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Unusual Dodecahedral Coordination in the Structure of Ammonium Tetrakis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione]praseodymate(III) Monohydrate, $NH_4Pr(C_8H_4F_3O_2S)_4 \cdot H_2O$[1]

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The crystal and molecular structure of ammonium tetrakis[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione]praseodymate(III) monohydrate, $NH_4Pr(C_8H_4F_3O_2S)_4 \cdot H_2O$, has been determined from 2969 observed three-dimensional X-ray film data. The material crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system, with two molecules per unit cell. The cell dimensions are: $a = 10.10\ (2)$, $b = 17.90\ (3)$, $c = 12.14\ (2)$ A; $\alpha = 78.57\ (10)$, $\beta = 103.97\ (10)$, and $\gamma = 86.95\ (10)°$. ($\rho_{obsd} = 1.65$ g cm^{-3}; $\rho_{calcd} = 1.67$ g cm^{-3}.) The molecules are monomeric with the metal dodecahedrally coordinated by the oxygens of the four bidentate ligands (Pr–O, 2.42–2.49 (2) A). The essentially coplanar ligands all show dihedral folding of 10–24° about the O–O line in the six-membered chelate ring. In contrast to other structures displaying similar bidentate coordination, each ligand bridges adjacent vertices between the two orthogonal trapezoids in the dodecahedron. The intramolecular sulfur–oxygen distances are 2.8–2.9 A, 0.4 A shorter than the sum of the van der Waals radii, indicating some interaction between these atoms. The structure was refined by the least-squares method to a conventional crystallographic R factor of 11.1%. Molar susceptibilities, measured from 68 to 297°K, obey Curie's law and yield a moment of 3.59 BM.

Introduction

During the preparation of a series of β-diketone chelates of praseodymium, a compound containing 4 moles of β-diketone/mole of metal was isolated. The compound 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (common name: 2-thenoyltrifluoroacetone, referred to as HTTA) (see Figure 1) is the ligand which produced this anomalous chelate with presumed formula $Pr(TTA)_4$.

Magnetic susceptibility measurements indicated that the metal was trivalent. It was assumed that an adduct compound of the tris-TTA chelate of praseodymium had been formed. A single-crystal X-ray analysis of the compound was performed in order to elucidate the position of the four ligands and the coordination sphere of the metal atom. It was found that an ammonium ion and a water of hydration are necessary to stabilize this chelate.

Experimental Section

Preparation.—The complex was prepared by mixing stoichiometric quantities of anhydrous $PrCl_3$ and HTTA in 95% ethanol and neutralizing the solution with NH_4OH in ethanol. The solution was allowed to evaporate slowly under a dry nitrogen atmosphere. The crystalline product was dried under vacuum. *Anal.* Calcd for $C_{32}H_{22}F_{12}NO_9PrS_4$: NH_3, 1.60; Pr, 13.27. Found: NH_3, 1.64; Pr, 13.20.

Magnetic Susceptibility.—These measurements were carried out on a Gouy balance. The molar susceptibilities, including a diamagnetic correction of -460×10^{-6} cm^3 mole^{-1}, are given in Table I. These results correspond to Curie's law, $\bar{\chi} = C/T$, with $C = 1.607$, and lead to a calculated magnetic moment on the Pr^{3+} ion of 3.59 BM, which is in agreement with the results given by Van Vleck.[3]

X-Ray.—The transparent pale yellow-green crystals were assigned to the triclinic system as a result of an optical examination and preliminary X-ray photography. A Delaunay reduction failed to suggest the presence of hidden symmetry. The cell chosen is a primitive one of dimensions: $a = 10.10\ (2)$, $b = 17.90\ (3)$, $c = 12.14\ (2)$ A; $\alpha = 78.57\ (10)$, $\beta = 103.97\ (10)$, and $\gamma = 86.95\ (10)°$. The cell dimensions were determined from precession photographs taken with Mo Kα radiation (0.7107 A) at approximately 22°. The errors quoted reflect the internal consistency from a series of measurements.

The "Delaunay cell" (for which α, β, and γ are all ≥90° and the direction cosines of [111] are all positive) is

$$\begin{aligned} a &= 20.13\ \text{A} & \alpha &= 101.43° \\ b &= 17.90\ \text{A} & \beta &= 107.80° \\ c &= 12.14\ \text{A} & \gamma &= 138.00° \end{aligned}$$

The transformation is given by

$$\begin{bmatrix} a \\ b \\ c \end{bmatrix}_{\text{Delaunay}} = \begin{bmatrix} 1 & -1 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

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[2] (a) Fordham University and Brookhaven National Laboratory; (b) Fordham University; (c) Brookhaven National Laboratory.

[3] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, p 243.

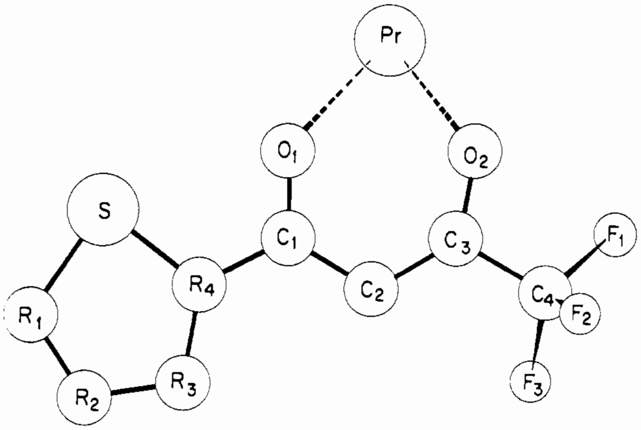

Figure 1.—Atom designation for TTA ligand.

