Inorganica Chimica Acta, 139 (1987) 51–53

Crystal Structure of the Adduct of Thorium(IV) Tetrakisacetylacetonate with Aniline, $[Th(C_5H_7O_2)_4]_2 \cdot C_6H_5NH_2$*

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The title compound has been synthesized from thorium tetrakisacetylacetonate (ThA_4) and aniline in ether, and its crystal structure determined. The cell is triclinic with $a = 20.417(26)$, $b = 9.268(7)$, $c = 14.166(10)$ Å, $\alpha = 86.19(6)$, $\beta = 101.06(8)$, $\gamma = 85.65(8)^\circ$, $U = 2614.3$ Å^3, $Z = 2$, space group $I1$ (non-centrosymmetric). There are two independent ThA_4 molecules, each with square antiprism coordination. The aniline is intercalated and not even hydrogen-bonded but does cause some disturbance of certain of the ligand planes.

Biltz [1] reported the compounds $2ThA_4 \cdot NH_3$ and $2ThA_4 \cdot C_6H_5NH_2$, neither of which seems to have received much attention over the past 80 years. Lenner [2] reported the crystal structure of the clathrate compound $2ThA_4 \cdot C_6H_6$. Biltz's compounds seemed to us worthy of further investigation in order to determine whether: (i) the nitrogen was within the thorium coordination sphere; (ii) a hydrogen-bonded structure was formed; or (iii) they were clathrates like the benzene adduct. We now report on the aniline adduct.

Experimental

We obtained brownish, mostly plate-like, crystals of the adduct by reacting ThA_4 with aniline in hot ether and then cooling. We were unable to recrystallize the product without loss of aniline, but analysis confirmed the nature of the crude material. *Anal.* Found: C, 40.45; H, 5.09; N, 0.94. Calc. for $C_{46}H_{63}O_{16}NTh_2$: C, 40.92; H, 4.70; N, 1.04%. The crystals slowly deteriorated on standing (over a period of weeks to months, depending on storage conditions).

A slab-shaped crystal measuring about 0.35 × 0.35 × 0.25 mm was used to collect X-ray intensities by $\theta/2\theta$ scans on a Nicolet R3M 4-circle automatic diffractometer with Mo Kα radiation (graphite monochromator, $\lambda = 0.71069$ Å). The non-standard I-centred cell quoted above was used because of its near-orthogonality and its similarity to the monoclinic cell of β-ThA_4 ($a = 20.36$, $b = 8.55$, $c = 14.56$ Å, $\beta = 104.33^\circ$) [3]. The primitive Delaunay cell for the title compound has $a = 11.687(14)$, $b = 14.367(14)$, $c = 9.268(7)$ Å, $\alpha = 110.10(6)$, $\beta = 106.86(8)$, and $\gamma = 102.71(8)^\circ$, and is obtained from the I cell by the transformation:

$$\begin{matrix} \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\ 0 & 1 & 0 \end{matrix}$$

3511 independent reflexions with $|F| \geqslant 3\sigma(F)$ were measured and corrected for Lorentz, polarization and absorption effects, the last empirically using azimuthal scans on 10 selected reflexions (360 measurements). Crystal decay, amounting to 29.5% during the data collection, was corrected by reference to two check reflexions monitored every 100 reflexions.

The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-diagonal least squares, with surprisingly little trouble from the obvious pseudo-symmetry. The aniline was clearly located in one orientation and all the atomic positions were refined satisfactorily (Table I). The thermal parameters must remain subject to some doubt, particularly where pairs of pseudo-related atoms show markedly different values (e.g., O(6) and O(14), C(15) and C(41)) (Table I). An enantiomer test [4] confirmed our model with $\eta = 0.81(2)$. Sufficient hydrogen atoms were found from low-θ difference maps to define approximate torsion angles for the methyl and amino groups. During refinement all hydrogens were constrained to ride on their adjacent heavy atoms at calculated distances and angles and with isotropic thermal factors held at 1.2 times U_{eq} of the neighbour. An extinction correction of the form $F^x = F_c/[1.0 + (3.2 \times 10^{-7})F^2/\sin(2\theta)]^{0.25}$ gave a significant reduction in R. Weights used were $w_i = 1/[\sigma^2(F_i) + 0.00138F_i^2]$ and the final R value was 0.0451.

