prescribed by lattice forces which would not be duplicated in the isolated molecule.[29]

Acknowledgments. We thank Dr. R. H. Boyd for making his minimization program available to us. Also, program ORTEP (Carroll K. Johnson, Oak Ridge, 1965) was used to draw the molecular diagrams for Figures 1 and 4. The calculations were carried out on an IBM 360/50 computer and a CDC-3600 computer. In this regard the assistance of the ANU and CSIRO computer centers is gratefully acknowledged. Drs. M. R. Osborne and G. S. Chandler are thanked for helpful discussions.

[29] M. R. Snow, Proceedings of the XIIth International Conference on Coordination Chemistry, Sydney, 1969, p 92.

Stereochemistry of Tropolonato Complexes Utilizing the Higher Coordination Numbers. I. Nine-Coordinate Tetrakis(tropolonato)-N,N'-dimethylformamidethorium(IV)[1]

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Abstract: Molecular crystals of (DMF)ThT$_4$ (DMF is N,N'-dimethylformamide, T$^-$ is the bidentate $C_7H_5O_2^-$ tropolonate ion) utilize a two-molecule unit cell, space group $P\bar{1}$, having a = 15.222 (9), b = 10.922 (6), c = 9.452 (5) Å, α = 113.40 (1), β = 96.40 (2), γ = 87.53 (2)°. The intensities of 7476 independent reflections having $(\sin \theta)/\lambda \lesssim 0.69$ were measured with Mo Kα radiation by the θ–2θ scanning technique on an automated Picker four-circle diffractometer; the 6792 data statistically retained as observable were employed for structure determination and anisotropic refinement to an R of 0.047; all hydrogen atoms were directly placed. The nine-coordinate (DMF)ThT$_4$ molecule in the crystal approximates closely to C_s-m symmetry; it occurs as one of seven theoretical stereoisomers that utilize the monocapped square antiprism as coordination polyhedron. One tropolonato ligand spans a slant edge of the pyramidal cap while the monodentate ligand takes the one other vertex, also in the cap, that allows retention of C_s symmetry. A second tropolonato ligand spans the basal edge of the polyhedron opposite to the monodentate ligand, and the two other tropolonato ligands span a mirrored pair of lateral edges of the polyhedron. Dimensional variations from the ideal C_{4v} geometry of the polyhedron are required by the small "bite" of the tropolonato ligand (2.52–2.56 Å); inter-ring O···O contacts range upward from 2.79 Å. The length of the Th–O bond to the apical oxygen, 2.485 (5) Å, is significantly greater than the average, 2.445 Å, for the other seven bonds to tropolonato oxygen; the bond to the uncharged DMF ligand at 2.519 (6) Å is still longer. Bond parameters in the tropolonato ligands compare favorably with those reported from simpler structures.

Stable mononuclear complexes that utilize coordination numbers greater than six are predominantly chelated species. It is, nonetheless, the configurational geometries theoretically attainable with monodentate ligands that provide the most illuminating basis for the stereochemical discussion of experimentally preparable complexes. The geometry of packing N spherically symmetric, chemically identical, monodentate ligands around a central cation affords a decisive preference for a particular coordination polyhedron when N is 4, 6, or 12, corresponding to any one of the three regular polyhedra with triangular faces (tetrahedron, octahedron, and icosahedron). In Figure 1 the ratio (ρ) of polyhedron radius or complexing bond length (M–L) to polyhedron edge length or ligand packing diameter (L–L) is plotted against coordination number (N) for the more probable coordination polyhedra.[4] Points representing the three regular polyhedra with triangular faces and the three-coordinate equilateral triangle define the straight line that represents a uniformly excellent stereochemistry; for a fixed ligand diameter or polyhedron edge length (L–L), the slope of this line gives the fractional increment in the complexing bond length (M–L) with unit increase in the coordination number (N) that maintains steric excellence. It is evident that the transition from the octahedron to the best of the seven-coordination polyhedra is not taken easily, whereas the step from seven- to eight-coordination (the cube excluded) is a small one. Within the wide gap separating the octahedron and the icosahedron, the better eight- and nine-coordination polyhedra are approximately equal in steric merit, as are also, at a lower level of merit, the better seven- and ten-coordination polyhedra.

For each of the coordination numbers, five and seven–ten inclusive, there are two (at least) coordination polyhedra that differ radically in symmetry type, but only modestly in the value of (M–L)/(L–L). Each

[1] This investigation was supported in part by National Science Foundation Grant No. GP-6710X, by Public Health Research Grant No. 2-RO1-GM09370 from the National Institutes of Health, General Medical Sciences, and by the Advanced Research Projects Agency.

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[4] Figure 1 is an alternative, easily grasped representation of the Pauling minimum radius ratios for the stability of various coordination polyhedra;[5] it is empirically useful irrespective of the nature of the complexing bonds.

[5] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 544–546. Pauling has employed his "univalent" ionic radii for the prediction of maximum coordination numbers with marked success.[6]

[6] L. Pauling, *J. Amer. Chem. Soc.*, 55, 1895 (1933).

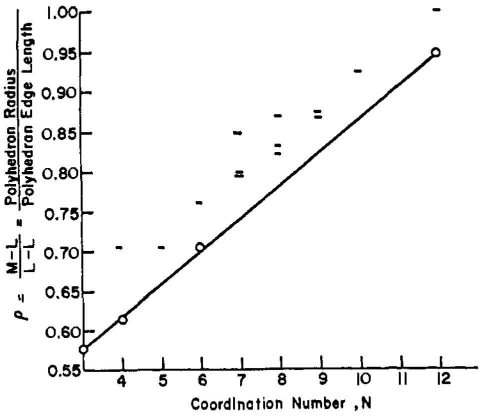

Figure 1. The ratio (ρ) of polyhedron radius (M–L) to polyhedron edge length (L–L) plotted against coordination number (N) for various coordination polyhedra. Reading upward (increasing ρ) for each coordination number the polyhedra represented are as follows: $N = 4$, the regular tetrahedron and the square; $N = 5$, the trigonal bipyramid and (coincidentally) the tetragonal pyramid; $N = 6$, the regular octahedron and the trigonal prism; $N = 7$, the C_{3v} monocapped octahedron, the C_{2v} monocapped trigonal prism, and the D_{5h} pentagonal bipyramid; $N = 8$, the D_{4d} square antiprism, the D_{2d} tetragonal dodecahedron, and the cube; $N = 9$, the D_{3h} tricapped trigonal prism and the C_{4v} monocapped square antiprism; $N = 10$, the D_{4d} bicapped square antiprism; $N = 12$, the regular icosahedron and the O_h cuboctahedron. (The special status of the pentagonal bipyramid is discussed in the accompanying paper.[14])

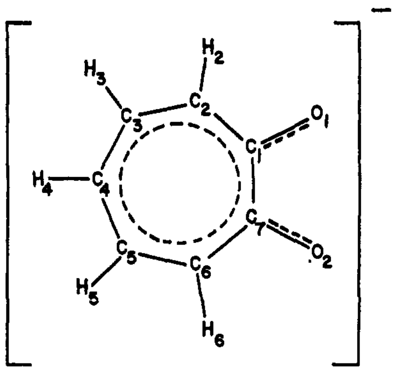

Figure 2. Diagram of the tropolonate ion (T^-) showing the numbering scheme used for the atoms. An additional literal subscript (a, b, c, or d) to the numbered atomic symbol is used to identify the pertinent tropolonato ligand within the $(DMF)ThT_4$ molecule.

such pair of polyhedra differs, for a fixed bond distance, in the value of the shortest L–L contact and in the number of shortest contacts; the polyhedron that has the larger value of the shortest L–L contact (or ligand packing diameter) has invariably a larger number of these contacts. In the hard-sphere model, only the shortness of the L–L contact is significant, but in a more realistic model that takes account of the compressibility of the ligands the number of such contacts assumes comparable importance. Several investigators have used the familiar Born relation for the ligand nonbonding repulsive energy to compare relative values of this energy for competing polyhedra in both the seven-[7] and the eight-coordination[8] categories. It turns out that, for a physically plausible range in the value of the Born parameter, the differences in the repulsive energies among three seven-coordination polyhedra and between two eight-coordination polyhedra (the cube remains highly improbable) are too small to serve as definitive criteria of stereochemical preferences. A similar conclusion quite surely applies for $N = 9$ and, perhaps, for $N = 10$. Attainment of the maximum coordination number allowed by nonbonding repulsions within the range $N = 7–10$ generally is signalized by a ligand packing diameter that is significantly smaller than the van der Waals value.[9] The coordination number of a complex in a crystal may be smaller than the value preferred in solution because the selection of the crystalline arrangement that maximizes the crystal energy may be overriding; in such a case, nonbonding repulsions within the complex become rather unimportant.

