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A New Hydroxo-bridged Thorium(IV) Dimer: Preparation and Structure of Di-μ-hydroxo-bis[aquanitrato(2,6-diacetylpyridinedisemicarbazone)thorium(IV)] Nitrate Tetrahydrate

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Abstract

The pentadentate ligand 2,6-diacetylpyridinedisemicarbazone, DAPSC, reacts with $Th(NO_3)_4$ in ethanol–water mixture and a di-μ-hydroxo Th(IV) dimer is formed. The compound $[Th_2(OH)_2(DAPSC)_2(NO_3)_2(H_2O)_2](NO_3)_4 \cdot 4H_2O$ (I) is monoclinic, space group $P2_1/n$ with $a = 10.705(1)$, $b = 19.008(2)$, $c = 11.782(1)$ Å, $\beta = 107.82(2)°$, $V = 2282(1)$ Å^3 and $Z = 2$. Detailed X-ray structural analysis showed that each thorium atom in the complex is coordinated to one pentadentate DAPSC ligand, which is subjected to a considerable distortion, one bidentate nitrate group, one water ligand and two bridging hydroxo groups. The coordination number is ten and the best presentation of the polyhedron is that of a distorted bicapped square antiprism. The Th–Th separation is 4.0181(6) Å and the average Th–O(H) bridge is 2.366 Å. The structure was refined using 3185 reflections to an R value of 5.0%.

Introduction

It is known that aqua ions of Th(IV) undergo extensive hydrolysis in solutions with pH > 3. The hydrolytic products have been investigated in several laboratories using X-ray techniques in solutions and in the solid state [1–3]. Polymerization of monomeric hydrolized Th(IV) species proceeds by the formation of μ-OH or μ-O bridges. Infinite chains of the $Th(OH)_2$ units exist in the solids of $Th(OH)_2SO_4$ and $Th(OH)_2CrO_4(H_2O)$ in which the thorium atoms are bridged by μ-hydroxo bridges and the Th–Th distances are about 4 Å [4, 5]. The structure of a discrete di-μ-hydroxo dimer, $[Th_2(OH)_2(NO_3)_6(H_2O)_6]$, was reported by Johanssen [6]. The coordination number of each of the Th(IV) atoms is 11 and the Th–Th separation is 3.988 Å. A similar U(IV) dimer, $U_2(OH)_2(ClO_4)_6 \cdot xH_2O$ was prepared and the X-ray study showed that the two uranium atoms are bridged by two hydroxo units with a U–U distance of 4 Å [7].

Recently, the structure of the first discrete oxo-bridged dimer of Th(IV) was reported by Palenik *et al.* [8]. The compound μ-oxo-bis[aquanitrato-(2,9-diformyl-1,10-phenanthrolinedisemicarbazone)-thorium(IV)] contains an almost linear Th–O–Th unit. Each Th atom is coordinated to the planar hexadentate ligand, to a bidentate O_2NO^- ligand, to an H_2O ligand and one bridging oxo ligand. The Th atoms are ten-coordinated with a quite unusual 1–6–3 geometry.

We report here the preparation and structure of another discrete, ten-coordinated Th(IV) dimer with a di-μ-hydroxo bridging system and distorted bicapped square antiprism polyhedron structure. The compound contains the pentadentate ligand 2,6-diacetylpyridinedisemicarbazone, DAPSC.

Experimental

Preparation of Di-μ-hydroxo-bis[aquanitrato(2,6-diacetylpyridinedisemicarbazone)thorium(IV)] Nitrate Hydrate, $[Th(OH)(DAPSC)(NO_3)(H_2O)]_2(NO_3)_4 \cdot 4H_2O$, I

$Th(NO_3)_4 \cdot H_2O$ (0.1 g) and DAPSC (0.057 g) were added to 10 ml of EtOH. The solution was stirred and heated for 1 h. H_2O (20 ml) was added and the solution was filtered. Slow evaporation yielded very pale yellow crystals suitable for X-ray study.