TABLE I

MAGNETIC SUSCEPTIBILITY *vs.* TEMPERATURE

	Temp, °K				
	68	76	168	195	297
$10^6\chi_M$, cm^3 mole^{-1}	11,929	10,525	6452	5714	4150

The unit cell volume of 2076 A^3 with two molecules per cell leads to a calculated density of 1.67 g cm^{-1} (observed, 1.65 g cm^{-3} by flotation using a bromoform–iodoform mixture). In the absence of a piezoelectric effect, the space group C_i^1-P$\bar{1}$ (origin at $\bar{1}$) was assumed and seems justified in view of the agreement between observed and calculated structure amplitudes. Since there are two molecules per cell, no crystallographic symmetry conditions need be imposed on the molecules. Multiple-film intensity data were collected at approximately 22° from a spherical crystal of 0.38 (2)-mm diameter (μr = 0.28); the *a* axis of the crystal was parallel to the goniometer head axis. Zirconium-filtered Mo Kα radiation (λ 0.7107 A) was employed for both the equiinclination Weissenberg zones 0*kl* through 7*kl* and the precession zones *hk*0 and *h*0*l*. The intensities of 2969 nonzero reflections within the limiting sphere $\theta_{Mo} = 20.0°$ were estimated by visual comparison with a series of timed exposures of a selected reflection. These represent approximately 75% of the reflections that can occur within this range. The geometrical Lorentz-polarization correction (Lp) and Phillips[4,5] spot distortion factors were applied to these intensities. No spherical absorption correction was applied: for the range $0 < \theta \leq 20°$, this correction varied from 1.55 to 1.56.

The $|F_o|$ values were subsequently brought to an approximate absolute scale using Wilson's method.

Solution and Refinement of the Structure

The positional parameters of the praseodymium atom were easily obtained from a three-dimensional origin-removed sharpened Patterson–Fourier synthesis. The coefficients used in this summation were derived from $F_{\text{modified}}^2 = KF_{\text{obsd}}^2(\Sigma_i Z_i^2/\Sigma_i f_i^2)$ exp $(2B(\sin^2\theta)/\lambda^2) - \Sigma_i Z_i^2$, where the scale factor K and the over-all temperature factor B were obtained from the Wilson plot; Z_i and f_i are the atomic number and scattering factor of the *i*th atom, respectively. A structure factor calculation based on the position of the praseodymium atom led to a residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.33$. All of the remaining light atoms of the four TTA ligands were found in subsequent difference-Fourier syntheses. Dodecahedral octacoordination of the metal atom to the eight oxygen atoms of the four TTA groups was immediately evident.

In addition to the four TTA ligands, a final difference-Fourier synthesis revealed two additional nonbonded light-atom peaks. These were assumed to be an ammonium cation and a water of hydration, referred to as X1 and X2; this structural determination could not be used to distinguish between the two.

The structural parameters obtained from the Fourier synthesis were refined by the full-matrix least-squares method, minimizing the quantity $\Sigma_i w_i(||F_{o_i}| - |F_{c_i}||)^2$, where w_i is the weighting factor. For the initial cycles of refinement, the weights, w, were assigned in the following way: w is proportional to $(I_o/5|F_o|)^2$ for $I_o < 100$; w is proportional to $(20/|F_o|)^2$ for $I_o > 100$. The atomic scattering factor for praseodymium was taken from the Dirac–Slater calculations of Cromer and Waber;[6] scattering factors for the other atoms were those tabulated in the "International Tables for X-Ray Crystallography."[7] The anomalous parts of the praseodymium and sulfur scattering factors given by Cromer[8] were included in the calculated structure factors.

Owing to the large number of atoms (59), the structure had to be refined in blocks: the positional and thermal parameters of the praseodymium atom, the individual scale factors, and three of the four TTA ligands were refined at one time, with the fourth held fixed. Upon obtaining the new parameters, another of the TTA ligands was held fixed, and the other three were refined. This procedure was repeated until the parameters of all of the atoms remained constant. With praseodymium-allowed anisotropic thermal parameters and all other atoms assigned a single variable isotropic thermal parameter, the refinement converged to values of the residual, R, of 0.111, and of the weighted residual, $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2} = 0.159$. The error of fit function $[\Sigma w(||F_o| - |F_c||)^2/(n - m)]^{1/2}$, where n is the number of observations and m is the number of variable parameters, is 1.28.

Near the end of the refinement, it seemed desirable to check the reasonableness of the weighting function, particularly in its dependence on $|F_o|$. For a proper weighting function, the mean value of $|\Delta F|/\sigma$ should be independent of $|F_o|$. From a smoothed plot of the average values of $|\Delta F|/|F_o|$ for various ranges of $|F_o|$, an empirical weighting function was derived. For the final cycles of refinement the $\sigma(F)$ values derived from this function were: $0 < F \leqslant 36$, $\sigma(F) = -0.00305F^2 + 0.241F$; $36 < F \leqslant 65$, $\sigma(F) = -0.0008F^2 + 0.146F$; and $F > 65$, $\sigma(F) = -0.00011F^2 + 0.101F$.

The final parameters from the last least-squares refinement, together with their standard deviations, are listed in Table II. Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digits. The observed and calculated structure amplitudes, $|F_o|$ and $|F_c|$, in electrons, are given in Table III. The highest peak on a final difference-Fourier synthesis is 1.5 electrons A^{-3} in the

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(4) D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

(5) D. C. Phillips, *ibid.*, **9**, 819 (1956).

(6) D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

(7) "International Tables for X-Ray Crystallography," Vol. III, The Knyoch Press, Birmingham, England, 1962, p 202.