The foregoing considerations do not apply if the electronic structure of the central atom in the complex is quite inconsistent with quasi-spherical behavior, nor do they apply without modification to chelated species, quasi-spherical character of the central atom notwithstanding; a multidentate chelating agent may indeed dictate the stereochemistry of the coordination group.[10] Given the paucity of stable complexed species that use only monodentate ligands to attain coordination numbers greater than six and the visible shortcomings of current electronic theories for the prediction of configurational geometry, the experimental study of the more subtle factors that influence the choice of configurational type is best carried out on complexes that involve, at most, bidentate chelation.

The tropolonate ion, $C_7H_5O_2^-$ (hereinafter written T^-), with the structural formula displayed in Figure 2, has been shown by Muetterties and coworkers to form stable complexes with a wide variety of cations.[11–13] They point out that the low resultant charge, compact planar conformation, and relatively small "bite" of the bidentate tropolonato ligand are conducive to the use of higher coordination numbers, seven through ten, by the larger triply and quadruply charged cations; and their experimental investigations provide strong evidence for the existence in solution of such varied species as ten-coordinate ThT_5^-, nine-coordinate $(DMSO)ThT_4$ (DMSO = dimethyl sulfoxide), eight-coordinate T_4Ta^+, SnT_4, LnT_4^- (Ln = lanthanide), and seven-coordinate T_3SnCl and T_3SnOH.

A program to determine the stereochemical preferences of selected tropolonato complexes as these are observed in crystalline phases is well along in this laboratory. Single crystals of adequate size and quality to provide X-ray data having the range $(0 < (\sin\theta)/\lambda \lesssim$

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[7] (a) D. Britton, *Can. J. Chem.*, 41, 1632 (1963); (b) T. A. Claxton and G. C. Benson, *ibid.*, 44, 157 (1966).

[8] (a) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963); (b) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).

[9] When the ligand packing diameter is quite significantly below the van der Waals value the repulsive energy may reach ~15% of the total bond energy and the shape parameters of any coordination polyhedron that is not one of the regular polyhedra are markedly affected by the nonbonding repulsions.[8a]

[10] See (a) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman and Co., San Francisco, Calif., 1968, pp 573–594; (b) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, 3, 34 (1964), for multidentate chelates in which the high-spin Fe^{3+} ion is constrained to five- and seven-coordination, respectively.

[11] (a) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, 86, 5132 (1964); (b) *ibid.*, 87, 21 (1965); (c) *ibid.*, 87, 4706 (1965); (d) *Quart. Rev.* (London), 21, 109 (1967).

[12] (a) E. L. Muetterties, *J. Pure Appl. Chem.*, 10, 54 (1965); (b) *J. Amer. Chem. Soc.*, 88, 305 (1966).

[13] E. L. Muetterties, H. Roesky, and C. M. Wright, *ibid.*, 88, 4856 (1966).

0.65 Å^{-1}) and number (4000–10,000) needed for quantitatively precise determinations of the rather complicated structures have thus far been obtained for five different compounds. The results of our structure determination for tetrakis(tropolonato)-N,N′-dimethylformamidethorium(IV), written hereafter as (DMF)ThT$_4$, are presented herein, and structure analyses for crystalline solvates of T$_3$SnCl and T$_3$SnOH are reported in the accompanying paper.[14] The structures of T$_4$TaPF$_6$ and NH$_4$HoT$_4$ also are known and are currently being refined. The structural principles outlined in connection with Figure 1 will be elaborated and expanded on the basis of our structural results.

Experimental Section

The crystals of (DMF)ThT$_4$ used for structure determination were obtained as an incidental product of attempts to recrystallize a fine powder of NaThT$_5$, kindly furnished by Dr. E. L. Muetterties, from various solvents. A small portion of the NaThT$_5$ sample was dissolved in hot dimethylformamide (DMF); upon slow isothermal evaporation of this solution to dryness, yellow-brown platelike crystals of (DMF)ThT$_4$ distributed within a powder (presumably NaT) were obtained. A nearly cube-shaped specimen ~0.125 mm on an edge was cut from one such platelet under a microscope. Prior to mounting on a goniometer head, this specimen received a (probably unnecessary) protective coating of shellac; it gave no evidence of deterioration during the extended process of recording the X-ray data.

Preliminary X-ray study by photographic methods together with the negative results of sensitive tests for piezoelectricity assigned the crystal to the triclinic system with $P\bar{1}$ as the probable space group;[15] this assignment was fully confirmed during the subsequent determination of structure. The crystal was then accurately centered on a Picker four-circle diffractometer and 40 reflections, chosen to give a good sampling of reciprocal space and instrument settings, were used to align the crystal and determine precise lattice constants as a basis for calculating angular settings for the recording of intensity data. A least-squares refinement[16] of the diffraction geometry for these 40 reflections, recorded at the ambient laboratory temperature of 21 ± 1°, gave the lattice constants (λ 0.71069 Å): $a = 15.222$ (9), $b = 10.922$ (6), $c = 9.452$ (5) Å, $\cos \alpha = -0.3972$ (1) or $\alpha = 113.40°$, $\cos \beta = -0.1114$ (3) or $\beta = 96.40°$, and $\cos \gamma = 0.0430$ (4) or $\gamma = 87.53°$. A Delauney reduction using these parameters confirmed the triclinic description. A cell content of two (DMF)ThT$_4$ molecules gave excellent agreement between calculated and measured densities, 1.830 and 1.826 g/cc, respectively.

Intensity measurements utilized Zr-filtered Mo Kα radiation and the θ–2θ scanning technique on a card-controlled Picker diffractometer. Each scan (1°/min) included a variable increment in angle above the 2.2° minimum to allow for spectral dispersion; background counts each of 40-sec duration were taken at both limits of the scan. A total of 7476 independent reflections having $(\sin \theta)/\lambda \lesssim 0.69$ were measured in concentric shells of increasing 2θ; intensity measurement was involuntarily terminated at this limit by the final failure of the programming unit in the diffractometer assembly. Ten standard reflections representing a judicious sampling of reciprocal space, machine settings, and intensities were employed as a monitor for possible misalignment and/or deterioration of the crystal; no evidence of either developed at any time. Three interruptions of the measurements were required by electronic and mechanical failures of the equipment. The replacement of a vacuum tube in the power detector supply produced a uniform increase in the intensities of ~50%; repairs effected on two other occasions produced quite minor alterations in the scale of intensities. Consequently, four distinct scale factors, divided into two groups within each of which the factors differed very little, were used in the subsequent least-squares refinement.

The linear absorption coefficient of the crystal for Mo Kα radiation is 6.02 mm^{-1}, yielding a μR of 0.466 for a spherical crystal having the same volume as the cube-shaped specimen used for intensity measurements. The absorption of X-rays by a spherical crystal having $\mu R = 0.466$ is virtually independent of scattering angle, and deviations from this absorption occasioned by the use of the cube-shaped specimen are practically negligible except for a trivial fraction of the reflections. Under these circumstances no absorption correction was made and the intensities were reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. Of the 7476 reflections examined, 684 were rejected as objectively unobserved by applying the criterion, $|F_o| < 0.5\sigma(|F_o|)$, wherein $\sigma(|F_o|)$ is the standard deviation computed from

$$\sigma^2(|F_o|) = (C_t + k^2B)/4|F_o|^2Lp^2$$

C_t being the total count from the scanning, k the ratio of scanning time to total background counting time, B the total background count, and Lp the Lorentz–polarization correction. The remaining 6792 observed intensities were used in the determination and refinement of structure.[17]

Structure determination was achieved through a combination of the heavy-atom technique, difference Fourier syntheses, and least-squares refinement. The wholly straightforward interpretation of the Patterson synthesis of the 2592 $|F_o|^2$ data having $(\sin \theta)/\lambda < 0.48$ placed the thorium atoms in twofold general positions, $\pm(x,y,z)$. These atomic coordinates and an isotropic temperature factor assigned to the thorium atom were varied with a scale factor in two cycles of full-matrix least-squares refinement which resulted in a conventional unweighted residual, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 0.226 for these low angle data. A single difference Fourier synthesis based on these refined parameters was sufficient to locate all other atoms (excluding hydrogens) in the asymmetric unit. A full-matrix least-squares refinement[18] with anomalous dispersion corrections and anisotropic temperature factors for the thorium atom, but isotropic thermal parameters for all other atoms, gave $R = 0.046$ for 2592 reflections. All of the 6792 independent reflections were then included in a fully anisotropic refinement of the 382 parameters through block-diagonal[19] least-squares minimization of the function $\Sigma w(|F_o| - k|F_c|)^2$ to give, with unit weighting ($w = 1$), $R = 0.051$. A Fourier difference synthesis based on the refined parameters afforded direct evidence for the placement of all 27 hydrogen atoms in chemically anticipated positions, most satis-

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[14] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3636 (1970).

[15] "International Tables for X-Ray Crystallography," Vol. I, "Symmetry Groups," The Kynoch Press, Birmingham, England, 1952, p 75.

[16] Use was made of the PICK II computer program, a revision of W. C. Hamilton's MODE 1 program.

