On the Formation and Properties of Tetrakis(acetylacetonato)-thorium(IV) Hemibenzene

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Lattice parameters have been determined for tetrakis(acetylacetonato)thorium(IV) hemibenzene, $[\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6]$. The unit cell is triclinic with the dimensions $a = 9.234(4)$ Å, $b = 11.093(6)$ Å, $c = 16.602(10)$ Å, $\alpha = 119.06(4)^\circ$, $\beta = 120.16(3)^\circ$, $\gamma = 74.81(3)^\circ$ and $Z = 2$. The infrared spectrum has been measured. The bonding interaction between the chelate complex and the benzene molecule is very weak as indicated by thermogravimetric analysis and solution behaviour. The solvate can probably best be described as a clathrate. Similar compounds were not found, however, if the central atom was changed to Zr(IV), Ce(IV), Hf(IV), U(IV), or Np(IV), nor could any solvate formation be found with other aromatic compounds like toluene, pyridine, or with solvents with a smaller molecular volume or with acetylacetone.

In the course of preparing and studying the acetylacetonates of tetravalent metals¹ it was observed that crystals obtained from a benzene solution of $\text{Th}(\text{AA})_4$ (AA = the acetylacetonate ligand) contained one molecule of the solvent for every two molecules of $\text{Th}(\text{AA})_4$. Since an investigation of the molecular packing of such a solvated species would be of considerable interest, especially with regard to the influence of the benzene molecule on the geometry of the coordination sphere around the thorium atom, a structure determination was begun. Some other properties were also studied in order to find out if there were any indications of bonding interactions between the benzene molecule and the conjugated ring system of the ligand. In order to determine if the benzene coordinating ability of $\text{Th}(\text{AA})_4$ is unique, a search for similar solvates with other tetravalent metal acetyl-

acetonates and with other solvents were performed.

EXPERIMENTAL

Preparation of the compound. $\text{Th}(\text{AA})_4$ was precipitated by mixing an aqueous solution of $\text{Th}(\text{NO}_3)_4$ and an aqueous solution of ammonia and acetylacetone.² In a similar way or by using an extraction procedure previously described³ $\text{Zr}(\text{AA})_4$, $\text{Ce}(\text{AA})_4$, $\text{Hf}(\text{AA})_4$, $\text{U}(\text{AA})_4$, and $\text{Np}(\text{AA})_4$ were also prepared. The complexes were crystallized from benzene at room temperature.

In the search for other solvates crystallization of $\text{Th}(\text{AA})_4$ was performed from both aromatic and non-aromatic diluents with molecular volumes similar to or less than the volume of benzene (148.4 Å³/molecule at 25°C). The following solvents were used (molecular volumes within parentheses obtained from density data): Water (30.0), ethanol (97.4), carbon disulfide (101.3), acetone (122.9), chloroform (133.9), pyridine (134.3), tetrahydrofuran (134.6), carbon tetrachloride (161.2), acetylacetone (171.0), diethyl ether (173.9), toluene (177.4), cyclohexane (180.5) and hexane (218.5).

Analysis. The thorium content of the complex was determined by α -counting in a TriCarb Liquid Scintillation Spectrometer on tracer amounts of ²³⁰Th, which was added before preparation of the complex. The amount of solvated benzene was determined from thermogravimetric measurements and by absorbance measurements of the solvated complex at ~ 675 cm⁻¹ in carbon tetrachloride solutions.

Thermogravimetric measurements. TGA and DTA curves were recorded with a Mettler Recording Vacuum Thermoanalyzer for the solvated and unsolvated $\text{Th}(\text{AA})_4$.

Structure investigations. Preliminary lattice parameters were determined from diffraction measurements using the Weissenberg single crystal technique. X-Ray photographs were

taken of the solvated and unsolvated $\text{Th}(\text{AA})_4$, using a Guinier focusing camera with $\text{CuK}\alpha$ radiation.

Infrared spectra. Infrared spectra of the solvated and unsolvated $\text{Th}(\text{AA})_4$ were recorded in the range $4000-400\text{ cm}^{-1}$ with a Perkin-Elmer 337 Grating IR Spectrophotometer, using a KBr pellet technique.

Density measurements. The density of dilute solutions of $\text{Th}(\text{AA})_4$ in benzene and toluene was measured pycnometrically.