X-ray Crystallography

Data were collected at 20 ± 2 °C on a Philips PW 1100 four-circle diffractometer. Mo Kα ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range $12° < \theta < 16°$. Data were measured by using ω–2θ motion. Crystallographic data and

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other pertinent information are given in Table I. Lorentz and polarization corrections were applied. Intensity data were corrected for absorption by the empirical ψ-scan method. The heavy atom positions were obtained from a three-dimensional Patterson function and the structure was refined in the space group $P2_1/n$ to convergence using anisotropic thermal parameters for all non-hydrogen atoms*. All the hydrogen atoms of the dimeric cation were located from the difference Fourier map and they were included in the final refinement cycles using the riding model with $U = 0.05$. The positional parameters of the hydrogen atoms are included in the 'Supplementary Material'.

The discrepancy indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table I.

TABLE I. Crystallographic Data

Formula	$C_{22}H_{44}N_{20}O_{30}Th_2$
Formula weight	1532.78
Space group	$P2_1/n$
a (Å)	10.705(1)
b (Å)	19.008(2)
c (Å)	11.782(1)
β (deg)	107.82(2)
V (Å^3)	2282(1)
Z	2
D_{calc} (g cm^{-3})	2.23
μ (cm^{-1})	63.18
Crystal size (mm)	0.2 x 0.15 x 0.07
2θ range (deg)	4-50
No. unique data	3948
Data with $F_o^2 > 3\sigma(F_o)^2$	3185
No variables	334
R	0.050
R_w	0.061

Results and Discussion

The atomic positional parameters are listed in Table II. Table III presents important bond lengths and angles in the dimer. Figure 1 shows the structure and the numbering scheme in the complex and Fig. 2 presents a stereoview of the dimer. With two molecules in the unit cell of space group $P2_1/n$ there is only a half $[Th_2(OH)_2(DAPSC)_2(NO_3)_2(H_2O)_2]^{4+}$ ion in the asymmetric unit with the other half related to it by a crystallographic inversion center. Each thorium atom is coordinated to the pentadentate DAPSC ligand which appears in its fully protonated form. The ligand, which in many other complexes adopts a planar geometry, is substantially distorted in order to form a favored polyhedron for ten-coordination. The deca-coordination sphere is completed by the two bridging hydroxo oxygen atoms, one coordinated water oxygen and two oxygen atoms of a coordinated nitrate group. The best presentation of the polyhedron is as a distorted bicapped square antiprism, BCSAP [11]. The atoms N(5), O(12), O(4), O(3)′ and N(1), O(11), O(1), O(3) form the two

TABLE II. Positional Parameters and Estimated Standard Deviations[a]

Atom	x	y	z	Atom	x	y	z
Th	0.59267(5)	0.40824(2)	0.49862(4)	N(4)	0.523(1)	0.3758(7)	0.097(1)
O(1)	0.543(1)	0.3666(5)	0.2932(9)	N(5)	0.754(1)	0.3926(5)	0.721(1)
O(2)	0.516(1)	0.3464(5)	0.6497(9)	N(6)	0.717(1)	0.3422(6)	0.788(1)
O(3)	0.4515(9)	0.4966(5)	0.3891(8)	N(7)	0.540(1)	0.2866(7)	0.818(1)
O(4)	0.378(1)	0.3473(6)	0.4209(9)	N(8)	0.672(1)	0.4972(7)	−0.065(1)
O(5)	0.702(1)	0.5266(6)	−0.148(1)	N(9)	0.774(1)	0.2828(7)	0.101(1)
O(6)	0.731(1)	0.5130(7)	0.040(1)	N(10)	0.764(1)	0.2821(8)	0.489(1)
O(7)	0.582(1)	0.4534(6)	−0.089(1)	C(1)	0.836(1)	0.5354(7)	0.506(1)
O(8)	0.723(1)	0.2340(6)	0.031(1)	C(2)	0.932(1)	0.5866(8)	0.549(1)
O(9)	0.785(1)	0.2798(6)	0.2056(9)	C(3)	1.006(2)	0.5857(8)	0.667(2)
O(10)	0.813(2)	0.3349(8)	0.057(1)	C(4)	0.986(2)	0.5320(8)	0.739(1)
O(11)	0.801(1)	0.3455(6)	0.479(1)	C(5)	0.890(1)	0.4822(7)	0.692(1)
O(12)	0.660(1)	0.2754(5)	0.512(1)	C(6)	0.764(1)	0.5302(7)	0.378(1)
O(13)	0.828(2)	0.2327(7)	0.470(1)	C(7)	0.770(2)	0.5877(8)	0.291(1)
OL(1)	0.218(1)	0.3395(6)	0.195(1)	C(8)	0.568(1)	0.3963(7)	0.209(1)
OL(2)	0.512(3)	0.216(1)	0.221(3)	C(9)	0.863(1)	0.4247(7)	0.768(1)
N(1)	0.814(1)	0.4849(6)	0.579(1)	C(10)	0.954(2)	0.410(1)	0.887(1)
N(2)	0.698(1)	0.4726(6)	0.348(1)	C(11)	0.586(1)	0.3249(7)	0.746(1)
N(3)	0.645(1)	0.4558(6)	0.231(1)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