[17] Some 550 reflections having quasi-absolute magnitudes of F_o (for a primitive cell) in the range 5–10 electrons were thereby retained in the analysis. The average value of $||F_o| - |F_c||$ for these reflections, which were for the most part to be seen as definite peakings on the strip recorder chart, was not significantly different from that of the bulk of the data. We consider that the refined model of the structure should take cognizance of these particularly structure-sensitive data, the somewhat deleterious effect on the conventional residual (R) notwithstanding.

[18] Following W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962. Atomic form factors from D. T. Cromer and J. L. Mann, *Acta Crystallogr.*, **A24**, 321 (1968), and anomalous dispersion corrections from D. T. Cromer, *ibid.*, **18**, 17 (1965), were used in this and all subsequent least-squares refinements of the structural parameters.

[19] Block-diagonal least-squares refinement utilized the computer program REFINE, written by J. J. Park in this laboratory; it embodies features of P. A. Vaughn's REFINE-XK3 program and of the analysis given by L. I. Hodgson and J. S. Rollett, *ibid.*, **16**, 329 (1963). One fully elaborated cycle of this block-diagonal least-squares refinement of the (DMF)ThT$_4$ structure on the IBM 360/65 computer required 28 min. To approximate to one full cycle of the standard Busing–Martin–Levy full-matrix fully anisotropic refinement[18] the problem had to be split into a three-stage operation with sequential refinements by parts, requiring a total of 135 min. Upon feeding the final results of our block-diagonal refinement into this three-stage operation, with the parameters of the thorium atom allowed to refine in all three stages, it was found that (1) no bond length involving a tropolonato ligand (C–H bonds excluded) was altered by more than 0.003 Å, the averaged shift was 0.0011 Å; (2) no bond length involving the DMF ligand was altered by more than 0.005 Å, the averaged shift was 0.0020 Å; (3) it is also of interest that changes in the thermal parameters of the thorium atom, appreciable only in the first partial cycle, were rather less than 0.01 Å^2. Comparisons between the block-diagonal and full-matrix refinements for simpler structures that do not require the latter procedure to be applied in partial cycles are not less emphatic in suggesting the absence of significant differences. Such comparisons, however, have been made only with data having a scope (number and range in $(\sin \theta)/\lambda$) comparable with those of this paper; we do not recommend the use of block-diagonal refinement with the scanty chromium sphere data that allow the apparent atomic positions to vary significantly with every elaboration of, or correction to, an approximate model.

Table I. Atomic Coordinates in Crystalline (DMF)ThT$_4$[a]

Atom type[b]	Coordinates 10^4x	10^4y	10^4z
O_m	1472 (4)	2410 (6)	−741 (7)
O_{a1}	1238 (4)	1615 (5)	1849 (7)
O_{a2}	802 (3)	4067 (5)	2578 (7)
O_{b1}	2859 (3)	1028 (5)	596 (6)
O_{b2}	3400 (4)	3020 (5)	170 (6)
O_{c1}	3699 (3)	3102 (6)	3375 (6)
O_{c2}	2277 (3)	3507 (6)	4640 (6)
O_{d1}	2809 (4)	5524 (5)	3580 (6)
O_{d2}	1945 (4)	5075 (5)	988 (6)
N_m	638 (5)	2336 (7)	−2900 (8)
C_{m1}	825 (7)	2780 (9)	−1376 (10)
C_{m2}	1242 (8)	1458 (12)	−3946 (12)
C_{m3}	−191 (8)	2702 (13)	−3572 (13)
C_{a1}	432 (5)	1897 (8)	2121 (8)
C_{a2}	−154 (6)	850 (8)	1875 (9)
C_{a3}	−1046 (6)	872 (10)	2075 (10)
C_{a4}	−1581 (6)	1954 (11)	2751 (11)
C_{a5}	−1368 (5)	3281 (10)	3301 (10)
C_{a6}	−610 (5)	3877 (9)	3214 (10)
C_{a7}	193 (5)	3305 (8)	2618 (8)
C_{b1}	3465 (5)	763 (7)	−320 (8)
C_{b2}	3814 (5)	−527 (8)	−922 (10)
C_{b3}	4471 (6)	−1070 (8)	−1914 (10)
C_{b4}	4945 (6)	−478 (10)	−2655 (10)
C_{b5}	4858 (6)	805 (9)	−2577 (11)
C_{b6}	4331 (6)	1847 (9)	−1688 (10)
C_{b7}	3738 (5)	1907 (7)	−612 (8)
C_{c1}	3799 (5)	3668 (7)	4869 (8)
C_{c2}	4645 (5)	3976 (9)	5647 (10)
C_{c3}	4925 (6)	4740 (10)	7187 (11)
C_{c4}	4414 (7)	5299 (10)	8435 (10)
C_{c5}	3524 (7)	5109 (10)	8416 (10)
C_{c6}	2896 (6)	4474 (10)	7201 (10)
C_{c7}	2962 (5)	3891 (8)	5588 (9)
C_{d1}	2697 (5)	6555 (7)	3255 (8)
C_{d2}	3026 (6)	7790 (8)	4274 (10)
C_{d3}	2981 (7)	9030 (8)	4207 (11)
C_{d4}	2574 (7)	9413 (9)	3050 (12)
C_{d5}	2135 (7)	8591 (9)	1674 (11)
C_{d6}	1958 (7)	7245 (9)	1099 (10)
C_{d7}	2183 (5)	6274 (7)	1737 (8)
Th	10^5x = 22918 (2)	10^5y = 32688 (3)	10^5z = 19344 (3)

[a] Figures in parentheses are the estimated standard deviations. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, c, or d) and a numerical subscript that follows the numbering scheme given in Figure 2 for the tropolonate ion. The atoms of the unique monodentate DMF ligand are denoted by the literal subscript m.

factorily so for the tropolonato hydrogen atoms. Final cycles of block-diagonal least-squares refinement, which employed unit weighting included the hydrogen atoms with isotropic thermal parameters, but was otherwise anisotropic, led to R = 0.047 and a conventional weighted residual, $\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$, of 0.052. Examination of a $|\Delta F|$ *vs.* $|F_o|$ plot showed that little or nothing was to be gained by departing from unit weighting.[20]

Two further points regarding the hydrogen atoms may be made. Excepting those in the peripheral methyl groups of the dimethylformamide ligands, the hydrogen positions given by the difference synthesis were quite resistant to undue movement during the subsequent ruthless process of overall least-squares minimization. Because the determination of the positions and the thermal parameters of all atoms except hydrogen was quite dominated by the very numerous (~5500) data from beyond the chromium Kα sphere, the inclusion of the hydrogen contributions in the final stages of refinement had no objectively significant effect upon the parameters of any individual C, O, or N atom, even though every carbon atom except those of the C_1 and C_7 classes (Figure 2) carried one or more hydrogen atoms. A cumulative effect of the hydrogen contributions, nonetheless, was displayed in an apparent quasi-uniform shrinkage of every tropolonato carbon skeleton amounting, on the average, to a decrease of ~0.010 Å in six of the seven C–C bond lengths within each ring; the unique C_1–C_7 and the C–O bond lengths involving unhydrided carbon atoms were not thus affected. C–N and C–O bond distances involving the hydrided carbon atoms of the DMF ligand also displayed apparent shrinkage of $\lesssim$0.01 Å upon inclusion of the hydrogen contributions. Apparent alterations in the complexing Th–O bond lengths were trivial in magnitude ($\lesssim$0.002 Å) and random in sign.

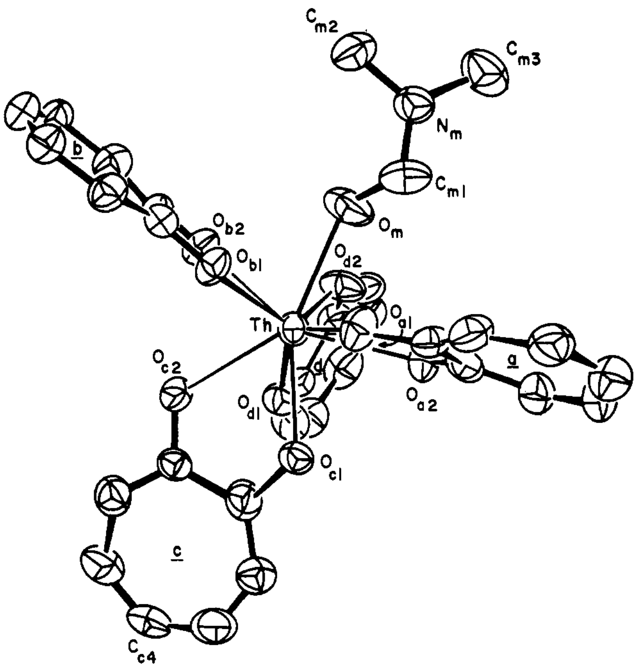

Figure 3. Model in perspective of the (DMF)ThT$_4$ molecule. The quasi-mirror plane includes all atoms of ligand d, the O_m and Th atoms, and the C_{c4} atom of ligand c.

