Chelate Chemistry. IV. Ten-Coordinate Thorium and Uranium(IV)

E. L. Muetterties

Contribution No. 1128 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. *Received August 18, 1965*

Abstract: Pentakis(tropolono)thorium(IV), pentakis(tropolono)uranium(IV), and pentakis(γ-isopropyltropolono)thorium(IV) anions have been prepared by reaction of the neutral tetrakis chelates of thorium or uranium with the sodium salt of the corresponding tropolone anion.

In earlier studies[1-3] it was established that the tropolone anion is a particularly effective bidentate donor in generating high-coordinate structures with a wide variety of ions. Seven- and eight-coordinate chelates were characterized for elements ranging from scandium to thorium. Recently, the thorium system has been examined in more detail, at the suggestion of Professor Roland Ward, for the possibility of ten coordination. There is precedent for ten coordination in a molecular structure. Lind, Lee, and Hoard[4] have established that in the tetrahydrated lanthanum salt of ethylenediaminetetraacetic acid the lanthanum is within bonding distance of ten donor atoms.

Results and Discussion

Tetrakis(tropolono)thorium(IV)[2] and sodium tropolonate dispersed in aqueous methanol react to yield a crystalline solid that retains its identity on recrystallization from aqueous media and from dimethyl sulfoxide. Analysis established the composition as $NaTh(O_2C_7H_5)_5$. A similar reaction course followed on substitution with lithium or potassium tropolonate, but attempts to isolate cesium and tetramethylammonium salts were unsuccessful.[5] The cation dependency was accentuated with the smaller uranium(IV) ion and only the lithium salt was successfuly isolated. This inverse relation of stability for the high-coordination lattice with cation size is formally analogous to that found for alkali metal salts of fluorotantalates: sodium ion yields Na_3TaF_8 and potassium, K_2TaF_7, while cesium gives the hexafluorotantalate lattice. Hoard and Silverton[6] have pointed out that in the fluorotantalate system the particular combination of cation and complex anion leads to an excellent salt-like arrangement in the crystal. An analogous phenomenon may operate in the tropolonothorium system.

γ-Isopropyltropolone (γ-thujaplicin) proved chemically identical with tropolone for the thorium system, and, fortunately, the salt $NaTh(O_2C_7H_4\text{-}i\text{-}C_3H_7)_5$ was sufficiently soluble for molecular weight studies. In chloroform solution, the chelate is highly associated; molecular weight ranges from 9300 in a saturated solution to the extrapolated value of 1556 for infinite dilution, which data are to be compared with a molecular weight of 1071 for a simple ion-pair formulation. Since the parent tetrakis chelate is monomeric in chloroform solution, these data clearly establish that the anion does exist in chloroform solution, although largely in the form of ion aggregates. Ion-pairing tendencies of cationic tropolone chelates have been previously noted.[1-3]

Infrared spectra of the anionic derivatives are significantly less complex than those of the parent neutral species, clearly ruling out the possibility of solid solutions. The proton n.m.r. spectrum of the pentakis(tropolono)thorium anion in $(CD_3)_2SO$ is quite similar to those of tetrakis(tropolono) chelates,[2b] and the β-proton triplet and α doublet are readily discernible. This datum might be taken as evidence that the ligands are identical; however, the possibility of facile dissociation leading to exchange equivalence cannot be excluded. In fact, at the low concentrations employed in cryoscopic molecular weight determinations the related thujaplicin chelate anion is dissociated in dimethyl sulfoxide.

The electron-acceptor activity of thorium in the tetrakis chelates was further evidenced in the formation of apparent nine-coordinate complexes with strong donor molecules, such as dimethyl sulfoxide. Formation of the latter complex may account for the dissociation of the pentakis chelate anion in dimethyl sulfoxide solution

$$(CH_3)_2SO + Th(O_2C_7H_5)_5^- \rightleftharpoons Th(O_2C_7H_5)_4 \cdot OS(CH_3)_2 + O_2C_7H_5^-$$

However, such solutions do yield on concentration only the salt of the pentakis chelate anion.

Attempts to prepare pentakis(tropolono) chelate anions of zirconium, hafnium, and cerium(IV) were unsuccessful. Large cation size and f^0 electronic configuration are probably two of the major considerations for formation of ten-coordinate molecular structures. In this context, thorium(IV) is certainly the most favorable of the ions investigated. The possibility of twelve-coordinate molecular structures would seem to be almost within grasp with the tropolone anion as the ligand. Hexakis anionic derivatives of such species as protactinium(V) may be isolable.

Conclusions

We propose that the pentakis(tropolono) derivatives are ten-coordinate. Possible idealized geometries for

---

(1) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964).

(2) (a) E. L. Muetterties and C. M. Wright, *ibid.*, **87**, 21 (1965); (b) *ibid.*, **87**, 4706 (1965).

(3) E. L. Muetterties, *Pure Appl. Chem.*, **10**, 53 (1965).

(4) M. D. Lind, B. Lee, and J. L. Hoard, *J. Am. Chem. Soc.*, **87**, 1611 (1965).

(5) The neutral tetrakis chelate was recovered, unchanged, as the sole insoluble phase.