(8) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

TABLE II

X-RAY POSITIONAL AND THERMAL PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS (σ) FOR $NH_4Pr(TTA)_4 \cdot H_2O$[a]

PRASEODYMIUM

x(σ)	y(σ)	z(σ)
0.0888(1)	0.2755(1)	0.1957(1)

$\beta_{11}(\sigma)$[b]	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
0.0103(5)	0.0039(1)	0.0083(1)	-0.0001(1)	0.0017(1)	-0.0022(1)

Ligand 1[c]

Atom[d]	x(σ)	y(σ)	z(σ)	B(Å²)(σ)
S	0.2744(10)	-0.1647(5)	0.0762(7)	7.9(2)
R1	0.3498(38)	-0.1026(19)	0.1583(29)	7.9(8)
R2	0.2465(39)	-0.0582(19)	0.1849(30)	8.1(8)
R3	0.1134(31)	-0.0679(16)	0.1330(24)	6.2(6)
R4	0.1099(29)	-0.1301(15)	0.0694(23)	5.7(6)
O1	-0.0293(19)	0.2197(10)	0.0348(15)	6.0(4)
O2	0.2559(20)	0.2140(10)	0.1156(15)	6.1(4)
C1	-0.0024(27)	-0.1658(14)	0.0111(21)	4.8(5)
C2	-0.1383(37)	-0.1387(18)	0.0074(27)	7.4(7)
C3	0.2447(36)	0.1682(18)	0.0441(27)	7.1(7)
C4	0.4013(55)	0.1399(30)	0.0481(45)	11.0(13)
F1	0.3839(37)	0.0876(18)	-0.0204(28)	14.5(9)
F2	0.4654(40)	0.1028(20)	0.1459(32)	15.5(10)
F3	0.4484(42)	0.1973(21)	0.0075(32)	16.3(10)

Ligand 2

Atom[d]	x(σ)	y(σ)	z(σ)	B(Å²)(σ)
S	-0.1484(14)	0.0382(7)	0.2560(11)	10.9(3)
R1	-0.1742(47)	-0.0546(23)	0.2939(37)	10.0(10)
R2	-0.0666(51)	-0.0935(25)	0.3655(38)	10.5(11)
R3	0.0575(26)	-0.0585(13)	0.4018(21)	4.9(5)
R4	0.0101(31)	0.0233(16)	0.3388(24)	6.2(6)
O1	0.0301(20)	0.1509(10)	0.2769(15)	6.1(4)
O2	0.2835(21)	0.2096(11)	0.3542(16)	6.6(4)
C1	0.0970(31)	0.0884(16)	0.3409(24)	6.0(6)
C2	0.2239(36)	0.0823(18)	0.4022(27)	6.8(7)
C3	0.3053(39)	0.1423(20)	0.4129(30)	7.6(8)
C4	0.4638(48)	0.1275(25)	0.4909(39)	9.6(10)
F1	0.4700(34)	0.0627(18)	0.5693(26)	13.9(8)
F2	0.5486(65)	0.1317(27)	0.4439(43)	21.1(16)
F3	0.4558(43)	0.1757(22)	0.5613(33)	16.7(11)

Ligand 3

Atom[d]	x(σ)	y(σ)	z(σ)	B(Å²)(σ)
S	-0.2885(10)	-0.4027(5)	0.1284(8)	7.7(2)
R1	-0.3017(35)	-0.4592(17)	0.2554(27)	7.1(7)
R2	-0.1834(34)	0.4950(17)	0.3076(26)	6.9(7)
R3	-0.0686(34)	-0.4980(17)	0.2460(26)	6.8(7)
R4	-0.1189(30)	-0.4403(15)	0.1418(23)	5.6(6)
O1	0.1289(18)	0.3705(9)	0.0362(15)	5.6(4)
O2	-0.1294(18)	0.3587(9)	0.0961(14)	5.3(4)
C1	-0.0514(28)	-0.4130(14)	0.0572(21)	4.8(5)
C2	0.0862(30)	-0.4306(15)	0.0757(22)	5.5(6)
C3	0.1623(25)	-0.4017(13)	0.0015(20)	4.2(5)
C4	0.3114(35)	-0.4234(18)	0.0375(28)	7.1(7)
F1	-0.3791(34)	0.3690(17)	-0.0885(26)	13.5(8)
F2	-0.3720(24)	0.4254(12)	0.0470(19)	9.6(5)
F3	-0.3558(27)	0.4920(14)	-0.1118(20)	11.1(6)

Ligand 4

Atom[d]	x(σ)	y(σ)	z(σ)	B(Å²)(σ)
S	-0.1830(11)	0.2758(6)	0.5057(9)	8.9(2)
R1	0.2063(45)	-0.2733(22)	0.3754(34)	9.3(9)
R2	0.1029(38)	-0.2992(19)	0.2987(30)	7.9(8)
R3	-0.0134(30)	-0.3220(15)	0.3443(22)	5.6(6)
R4	0.0223(27)	-0.3087(13)	0.4621(21)	5.0(5)
O1	-0.0032(17)	0.3030(9)	0.3552(13)	5.0(3)
O2	0.2239(18)	0.3694(9)	0.2860(14)	5.3(4)
C1	0.0458(25)	0.3216(12)	0.4487(20)	4.2(5)
C2	0.1775(30)	0.3546(15)	0.4729(24)	6.0(6)
C3	0.2492(27)	0.3739(14)	0.3947(22)	5.0(5)
C4	0.3677(44)	0.4150(23)	0.4290(35)	8.8(10)
F1	0.3447(35)	0.4885(18)	0.3855(26)	14.2(8)
F2	0.4234(31)	0.4064(15)	0.5377(25)	12.7(7)
F3	0.4738(29)	0.3973(14)	0.3876(22)	11.6(7)
X1[e]	0.4489(34)	0.3144(18)	0.1909(26)	11.6(7)
X2	-0.2811(56)	0.2557(26)	0.2206(39)	16.7(14)

[a] Due to computer limitations, all parameters could not be varied simultaneously, and the standard deviations for the thermal parameters are obtained from more than one cycle of refinement. They are thus likely to be somewhat low.

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

[c] Ligands of TTA in this and following tables are numbered as shown in Figure 2.

[d] Atoms in this and following tables are numbered as shown in Figure 1.

[e] X1 or X2 denotes the water of hydration, and the other denotes the ammonium ion. Since hydrogen atoms were not located, these groups could not be distinguished.

vicinity of the praseodymium atom. Other peaks of approximately 0.8–1.2 electrons A^{-3} occur in the region of the CF_3 groups, presumably owing to the inadequacy of the isotropic temperature parameter model. Less pronounced but still readily evident from the difference map was the anisotropy of the other light atoms. In agreement with the generally high temperature factors indicated by the least-squares refinement, the observed peak heights are: sulfur, 7–10 electrons A^{-3}; fluorine, 2–4 electrons A^{-3}; and the other light atoms, intermediate between these values. The hydrogen atoms could not be located.