Solubility measurements. The solubility of $\text{Th}(\text{AA})_4$ in hexane, carbon tetrachloride, hexone (4-methyl-2-pentanone), benzene, toluene, and chloroform was determined from measurements of the $\text{Th}(\text{AA})_4$ concentration in saturated solutions using liquid scintillation technique and ^{230}Th .

PROPERTIES

Properties and stability in the solid state. The only solvate that was obtained was $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$. Freshly made crystals of the solvate became opaque within a few hours exposure to air at room temperature, due to the loss of benzene and destruction of the structure. Because of this rapid decomposition of the solvate and since any non-stoichiometric solvent inclusions in the crystals had to be removed by washing and drying of the crystals before analysis, definitive reproducible values of the $\text{Th}/\text{C}_6\text{H}_6$ ratio were difficult to obtain. The measured values of this ratio were, however, close to and never less than two and did not exceed three indicating a solvate with the composition $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$.

Fig. 1. DTA recording for $\alpha\text{-Th}(\text{AA})_4$ and $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$.

Two forms of $\text{Th}(\text{AA})_4$ exist, both being monoclinic.^{1,4} The formation of a new stoichiometric compound distinguishable from the unsolvated $\text{Th}(\text{AA})_4$ was confirmed from comparison of Guinier photographs.

The suggested composition of the solvate was confirmed by thermogravimetric measurements. The weight decrease due to decomposition and to evaporation of benzene began already at room temperature and was complete at about 70°C (cf. the boiling point of benzene: 80.1°C). A small endothermic peak was observed in the DTA recording at a temperature just below the point of complete loss of benzene, as can be seen in Fig. 1. Another endothermic peak around 130°C was also found, possibly due to destruction of the lattice, and after this point a loss of weight which increased rapidly after the melting point, around 170°C , began and indicated a sublimation. For the unsolvated $\alpha\text{-Th}(\text{AA})_4$ complex an endothermic transition occurred around 140°C , after which sublimation was noticeable. This reaction might be due to a destruction of the high-density $\alpha\text{-Th}(\text{AA})_4$ lattice. The low-density $\beta\text{-Th}(\text{AA})_4$ form is more stable at high temperatures and is usually obtained by sublimation

Fig. 2. Infrared spectra of $\alpha\text{-Th}(\text{AA})_4$ and $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$.

of $\text{Th}(\text{AA})_4$ at low pressure just below the melting point.¹

From the preliminary structure investigation, the cell volume $1284.8 \text{ \AA}^3$ was calculated for two formula units. A possible set of lattice parameters for the triclinic cell is $a = 9.234(4) \text{ \AA}$, $b = 11.093(6) \text{ \AA}$, $c = 16.602(10) \text{ \AA}$, $\alpha = 119.06(4)^\circ$, $\beta = 120.16(3)^\circ$, $\gamma = 74.81(3)^\circ$ and $Z = 2$. A full three-dimensional structure investigation is in progress,⁵ and possibly a better choice of unit cell parameters will be selected. The molecular volume of benzene based on the density of the liquid at 25°C is $148.4 \text{ \AA}^3$ and from structure data $122.2 \text{ \AA}^3$. The molecular volume of two molecules of the unsolvated $\alpha\text{-Th}(\text{AA})_4$ molecule, as given by structure data,¹ is $1187.0 \text{ \AA}^3$. The sum of these volumes is 1335.5 and $1309.2 \text{ \AA}^3$, respectively, which is greater than the measured $1284.8 \text{ \AA}^3$ and thus suggests that the efficiency of packing of the molecule is better in the solvated than the unsolvated structure.

Infrared spectra have been recorded for solvated and unsolvated $\text{Th}(\text{AA})_4$ and portions of these spectra are shown in Fig. 2. The assignment of the bands in the infrared spectrum of $\text{Th}(\text{AA})_4$ is given in the literature.⁶ Some minor differences between the two spectra are noticeable. A new peak appearing around 690 cm^{-1} in the spectrum of $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ and corresponding to the solvated benzene is shifted towards a higher frequency in comparison to the value for free benzene. The band around 1350 cm^{-1} due to CH_2 deformation is shifted to a lower frequency and the band around 1021 cm^{-1} assigned to CH_2 rocking is split. The slightly metal sensitive band around 660 cm^{-1} probably corresponding to ring deformation is shifted to a lower frequency. The bands around $750 - 800 \text{ cm}^{-1}$ corresponding to CH out-of-plane bending appear as a single peak with shoulders while four peaks are distinguishable for the unsolvated species. Neither the bands at 530 cm^{-1} and 400 cm^{-1} which are sensitive to $\text{M}-\text{O}$ vibrations, nor the bands around $1500 - 1600 \text{ cm}^{-1}$ from $\text{C}=\text{C}$ and $\text{C}=\text{O}$ vibrations or any other pure in-plane stretchings have changed significantly. This indicates that the ligand ring geometry is more or less unperturbed in the presence of benzene molecules in the crystal lattice. Any change of the inner coordination would have