(6) J. L. Hoard and J. B. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

ten coordination are a symmetrically bicapped, square antiprism and a closely related one generated from the D_{2d} dodecahedral model with the ninth and tenth positions on a C_2 axis. Professor J. L. Hoard plans to study the geometries of our thorium chelates for the highly perturbed solid state. In solution, conformational interconversions should be even more facile processes than for seven-, eight-, or nine-coordinate structures; *i.e.*, the lifetime of the ground-state geometries should be quite short.[7]

Ten-coordinate thorium structures have been proposed by Bohigian and Martell[8] for the thorium derivative of triethylenetetraminehexaacetic acid and by Goldstein, Menis, and Manning[9] for a bis(acetic acid) complex of tetrakis(thenoyltrifluoroaceto)thorium. We suggest that ten coordination may be relatively common in thorium, protactinium, and uranium(IV) chelates.

Experimental Section

Preparation of ThT_4. A solution of tropolone (5.2 g., 0.0425 mole) in 20 ml. of methanol was added to a solution of thorium tetranitrate tetrahydrate (5.52 g., 0.01 mole) in 100 ml. of water and 50 ml. of methanol. A clear solution was obtained on mixing, but very soon afterward a pale yellow solid began to separate. After 0.5 hr., the reaction slurry was placed on a steam bath for 2 hr. The solution was filtered, and the collected solid was washed with aqueous methanol. The solid was dried at 80° (0.01 μ) for 4 hr. The weight of crude tetrakis(tropolono)thorium was 6.95 g.

This is a simpler procedure for the preparation of ThT_4 than was detailed in paper III.[2b]

Preparation of $(C_{10}H_{11}O_2)_4Th$. A solution of γ-$C_3H_7C_7H_4O_2H$ (6.52 g., 0.04 mole) in 20 ml. of warm ethanol was added to a solution of thorium nitrate tetrahydrate (5.52 g., 0.01 mole) in 80 ml. of water and 20 ml. of ethanol. A yellow solid separated from the reaction solution which was then warmed on a steam bath for 15 min. The yellow solid initially turned to an oil and then slowly resolidified. The solid was recovered by filtration and was recrystallized from 95% methanol, m.p. 350–354° dec.

Anal. Calcd. for $(C_{10}H_{11}O_2)_4Th$: C, 54.3; H, 5.02; Th, 26.3; mol. wt., 884.9. Found: C, 54.2; H, 5.06; Th, 26.6; mol. wt., 886 (chloroform solution by vapor pressure osmometry), 843 (cryoscopic in benzene).

The 60-Mc. proton n.m.r. spectrum of $(C_{10}H_{11}O_2)_4Th$ in $(CD_3)_2SO$ consisted of an AB pattern for the α and β aromatic protons and a septet–doublet for the aliphatic CH and CH_3 protons, respectively ($J_{H\alpha H\beta} = 14$ c.p.s., $J_{HCHHCH_3} = 9$ c.p.s.). In chloroform, the spectrum is altered in that the α and β aromatic protons are indistinguishable.

Preparation of $NaThT_5$. A slurry of tetrakis(tropolono)thorium (3.84 g., 0.0054 mole) and sodium tropolonate (1.2 g., 0.0085 mole) in a mixture of acetonitrile (200 ml.), water (75 ml.), and ethanol (75 ml.) was warmed on a steam bath for 17 hr. Reaction occurred within the first half-hour as evidenced by a change in the color and an increase in particle size of the solids. The slurry was filtered while hot, and the pale yellow solid was washed with warm aqueous ethanol and vacuum dried at 150° for 2 hr., m.p. >400°.

Anal. Calcd. for $Na^+Th(O_2C_7H_5)_5^-$: Na, 2.68; Th, 27.0; C, 48.9; H, 2.93. Found: Na, 2.70; Th, 26.9; C, 49.0; H, 2.78.

Recrystallization was effected from a hot mixture of ethanol, water, and acetonitrile.

Anal. Found: C, 48.9; H, 3.03.

The salt was also recrystallized from hot dimethyl sulfoxide by adding a mixture of ethanol and water to the hot solution. Slow addition of the latter solvent mixture gave rise to a slow crystallization of solid from the solution. The crystals were analytically and spectrally identical with the above-described salt. The infrared spectrum of all samples of the sodium salt in Nujol mulls indicated the possible presence of water in the lattice although the analytical data corresponded closely to the anhydrous formulation. Principal infrared absorptions exclusive of the Nujol bands are at 3430 (vw), 1680 (vw), 1595 (s), 1520 (s), 1490 (m), 1250 (m), 1230 (m), 998 (vw), 970 (w), 920 (w), 910 (w), 875 (m), 760 (w), 735 (s, broad), and 700 (m) cm.$^{-1}$.

Preparation of $LiThT_5$. Tropolone (1.1 g., 0.009 mole), lithium hydroxide (10.2 g., 0.4 mole), and tetrakis(tropolono)thorium (3.58 g., 0.005 mole) were added to a mixture of ethanol (100 ml.), water (100 ml.), and acetonitrile (200 ml.). The reaction mixture was heated on a steam bath for 2 days. The slurry was filtered while hot, and the collected yellow solid was washed with a hot mixture of ethanol and water and then vacuum dried, m.p. >400°.