Programs for the IBM 7094 and CDC 6600 computers used in this work, in addition to those of local origin, are modifications of Zalkin's FORDAP program,[9] Busing, Martin, and Levy's ORFLS least-squares[10] and ORFFE error function[11] programs, and Johnson's ORTEP ellipsoid plot program.[12]

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(9) A. Zalkin, "A FORTRAN Crystallographic Program for Fourier Analysis," University of California, Livermore, Calif., unpublished.

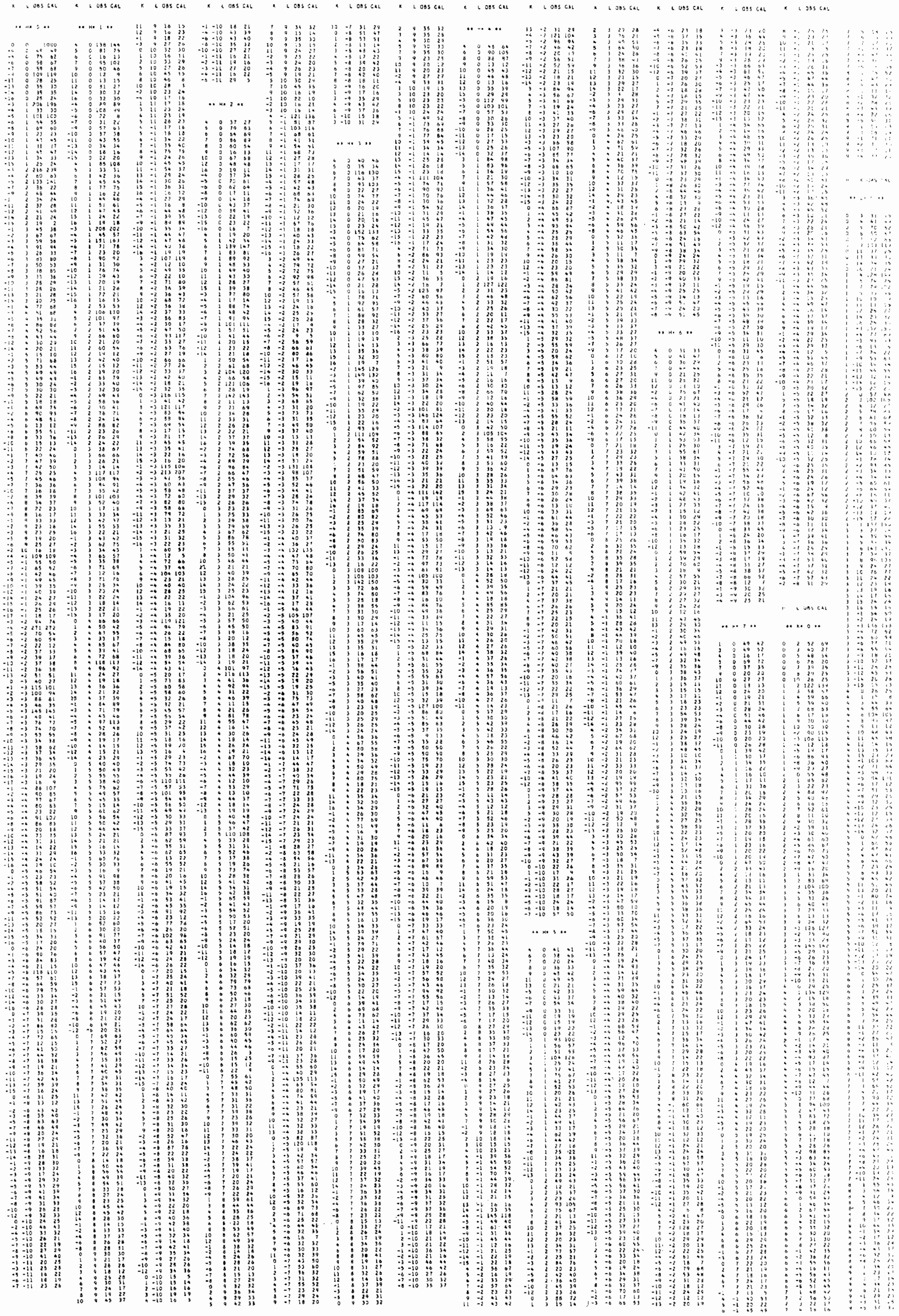
(10) W. R. Busing, K. O. Martin, and H. A. Levy, "A FORTRAN Crystallographic Least-Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962, Report TM-305.

(11) W. R. Busing, K. O. Martin, and H. A. Levy, "A FORTRAN Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964, Report TM-306.

(12) C. K. Johnson, "A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, Report 3794.

TABLE III

X-RAY OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS) FOR $NH_4Pr(TTA)_4 \cdot H_2O$[a]



[a] The above reflections are both Weissenberg and precession data, and therefore some of the above are not unique.

Description and Evaluation of the Structure

The structure described by the cell dimensions, symmetry operations of the space group, and parameters of Table II consist of the packing of discrete monomeric $Pr(TTA)_4^-$ anions, possibly bound together through weak water and ammonium hydrogen bonds. The molecular structure of the molecule is shown in Figure 2, and the inner coordination geometry is displayed in Figure 3.

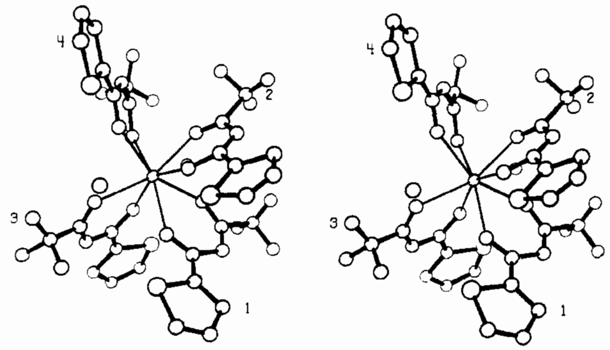


Figure 2.—The molecular structure of $NH_4Pr(TTA)_4\cdot H_2O$. The two views constitute a stereoscopic pair and can be viewed with a small hand stereoscope. The numerals denote the four distinct TTA ligands. The two isolated spheres represent X1 and X2—the ammonium ion and the water of hydration.