caused shifts at least in the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ vibrations.⁷ It may be concluded that any interaction between the solvated benzene and the metal or ligand ring must be weak.

Properties in solution. From density measurements of dilute $\text{Th}(\text{AA})_4$ -solutions the apparent molar volume could be estimated. With the assumption that the solutions of $\text{Th}(\text{AA})_4$ in the inert solvents benzene and toluene could be regarded as regular,⁸ a simple mass balance consideration would give.

$$v_A = (m_m/\rho_m - m_s/\rho_s)M_A/m_A \quad (1)$$

where v , m , ρ and M are molar volume, weight, density and formula weight, respectively, and subscripts A, S and m denote the complex, the pure solvent and the mixture of solute and solvent, respectively. Any interaction would of course give a volume change. Significant changes of the molar volume v_A as defined above for solutions of the same concentration but consisting of different solvents would be an indication of differences in the solvent-solute interaction.

For a dilute solution of $\text{Th}(\text{AA})_4$ a molar volume of $350 \pm 10 \text{ cm}^3/\text{mol}$ was measured in benzene and $370 \pm 10 \text{ cm}^3/\text{mol}$ in toluene which possibly indicates a slightly stronger interaction or smaller intermolecular distances in benzene than in toluene. (In solid state the molar volumes obtained from structure investigations¹ are 357 and $368 \text{ cm}^3/\text{mol}$, for α - and β - $\text{Th}(\text{AA})_4$, respectively.) The only conclusion of these measurements is that any difference that might exist between the coordination of $\text{Th}(\text{AA})_4$ in benzene, which is capable of forming solid solvates, and $\text{Th}(\text{AA})_4$ in toluene, which does not form solid solvates, is small.

From comparative studies of the distribution of tetravalent acetylacetonates ($\text{Th}(\text{AA})_4$, $\text{U}(\text{AA})_4$, $\text{Np}(\text{AA})_4$, and $\text{Pu}(\text{AA})_4$) between an aqueous phase and benzene it was found that $\text{Th}(\text{AA})_4$ differs from the others.⁹ A slightly different coordination for the $\text{Th}(\text{AA})_4$ complex might be the explanation for this phenomena. If, however, there is an explicit interaction between benzene and $\text{Th}(\text{AA})_4$, possibly due to some favourable steric circumstances, which does not occur with the other tetravalent acetylacetonates (with smaller molecular volumes), then this behaviour might be detected from solubility data. For this reason the solu-

bility of $\text{Th}(\text{AA})_4$ was measured in hexane, carbon tetrachloride, hexone, benzene, toluene, and chloroform. Solvent-solute interaction with hexane and carbon tetrachloride would be small, while hexone and chloroform are very likely to interact with $\text{Th}(\text{AA})_4$.^{10,11}

According to the theory of regular solutions, the following relation should be valid:^{8,12}

$$RT \ln a_2 = RT \ln x_2 + v_2 \phi_1^2 (\delta_1 - \delta_2)^2 \quad (2)$$

where R is the gas constant, T is the absolute temperature, a is the activity, x is the mol fraction, ϕ is the volume fraction, v is the molar volume, and δ is the solubility parameter. Subscript 2 denotes solute and 1 solvent. In a regular solution interactions between solvent and solute are mainly of a dispersion type. The heat of mixing and solution is non-zero while the entropy is that of an ideal solution. Significant interactions between solvent and solute, e.g. hydrogen bonding, would violate the basic postulates in the theory and hence would be expected to cause deviations. Deviations from eqn. (2) would consequently indicate the degree of solvent-solute interaction.¹³