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*All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

TABLE III. Important Bond Lengths (Å) and Angles (°)

Bond lengths

Th–Th'	4.0181(6)	N(2)–C(6)	1.29(1)
Th–O(1)	2.445(9)	N(3)–C(8)	1.37(1)
Th–O(2)	2.48(1)	N(4)–C(8)	1.31(1)
Th–O(3)	2.361(8)	N(5)–N(6)	1.38(1)
Th–O(3)'	2.372(9)	N(5)–C(9)	1.28(1)
Th–O(4)	2.49(1)	N(6)–C(11)	1.38(1)
Th–O(11)	2.61(1)	N(7)–C(11)	1.32(2)
Th–O(12)	2.62(1)	C(1)–C(2)	1.39(1)
Th–N(1)	2.69(1)	C(1)–C(6)	1.47(1)
Th–N(2)	2.68(1)	C(2)–C(3)	1.38(2)
Th–N(5)	2.68(1)	C(3)–C(4)	1.38(2)
O(1)–C(8)	1.24(1)	C(4)–C(5)	1.39(1)
O(2)–C(11)	1.23(1)	C(5)–C(9)	1.50(2)
N(1)–C(1)	1.36(1)	C(6)–C(7)	1.52(2)
N(1)–C(5)	1.32(1)	C(9)–C(10)	1.48(1)
N(2)–N(3)	1.36(1)	O(11)–N(10)	1.29(1)
		O(12)–N(10)	1.24(2)
		O(13)–N(10)	1.22(2)