The final coordinates and anisotropic thermal parameters for all atoms except hydrogen are listed in Tables I and II, respectively; the refined positions and isotropic thermal parameters of the hydrogen atoms are given in Table III.[20] The numbering scheme used to designate atoms of the (DMF)ThT$_4$ molecule is as follows. Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, c, or d), and a numerical subscript that follows the numbering scheme given in Figure 2 for the tropolonate ion. Symbols for the atoms in the DMF ligand carry the unique subscript m and the numerical subscripts shown in Figure 3. Each symbol for a hydrogen atom carries the two subscripts of the carbon to which it is attached and, for the hydrogen atoms of the DMF methyl groups, a third subscript to distinguish among hydrogens attached to the same carbon atom.

Discussion of Results

A model seen in perspective of the nine-coordinate (DMF)ThT$_4$ molecule, lacking only the hydrogen atoms, is illustrated in Figure 3; each atom is represented by an ellipsoid[21] having the shape, orientation, and relative size concomitant with the thermal parameters listed in Table II. We note first that the geometry of the complexing pattern is fully compatible with the ideal symmetry of C_s-m—but no more than this—for the molecule as a whole when freed of environmental constraints; apart from the orientation of the DMF

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(20) A table of the 6792 observed and calculated amplitudes from this refinement has been deposited as Document No. NAPS-00875 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $3.00 for photoprints or $1.00 for microfiche. Advance payment is required. Make checks or money order payable to: ASIS–NAPS.

(21) C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table II. Thermal Parameters in Crystalline (DMF)ThT$_4$[a]

Atom type[b]	Anisotropic Parameters, Å^2						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
Th	3.06 (1)	2.84 (1)	2.85 (1)	0.32 (1)	0.36 (1)	1.15 (1)	2.9
O_m	6.0 (3)	4.8 (3)	3.9 (3)	0.4 (2)	−1.6 (2)	1.2 (2)	4.7
O_{a1}	3.9 (2)	3.0 (2)	5.2 (3)	0.3 (2)	1.3 (2)	1.4 (2)	3.9
O_{a2}	3.2 (2)	3.5 (2)	5.2 (3)	0.7 (2)	0.8 (2)	1.8 (2)	3.8
O_{b1}	3.9 (2)	3.2 (2)	4.0 (2)	0.8 (2)	1.3 (2)	1.4 (2)	3.5
O_{b2}	4.4 (2)	3.5 (2)	3.4 (2)	0.6 (2)	1.5 (2)	1.4 (2)	3.5
O_{c1}	3.7 (2)	5.1 (3)	3.0 (2)	1.5 (2)	0.6 (2)	1.5 (2)	3.7
O_{c2}	3.1 (2)	6.6 (3)	3.4 (2)	−0.3 (2)	0.1 (2)	2.9 (2)	3.7
O_{d1}	4.3 (2)	3.5 (2)	3.4 (2)	0.2 (2)	−0.1 (2)	1.7 (2)	3.6
O_{d2}	5.2 (3)	3.4 (2)	3.3 (2)	0.2 (2)	−0.3 (2)	1.6 (2)	3.9
N_m	4.9 (3)	4.5 (3)	3.3 (3)	0.2 (3)	−0.1 (2)	1.7 (2)	4.1
C_{m1}	6.1 (5)	4.6 (4)	3.3 (3)	−0.3 (3)	0.6 (3)	1.6 (3)	4.5
C_{m2}	6.7 (6)	7.0 (6)	4.4 (4)	1.3 (5)	1.7 (4)	1.6 (4)	5.9
C_{m3}	6.7 (6)	8.8 (7)	5.6 (5)	1.1 (5)	−1.6 (5)	3.4 (5)	6.3
C_{a1}	3.7 (3)	4.0 (3)	2.6 (3)	0.3 (3)	0.4 (2)	1.1 (2)	3.4
C_{a2}	4.5 (4)	4.1 (4)	3.3 (3)	−0.4 (3)	0.9 (3)	0.8 (3)	4.0
C_{a3}	4.6 (4)	5.9 (5)	3.9 (4)	−1.3 (3)	0.2 (3)	1.6 (3)	4.7
C_{a4}	3.6 (4)	7.0 (5)	4.4 (4)	−0.0 (3)	0.6 (3)	2.5 (4)	4.7
C_{a5}	3.3 (3)	5.9 (5)	4.2 (4)	1.0 (3)	0.5 (3)	1.9 (3)	4.3
C_{a6}	3.5 (3)	4.4 (4)	4.3 (4)	0.7 (3)	0.4 (3)	1.6 (3)	4.1
C_{a7}	3.8 (3)	3.8 (3)	2.7 (3)	0.3 (3)	−0.4 (2)	1.0 (2)	3.4
C_{b1}	2.9 (3)	3.5 (3)	3.2 (3)	0.0 (2)	−0.0 (2)	1.4 (2)	3.2
C_{b2}	4.1 (3)	3.4 (3)	3.7 (3)	0.2 (3)	0.3 (3)	1.1 (3)	3.8
C_{b3}	4.2 (4)	4.0 (4)	4.0 (4)	1.1 (3)	0.3 (3)	0.7 (3)	4.2
C_{b4}	4.3 (4)	5.5 (5)	4.3 (4)	1.3 (3)	1.1 (3)	1.2 (3)	4.7
C_{b5}	4.0 (4)	5.2 (4)	4.5 (4)	0.2 (3)	1.5 (3)	1.2 (3)	4.5
C_{b6}	4.5 (4)	4.4 (4)	3.8 (3)	0.1 (3)	1.1 (3)	1.5 (3)	4.2
C_{b7}	3.5 (3)	3.4 (3)	3.0 (3)	0.1 (2)	0.0 (2)	1.1 (2)	3.3
C_{c1}	3.5 (3)	3.6 (3)	3.3 (3)	0.5 (2)	0.7 (2)	1.8 (2)	3.3
C_{c2}	3.6 (3)	5.0 (4)	4.7 (4)	0.1 (3)	0.3 (3)	2.7 (3)	4.1
C_{c3}	4.7 (4)	5.4 (4)	4.6 (4)	−0.5 (3)	−0.4 (3)	2.7 (4)	4.6
C_{c4}	6.7 (5)	5.5 (5)	3.6 (4)	−0.4 (4)	−0.7 (3)	2.2 (3)	4.9
C_{c5}	6.5 (5)	6.1 (5)	2.9 (3)	1.2 (4)	0.6 (3)	1.7 (3)	4.8
C_{c6}	4.6 (4)	6.3 (5)	3.5 (3)	1.1 (3)	1.1 (3)	2.8 (3)	4.2
C_{c7}	3.5 (3)	4.1 (3)	3.7 (3)	0.6 (3)	0.8 (2)	2.3 (3)	3.4
C_{d1}	3.2 (3)	3.6 (3)	3.0 (3)	0.5 (2)	1.1 (2)	1.5 (2)	3.0
C_{d2}	4.4 (4)	3.9 (3)	4.2 (4)	0.1 (3)	0.1 (3)	1.5 (3)	4.2
C_{d3}	5.6 (5)	3.3 (3)	5.4 (4)	−0.2 (3)	0.6 (4)	1.4 (3)	4.7
C_{d4}	6.0 (5)	4.0 (4)	6.5 (5)	0.6 (3)	1.8 (4)	2.6 (4)	5.0
C_{d5}	6.3 (5)	4.6 (4)	5.3 (5)	1.0 (4)	1.6 (4)	2.8 (4)	4.9
C_{d6}	6.1 (5)	4.6 (4)	3.9 (4)	1.3 (3)	1.1 (3)	2.2 (3)	4.5
C_{d7}	4.1 (3)	3.5 (3)	3.1 (3)	0.7 (3)	0.9 (2)	1.5 (2)	3.4

[a] The number in parentheses that follows each B_{ij} value is the estimated standard deviation in the last significant figure. The B_{ij}'s in Å^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, c, or d) and a numerical subscript that follows the numbering scheme given in Figure 2 for the tropolonate ion. The atoms of the unique monodentate DMF ligand are denoted by the literal subscript m. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

ligand around the complexing Th–O_m bond, the molecule in the crystal otherwise approximates to the requirements of a mirror plane in which the Th and O_m atoms, the C_{c4} and H_{c4} atoms of tropolonato ligand c, and all atoms of tropolonato ligand d ideally would be centered. Examination of Figure 3 in conjuction with the atomic displacements from the quasi-mirror plane listed in Table IV shows that the Th and O_m atoms lie out of the plane by 0.02 and −0.05 Å, respectively, that all atoms of ligand d lie within $\lesssim$0.03 Å of the mean plane, and that ligand c, lying perpendicular to the quasi mirror, is split along its principal axis into virtually enantiomorphic halves. The mirror-image relationship between ligands a and b is rather less closely approximated because the mean planes of these ligands are differently inclined, by 11.6 and 15.0°, respectively, to the quasi-mirror plane. Inasmuch as the reality of C_s symmetry for the unconstrained molecule is beyond reasonable doubt, the presence of a mirror plane is assumed in the following discussion of the coordination group.

