Acta Cryst. (1959). **12**, 817

Dimorphism and isomorphism of zirconium(IV), cerium(IV), thorium(IV) and uranium(IV) acetylacetonates.

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(*Received* 20 *April* 1959)

It has been established recently by means of X-ray crystal analysis of thorium(IV) acetylacetonate that the coordination polyhedron for thorium is an Archimedean antiprism (Grdenić & Matković, 1958). The position of four chelate rings has also been determined and a configuration with the symmetry D_2 has been established for the complex. The question still remained whether a tetravalent metal other than thorium in actylacetonate or in any analogous chelate complex occurs in the same co-ordination, or is surrounded with the oxygen atoms in a different way. The answer to this question is of interest for the development of our knowledge on the eight-coordinated complexes.

Results and discussion

It might be taken with certainty that the crystal isomorphism of a variety of compounds is the sufficient proof for the identity of their molecular structure and, consequently, for the identity of the co-ordination polyhedra in which a central metal atom occurs. For this reason the lattice constants for zirconium(IV), cerium(IV) and uranium(IV) acetylacetonates have been determined and supplementary crystallographic measurements on thorium(IV) acetylacetonate have been made. The results are given in Table 1.

Thorium(IV) acetylacetonate is dimorphic. The modifications are both monoclinic but have different unit cells and space groups, i.e. $P2_1/c$ for α-modification and $C2/c$ for β-modification. The crystal structure of only the α-modification has been determined (Grdenić & Matković, 1958). Cerium(IV) and uranium(IV) acetylacetonate occur in the same modification with lattice parameters very close to those of the thorium compound, so that isomorphism of the thorium and cerium compound previously observed (Scagliarini, 1926) has been confirmed. Consequently, the identity of the molecular structure as well as the identity of the co-ordination polyhedron for cerium(IV), thorium(IV) and uranium(IV) acetylacetonates may be taken as established.

For zirconium(IV) acetylacetonate only the β-modification has so far been observed, with the lattice parameters very close to those of β-modification of the thorium compound. The space group $C2/c$, which has been independently determined by Silverton (1959), for $Z=4$ necessitates $\bar{1}$ or 2 as the lowest molecular symmetry. Since no extra conditions limiting possible reflexions have been observed, the molecular symmetry in crystals of β-modification should be 2 at least, which is compatible with the symmetry D_2 found for the molecule of the thorium compound. Thus, the identity of the molecular structure and also of the co-ordination polyhedron of thorium(IV) and zirconium(IV) acetylacetonate could be taken as established, the more so since the transition from β- to α-modification in the case of the thorium compound occurs spontaneously, so that it could be taken as fairly certain that the transition consists only in the packing rearrangement of the molecules without any change of configuration.

Experimental

The acetylacetonates were prepared by the methods already known (Fernelius & Bryant, 1957). Single crystals of the α-modification of thorium compound were obtained by slow evaporation of petrol–ether solution at room temperature. From the warm solution or by sublimation in a high vacuum, crystals of β-modification were sometimes formed. Single crystals of the zirconium as well as those of the uranium compound were grown from benzene solution. Since no precaution was taken, yellow crystals of uranyl compound formed by oxidation with atmospheric oxygen always occurred in large quantities. Single crystals of the cerium compound were obtained directly from the reaction mixture (Job & Goissedet, 1913). Crystals of the α-modification occur in two distinct habits (Fig. 1(*a*), (*b*)). Crystals of β-modification were observed in the shape of needles or thick prisms (Fig. 1(*c*)). The β-modification of the thorium compound transforms slowly at room temperature into the α-modification; the transformation can be neatly followed by leaving crystals

Table 1. *Crystallographic data*

	α-modification				β-modification			
Compound	*a* (Å)	*b* (Å)	*c* (Å)	β	*a* (Å)	*b* (Å)	*c* (Å)	β
$Zr(C_5H_7O_2)_4$		not observed			19·80	8·35	14·10	102° 30′
						($D_m=1·37$;	$D_x=1·42$)	
$Ce(C_5H_7O_2)_4$	11·70	12·64	16·93	112° 15′		not observed		
		($D_m=1·53$;	$D_x=1·54$)					
$Th(C_5H_7O_2)_4$	11·72	12·76	17·02	112° 15′	20·36	8·52	14·56	104° 20′
		($D_m=1·76$;	$D_x=1·77$)			($D_x=1·71$)		
$U(C_5H_7O_2)_4$	11·65	12·68	16·95	112° 15′		not observed		
		($D_x=1·82$)						
Space group		C^5_{2h}–$P2_1/c$; $Z=4$				C^6_{2h}–$C2/c$; $Z=4$		

D_m = measured density in g.cm.$^{-3}$. D_x = calculated density in g.cm.$^{-3}$

in petrol–ether mother liquor. The crystals of the α-modification are also unstable since they gradually loose their transparency and eventually become amorphous to X-rays. The densities were determined by the suspension method using Thoulet solution, or pycnometrically using the saturated petrol–ether solution or paraffin oil as liquid.