Important angles

O(1)–Th–O(2)	122.6(3)	O(3)'–Th–O(2)	78.1(3)
O(1)–Th–O(3)	77.3(3)	O(3)'–Th–O(3)	63.8(3)
O(1)–Th–O(4)	65.7(3)	O(3)'–Th–O(4)	103.9(3)
O(1)–Th–O(11)	72.3(4)	O(3)'–Th–O(11)	136.2(4)
O(1)–Th–O(12)	73.9(4)	O(3)'–Th–O(12)	143.0(4)
O(1)–Th–N(1)	115.3(3)	O(3)'–Th–N(1)	72.2(3)
O(1)–Th–N(2)	59.9(3)	O(3)'–Th–N(2)	102.6(3)
O(1)–Th–N(5)	144.4(3)	O(3)'–Th–N(5)	73.6(4)
O(2)–Th–O(3)	115.6(3)	Th–O(1)–C(8)	127.6(9)
O(2)–Th–O(4)	64.5(4)	Th–O(2)–C(11)	125.6(9)
O(2)–Th–O(11)	109.3(4)	Th–O(3)–Th'	116.2(4)
O(2)–Th–O(12)	69.0(3)	Th–O(11)–N(10)	97.0(9)
O(2)–Th–N(1)	116.9(4)	Th–O(12)–N(10)	97.8(9)
O(2)–Th–N(2)	174.8(4)	Th–N(1)–C(1)	117(1)
O(2)–Th–N(5)	60.0(4)	Th–N(1)–C(5)	122.6(8)
O(3)–Th–O(4)	76.4(4)	C(1)–N(1)–C(5)	119(1)
O(3)–Th–O(11)	134.4(3)	Th–N(2)–N(3)	115.7(8)
O(3)–Th–O(12)	146.9(4)	Th–N(2)–C(6)	120.6(9)
O(3)–Th–N(1)	98.9(4)	N(3)–N(2)–C(6)	120(1)
O(3)–Th–N(2)	69.0(3)	N(2)–N(3)–C(8)	115(1)
O(3)–Th–N(5)	136.6(3)	Th–N(5)–N(6)	115.2(1)
O(4)–Th–O(11)	118.4(4)	Th–N(5)–C(9)	126.6(9)
O(4)–Th–O(12)	77.2(4)	N(6)–N(5)–C(9)	118(1)
O(4)–Th–N(1)	175.0(4)	N(5)–N(6)–C(11)	114(1)
O(4)–Th–N(2)	120.0(4)	N(1)–C(1)–C(2)	121(2)
O(4)–Th–N(5)	123.7(3)	N(1)–C(1)–C(6)	118(1)
O(11)–Th–O(12)	48.5(4)	C(2)–C(1)–C(6)	121(1)
O(11)–Th–N(1)	66.1(4)	C(1)–C(2)–C(3)	120(1)
O(11)–Th–N(2)	66.5(4)	C(2)–C(3)–C(4)	118(2)
O(11)–Th–N(5)	74.0(4)	C(3)–C(4)–C(5)	120(2)
O(12)–Th–N(1)	107.8(4)	N(1)–C(5)–C(4)	122(1)
O(12)–Th–N(2)	108.6(3)	N(1)–C(5)–C(9)	117(1)
O(12)–Th–N(5)	75.5(4)	C(4)–C(5)–C(9)	121(2)
N(1)–Th–N(2)	58.9(4)	N(2)–C(6)–C(1)	114(1)
N(1)–Th–N(5)	58.7(3)	N(2)–C(6)–C(7)	124(2)
N(2)–Th–N(5)	115.1(4)	C(1)–C(6)–C(7)	122(1)
O(3)'–Th–O(1)	141.1(4)	O(1)–C(8)–N(3)	119(1)
O(1)–C(8)–N(4)	124(1)	C(5)–C(9)–C(10)	121(1)
N(3)–C(8)–N(4)	117(1)	O(2)–C(11)–N(6)	121(1)
N(5)–C(9)–C(5)	114(1)	O(2)–C(11)–N(7)	123(2)
N(5)–C(9)–C(10)	125(1)	N(6)–C(11)–N(7)	116(1)
		O(11)–N(10)–O(12)	116(1)
		O(11)–N(10)–O(13)	120(1)
		O(12)–N(10)–O(13)	124(1)

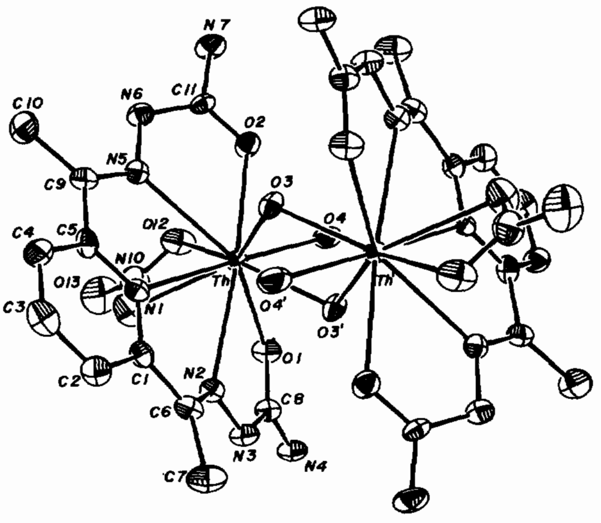

Fig. 1. The structure and numbering scheme in $[Th_2(OH)_2 \cdot (DAPSC)_2(NO_3)_2(H_2O)_2]^{4+}$.

square faces with O(2) and N(2) as the capping atoms. Figure 3 shows a stereoview of the BCSAP. A similar BCSAP geometry exists in the ten-coordinated $[Ce(III)(DAPSC)_2]^{3+}$ complex in which a remarkable distortion of the DAPSC ligand occurs [12]. In **I**, the dihedral angles between the aromatic ring and the planes of the side arms defined by C(10), C(9), N(6), N(7), C(11), O(2) and C(7), C(6), N(3), N(4), C(8), O(1) are 21.15° and 21.28°, respectively. Such distortions are possible only when the ligand is fully protonated because when a deprotonation of the semicarbazone NH groups occurs, conjugated systems are formed and the ligand tends to be planar [10].

