with increasing distance from the oxygen atoms and indicate symmetrical bonding. The C_1-C_7 distance is longest, this being attributed to the small aromatic character in this bond, and the oxygen atom separations (2.495 (4), 2.504 (4) Å) are among the shortest found for tropolonato ligands. Carbon-hydrogen distances in all four ligands are all identical within the accuracy of the determination and average 0.96 (3) Å.[6b]

As a consequence of the hydrogen bond, the ligand parameters in ligands 1 and 2 are different from those in ligands 3 and 4. The asymmetry of the bond is reflected in the bond lengths around the tropolonato ligands. The C_7 ring in ligand 2 has bond lengths which alternate (the differences are significant), and this can be explained by assuming a bond between the O_3 and H atoms which leads to double-bond character in C_1-C_2 (1.332 (5) Å), C_3-C_4 (1.349 (7) Å), and C_5-C_6 (1.357 (2) Å) and single-bond character in C_1-C_7 (1.463 (5) Å), C_2-C_3 (1.403 (6) Å), C_4-C_5 (1.398 (7) Å), and C_6-C_7 (1.421 (6) Å). The bond lengths in the C_7 ring of ligand 1 indicate bonding which is intermediate between that of ligand 2 and the symmetrical ligands 3 and 4. The C_7 ring in ligand 1 is the only planar ring in the structure (within our limits of error) with the oxygen atoms placed on either side of this plane (as was found for the other rings). The C_7 ring of ligand 2 has the largest deviations from the least-squares plane for all four ligands.

The Hydrogen Bond. The effect of this bond on the associated tropolonato ligands and the Sc-O bond lengths has already been noted, and these results indicate clearly that this bond is not symmetrical.

Ibers and Hamilton[13] have published a graph relating O-H distance to O···O separation for hydrogen bonds based on neutron diffraction data. Their graph has two discontinuous curves—one for short O···O separations (2.38–2.55 Å) where the proton is symmetrically placed and the other for O···O distances of 2.48–2.87 Å where the proton is asymmetric.

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(13) W. C. Hamilton and J. A. Ibers, "The Hydrogen Bond," W. A. Benjamin, New York, N. Y., 1968, p 53.

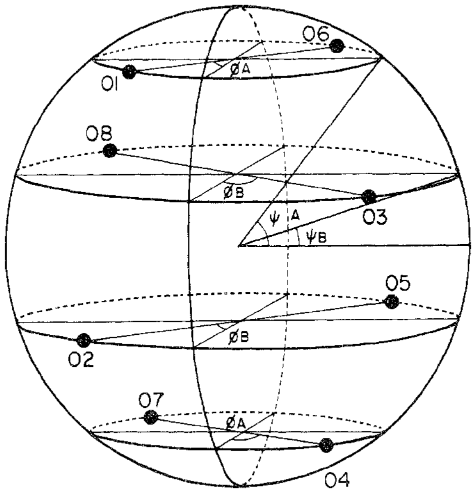

Figure 3. Generalized eight-coordination adapted from ref 5.

Our O···O separation (2.484 (4) Å) falls in the region where there is overlap between both curves. While our O–H distance of 1.17 (6) Å is within the limits of error of *either* the symmetric or the asymmetric curve, we consider the data from the tropolone rings indicate very strongly an asymmetric proton position.

Infrared stretching frequencies as a function of distances in hydrogen-bonded systems have been reviewed,[14] and for an O···O distance of 2.48 Å, an O–H stretching frequency of 1975 cm^{-1} is predicted on the basis of other results. The infrared spectrum of the acid dimer presented here shows a small, broad band at 1976 cm^{-1} in agreement with this prediction.

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Addendum

The structure of this compound has also been determined independently by Anderson, Neuman, and Melson (following paper).[15] Our unit cell is related to theirs by the transformation

$$\begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$$

The results of the two crystal structures are the same within the limits of the combined errors. The main differences are (1) the alternation of bonds in the C_7 ring of ligand 2 (their ligand 4) is not so pronounced and (2) the reduced thermal motion of the tropolonate ligands involved in hydrogen bonding is not so apparent from their rigid-body analysis.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. (Unobserved reflections are indicated by asterisks.) Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× 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 $5.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1880.

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[14] K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, 77, 6480 (1955).

[15] T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 13, 1884 (1974).

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Coordination Chemistry of Scandium. VII.[1] Crystal and Molecular Structure of Hydrogentetrakis(tropolonato)scandium(III), a Scandium(III) Complex with Approximate D_{2d} Dodecahedral Stereochemistry

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The crystal and molecular structure of hydrogentetrakis(tropolonato)scandium(III), HSc($C_7H_5O_2$)$_4$, has been determined by a single-crystal X-ray diffraction technique. The compound crystallizes in the space group $P\bar{1}$, with cell constants a = 10.022 (4), b = 11.515 (3), and c = 12.004 (4) Å; α = 72.74, β = 84.58, and γ = 65.04°; Z = 2. Least-squares refinement of the counter data give a final R factor of 0.027 for 2539 significant reflections. The compound exists as a hydrogen-bonded dimer with each scandium atom coordinated by eight oxygen atoms. The coordination environment about the scandium ion is close to that of a D_{2d} dodecahedron. In the crystal, the two dodecahedra are held together about the center of symmetry by two almost linear hydrogen bonds, with an O–H distance of 1.00 Å, a hydrogen-bonded O- - -H distance of 1.49 Å, and an O–H- - -O angle of 175.9°.

Introduction

As part of our program concerning the structural characterization of scandium coordination compounds, we recently reported the crystal and molecular structures of two six-coordinated scandium(III) species, *viz.*, tris(acetylacetonato)-scandium(III),[2] Sc(acac)$_3$ (acac = acetylacetonato anion, $C_5H_7O_2^-$), and tris(tropolonato)scandium(III),[1] Sc(trop)$_3$ (trop = tropolonato anion $C_7H_5O_2^-$). In Sc(acac)$_3$, the coordination environment for the scandium(III) ion is close to trigonal antiprismatic, whereas in Sc(trop)$_3$, the stereochemistry is almost midway between trigonal antiprismatic and trigonal prismatic. From these structures, we concluded that in the solid state, the coordination environment of the scandium(III) ion (d^0 configuration) is influenced by the nature of the ligands coordinated to it and by interactions between the ligands.

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[1] Part VI: T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 13, 158 (1974).

[2] T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 12, 927 (1973).