Ignoring, for the moment, the bidentate character of the tropolonato ligands, we ask whether the ThO_9 coordination group approximates the geometry and the symmetry of either of the configurations theoretically preferred with monodentate ligands. The normal to the mirror plane through the thorium atom displays no semblance of rotational symmetry beyond the trivial C_1. There is, however, one (and only one) preferred direction in the coordination group that possesses quasi symmetry of higher order than C_1 and is simultaneously consistent with the presence of a required mirror plane: the Th–O_{d2} bond defines the principal axis of quasi-fourfold (C_4) symmetry within the monocapped square-antiprismatic coordination group illustrated in Figure 4. The maximum symmetry, with only monodentate ligands, of this nine-coordination polyhedron is C_{4v}. With four of the five ligands bidentate, as in (DMF)ThT$_4$, there are seven plausible stereoisomers: one of these, with the monodentate ligand on the unique axis, ideally retains C_4 symmetry, two others retain only a mirror plane

Table III. Refined Parameters for Hydrogen Atoms in Crystalline (DMF)ThT$_4$[a]

Atom type[b]	Fractional coordinates 10^3x	10^3y	10^3z	Isotropic thermal parameter B, Å^2
H_{m1}	35 (9)	378 (14)	−73 (16)	9 (4)
H_{m2-1}	87 (7)	52 (11)	−453 (13)	6 (3)
H_{m2-2}	131 (10)	147 (16)	−503 (18)	11 (5)
H_{m2-3}	183 (8)	132 (12)	−334 (14)	6 (3)
H_{m3-1}	−42 (11)	395 (16)	−280 (19)	11 (5)
H_{m3-2}	−22 (12)	284 (18)	−433 (21)	16 (6)
H_{m3-3}	−53 (8)	177 (13)	−380 (15)	7 (4)
H_{a2}	13 (6)	−3 (9)	146 (11)	3 (2)
H_{a3}	−131 (6)	−11 (9)	164 (11)	3 (2)
H_{a4}	−215 (9)	175 (14)	281 (16)	7 (4)
H_{a5}	−178 (5)	400 (8)	386 (9)	2 (2)
H_{a6}	−58 (5)	489 (8)	360 (9)	1 (2)
H_{b2}	352 (5)	−113 (7)	−63 (8)	1 (1)
H_{b3}	460 (7)	−206 (10)	−220 (12)	4 (3)
H_{b4}	551 (6)	−111 (9)	−316 (11)	3 (2)
H_{b5}	531 (8)	131 (11)	−283 (13)	6 (3)
H_{b6}	440 (5)	274 (8)	−172 (9)	2 (2)
H_{c2}	519 (7)	356 (11)	492 (13)	5 (3)
H_{c3}	565 (8)	491 (12)	741 (13)	6 (3)
H_{c4}	475 (7)	599 (11)	952 (13)	6 (3)
H_{c5}	326 (7)	561 (10)	951 (12)	5 (3)
H_{c6}	235 (7)	434 (10)	749 (12)	4 (2)
H_{d2}	332 (5)	765 (8)	503 (9)	3 (2)
H_{d3}	327 (7)	983 (10)	523 (12)	4 (3)
H_{d4}	264 (6)	1042 (9)	335 (11)	4 (2)
H_{d5}	182 (8)	928 (12)	111 (14)	8 (3)
H_{d6}	159 (8)	672 (11)	21 (13)	4 (3)

[a] Figures in parentheses are the estimated standard deviations. [b] Each symbol for a hydrogen atom carries the same two subscripts as the carbon atom to which it is bonded. In addition, methyl group hydrogens of the unique monodentate DMF ligand carry a third subscript to distinguish between hydrogens on the same carbon atom.

Table IV. Atomic Displacements from the Quasi-Mirror Plane in (DMF)ThT$_4$.[a] Equation of the Mean Plane:[b] $0.905X + 0.020Y - 0.424Z = 2.37$

Type[c]	Displacements from the Mean Plane, Å Ligand a	Ligand b	Ligand c	Ligand d	Ligand m
Th	0.02	0.02	0.02	0.02	0.02
O_{x1}	1.47	−1.32	−1.26	0.01	−0.05[d]
O_{x2}	2.35	−2.30	1.27	0.03	
C_{x1}	2.70	−2.57	−0.73	−0.01	0.55
C_{x2}	3.42	−3.29	−1.55	−0.03	−1.16
C_{x3}	4.74	−4.64	−1.25	−0.02	0.95
C_{x4}	5.76	−5.64	0.00	0.01	
C_{x5}	5.69	−5.51	1.23	0.00	
C_{x6}	4.59	−4.40	1.55	0.02	
C_{x7}	3.22	−3.10	0.74	0.02	
N					0.13

[a] The quasi mirror is the mean plane for the Th, O_m, C_{c4}, and all nine tropolonato skeleton atoms of ligand d. [b] X, Y, and Z are orthogonal coordinates measured in Å along ($b \times c^*$), b, and c^*, respectively, of the crystallographic coordinate system. [c] Atoms numbered in agreement with Figures 2 and 3, with x denoting the ligand (a, b, c, d, or m). [d] Displacement of the O_m atom.

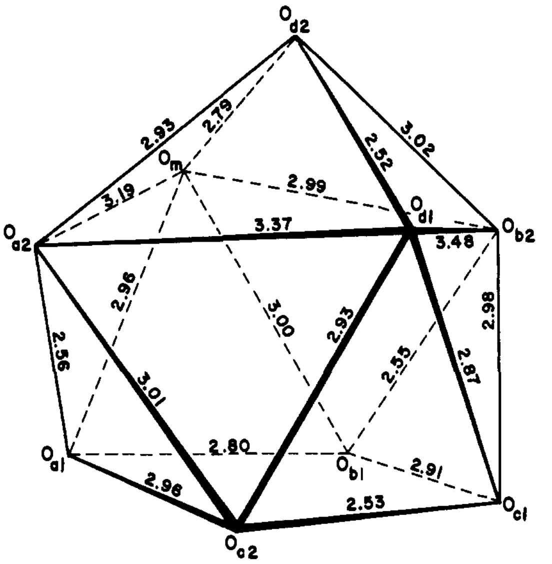

Figure 4. Perspective view (adapted from a computer-drawn diagram) of the monocapped square-antiprismatic coordination polyhedron as observed in the DMFThT$_4$ molecule. The four short edges of 2.52–2.56-Å length are those spanned by the bidentate ligands. The chelation pattern is primarily responsible for the quasi-S$_4$ ruffling in the arrangement of the four atoms (O_{a2}, O_{d1}, O_{b2}, and O_m) which define the base of the pyramidal cap. With vertices numbered 1–9 as suggested by Muetterties and Wright,[11d] this stereoisomer is fully specified as 1, 2 (O_{d2}, O_{d1}); 3, 7 (O_{a2}, O_{a1}); 4 (O_m); 5, 8 (O_{b2}, O_{b1}); 9, 6 (O_{c1}, O_{c2}).

(C_s), and the remaining four are reduced to the trivial onefold symmetry of C_1. As will now be shown, the observed configuration of the (DMF)ThT$_4$ molecule provides a good example of one of the C_s stereoisomers.

Table V is a listing of the complexing bond distances[22] and polyhedral edge lengths in the coordination group of the (DMF)ThT$_4$ molecule; rounded-off values of the edge lengths are also carried on Figure 4. The four polyhedral edges that correspond to the "bite" of the tropolonato ligands have lengths ≲2.56 Å, substantially below the pertinent van der Waals packing diameter (2.80 Å),[23] while the 16 interligand O···O contacts, by contrast, range from 2.79 to 3.48 Å, with just three of these below 2.90 Å. The inherently small bite of the tropolonato ligands contributes materially

Table V. Bond Distances and Polyhedral Edge Lengths in the Coordination Group of (DMF)ThT$_4$[a]

Type[b]	Length, Å	Type[b]	Length, Å	Type[b]	Length, Å
Th–O_{d2}	2.485 (5)	O_{d2}–O_{d1}[c]	2.521 (7)	O_{a1}–O_{b1}	2.795 (7)
		O_{d2}–O_{a2}	2.925 (8)	O_{b1}–O_{c1}	2.905 (8)
Th–O_{d1}	2.441 (5)	O_{d2}–O_m	2.793 (8)	O_{c1}–O_{c2}[c]	2.527 (7)
Th–O_{a2}	2.447 (5)	O_{d2}–O_{b2}	3.019 (8)	O_{c2}–O_{a1}	2.958 (8)
Th–O_m	2.519 (6)				
Th–O_{b2}	2.435 (5)	O_{d1}–O_{c1}	2.866 (7)	O_{b1}–O_m	2.996 (8)
		O_{d1}–O_{c2}	2.932 (8)	O_{a1}–O_m	2.964 (9)
Th–O_{a1}	2.439 (5)	O_{c1}–O_{b2}	2.979 (7)	O_m–O_{b2}	2.992 (9)
Th–O_{b1}	2.436 (5)	O_{c2}–O_{a2}	3.011 (7)	O_m–O_{a2}	3.194 (9)
Th–O_{c1}	2.447 (5)	O_{a1}–O_{a2}[c]	2.564 (7)	O_{d1}–O_{a2}	3.366 (8)
Th–O_{c2}	2.468 (5)	O_{b1}–O_{b2}[c]	2.550 (7)	O_{d1}–O_{b2}	3.480 (7)

[a] Figures in parentheses are the estimated standard deviations. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, c, or d) and a numerical subscript that follows the numbering scheme given in Figure 2 for the tropolonate ion. Atoms in the monodentate DMF ligand carry the literal subscript m. [c] The "bite" of the ligand.

