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The Crystal Structure of Thorium (IV) Acetylacetonate (A Preliminary x-Ray Examination)

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Little is known about the stereochemistry of metal complexes having the coordination number of eight. There are only a few structures of eight coordinated metal complexes hitherto determined with the use of x-ray methods. The square Archimedean antiprism and trigonal dodecahedron were established as the coordination polihedra for $(TaF_8)^{3-}$ and $[Mo(CN)_8]^{4-}$ respectively[1]. The stereochemistry of uranium (IV) oxalate was investigated by chemical methods[2], but without conclusive results. The present communication is a part of the investigation on uranium and thorium complexes which is now in progress.

It was found during the preliminary work that uranium (IV) - and thorium (IV) acetylacetonate are isomorphous. Thereafter it was decided to carry out the whole x-ray analysis on the thorium complex first. The thorium (IV) acetylacetonate can be prepared more easily and it crystallises in large beautiful crystals. Contrary to the uranium (IV) complex which oxidises readily it does not oxydise in solution by atmospheric oxygen.

The first stage of the x-ray analysis did not allow any conclusion about the symmetry of the molecule: four molecules are located in a general position in the unit cell with the space group of C_{2h}^5 . Therefore the investigation followed the ordinary x-ray methods. Special atention was given to the absorption factor. For this purpose, a cylindrical shape was given to the specimen used for the recording of x-ray by grinding a large single crystal. The intensities of *h0l* reflexions were obtained and the Patterson projection ($x0z$) was evaluated. The contour map of this projection is given in Fig. 1. The position of the thorium atom, determined from the projection, has the coordinates $x = 0.19$, $z = 0.20$. Since those coordinates had been obtained from the Patterson synthesis, they are, of course, not very accurate. They will be used only as preliminary parameters for evaluating the signs of the coefficients in the first Fourier synthesis. The further structure analysis is now in progress and the results will be published elsewhere.

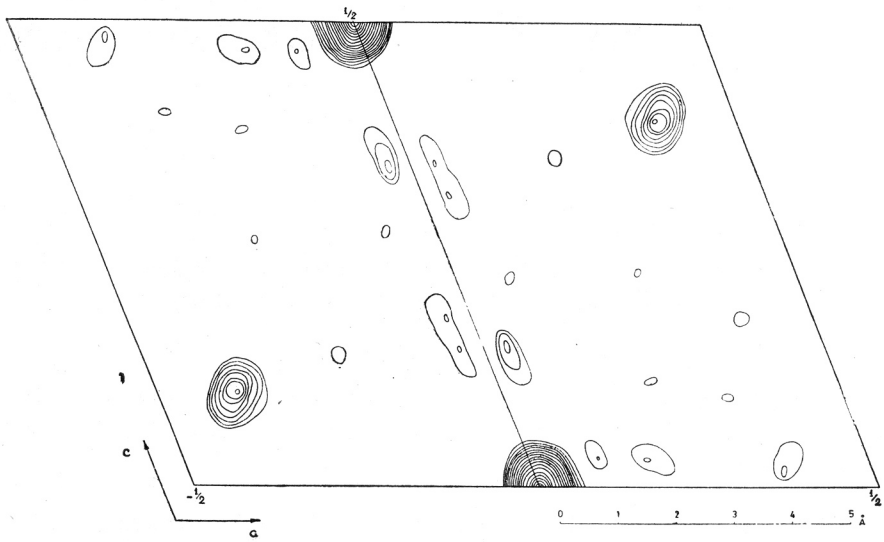

Fig. 1. Patterson synthesis (*xoz*) of the crystal of thorium(IV) acetylacetonate. Contours at equal arbitrary levels.

EXPERIMENTAL

The prepaparation of the crystals of thorium (IV) acethylatonate

Thorium acetylacetonate was prepared by the method formerly described[3]. The crystals used in this investigation were obtained by slow evaporation at room temperature from a solution in petroleum ether. Subsequently it was observed that larger crystals (up to 5 mm.) did grow from a solution in a petroleum ether — ethyl ether (1 : 1) mixture.

Crystallographic and x-ray data

The crystals of thorium(IV) acetylacetonate are bright, colourless and transparent short monoclinic prisms. The monoclinic angle as determined by means of an optical goniometer amounts to $\beta = 112^0\,15'$.

The density was determined both pycnometrically and by the suspension method. Paraffin oil saturated with thorium acetylacetonate was used as pycnometer liquid and Thoulet's solution for the suspension method. The value of $\varrho = 1.76$ g.cm.$^{-3}$ was obtained as the mean value for density.

The unit cell dimensions were determined by means of the oscillation photographs about all three axes. Nickel - filtered CuK - radiation was used. The values are as follows:

$a = 11.67$ Å, $b = 12.69$ Å, $c = 16.95$ Å, $\beta = 112^0\,15'$. This unit cell contains four molecules $Th(C_5H_7O_2)_4$ (calculated density $\varrho = 1.78$ gcm^{-3}).

The observed systematic absences of reflexions are: $h0l$ with l odd and $0k0$ with k odd only, so that the space group is $C_{2h}^5 - P2_1/c$.

All reflexions of the [010] zone were recorded on four films simultaneously using the Weissenberg goniometer. The relative $h0l$ intensities were determined from the optical densities measured at the centre of each spot using a microdensitometer and with the help of the characteristic curve of the film. The absorption correction ($\mu = 223$ cm^{-1}) for the cylindrical specimen ($r = 0.12$ mm) was carried out according to Bradley[4]. The corrections for polarization and Lorentz factors were made in the usual way. The Patterson projection was evaluated with the use of Beevers & Lipson strips at intervals of 1/60 of the cell edge. The synthesis was »sharpened« by an arbitrary chosen factor of exp ($4\sin^2\theta/\lambda^2$).

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IZVOD

Kristalna struktura torij(IV) acetilacetonata. (Preliminarno rentgenografsko istraživanje)

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Monokristali torij(IV) acetilacetonata ispitivani su rentgenografskom metodom. Određene su dimenzije elementarne ćelije:

$$a = 11{,}67 \text{ Å}, \quad b = 12{,}69 \text{ Å}, \quad c = 16{,}95 \text{ Å}, \quad \beta = 112^0\,15'.$$

Ispitivani kristali su monoklinskog sustava i pripadaju prostornoj grupi $C_{2h}^5 - P2_1/c$. Izračunata je Pattersonova projekcija ($x0z$). Dalje istraživanje strukture ovog spoja je u toku.

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