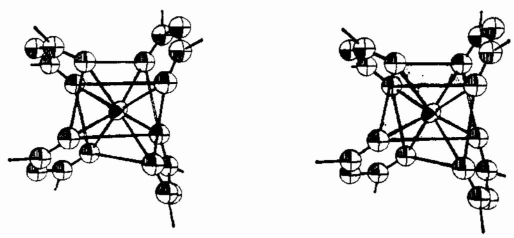


Figure 3.—Bisdiphenoidal arrangement of the inner coordination of $NH_4Pr(TTA)_4\cdot H_2O$. The two views constitute a stereoscopic pair and can be viewed with a small hand stereoscope. The atoms are drawn as spheres of arbitrary radius.

The coordination sphere around praseodymium consists of eight essentially equidistant (2.42–2.49 A) oxygen atoms, located at the vertices of a bisdiphenoid (two trapezoids lying in mutually perpendicular mirror planes). Figure 4 shows the two equivalent trapezoids BAAB. The site of the metal atom is the center of the polyhedron. In other structures, four bidentate coordinating ligands are found to be bound across vertices A–B along edges *m* of a single trapezoid.[13,14] In $NH_4Pr(TTA)_4\cdot H_2O$, each unsymmetrically substituted acetylacetone ligand bridges *adjacent* vertices A–B of the *two* orthogonal trapezoids, along edges *g* of the dodecahedron. Four such bidentate ligands could possibly produce 110 optically active isomers,[15] of which the arrangement here described is one. However, owing to the presence of a center of symmetry in the unit cell, $P\bar{1}$, the two molecules exist as a *dl* pair (*i.e.*, a racemate) in the crystal.

The angles θ_A and θ_B which the bonds metal–A and metal–B (Figure 4) make with the idealized unique $\bar{4}$ axis as found in this dodecahedron are 41.4 and 65.7°, respectively. As has been shown in other structures,[13,16,17] there is a large diversity of angle available for θ_A and for θ_B (θ_A ranges between 35 and 47°, and θ_B ranges between 73 and 93°). Intramolecular packing and the size and shape of the coordinating groups define the total size and final shape of these dodecahedra.

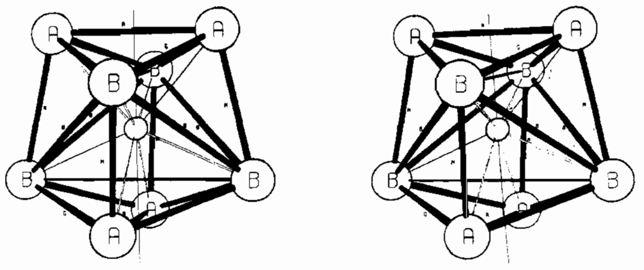


Figure 4.—The idealized D_d-$\bar{4}2m$ dodecahedron. The two views constitute a stereoscopic pair and can be viewed with a small hand stereoscope.

The best least-squares planes through each of the two trapezoids BAAB, given by the equation $Ax + By + Cz - D = 0$ in the triclinic coordinate system, are indicated in Table IV, along with the mean displacement of the atoms from the plane. The angle between these least-squares planes of the two trapezoids is 86.8°. This agrees well with the idealized angle of 90°. Using Hoard's notation for the idealized D_{2d} model of the dodecahedron,[13] all previously reported structures have sides $g > a = m$. However, $NH_4Pr(TTA)_4\cdot H_2O$ exhibits $g = m < a$, which, along with the structure of cesium tetrakis(hexafluoroacetylacetone)-yttrate(III),[18] represents the first cases of this type of dodecahedral coordination. It should be noted that this particular conformation is one which Hoard and Silverton, in their analysis of relative stabilities of ground-state geometries of chelates,[13] had predicted as a reasonable stereoisomer.

The best least-squares planes through each of the thienyl rings, and through each of the six-membered chelate rings (but excluding the metal), are given in Table IV along with the mean displacement of the atoms from these planes. Also shown in Table IV are the dihedral angles which are formed by the slight twisting of the thienyl ring away from the plane of the six-membered chelate ring.

The essentially coplanar ligands all show folding about the oxygen–oxygen line in the six-membered chelate rings. The dihedral angles thus formed between planar (*i.e.*, best least-squares plane) β-diketone and the plane bounded by oxygen–oxygen–praseodymium are 13.1, 10.5, 13.8, and 23.6° for molecules 1, 2, 3, and 4, respectively. This folding apparently is an aid for good packing within and between molecules. Tables V and VI give all pertinent intramolecular distances and angles, respectively.

Because the standard deviations in the positional parameters of the light atoms are high (0.03–0.05 A), any speculation with regard to bond character in the TTA ligand would be meaningless. However, it should be noted that the nearly planar thienyl ring remains essentially coplanar with the remainder of the chelate molecule. The thienyl ring bends toward O1

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

(14) (a) S. J. Lippard, *Progr. Inorg. Chem.*, in press; (b) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

(15) L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943).

(16) J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, **5**, 1208 (1966).

(17) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

(18) S. J. Lippard, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **88**, 5930 (1966).