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(22) Estimated standard deviations in the bond lengths and angles of (DMF)ThT$_4$ were calculated following W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(23) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

to the evident looseness of the ligand packing that, in turn, gives the molecular configuration a pronounced susceptibility to distortion in the asymmetric environment provided by the crystalline arrangement. Inasmuch as the spanning of one of the capping edges (Figure 4) of the coordination polyhedron by a tropolonato ligand (d) limits the maximum symmetry to C_s, the retention of a quasi-mirror plane in the crystal by the deformable complex bespeaks a real preference for the observed stereoisomeric form. The mean planes for the atoms (O_{a1}, O_{b1}, O_{c1}, and O_{c2}) comprising the "square" base of the coordination polyhedron and for the atoms (O_{a2}, O_m, O_{b2}, and O_{d1}) comprising the "square" base of the pyramidal cap (with the O_{d2} atom at the apex) are given in Table VI along with the displacements from these planes of all atoms in the coordination group. It is seen that each of these "square" arrays displays a quasi-S_4 ruffling from its mean plane, averaging 0.06 and 0.19 Å for the respective lower and upper "squares." The mean planes are nearly parallel with 1.3° as the angle between their normals. The addition of the ninth ligand on the unique axis of the square-antiprismatic coordination group requires a substantial spreading of the polyhedral face thus capped. Consequently, the average length of the four O···O edges delineating the base of the pyramidal cap is 3.26 Å, as compared with 2.93 Å for the other 12 interligand O···O edges and 2.54 Å for the four short edges spanned by the tropolonato ligands. The thorium atom (Table VI) lies only 0.87 Å below the base of the pyramidal cap, but 1.44 Å above the base of the coordination polyhedron.

Table VI. Atomic Displacements from the Mean Planes of the "Square" Bases of the Coordination Polyhedron and Its Pyramidal Cap

Equations of the Mean Planes[a]

A. Base of coordination polyhedron:[b] $0.173X - 0.915Y + 0.365Z = 0.12$

B. Base of pyramidal cap:[c] $0.179X - 0.905Y + 0.385Z = 2.35$

Atom type[d]	Displacement (Å) from Plane A	Displacement (Å) from Plane B	Atom type	Displacement (Å) from Plane A	Displacement (Å) from Plane B
O_{a1}	0.05	−2.23	O_{a2}	2.12	−0.19
O_{b1}	−0.05	−2.33	O_m	2.47	0.21
O_{c1}	0.06	−2.28	O_{b2}	2.10	−0.19
O_{c2}	−0.06	−2.41	O_{d1}	2.53	0.17
Th	1.44	−0.87	O_{d2}	3.92	1.61

[a] *X*, *Y*, and *Z* are orthogonal coordinates in Å along ($b \times c^*$), *b*, and c^*, respectively, in the crystal. [b] Comprises atoms O_{a1}, O_{b1}, and O_{c2}. [c] Comprises atoms O_{a2}, O_m, O_{b2}, and O_{d1}. [d] Atoms labeled in agreement with Figures 2–4.

Table VII. Bond Angles Subtended at the Th(IV) Atom in the Coordination Group of (DMF)ThT_4[a]

Type[b]	Angle, deg	Type[b]	Angle, deg	Type[b]	Angle, deg
$O_{a1}ThO_{a2}$	63.3	O_mThO_{a1}	73.4	$O_{c1}ThO_{d1}$	71.8
$O_{b1}ThO_{b2}$	63.1	O_mThO_{b1}	74.4	$O_{c2}ThO_{d1}$	73.4
$O_{c1}ThO_{c2}$	61.9	O_mThO_{d2}	67.9		
$O_{d1}ThO_{d2}$	61.6	$O_{a2}ThO_{c2}$	75.6	O_mThO_{a2}	80.0
		$O_{b2}ThO_{c1}$	75.2	O_mThO_{b2}	74.3
$O_{a1}ThO_{c2}$	74.1	$O_{a2}ThO_{d2}$	72.7	$O_{a2}ThO_{d1}$	87.1
$O_{b1}ThO_{c1}$	73.0	$O_{b2}ThO_{d2}$	75.7	$O_{b2}ThO_{d1}$	91.1
		$O_{a1}ThO_{b1}$	70.0		

[a] The estimated standard deviation of all angles listed is 0.2°. [b] Each symbol for an atom of a tropolonato ligand carries a literal subscript to identify the particular ligand (a, b, c, or d) and a numerical subscript that follows the numbering scheme given in Figure 2 for the tropolonate ion. The atoms of the unique monodentate DMF ligand are denoted by the literal subscript m.

Table VII lists the bond angles subtended at the thorium atom within the coordination group of the (DMF)ThT_4 molecule. Notable features of these angles are readily summarized as follows. (1) The angles subtended at the thorium atom by the four short edges spanned by the tropolonato ligands range from 61.6 to 63.3, averaging 62.5°; the somewhat larger pair of angles (63.1 and 63.3°), corresponding to bites (2.550 and 2.564 Å) appreciably larger than the average (2.541 Å), are subtended by the pair of tropolonato ligands that span two of the eight lateral edges connecting the base of the coordination polyhedron with the base of the pyramidal cap (Figure 4). (2) The bond angles at thorium subtended by the 12 interligand O···O edges of 2.93 Å averaged length (*vide supra*) range from 67.9 to 75.7, averaging 73.1°. (3) The angles subtended by the four long edges defining the base of the pyramidal cap range from 74.3 to 91.1, averaging 83.1°.

The hard-sphere model for the C_{4v} monocapped square antiprism with a polyhedron radius of 2.457 Å (the average of the nine Th–O bond lengths in Table V) has 16 edges of 2.82 Å length subtending angles of 70.1° at the polyhedron center and four long edges of 3.26 Å length subtending angles of 83.1°. Departures from this model that are observed in the coordination group of the (DMF)ThT_4 molecule are evidently attributable, in order of decreasing cogency, to the very small bite of the tropolonato ligands, to packing constraints imposed by the crystalline arrangement, and, rather trivially, to variations in the complexing bond lengths that may be theoretically required. Six of the nine Th–O bond lengths (Table V) average to 2.441 Å with a mean deviation of 0.004 Å as compared with the estimated standard deviation of 0.005 Å for the individual datum. The significantly longer Th–O_m bond (2.519 Å) to the uncharged, rather weakly complexed, DMF ligand is not unexpected. The slightly, but significantly, longer than expected Th–O_{c2} bond (2.468 Å) seems to arise from packing constraints in the crystal (*vide infra*). On the basis of idealized C_{4v} symmetry the unique axial bond (in (DMF)ThT_4 the Th–O_{d2} bond) might be expected to differ in length from the averaged value for all nine bonds. Inasmuch as this bond presumably can make good use of the thorium d_{z^2} valence shell orbital for σ bonding,[8a] the greater than average length of the Th–O_{d2} bond (2.485 Å) in (DMF)ThT_4 is perhaps surprising. The Th–O_{d1} bond in the same chelate ring is of "normal" length (2.441 Å) although, as shown later, this ring displays a moderate degree of angular strain. It is possible that both the angular strain and the enhanced length of the Th–O_{d2} bond arise from packing constraints to which ligand d is subjected in the crystal. Such constraints, however, do not seem to be unduly severe; it is rather more probable, we judge, that a slightly longer than average axial bond is characteristic of the unconstrained species.