Anal. Calcd. for $Li^+Th(O_2C_7H_5)_5^-$: Li, 0.82; Th, 27.5; C, 49.8; H, 2.97. Found: Li, 0.83; Th, 27.8; C, 50.2; H, 2.91.

Preparation of $KThT_5$. A slurry of tetrakis(tropolono)thorium (1.0 g., 0.0014 mole) and potassium tropolonate (0.8 g., 0.005 mole) in ethanol (100 ml.), water (100 ml.), and acetonitrile (200 ml.) was heated at reflux for 2 days. The slurry was filtered while hot, and the pale yellow solid was washed with a warm mixture of ethanol and water and then vacuum dried.

Anal. Calcd. for $K^+Th(O_2C_7H_5)_5^-$: K, 4.46; Th, 26.5; C, 48.0; H, 2.85. Found: K, 3.32; Th, 26.3; C, 48.0; H, 2.90.

Preparation of $Na^+Th(O_2C_{10}H_{11})_5^-$. A solution of $(C_{10}H_{11}O_2)_4Th$ (1.768 g., 0.002 mole) in 40 ml. of methanol was added to a solution of γ-$C_3H_7C_7H_4O_2H$ (0.38 g., 0.023 mole) and sodium hydroxide (0.081 g., 0.0021 mole) in a warm mixture of 20 ml. of methanol, 20 ml. of ethanol, and 10 ml. of water. A yellow precipitate formed on mixing the two solutions. The reaction mixture was warmed on a steam bath, and the yellow precipitate turned to an oil. Ethanol was added until the solution cleared and solids began to form. The solution was taken to near reflux and then cooled with vigorous stirring. The off-white solid that separated was collected and vacuum dried at 100°, m.p. 273–278° dec.

Anal. Calcd. for $Na^+Th(O_2C_{10}H_{11})_5^-$: Na, 2.15; Th, 21.6; C, 56.0; H, 5.18; mol. wt., 1071. Found: Na, 1.99; Th, 22.1; C, 55.8; H, 5.36; mol. wt., 1556 at infinite dilution and 9300 for a saturated solution (chloroform solution by vapor pressure osmometry).

Preparation of $ThT_4 \cdot OS(CH_3)_2$. Tetrakis(tropolono)thorium (1 g., 0.0014 mole) was dissolved in 20 ml. of dimethyl sulfoxide heated to 150°. The solution was filtered through a fine filter disk into 100 ml. of toluene warmed to 70°. On cooling, yellow crystals appeared. These were collected and vacuum dried at 60°.

Anal. Calcd. for $Th(O_2C_7H_5)_4OS(CH_3)_2$: C, 45.4; H, 3.30; S, 4.03. Found: C, 45.5; H, 3.33; S, 3.97.

Preparation of UT_4. Tropolone (2.5 g., 0.02 mole) was added to a slurry of uranium(IV) acetate (2 g., 0.004 mole) in 100 ml. of acetonitrile. There was an immediate reaction with the development of a red-orange color. The reaction mixture was heated to reflux for 45 min., then filtered hot. The orange-brown insoluble material was recrystallized from a number of organic solvents but attempts to free the chelate from excess solvent by vacuum drying at elevated temperatures were unsuccessful. The chelate was purified by sublimation at 340° (0.01 μ).

Anal. Calcd. for $U(O_2C_7H_5)_4$: C, 46.5; H, 2.77. Found: C, 47.2; H, 3.11.

This compound has an infrared spectrum very similar to that of tetrakis(tropolono)cerium(IV) and the X-ray powder pattern was isomorphous with that of the cerium derivative.[2b]

Preparation of $LiUT_5$. Tetrakis(tropolono)uranium(IV) (0.8 g., 0.001 mole) and lithium tropolonate (0.3 g., 0.002 mole) were added to a mixture of 50 ml. of methanol, 50 ml. of water, and 80 ml. of acetonitrile. The reaction mixture was refluxed for 20 hr., then filtered; the insoluble material was washed with methanol and acetonitrile, then dried at 100° (0.01 μ) for 1 hr., m.p. 410° dec.

Anal. Calcd. for $LiU(O_2C_7H_5)_5$: Li, 0.82; U, 28.1; C, 49.5; H, 2.95. Found: Li, 0.65; U, 27.7; C, 49.0; H, 3.08.

The X-ray powder pattern of this lithium salt is isomorphous with that of $LiThT_5$.

Analytical Procedures. Thorium was determined after acid degradation by addition of excess ethylenediaminetetraacetic acid and back titration with copper(II) ion. The alkali metals were analyzed by flame photometry.

Acknowledgment. The author is indebted to Miss C. M. Wright, who separated γ-thujaplicin from a natural mixture of isopropyltropolones.

---

(7) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

(8) T. A. Bohigian, Jr., and A. E. Martell, *ibid.*, **4**, 1264 (1965).

(9) G. Goldstein, O. Menis, and D. L. Manning, *Anal. Chem.*, **32**, 400 (1960).