The maximum parameter shift on the final cycle of refinement was 0.7 and the highest peak in the final difference map was 1.5 e Å^{-3}. These rather high values are due to the pseudo-symmetry and the effects (absorption and series termination) of the very heavy thorium atom. The final variance analysis and normal probability plot were devoid of unusual features. The SHELXTL suite of crystallographic programs [5] was used throughout on a NOVA 3 computer.

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*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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0020-1693/87/$3.50

TABLE I. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}[a]
Th(1)	52(2)	2547(5)	2544(3)	35(1)
Th(2)	−105(2)	7489(5)	7459(3)	36(1)
O(1)	461(11)	3866(29)	3907(16)	55(8)
O(2)	1301(11)	1932(27)	3179(15)	51(8)
O(3)	237(8)	−61(15)	2888(10)	62(6)
O(4)	−577(8)	1774(16)	3789(8)	59(5)
O(5)	−753(7)	4474(17)	2310(10)	65(6)
O(6)	−955(6)	1823(12)	1668(8)	35(4)
O(7)	334(8)	1762(16)	1136(12)	73(6)
O(8)	529(7)	4465(14)	1688(8)	49(5)
O(9)	−483(13)	6167(21)	6085(16)	50(8)
O(10)	−1243(13)	8053(24)	6905(19)	80(10)
O(11)	−217(6)	10016(13)	7209(11)	56(5)
O(12)	485(6)	8258(13)	6250(9)	46(5)
O(13)	826(6)	5508(14)	7757(11)	55(5)
O(14)	952(8)	8278(23)	8323(16)	108(9)
O(15)	−356(7)	8278(15)	8910(9)	52(5)
O(16)	−510(8)	5571(16)	8282(11)	65(6)
C(1)	913(11)	5029(25)	5275(16)	71(9)
C(2)	1073(10)	4007(22)	4412(14)	49(7)
C(3)	1676(11)	3247(27)	4408(14)	62(9)
C(4)	1727(8)	2385(21)	3862(13)	40(6)
C(5)	2448(11)	1691(28)	3796(17)	80(10)
C(6)	114(11)	−2559(21)	2957(22)	82(11)
C(7)	−26(8)	−1003(22)	3181(15)	49(7)
C(8)	−557(14)	−735(30)	3740(21)	96(13)
C(9)	−731(8)	543(22)	4043(12)	38(6)
C(10)	−1306(16)	840(36)	4700(17)	102(14)
C(11)	−1821(15)	6182(28)	2052(18)	86(12)
C(12)	−1416(9)	4680(25)	2065(16)	62(8)
C(13)	−1832(9)	3455(22)	1800(17)	60(8)
C(14)	−1638(15)	2353(27)	1543(22)	92(12)
C(15)	−2007(11)	1086(26)	1290(19)	76(10)
C(16)	695(14)	911(29)	−215(20)	95(13)
C(17)	624(10)	2090(25)	412(19)	71(9)
C(18)	824(9)	3553(23)	258(14)	52(7)
C(19)	791(8)	4628(20)	1016(12)	38(6)
C(20)	1050(10)	6042(21)	826(13)	49(7)
C(21)	2275(33)	8713(49)	2102(34)	96(19)
C(22)	1876(29)	8152(69)	2824(38)	108(21)
C(23)	2072(24)	6921(56)	3257(45)	107(20)
C(24)	2708(29)	6133(80)	3046(53)	144(30)
C(25)	2988(28)	6722(66)	2330(43)	101(24)
C(26)	2768(27)	7898(71)	1910(44)	104(23)
N(1)	2068(21)	9879(45)	1579(23)	145(18)
C(27)	−1024(10)	4881(25)	4779(16)	64(9)
C(28)	−969(11)	5983(20)	5464(13)	49(7)
C(29)	−1596(10)	6737(24)	5492(17)	60(8)
C(30)	−1749(12)	7851(22)	6250(18)	68(9)
C(31)	−2402(12)	8590(32)	6083(26)	107(15)
C(32)	−119(18)	12583(26)	7046(21)	103(14)
C(33)	197(13)	11058(22)	6817(16)	64(9)
C(34)	583(11)	10788(22)	6278(14)	51(7)
C(35)	747(15)	9465(23)	5970(16)	87(11)
C(36)	1213(9)	9343(19)	5321(13)	43(7)
C(37)	1725(9)	3809(23)	7823(21)	80(11)
C(38)	1442(15)	5306(25)	7951(15)	74(10)
C(39)	1816(14)	6301(31)	8293(19)	89(12)
C(40)	1577(7)	7899(21)	8455(11)	37(6)
C(41)	2130(14)	8849(46)	8905(28)	175(24)
C(42)	−664(13)	8752(23)	10381(14)	65(9)
C(43)	−578(9)	7724(22)	9591(11)	46(7)
C(44)	−751(13)	6395(26)	9716(20)	79(11)
C(45)	−745(11)	5363(29)	9163(18)	70(10)
C(46)	−982(14)	3868(25)	9283(23)	95(13)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Results and Discussion

