On the Crystal Structures of the Zirconium and Hafnium "Cupferrates"

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Recently Dyressen investigated the formation of complexes between Th⁴⁺ ions and the anions of N-nitroso-N-phenylhydroxylamine (C₆H₅N(NO)OH). The question as to how the ligands are arranged in the complexes then arose and, as a hypothesis, Dyressen suggested a "fourblade propeller" arrangement for Th(C₃H₅N₄O₄)₄. The organic ligands could then be arranged either in the syn form with both their oxygens in contact with the metal ion or in the anti form with one oxygen and one nitrogen per ligand in contact with the metal ion. Dyressen preferred the first possibility. By investigating the crystal structure of a compound of this formula, it should be possible to reveal the actual structure of the complexes. The heavy thorium atoms, which dominate the X-ray scattering too much, should then preferably be replaced by a lighter tetravalent atom, i.e., Zr⁴⁺.

From Dr. Dyressen we obtained crystals of Me(C₆H₅N₄O₄)₄, Me being Zr⁴⁺, Hf⁴⁺ and also a mixture of these ions in the

**Fig. 1.** The Patterson projections P(uvp), P(upw), and P(pvw) for Zr(C₆H₅N₄O₄)₄. The negative parts and the trivial, large maxima at (000) and (±10) have been omitted in all projections.

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Atomic ratio 1:1. These compounds had been prepared by precipitating water solutions of \( \text{Me}^{4+} \) perchlorates with the equivalent of "cupferron" (= \( \text{NH}_2\text{C}_6\text{H}_4\text{N}_2\text{O}_4 \)), dissolving the compounds obtained, preferably in chloroform, and slowly evaporating the solutions. The crystals were light yellow for \( \text{Me} = \text{Zr}^{4+} \), light yellowish brown for \( \text{Me} = (\text{Zr, Hf})^{4+} \) and light brown for \( \text{Me} = \text{Hf}^{4+} \). They were all rather long rods with a rhombic cross-section.

From single crystal photographs of \( \text{Zr(C}_8\text{H}_8\text{N}_2\text{O}_4)_4 \) \( (h00, h00, 0kl, 0kl) \) taken in Weissenberg cameras with CuK radiation, it was concluded that it is orthorhombic with the following dimensions:

\[
\begin{align*}
a &= 16.7 \pm 0.2 \ \AA \\
b &= 11.2 \pm 0.1 \ \AA \\
c &= 14.4 \pm 0.2 \ \AA \\
V &= 2.69 \cdot 10^4 \ \AA^3
\end{align*}
\]

From a few Weissenberg photographs of the \( (\text{Zr, Hf}) \) and Hf compounds, it was found that the three compounds are isomorphous and that their cell dimensions, within the experimental errors, are identical. For all three compounds, the \( c \) axis coincides with the needle axis of the crystals.

From the density of the zirconium compound, \( 1.573 \pm 0.002 \ \text{g/ml} \) as determined by flotation methods, the cell content was found to be 3.99 = 4 formula units \( \text{Me}(\text{C}_8\text{H}_8\text{N}_2\text{O}_4)_4 \).

The following reflections are systematically absent:

\[
\begin{align*}
&h00 \text{ with } h + k = \text{odd} \\
&h0l \text{ with } l = \text{odd} \\
&0kl \text{ with } k = \text{odd}
\end{align*}
\]

which is characteristic for the space group No. 60 \( \text{Pbcn} \).

The positions of the metal atoms were determined from the three Patterson projections \( P(wpw), P(pqw), \) and \( P(wwp) \) of the zirconium compound (cf. Fig. 1). Their parameters were found to be:

\[
\begin{align*}
&4 \text{ Zr in } \text{Pbcn} \ 4(e) \pm (0, y, \frac{1}{2}) \\
&\pm (\frac{1}{2}, \frac{1}{2} + y, \frac{1}{2}) \text{ with } y = 0.074
\end{align*}
\]

They are thus situated on the twofold axes in the unit cell and consequently have the special extinction: \( hkl \) absent for \( h + k = \text{odd} \). The fact that the metal ions are situated in this way is also consistent with a "propeller" arrangement since the organic ligands, lacking twofold symmetry, must be situated outside the twofold axes and, consequently, must be paired within the complexes.

Chromatographic Separation of Aliphatic Monocarbonyl Compounds

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In work on the chromatographic separation of the 2,4-dinitrophenyldihydrozones of aliphatic methylketones and aldehydes, Meigh's two-phase methanol-heptane system \( ^{1,2} \) gave promising results. The separation and identification of components in a mixture was, however, impossible owing to the trailing of the spots. Addition of 10 % glacial acetic acid to the moving phase resulted in well concentrated spots. Ligroin (B.D.H., b.r. 90—110°C) and even a technical petrol fraction (Shell, b.r. 80—110°C) were as effective as pure heptane.

Chromatographic method. The paper (Whatman No. 1) is soaked in methanol, the excess methanol allowed to drip off, and the paper dried for 10—15 minutes at 80°C. It should be used within two hours after this procedure. The hydrazones (0.5—30 μg may be used) are then pipetted on to the paper, which is suspended in a dry trough and left to stand overnight. The chamber should be airtight and the cover provided with holes for filling the troughs. The chamber holds two containers, the one with heptane(ligroin)-in-

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