TABLE IV

TABLE OF WEIGHTED LEAST-SQUARES PLANES AND OF DIHEDRAL ANGLES

$Ax + By + Cz - D = 0$[a]

Atoms	A	B	C	D	Mean dev, A	Mean σ, A
Planes through the Two Trapezoids						
O1 (2), O1 (1), O2 (4), O1(3)[b]	8.744	−8.105	−3.843	−2.087	0.07	0.02
O2 (2), O2 (1), O1 (4), O2 (3)	5.535	15.473	0.261	4.816	0.06	0.02
Planes through the Thienyl Rings						
S, R1, R2, R3, R4 (1)	−2.357	−9.334	8.897	−1.569	0.02	0.03
S, R1, R2, R3, R4 (2)	5.247	−6.018	−11.340	−3.914	0.01	0.03
S, R1, R2, R3, R4 (3)	2.781	15.046	6.962	5.964	0.01	0.03
S, R1, R2, R3, R4 (4)	3.202	−15.613	0.541	−4.616	0.01	0.03
Planes through the Chelate Rings						
O1, C1, C2, C3, O2 (1)	−2.447	−9.993	8.530	−1.805	0.04	0.02
O1, C1, C2, C3, O2 (2)	5.112	−6.691	−11.286	−3.969	0.03	0.03
O1, C1, C2, C3, O2 (3)	0.875	16.227	6.901	6.370	0.01	0.02
O1, C1, C2, C3, O2 (4)	4.235	−14.891	0.067	−4.518	0.03	0.02

Dihedral Angles between the Plane of the Thienyl Ring and the Plane of the Chelate Ring

Ligand	Dihedral angle, deg	Ligand	Dihedral angle, deg
1	2.6	3	12.4
2	2.3	4	6.3

[a] x, y, and z are fractional coordinates in the triclinic system. [b] Numbers in parentheses denote ligand.

TABLE V

BOND DISTANCES (IN A) FOR $NH_4Pr(TTA)_4 \cdot H_2O$

Ligand	Pr–O1	Pr–O2	S–R1	S–R4
1	2.45 (2)	2.45 (2)	1.72 (3)	1.72 (3)
2	2.42 (2)	2.45 (2)	1.69 (4)	1.65 (3)
3	2.44 (2)	2.49 (2)	1.71 (3)	1.76 (3)
4	2.46 (2)	2.48 (2)	1.63 (4)	1.74 (3)

	R1–R2	R2–R3	R3–R4	R4–C1
1	1.41 (5)	1.38 (4)	1.47 (4)	1.44 (4)
2	1.28 (5)	1.44 (5)	1.50 (4)	1.50 (4)
3	1.35 (4)	1.52 (5)	1.43 (4)	1.39 (4)
4	1.32 (5)	1.46 (4)	1.46 (3)	1.40 (3)

	C1–O1	C1–C2	C2–C3	C3–O2
1	1.27 (3)	1.42 (4)	1.30 (4)	1.30 (3)
2	1.28 (3)	1.30 (4)	1.40 (4)	1.25 (3)
3	1.28 (3)	1.36 (4)	1.36 (4)	1.24 (3)
4	1.24 (2)	1.47 (4)	1.33 (4)	1.30 (3)

	C3–C4	C4–F1	C4–F2	C4–F3	O1–O2(g)[a]
1	1.62 (6)	1.36 (5)	1.24 (5)	1.22 (5)	2.80 (3)
2	1.63 (6)	1.33 (4)	1.14 (6)	1.34 (5)	2.84 (3)
3	1.47 (4)	1.38 (4)	1.32 (4)	1.35 (3)	2.88 (3)
4	1.46 (5)	1.30 (4)	1.28 (4)	1.34 (4)	2.87 (2)

Edge g[a]		Edge b		Edge m	
O1 (2)–O1 (4)[b]	3.09	O2 (4)–O2 (1)	3.83	O1 (1)–O1 (2)	2.85
O2 (2)–O2 (4)	2.81	O2 (4)–O2 (3)	3.79	O1 (3)–O2 (4)	2.95
O2 (3)–O1 (1)	2.93	O1 (2)–O2 (3)	3.96	O2 (3)–O1 (4)	3.03
O1 (3)–O2 (1)	2.89	O1 (2)–O2 (1)	3.44	O2 (1)–O2 (2)	2.83

Edge a	
O1 (1)–O1 (3)	3.21
O2 (2)–O1 (4)	3.27

[a] Edges of the dodecahedron follow the nomenclature of Figure 4. [b] Numbers in parentheses denote the TTA ligand.

TABLE VI

INTRAMOLECULAR ANGLES (IN DEGREES) FOR $NH_4Pr(TTA)_4 \cdot H_2O$

Ligand	O1–Pr–O2	R1–S–R4	S–R1–R2	R1–R2–R3
1	69.6 (6)	94 (2)	109 (3)	116 (3)
2	71.4 (6)	93 (2)	111 (4)	122 (4)
3	71.5 (6)	95 (2)	110 (3)	117 (3)
4	70.9 (5)	94 (2)	111 (3)	119 (3)

	R2–R3–R4	R3–R4–S	S–R4–C1	R3–R4–C1
1	111 (3)	110 (2)	119 (2)	132 (3)
2	100 (3)	115 (2)	120 (2)	125 (2)
3	107 (3)	111 (2)	120 (2)	128 (3)
4	104 (2)	111 (2)	117 (2)	132 (2)

	R4–C1–O1	R4–C1–C2	O1–C1–C2	Pr–O1–C1
1	116 (2)	119 (3)	125 (3)	135 (2)
2	111 (3)	124 (3)	125 (3)	136 (2)
3	115 (3)	121 (2)	124 (2)	134 (2)
4	120 (2)	118 (2)	122 (2)	135 (2)

	C1–C2–C3	C2–C3–O2	Pr–O2–C3	O2–C3–C4
1	122 (3)	131 (3)	133 (2)	105 (3)
2	126 (3)	129 (3)	131 (2)	109 (3)
3	125 (2)	132 (2)	129 (2)	110 (2)
4	124 (2)	131 (3)	126 (2)	112 (3)

	C2–C3–C4	C3–C4–F1	C3–C4–F2	C3–C4–F3
1	124 (3)	102 (4)	112 (4)	105 (4)
2	122 (3)	105 (4)	118 (5)	99 (4)
3	118 (2)	111 (3)	116 (3)	117 (3)
4	117 (3)	113 (3)	118 (3)	114 (3)

	F1–C4–F2	F1–C4–F3	F2–C4–FC
1	105 (4)	114 (5)	117 (5)
2	116 (5)	97 (4)	118 (5)
3	101 (3)	107 (3)	104 (3)
4	107 (3)	100 (3)	103 (3)

O2 (2)–Pr–O1 (4)[a]	O2 (2)–Pr–O2 (1)	O2 (3)–Pr–O1 (4)
83.6 (6)	70.4 (6)	75.6 (5)
O2 (1)–Pr–O2 (3)	**O2 (4)–Pr–O1 (2)**	**O2 (4)–Pr–O1 (3)**
130.5 (6)	132.1 (6)	73:6 (2)
O1 (2)–Pr–O1 (1)	**O1 (1)–Pr–O1 (3)**	
71.7 (6)	82.1 (6)	

[a] Numbers within parentheses denote TTA ligand.