The two ThA_4 moieties each show square-antiprismatic coordination, as is found for ThA_4 itself [6] (Fig. 1). The aniline occupies a space in the lattice and there are no non-bonded contacts short enough to be remotely plausible as hydrogen-bonds. This is just as much a clathrate compound as is $2ThA_4 \cdot C_6H_6$.

The mean Th–O bond distance of 2.395 Å (Table II) is quite typical for complexes of this type as are also the mean dimensions of the acetylacetonate ligands and the dimensions of the aniline molecule. The mean θ angle of the antiprisms is also quite normal at 56.5°.

The interest in the present structure lies in the effect of the intercalated aniline molecule on the shape of the ThA_4 moieties. All the ligands are very close to planar (r.m.s. deviations of 0.02 to 0.09 Å) (Table III). In the parent compound ThA_4, these planes are inclined at about 30° to the mean equatorial plane of the antiprism. In the present compound the planes of two ligands on each thorium (the ones facing the aniline) are opened out to accommodate the included molecule, which lies between them (Fig. 2). These ligands show a mean dihedral angle, D, of 42.05° in comparison with 27.9° for the others. The mean hinge angles, H (the angles between the O–Th–O planes and the ligand planes) are 2.4°

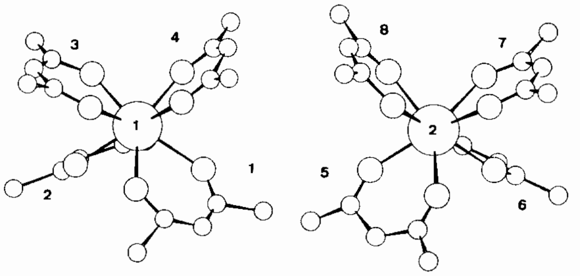

Fig. 1. The two ThA_4 molecules. The Th atoms are numbered and the ligands are numbered as in Table III.

TABLE II. Bond Lengths (Å)