The $Th(OH)_2Th$ system is similar to that found in $[Th_2(OH)_2(NO_3)_6(H_2O)_6]$ [6]. The average Th–O(H) bond distance, 2.366 Å, and the Th–Th separation, 4.0181(6) Å, in **I** are almost identical with the corresponding distances in the nitrate complex of 2.365 Å and 3.988 Å, respectively.

Supplementary Material

Tables of structure factors, thermal parameters and positional parameters of the hydrogen atoms (22 pages) are available from the Editor-in-Chief.

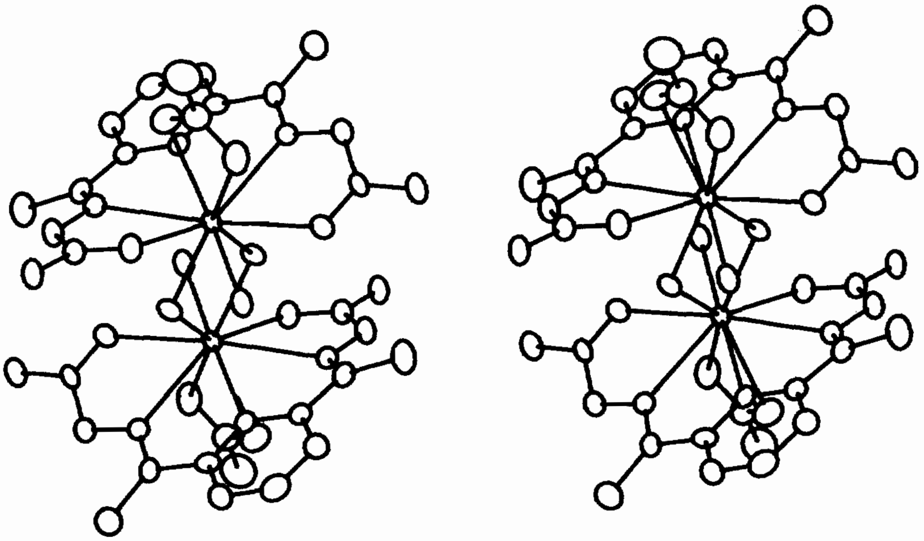

Fig. 2. A stereoview of $[Th_2(OH)_2(DAPSC)_2(NO_3)_2(H_2O)_2]^{4+}$.

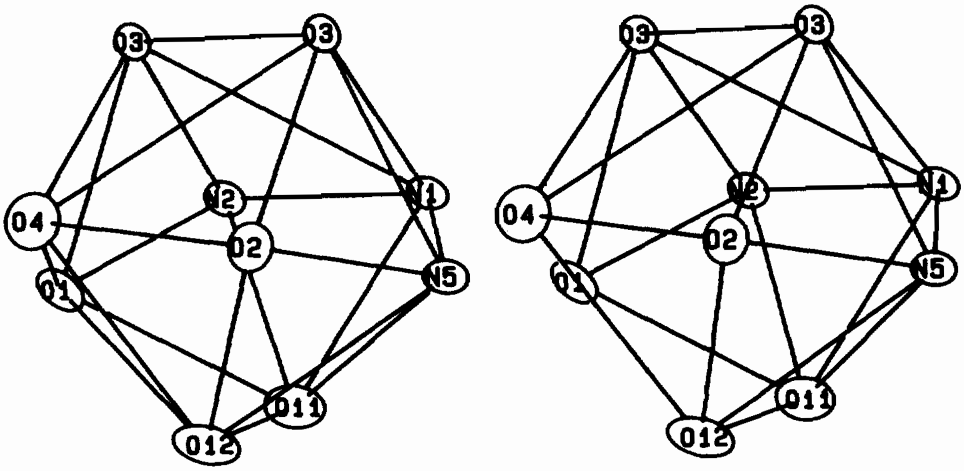

Fig. 3. A stereoview of the bicapped square antiprism polyhedron.

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