The solubility parameter of a chelate, ML_n , may be estimated by the relation¹⁴

$$\delta_{\text{ML}_n} = (n/n')^{1/2} \delta_{\text{HL}} \quad (3)$$

where $v_{\text{ML}_n} = n'v_{\text{HL}}$. From eqn. (3) the value $\delta_{\text{Th}(\text{AA})_4} = 11.38$ is obtained when using the molar volume of the chelate as given by the lattice parameters. [All δ -values in this report are given in $(\text{cal mol/cm}^3)^{1/2}$]. Eqn. (3) is in fact based on the assumption that the heat of evaporation of the chelate is simply obtained by addition of the contributions from the ligands. This is not unreasonable due to the

additive nature of the molar cohesive energy which has been demonstrated in other cases.¹⁵ Since the ligands in the complex are partly shielded the heat of evaporation should, however, be less than the value obtained from addition of the ligand contributions, which would change eqn. (3) to give

$$\delta_{\text{ML}_n} = (n''/n')^{1/2} \delta_{\text{HL}} \quad (4)$$

where $n'' \lesssim n$. For some tris acetylacetonates values of $n''/n \approx 0.73$ have been obtained.¹⁶ For the somewhat less symmetric tetrakis-acetylacetonates a higher value might be expected. For $n''/n = n'/n \approx 0.87$ the value for $\delta_{\text{Th}(\text{AA})_4} = \delta_{\text{HAA}} = 10.6$ would simply be obtained by assuming a volume reduction and a shielding effect of the same order.

In Table 1 calculated solubilities according to eqn. (2) are given using $\delta_{\text{Th}(\text{AA})_4} = 10.6$. In order to eliminate the activity a_2 in eqn. (2) only relative values have been calculated using hexane as an inert reference diluent. Good agreement between measured and calculated solubilities is obtained for carbon tetrachloride, toluene, and benzene, while deviations are found for hexone and chloroform. The requirements for regularity are not violated and any specific interaction with benzene is not indicated. As already stated, chloroform is known to interact strongly with $\text{Th}(\text{AA})_4$,¹¹ and mixed complexes with the composition $[\text{Th}(\text{AA})_n, \text{hexone}]^{4-n}$ are also known from distribution experiments.¹⁰ For both these solvents the calculated solubility values differ significantly from the measured values, due to a solvent-solute interaction. Evidently the basic postulates of the regular solution concept are not valid, and in order to obtain

Table 1. Measured and calculated solubilities. (For $\delta_{\text{Th}(\text{AA})_4} = 10.6$) (v from lattice parameters.¹)

Solvent	δ^a	Meas. log x	Meas. log x^b	Calc. log x^b
Hexane	7.27	-3.84	Ref.	Ref.
Carbon tetrachloride	8.58	-1.92	1.92	1.84
Hexone	8.65	-2.61	1.23	1.91
Toluene	8.99	-1.65	2.19	2.23
Benzene	9.16	-1.47	2.37	2.36
Chloroform	9.53	-1.43	2.41	2.61

^a Calculated from $\delta = [(\Delta H^v - RT)/v]^{1/2}$. ^b With hexane chosen as an inert reference solvent.

agreement between measured and calculated values the molar volumes and solubility parameters must be empirically modified.

CONCLUSIONS

Solid solvates between β -diketone complexes and benzene are not unique. Solvates with different solvent molecules including benzene are known for many rare earth complexes. A structure investigation of $[\text{Yb}(\text{AA})_3\text{H}_2\text{O} \cdot \frac{1}{2}\text{C}_6\text{H}_6]$ ¹⁷ shows that the benzene molecule in this compound is simply interstitially incorporated in the crystal lattice, the closest distance to any other carbon or oxygen atom from a benzene carbon atom being 3.53 Å. The volume of the solvate is very close to the sum of the volumes of the unsolvated complex and benzene indicating an efficiency of packing that is about equal.

In the case of $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ a volume reduction occurs, but only with a few per cent. The incorporation of benzene in the solid lattice seems to be mainly due to fortuitous packing relations in the solid state. Evidently the size of the central atom is of importance, since solid adducts of similar composition are not formed with the other, smaller tetravalent ions investigated. Benzene seems to have exactly the right size and geometry for entering the lattice, since no other of the studied solvents, including flat aromatics of smaller size, would form solid solvates. Thus no interaction responsible for the previously observed⁹ very pronounced differences between partition coefficients of tetravalent actinide acetylacetonates in the benzene/water system could be found, and these anomalies are consequently due either to changes in the aqueous phase or to some other parameter related to the distribution equilibrium.

A systematic investigation of the thermodynamics of the distribution process of these complexes in different two-phase systems is in progress.

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