The chemically unique Th–O_m bond to the monodentate DMF ligand can be taken as the preferred axis in a stereochemically superficial description of the $(DMF)ThT_4$ molecule. In this description, the nine oxygen atoms are "layered" in a one–five–three arrangement with the quasi-pentagonal and triangular layers each roughly normal to the axis defined by the $Th{-}O_m$ bond. Referring to Figures 3 and 4, atoms O_{b1}, O_{b2}, O_{d2}, O_{a1}, and O_{a2} constitute the "pentagonal girdle" around the thorium, and atoms O_{c1}, O_{c2}, and O_{d1} the triangular base of the polyhedron; the thorium atom lies ~0.68 Å below the mean plane of the strongly folded pentagonal girdle. The incomplete and superficial character of this description is then revealed by noting that such one–five–three layering of the oxygen atoms approximately normal to a preferred axis is observed if this axis be taken along any one of the four Th–O bonds to the oxygen atoms (O_{d1}, O_{a2}, O_{b2}, O_m) lying at the vertices of the pyramidal cap of the monocapped square-antiprismatic coordination group. Otherwise put, the axial $Th{-}O_{d2}$ bond of the one–four–four capped antiprismatic coordination group is an axis of quasi-C_4 symmetry for the fourfold reproduction of the one–five–three layering pattern that obtains along any one of the cited bond directions. Indeed, this observation provides a further easily applied criterion for the identification of monocapped square-antiprismatic nine-coordination.[24]

An excellent example of such coordination, involving the minimum distortions consistent with the rigorous constraints imposed by multidentate chelation, is to be found in the nine-coordinate ethylenediaminetetraacetatotriaquolanthanum(III) ion[25] and the other isostructural rare earth species of analogous chemical formula.[26]

Furthermore, the tetrakis(γ-isopropyltropolonato)-monaquothorium(IV) molecule, as observed in the crystal,[27] is best described as one of the four distinguishable C_1 stereoisomeric forms that are based upon monocapped square-antiprismatic coordination while being limited by the chelation pattern to onefold symmetry. Both this complex and the $(DMF)ThT_4$ molecule are limited to seven distinctive stereoisomeric forms by excluding the possibility that the tropolonato ligand, with its small quasi-rigid bite, can span any of the four long edges of the coordination polyhedron. Placement of the monodentate ligand in the capping position requires the spanning of four of the eight lateral edges of the polyhedron by tropolonato ligands to give the C_4 "pinwheel" stereoisomer. All other stereoisomers require the spanning of one slant edge of the pyramidal cap by a tropolonato ligand, thereby reducing the maximum symmetry to C_s. This symmetry is maintained in two stereoisomers wherein the monodentate ligand is positioned at the one other vertex that lies in the mirror plane; it is lost in the four C_1 stereoisomers that have the monodentate ligand positioned at any of the remaining six vertices of the polyhedron.

As remarked earlier, one of the C_s stereoisomers is exemplified by the $(DMF)ThT_4$ molecule; interchange of the positions occupied by atoms O_m and O_{d1}, both lying in the mirror plane (Figures 3 and 4), gives the other. The distribution of bond angle and packing strains in the observed stereoisomer of the $(DMF)ThT_4$ molecule seems to be at least as favorable as in any of the competing forms. Thus, for example, the C_4 and two of the C_1 stereoisomers (all unobserved as yet) concentrate four relatively tight interligand O···O packing contacts in the base of the coordination polyhedron. Such considerations by no means preclude the possibility that the mobile complex exists in several stereoisomeric forms in solution, and that the form observed in the crystal primarily reflects a dominating importance of crystalline stability. Lacking any sound basis for appraising the relative merits of the several grotesquely shaped stereoisomers as the packing units in crystalline phases, we note one feature of the observed $(DMF)ThT_4$ configuration that is favorable in this connection: the DMF ligand can take any arbitrary orientation around the $Th{-}O_m$ bond and the configuration of the ligand is otherwise subject only to the maintenance of standard bond parameters. In the C_4 stereoisomer, by contrast, the interaction of the H_{m1} hydrogen atom (Table III) with contiguous tropolonato oxygen atoms may severely restrict the freedom of orientation of the DMF ligand. Configurational constraints that are both more general and more restrictive are applicable to the DMF ligand in the unobserved alternative C_s stereoisomer.

From the least-squares fitting of mean planes to the seven-membered carbon ring and the $O_1{-}C_1{-}C_7{-}O_2$ moiety (Figure 2) of each tropolonato ligand one finds that there are significant departures from planarity in most of these subsystems. Ligand d, the exceptional case, is virtually planar in its entirety; the sums of the internal angles in the seven-membered carbon and five-membered chelate ($-Th{-}O_1{-}C_1{-}C_7{-}O_2{-}$) rings are 900.0 and 540.0°, respectively. Ligands a and b both display a torsional twisting around the ligand principal axis of quasi-twofold symmetry through the C_4 atom and the midpoint of the $C_1{-}C_7$ bond (Figure 2). This twisting gives rise to displacements from the mean plane of the carbon ring that, in the more severely affected ligand a, reach ±0.07 Å for carbon atoms, ±0.18 Å for O_1 and O_2 atoms. Superimposed upon the twisting is a quite minor folding of the five-membered chelate ring along the $O_1 \cdots O_2$ edge of the coordination polyhedron; the angle of fold between the plane defined by the Th, O_1, and O_2 atoms and the mean plane of the $O_1{-}C_1{-}C_7{-}O_2$ grouping is only 0.7° for ligand a, 1.0° for ligand b. Sums of the internal angles in the carbon rings are 898.6 and 899.5° for ligands a and b, respectively; the corresponding sums for the chelate rings have the same value, 539.7°, for both ligands.

Ligand c displays rather different behavior. Virtually free of twist about its quasi-twofold axis and rather closely adhering to the requirements of the quasi-mirror plane (*vide supra*) that divides it into nearly enantiomorphic halves, ligand c is folded along the

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(24) We note also that the coordination group is very roughly describable (but in purely dimensional terms) as tricapped trigonal prismatic with either of two different orientations of the principal quasi-threefold axis or, what amounts to the same thing, two different choices for the triad of oxygen atoms constituting the equatorial triangular girdle around the thorium atom. These choices, (O_{d2}, O_{b1}, O_{c2}) and (O_{d2}, O_{a1}, O_{c1}), are related through the mirroring operation that, in excellent approximation, characterizes the entire $(DMF)ThT_4$ molecule (*vide supra*). The observed quasi mirror does not coincide with either the horizontal or any of the three vertical symmetry planes in the D_{3h} tricapped trigonal prism; its presence, indeed, is inconsistent with the simultaneous existence of any of the symmetry elements that characterize the idealized polyhedron.

(25) J. L. Hoard, B. Lee, and M. D. Lind, *J. Amer. Chem. Soc.*, **87**, 1612 (1965), in which the monocapped square-antiprismatic geometry went unrecognized.

(26) B. Lee, M. D. Lind, and J. L. Hoard, manuscript in preparation.

(27) E. Huber-Buser, private communication based upon measurements taken in this laboratory.

Table VIII. Bond Lengths (Å) in the Tropolonato Ligands of (DMF)ThT$_4$[a]

Type[b]	Ligand a	Ligand b	Ligand c	Ligand d	Average[c]
O_1–C_1	1.281 (9)	1.281 (9)	1.291 (9)	1.280 (9)	1.277 (9, 9, 3)
O_2–C_7	1.286 (10)	1.267 (9)	1.264 (9)	1.263 (9)	
C_1–C_7	1.461 (11)	1.468 (10)	1.477 (10)	1.479 (10)	1.471 (7, 10, 5)
C_1–C_2	1.409 (11)	1.399 (11)	1.394 (11)	1.384 (11)	1.407 (12, 11, 4)
C_7–C_6	1.417 (11)	1.415 (11)	1.413 (11)	1.426 (11)	
C_2–C_3	1.389 (12)	1.395 (12)	1.387 (13)	1.380 (12)	1.385 (7, 13, 5)
C_6–C_5	1.376 (13)	1.399 (12)	1.377 (14)	1.377 (13)	
C_3–C_4	1.380 (14)	1.394 (14)	1.401 (14)	1.394 (14)	1.383 (10, 14, 5)
C_5–C_4	1.371 (14)	1.375 (14)	1.377 (15)	1.369 (15)	
O_1–O_2[d]	2.564 (7)	2.550 (7)	2.527 (7)	2.521 (7)	

[a] The figure in parentheses following each individual distance is the estimated standard deviation. [b] Atoms labeled in agreement with Figure 2 and Tables I and II. [c] The figures in parentheses following each averaged value are the mean deviation, the rms value of the estimated standard deviation for an individual datum, and the weighted standard deviation of the mean. [d] The "bite" of the ligand.

$O_1 \cdots O_2$ line (polyhedron edge) through an angle of 23.5°, a value quite comparable with the 22.6° foldings observed in the six-membered chelate rings of the tetrakis(acetylacetonato)zirconium(IV) molecule.[28] When viewed normal to the quasi-mirror plane so that, excepting the terminal C_4, the atoms superimpose in pairs, ligand c is seen to be curved into the form of a shallow boat, with the C_4 atom at the prow. Averaged displacements from the mean plane of the seven-membered carbon ring (see Figure 2) are: C_4, 0.07; C_3 and C_5, −0.02; C_2 and C_6, −0.07; C_1 and C_7, 0.05; O_1 and O_2, 0.16; Th, 1.16 Å. Accompanying sums of the internal angles in the respective chelate and carbon rings of ligand c are 531.1 and 898.2°. Both the curving of the tropolonato skeleton and the large folding of the chelate ring in ligand c are attributable to packing constraints in the crystalline arrangement. Ligand c is directly involved in 10 of the 13 intermolecular packing contacts that closely approach or attain to critical minimum values. The slightly greater than average value (by an apparent 0.027 Å) of the Th–O_{c2} bond length may also be attributed to intermolecular packing constraints.