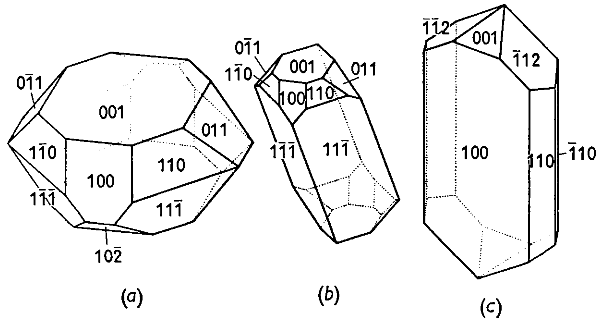

Fig. 1. (*a*) and (*b*) Crystal habits of α-modification of thorium (IV) acetylacetonate. (*c*) Crystal habit of zirconium(IV) acetylacetonate and β-modification of thorium(IV) acetylacetonate.

The lattice constants were determined from oscillation and Weissenberg photographs using Cu $K\alpha$ radiation.

The crystal structure determination of cerium(IV) acetylacetonate is now in progress.

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Acta Cryst. (1959). **12**, 818

Structure de $(CH_3NO)_2$-trans.

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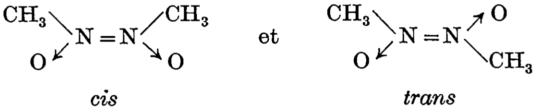
(*Reçu le* 8 *mai* 1959)

La photolyse du nitrite de butyle tertiaire permet de préparer les deux isomères géométriques de $(CH_3NO)_2$ (Gowenlock & Trotman, 1955):



$$\underset{O\swarrow}{\overset{CH_3\diagdown}{}}N=N\underset{\searrow O}{\overset{\diagup CH_3}{}} \quad \text{et} \quad \underset{O\swarrow}{\overset{CH_3\diagdown}{}}N=N\underset{\diagdown CH_3}{\overset{\nearrow O}{}}$$

cis *trans*

Nous avons déterminé la structure du *trans*-$(CH_3NO)_2$; P.F. = 122 °C. Données cristallographiques: orthorhombique; groupe spatial *Cmcm*.

$$a = 7{,}25;\quad b = 9{,}38;\quad c = 6{,}27\ \text{Å}.\quad Z = 4\ .$$

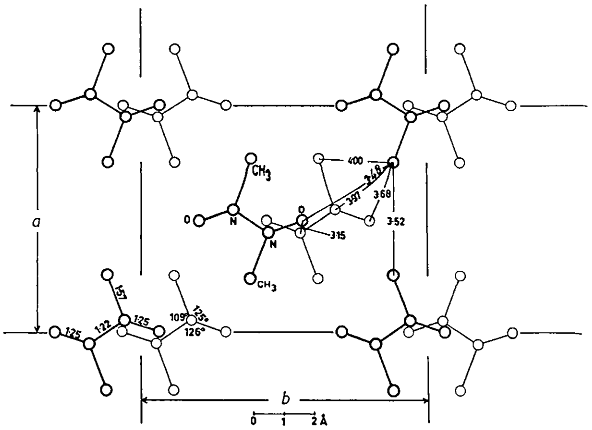


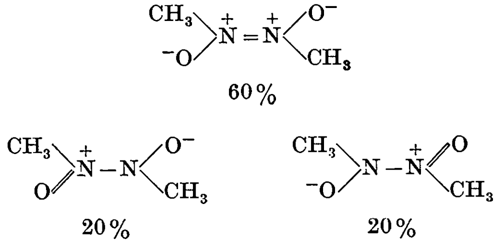
Fig. 1. Projection de la structure sur le plan (001). En trait mince, les molécules du plan $z = \frac{1}{4}$; en trait épais, celles du plan $z = \frac{3}{4}$.

Atomes en positions spéciales (hydrogènes exceptés) dans les plans de symétrie $z = \frac{1}{4}$ et $z = \frac{3}{4}$.

La structure a été résolue par la méthode de la transformée de Fourier puis affinée par séries de Fourier successives et moindres carrés jusqu'à $R(hk0) = 11{,}8\%$ et $R(hkl) = 11{,}3\%$.

La Fig. 1 montre la disposition des molécules dans la maille avec les distances intramoléculaires et intermoléculaires ainsi que les angles de valence. La structure présente un désordre quant à la distribution des atomes d'azote; ceux-ci peuvent occuper deux positions (visibles sur la Fig. 1) qui ne modifient ni la structure interne de la molécule ni les contacts intermoléculaires à l'intérieur des plans contenant les molécules.

Les distances interatomiques s'interprètent bien si on admet une mésomérie entre les trois formes suivantes:



$$\underset{^-O\diagup}{\overset{CH_3\diagdown}{}}\overset{+}{N}=\overset{+}{N}\underset{\diagdown CH_3}{\overset{\diagup O^-}{}}$$

60%

$$\underset{O\diagup\!\!\!\diagup}{\overset{CH_3\diagdown}{}}\overset{+}{N}-N\underset{\diagdown CH_3}{\overset{\diagup O^-}{}} \qquad \underset{^-O\diagup}{\overset{CH_3\diagdown}{}}N-\overset{+}{N}\underset{\diagdown CH_3}{\overset{\diagup\!\!\!\diagup O}{}}$$

20% 20%

Une analyse détaillée de ce travail sera publiée prochainement dans le Bulletin des Sociétés Chimiques Belges.

Référence

Gowenlock, B. G. & Trotman, J. (1955). *J. Chem. Soc.* p. 4190.