(Figure 1), apparently pivoting about R4 (the angle C1–R4–R3 is greater than the angle C1–R4–S) (Figure 1, Table VI). This leads to a short sulfur–oxygen distance of approximately 2.8 A. This distance is 0.4 A shorter than the sum of the van der Waals radii indicating some weak interaction between these two atoms. There is also the possibility of steric repulsion between the hydrogen located on R3 and the hydrogen located on C2 (hydrogens not shown in Figure 1). A normal intramolecular nonbonded hydrogen–hydrogen interaction (the hydrogens being separated by at least three carbon atoms) is always greater than 2.0 A. If the angle C1–R4–R3 were equal to the angle C1–R4–S, then the hydrogen–hydrogen distance would be approximately 1.6–1.7 A. Actually, it is found in these TTA ligands that these two hydrogens are at a distance of approximately 2.1 A and therefore presumably push the thienyl ring toward the oxygen denoted as O1. A short sulfur–oxygen distance has been previously noted in the structure of the methyl ester of *o*-nitrobenzenesulfenic acid, where short nonbonded sulfur–oxygen distances of 2.44 A were found.[19]

The angle O2–C3–C2 opens to 130.4°, whereas the angle O1–C1–C2 is 124.0°. Four independent measurements of these same quantities, all within three standard deviations, suggest that this difference is real. This difference in angle within the six-membered chelate ring has not been noted in the structure of zirconium(IV) acetylacetonate,[20] where these two angles were identical at 123.7°. The discrepancy of angle in this structure could be due to the strong electronegative CF_3 group of the TTA; it could also be due to the force exerted on the six-membered chelate ring by the pivoting of the thienyl ring toward O1. This difference in angle, however, was not observed in the structure of $Eu(TTA)_3 \cdot 2H_2O$[21] where these two angles were equal at approximately 124°. However, since considerable nonplanarity of each of the TTA molecules as a whole is evidenced in this tris(2-thenoyltrifluoroacetone)europium(III) dihydrate, this could serve to alleviate strain in the six-membered ring and allow these two angles to remain essentially equivalent.

The close proximity (2.75 A) of the extra atoms (X1 and X2)—the water of hydration and the ammonium ion—is shown in the packing diagram in Figure 5. Because of the high thermal motion, the low electron densities of the two sites (X1, 3.9 electrons A^{-3}; X2, 2.6 electrons A^{-3}) cannot be taken as an indication of which is the water of hydration and which is the ammonium ion. Since no unambiguous hydrogen-bonding scheme could be devised, the nearest neighbors of both X1 and X2 are listed in Table VII. This water–ammonium cation system fills the void between the large monomeric $Pr(TTA)_4^-$ units. Previous tetrakis(β-diketone)lanthanide(III) chelates have had large substituted ammonium cations (*i.e.*, tetraethylammonium, trimethylammonium), but have exhibited no water of hydration. The structure of ammonium tetrakis(2-thenoyltrifluoroacetone)-praseodymate(III) monohydrate seems to be stabilized by the combination of the water of hydration and the small cation (*i.e.*, effectively a larger cation).

The stereoview of Figure 2 shows readily the positions of the water of hydration and the ammonium ion (X1 and X2) in relation to the metal. X1 is located 3.7 A and X2 is located 3.9 A from the praseodymium atom. The line defined by X1–Pr–X2, which has an angle of 172.9°, corresponds to one of the two twofold axes of the idealized dodecahedron. Each of these axes passes through the midpoints of two opposed *b* edges and through the center of the polyhedron, and is normal to the unique $\bar{4}$ axis. The large distances between the ammonium ion and the metal and between the water of hydration and the metal seem to preclude any appreciable bonding to the metal.

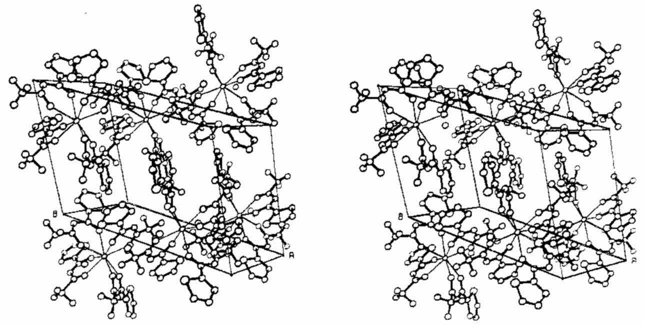

Figure 5.—Packing diagram for $NH_4Pr(TTA)_4 \cdot H_2O$. The two views constitute a stereoscopic pair and can be viewed with a small hand stereoscope.

TABLE VII

NEAREST NEIGHBORS OF X1 AND X2 (AMMONIUM AND WATER)

X1			X2		
Atom	Ligand	Distance, A	Atom	Ligand	Distance, A
X2		2.75	X1		2.75
O2	1	2.80	O2	3	2.82
F3	3	3.01	F3	2	3.15
F3	4	3.01	O1	4	3.23
O2	4	3.02	O1	2	3.50
F2	3	3.23	S	4	3.58
O1	3	3.25	F3	3	3.59
O2	2	3.32			
F1	3	3.33			

The metal to oxygen bond distances, which range from 2.42 to 2.49 A, are in very good agreement with other lanthanide β-diketone metal to oxygen distances: europium to oxygen distances of 2.45 A in tris(2-thenoyltrifluoroacetone)europium(III) dihydrate;[21] cerium to oxygen distances of 2.39 A in cerium(IV) acetylacetonate.[22] The mean value of the oxygen–oxygen distance of 2.85 A across the six-membered chelate ring agrees well with the mean value for cerium(IV) acetylacetonate of 2.81 A[22] and with the value found by Lippard in cesium tetrakis(hexafluoroacetylacetone)yttrate(III) of 2.85 A,[18] but is substantially larger than the mean value for zirconium(IV) acetylacetonate of 2.67 A,[20] as could be expected.