Bond lengths in the tropolonato ligands of the (DMF)ThT$_4$ molecule are given in Table VIII. The pairings of C–O and C–C distances in the listing and the averaged values of these parameters in the final column of Table VIII take cognizance of the quasi-twofold symmetry of the ligands (C_2 for a and b, C_s for c, and C_{2v} for d). For each of the five bond types thus obtained, the mean deviation from the averaged length (of either four or eight bonds) generally is as small as, or smaller than, the estimated standard deviation for an individual bond length. There is, moreover, no evidence for an alternation of bond lengths in the carbon ring similar to that reported for the bis(tropolonato)copper(II) molecule.[29] The merits of these averaged bond lengths and of the weighted standard deviations attached thereto (Table VIII) are supported by the comparisons given in Table IX with relevant data from structure determinations for sodium tropolonate[30] (NaT), tris(tropolonato)iron[31] (FeT$_3$), and the seven-coordinate T_3SnCl and T_3SnOH complexes of the accompanying paper.[14] Weighted standard deviations of the mean values are $\lesssim$0.005 Å for all of the data in Table IX except the C–C distances in FeT$_3$, for which 0.007 Å is estimated.[31]

Table IX. Comparative Bond Lengths in the Tropolonato Skeleton from Various Investigations

Bond type[a]	NaT	FeT$_3$	XSnT$_3$[b]	(DMF)-ThT$_4$	Average
C–O[c]	1.278	1.294	1.286	1.277	1.284
C_1–C_7	1.487	1.463	1.456	1.471	1.469
C_1–C_2[d]	1.426	1.397	1.396	1.407	1.407
C_2–C_3[e]	1.390	1.385	1.386	1.385	1.386
C_3–C_4[f]	1.388	1.379	1.386	1.383	1.384

Bond lengths (Å) from

[a] See Figure 2. [b] Averaged values from ClSnT$_3$ and OHSnT$_3$. [c] C_1–O_1 and C_7–O_2. [d] Also C_7–C_6. [e] Also C_6–C_5. [f] Also C_5–C_4.

From examination of Table IX, it is evident that the C–O bonds are strongly involved in the delocalization of π electron density that characterizes the aromatic system, largely at the expense of the unique C_1–C_7 bond; this latter, as pointed out by Hamor and Watkin,[31] is never substantially shorter than the 1.48 Å proposed for the length of a pure σ bond between trigonally hybridized carbon atoms.[32] The data do suggest, however, that increasing strength of the complexing bonds generally is accompanied by a modest lengthening of the C–O bonds and, perhaps less predictably, some shortening of the C_1–C_7 link. The data further suggest that the C_1–C_2 and C_7–C_6 bonds, each contiguous to the unique C_1–C_7 and one of the C–O bonds, are slightly longer (~0.02 Å) than are the four other aromatic C–C bonds. The overall averaged length for the six aromatic bonds is 1.392 Å.

Table X is a listing of the bond angles within the tropolonato ligands and the chelate rings of the (DMF)-ThT$_4$ molecule. The averaged values of the angles of each chemical type within the seven-membered carbon rings are listed in the last column of the table. Although the sum of these averaged values for the carbon ring is only 899.0°, a consequence of the small departures of three of the four rings from exact planarity, the pattern of four larger and three smaller bond angles ob-

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(29) W. M. Macintyre, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc. Ser. A.*, 289, 161 (1966).

(30) R. Shiono, *Acta Crystallogr.*, 14, 42 (1961); Y. Sasada and I. Nitta, *ibid.*, 9, 205 (1956).

(31) T. A. Hamor and D. J. Watkin, *J. Chem. Soc., D*, 440 (1969).

(32) D. W. J. Cruickshank, *Tetrahedron*, 17, 155 (1962).

Table X. Bond Angles (deg) in the Tropolonato Ligands of (DMF)ThT_4[a]

Type[b]	Ligand a	Ligand b	Ligand c	Ligand d	Average[c]
$C_7C_1C_2$	125.4 (7)	126.1 (7)	126.3 (7)	125.6 (7)	125.4 (5, 7, 2)
$C_1C_7C_6$	125.6 (7)	125.1 (7)	124.7 (7)	124.7 (7)	
$C_1C_2C_3$	130.7 (8)	131.2 (8)	131.1 (8)	132.2 (8)	131.0 (4, 8, 3)
$C_7C_6C_5$	130.4 (8)	131.1 (8)	130.4 (8)	131.1 (9)	
$C_2C_3C_4$	129.0 (9)	129.4 (8)	128.3 (9)	129.6 (9)	129.6 (5, 9, 3)
$C_6C_5C_4$	129.7 (8)	129.6 (8)	130.6 (8)	130.6 (9)	
$C_3C_4C_5$	127.8 (8)	127.0.(8)	126.8 (8)	126.2 (8)	127.0 (5, 8, 4)
$O_1C_1C_2$	118.8 (7)	119.7 (7)	119.8 (7)	121.3 (7)	119.8 (6, 7, 3)
$O_2C_7C_6$	119.4 (7)	119.0 (7)	120.6 (7)	120.0 (7)	
$O_1C_1C_7$	115.8 (7)	114.2 (6)	113.8 (7)	113.1 (6)	114.7 (8, 6, 2)
$O_2C_7C_1$	114.9 (7)	115.9 (6)	114.7 (6)	115.3 (6)	
ThO_1C_1	122.8 (5)	123.4 (4)	120.4 (4)	126.2 (4)	122.9 (13, 5, 2)
ThO_2C_7	122.9 (5)	123.1 (5)	120.3 (4)	123.8 (5)	
O_1ThO_2	63.3 (2)	63.1 (2)	61.9 (2)	61.6 (2)	62.5 (7, 2, 1)

[a] Figure in parentheses following each individual angle is the estimated standard deviation. [b] Atoms numbered in agreement with Figure 2. [c] Figures in parentheses following each averaged value are, in order, the mean deviation, the rms estimated standard deviation for an individual datum, and the weighted standard deviation of the mean.

Table XI. Bond Distances and Angles for the Unique Monodentate N,N'-Dimethylformamide Ligand in (DMF)ThT_4[a]

		Distances,[b] Å			
$Th-O_m$	2.519 (6)	$C_{m1}-N_m$	1.325 (11)	$C_{m3}-N_m$	1.461 (12)
O_m-C_{m1}	1.233 (11)	$C_{m2}-N_m$	1.455 (12)		
		Angles,[c] deg			
ThO_mC_{m1}	135.3 (6)	$C_{m1}N_mC_{m2}$	121.1 (8)	$C_{m2}N_mC_{m3}$	118.3 (8)
$O_mC_{m1}N_m$	123.6 (8)	$C_{m1}N_mC_{m3}$	120.6 (8)		

[a] Atoms numbered to agree with Figure 3, with the literal subscript m denoting atoms of the DMF ligand. [b] Figures in parentheses are the estimated standard deviations in units of 10^{-3} Å. [c] Figures in parentheses are the estimated standard deviations in units of 0.1°.

served in other tropolonato complexes[14,30,31] is closely maintained. Indeed, the variations in the values reported for any particular class of angle (<1.0°) by the several investigators are too small to have any obvious chemical significance. Bond angles in the chelate rings display objectively significant variations from the mean values. The O_1ThO_2 angles in a and b are ~1.6° smaller than in c and d. The bond angles at the oxygen atoms play their usual role of quasi-dependent variables. In the strongly folded chelate ring c the ThOC angles are ~2.5° below the general average, and in the planar, but internally strained, chelate ring d the ThO_1C_1 angle is ~3.3° above the average.

The bond parameters listed in Table XI for the monodentate DMF ligand are essentially those expected for the uncomplexed species. Weak complexing is suggested by the long, 2.519 (6) Å, $Th-O_m$ distance and by the observation that the O_m-C_{m1} bond length of 1.233 (11) Å apparently is unaltered from the double bond value. The striking feature is the evident readiness of the ThT_4 molecule to expand into nine-coordination by adding a monodentate oxo ligand, the weakly complexing nature of this latter notwithstanding.

All that is significant in respect to the apparent C–H bond lengths in (DMF)ThT_4, as calculated from the carbon positions (Table I) and the "refined" hydrogen positions (Table III), may be summarized as follows. The 21 C–H distances involving tropolonato or trigonal carbon atoms average 1.03 Å, with 0.07 and 0.10 Å as the respective values of the mean deviation and of the (root mean square) standard deviation for an individual datum. The six C–H distances in the peripheral methyl groups average 1.07 Å, with 0.11 and 0.14 Å as the respective mean and rms standard deviations.