Th(1)–O(1)	2.402(24)	Th(1)–O(2)	2.544(21)
Th(1)–O(3)	2.420(14)	Th(1)–O(4)	2.472(15)
Th(1)–O(5)	2.296(15)	Th(1)–O(6)	2.358(12)
Th(1)–O(7)	2.325(18)	Th(1)–O(8)	2.451(14)
Th(2)–O(9)	2.402(22)	Th(2)–O(10)	2.313(26)
Th(2)–O(11)	2.333(13)	Th(2)–O(12)	2.378(14)
Th(2)–O(13)	2.495(12)	Th(2)–O(14)	2.457(18)
Th(2)–O(15)	2.360(14)	Th(2)–O(16)	2.349(16)
O(1)–C(2)	1.335(29)	O(2)–C(4)	1.285(27)
O(3)–C(7)	1.153(25)	O(4)–C(9)	1.254(25)
O(5)–C(12)	1.326(23)	O(6)–C(14)	1.416(31)
O(7)–C(17)	1.310(32)	O(8)–C(19)	1.184(23)
O(9)–C(28)	1.224(29)	O(10)–C(30)	1.284(33)
O(11)–C(33)	1.480(29)	O(12)–C(35)	1.345(28)
O(13)–C(38)	1.231(32)	O(14)–C(40)	1.273(22)
O(15)–C(43)	1.241(23)	O(16)–C(45)	1.427(31)
C(1)–C(2)	1.661(32)	C(2)–C(3)	1.372(31)
C(3)–C(4)	1.161(31)	C(4)–C(5)	1.584(29)
C(6)–C(7)	1.515(29)	C(7)–C(8)	1.476(37)
C(8)–C(9)	1.333(35)	C(9)–C(10)	1.651(36)
C(11)–C(12)	1.562(34)	C(12)–C(13)	1.495(30)
C(13)–C(14)	1.173(35)	C(14)–C(15)	1.470(37)
C(16)–C(17)	1.469(39)	C(17)–C(18)	1.460(32)
C(18)–C(19)	1.519(28)	C(19)–C(20)	1.477(27)
C(21)–C(22)	1.516(87)	C(21)–C(26)	1.294(87)
C(21)–N(1)	1.265(57)	C(22)–C(23)	1.258(77)
C(23)–C(24)	1.530(85)	C(24)–C(25)	1.362(99)
C(25)–C(26)	1.217(83)	C(27)–C(28)	1.451(31)
C(28)–C(29)	1.419(29)	C(29)–C(30)	1.595(35)
C(30)–C(31)	1.421(33)	C(32)–C(33)	1.588(35)
C(33)–C(34)	1.221(36)	C(34)–C(35)	1.368(31)
C(35)–C(36)	1.446(36)	C(37)–C(38)	1.498(33)
C(38)–C(39)	1.301(39)	C(39)–C(40)	1.568(35)
C(40)–C(41)	1.550(40)	C(42)–C(43)	1.542(29)
C(43)–C(44)	1.317(32)	C(44)–C(45)	1.277(38)
C(45)–C(46)	1.511(37)		

TABLE III. Details Concerning the Ligand Planes[a]

Ligand No.	O	C	r.m.s. deviation	*d*Th	*D*	*H*
1	1,2	1–5	0.06	0.04	42.5	2.2
2	3,4	6–10	0.04	0.56	26.4	15.9
3	5,6	11–15	0.09	0.44	27.6	14.3
4	7,8	16–20	0.04	0.10	38.6	3.2
5	9,10	27–31	0.06	0.01	44.4	2.6
6	11,12	32–36	0.06	0.41	27.8	12.8
7	13,14	37–41	0.02	0.37	29.9	10.7
8	15,16	42–46	0.02	0.05	42.7	1.4

[a]See text for explanation of symbols.

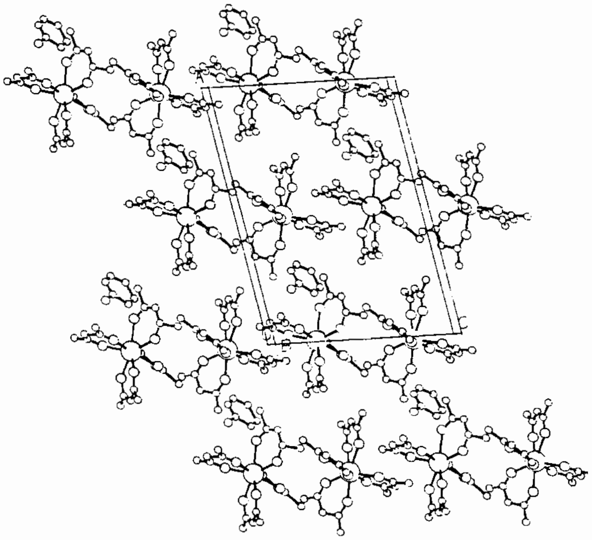

Fig. 2. Crystal packing for $2ThA_4 \cdot C_6H_5NH_2$.

and 13.4° respectively. The same effect is reflected in the distance of the thorium from the ligand plane, *d*Th. For the undisturbed ligands it averages 0.45 Å, but for those affected by the aniline it is 0.05 Å, close to the r.m.s. deviations of the planes themselves.

Supplementary Material

Tables of bond angles, anisotropic thermal factors, hydrogen positions, and observed and calculated structure factors are available from the authors on request.

Acknowledgements

We thank the Science and Engineering Research Council and the Royal Society for grants towards the purchase of the diffractometer equipment.

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