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The probable isomorphism of plutonium(IV) and thorium(IV) acetylacetonates.

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Grdenić & Matković (1959) have recently found that the acetylacetonates of zirconium (IV), cerium (IV), thorium (IV), and uranium (IV) crystallize in two different monoclinic modifications, α and β. Thorium acetylacetonate was prepared in both forms, cerium and uranium acetylacetonates only in the α-form, and zirconium acetylacetonate only in the β-form. Under suitable conditions it should be possible to prepare the acetylacetonates of all four quadrivalent metals in both forms.

Grdenić & Matković did not refer to plutonium (IV) acetylacetonate; but Dixon & Smith (1949), quoting unpublished work by Zachariasen, have stated that thorium and plutonium acetylacetonates are not isomorphous. Staritzky & Walker (1952) have published optical crystallographic data on the thorium and plutonium complexes, and they too have concluded that the complexes are not isomorphous.

From Grdenić & Matković's work it is now clear that the plutonium acetylacetonate crystals studied by Staritzky & Walker were isomorphous with the β-forms of zirconium and thorium acetylacetonates. Grdenić & Matković give the monoclinic angles β for the β-forms of zirconium and thorium acetylacetonates as 102° 30′ and 104° 20′ respectively; Staritzky & Walker give 103° for the plutonium complex. There is also a close correspondence between Staritzky & Walker's description of the crystals of the plutonium complex, and Grdenić & Matković's drawing of the crystal of the β-forms of the zirconium and thorium complexes. The thorium acetylacetonate crystals studied by Staritzky & Walker were probably in the α-form.

The puzzling non-isomorphism of the thorium and plutonium acetylacetonates reported by the American workers was thus probably due to the fortuitous circumstance that their crystals of the thorium complex belonged to the α-series, while those of the plutonium complex belonged to the β-series.

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Unit cell and space group of aconitine hydrochloride, hydrobromide, and hydroiodide.

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For the alkaloid aconitine the empirical formula

$$C_{34}H_{47}O_{11}N$$

is generally accepted. Although several suggestions have been made, the structure is not yet known.

Aconitine hydrochloride was crystallized from a solution of very pure aconitine in dilute hydrochloric acid. To obtain crystals of the hydrobromide and hydroiodide proved much more difficult because of the poor solubility of the two compounds and the strong tendency to form twins. By means of time-consuming diffusion methods sufficiently large single crystals were obtained for X-ray investigation.

Weissenberg photographs (Cu $K\alpha$ radiation) showed the three compounds to be isomorphous. From missing spectra the space group $P2_12_12_1$ was derived. Cell-dimensions were measured from Weissenberg diagrams, calibrated with sodium chloride powder lines, and gave the results tabulated below:

	a	b	c	(Å)	U (Å^3)	Z
aconitine–HCl–xH$_2$O	12·89	14·79	19·31	all ±0·02	3681	4
aconitine–HBr–xH$_2$O	12·93	14·85	19·39	all ±0·02	3723	4
aconitine–HI–xH$_2$O	12·98	14·95	19·48	all ±0·02	3780	4

The ratios

$$a:b:c = 0{\cdot}872:1:1{\cdot}306$$

and

$$a:b:c = 0{\cdot}871:1:1{\cdot}306$$

for the hydrochloride and the hydrobromide respectively agree with the values as given by Groth:

$$0{\cdot}8749:1:1{\cdot}3040$$

and

$$0{\cdot}8646:1:1{\cdot}3095$$

respectively.

The density of aconitine hydrobromide-xH$_2$O as measured by flotation is 1·419 g.cm.$^{-3}$. Calculation of the molecular weight, based on this value, gives 800·37. From this x is found to be 4·1, indicating four molecules H$_2$O per molecule of aconitine-hydrobromide. The density, calculated with the formula $C_{34}H_{47}O_{11}N.HBr.4\,H_2O$ is 1·416 g.cm.$^{-3}$.

The structure analysis of aconitine is in progress.