The relatively high degree of thermal motion exhibited by all of the light atoms is particularly pronounced in the CF_3 groups. The large parameter errors of all of these CF_3 groups can be ascribed to the fact that there probably exists a very high degree of anisotropic thermal motion, which was shown by a difference Fourier in the region of the CF_3 groups. It is worthwhile to mention that one of the fluorines of each CF_3 group lies in the plane of the remainder of the

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(19) W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964).

(20) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

(21) J. G. White, private communication.

(22) B. Matković and D. Grdenić, *Acta Cryst.*, **16**, 456 (1963).

ligand and away from O2 and that the other two fluorines bifurcate this oxygen, O2 (*i.e.*, take positions as far as possible from O2).

A close inspection of Figure 2 reveals that, since no. 2 TTA has its terminal groups (thienyl and CF_3) reversed, the over-all idealized (*i.e.*, neglecting the ring folding and the nonplanarity) symmetry including the total ligand is the minimum trivial symmetry of C_1. Considering only the eight oxygens of the four TTA ligands, the symmetry is very nearly S_4-$\bar{4}$, and not D_{2d}. The displacements, normal to the trapezoidal planes, amount to 0.06 A.

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$d\pi$–$p\pi$ Bonding and Conjugation Involving Group IV Elements

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The possibility of conjugation between aromatic residues linked by tetrahedral silicon, germanium, and tin atoms has been investigated. The experimental method used involved the measurement of the nmr contact shifts of suitably substituted paramagnetic nickel chelates. The results show that there is a negligible amount of conjugation. The significance of this result relative to the evidence for $d\pi$–$p\pi$ bonding involving group IV elements obtained by other experimental methods is discussed. In contrast to $p\pi$–$p\pi$ bonding, $d\pi$–$p\pi$ bonding with a central atom does not necessarily lead to conjugation. The synthesis of a five-coordinated tin chelate is also described, and nmr evidence for analogous germanium and silicon compounds is reported.

Introduction

The electronic structures of the second-, third-, and fourth-row elements—Si, Ge, and Sn—differ from that of their first-row analog C in that they have valence-shell d orbitals available for bond formation. The utilization of these orbitals to form σ bonds is well established. Thus, in an ion such as SiF_6^{2-} the coordination number six can only be attained by involving the Si 3d orbitals in the bonding process. The situation with respect to π bonding is less clear, although evidence for such interactions has been sought by a large number of physical techniques. Thus at various times bond length determinations,[1] dipole moment determinations,[2] infrared spectroscopy,[3] nuclear magnetic resonance,[4–6] chemical reactivity,[7] electronic spectroscopy,[8,9] and electron spin resonance[10–15] have all been utilized to obtain information bearing on this problem. Much of the earlier work has been summarized in a review by Stone and Seyferth.[16] These various investigations have not led to uniform conclusions regarding $d\pi$–$p\pi$ bonding—in some cases the results have indicated important contributions from such interactions (*e.g.*, see ref 8) while in other cases the effects appear to be negligible (*e.g.*, see ref 6). Part of this lack of uniformity can no doubt be ascribed to the use of different compounds in different experiments. It is certainly very possible that $d\pi$–$p\pi$ bonding may be important in one bonding situation but negligible in another. However, it also appears that some degree of confusion has arisen from drawing too close an analogy between $d\pi$–$p\pi$ bonding and $p\pi$–$p\pi$ bonding. In particular, the latter bonding is closely associated with conjugation, whereas the former may not be. There have been several theoretical papers in which this distinction has been pointed out, such as that of Craig and Mitchell[17] on "island" and cyclic delocalization in $p\pi$–$d\pi$ systems and the more general theoretical treatment of Jaffé[18] on multiple bonds involving d orbitals. In this latter paper the case of a tetrahedral central atom has been specifically treated. In concurrence with the theory, there is a variety of experimental evidence suggesting that when the central atom is one of the group IV elements—Si, Ge, or Sn—$d\pi$–$p\pi$ bonding is of some significance. Whether there

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(1) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(2) H. Soffer and T. DeVries, *J. Am. Chem. Soc.*, **73**, 5817 (1951).

(3) E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *Spectrochim. Acta*, **13**, 202 (1958).

(4) D. J. Blears, S. S. Danyluk, and S. Cawley, *J. Organometal. Chem.* (Amsterdam), **6**, 284 (1966).

(5) E. A. V. Ebsworth and S. G. Frankiss, *J. Am. Chem. Soc.*, **85**, 3516 (1963).

(6) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, *ibid.*, **88**, 622 (1966).

(7) R. Breslow and E. Mohacsi, *ibid.*, **83**, 4100 (1961); **84**, 684 (1962).

(8) L. Goodman, A. H. Konstam, and L. H. Sommer, *ibid.*, **87**, 1012 (1965).

(9) J. Nagy, J. Reffy, A. Kusgmann-Borbely, and K. Palossy-Becker, *J. Organometal. Chem.* (Amsterdam), **7**, 393 (1967).

(10) M. D. Curtis and A. L. Allred, *J. Am. Chem. Soc.*, **87**, 2554 (1965).

(11) R. Gerdil and E. A. C. Lucken, *ibid.*, **87**, 213 (1965).

(12) G. R. Hush and R. West, *ibid.*, **87**, 3993 (1965).

(13) M. G. Townsend, *J. Chem. Soc.*, 51 (1962).

(14) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).

(15) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 822 (1963).

(16) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(17) D. P. Craig and K. A. R. Mitchell, *J. Chem. Soc.*, 4682 (1965).

(18) H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).