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

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Recently Dyrssen investigated the formation of complexes between Th^{4+} ions and the anions of N-nitroso-N-phenylhydroxylamine ($C_6H_5N(NO)OH$) [1]. The question as to how the ligands are arranged in the complexes then arose and, as a hypothesis, Dyrssen suggested a "fourblade propeller" arrangement for $Th(C_6H_5N_2O_2)_4$. 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. Dyrssen 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.* Zr^{4+}.

From Dr. Dyrssen we obtained crystals of $Me(C_6H_5N_2O_2)_4$, Me being Zr^{4+}, Hf^{4+} and also a mixture of these ions in the

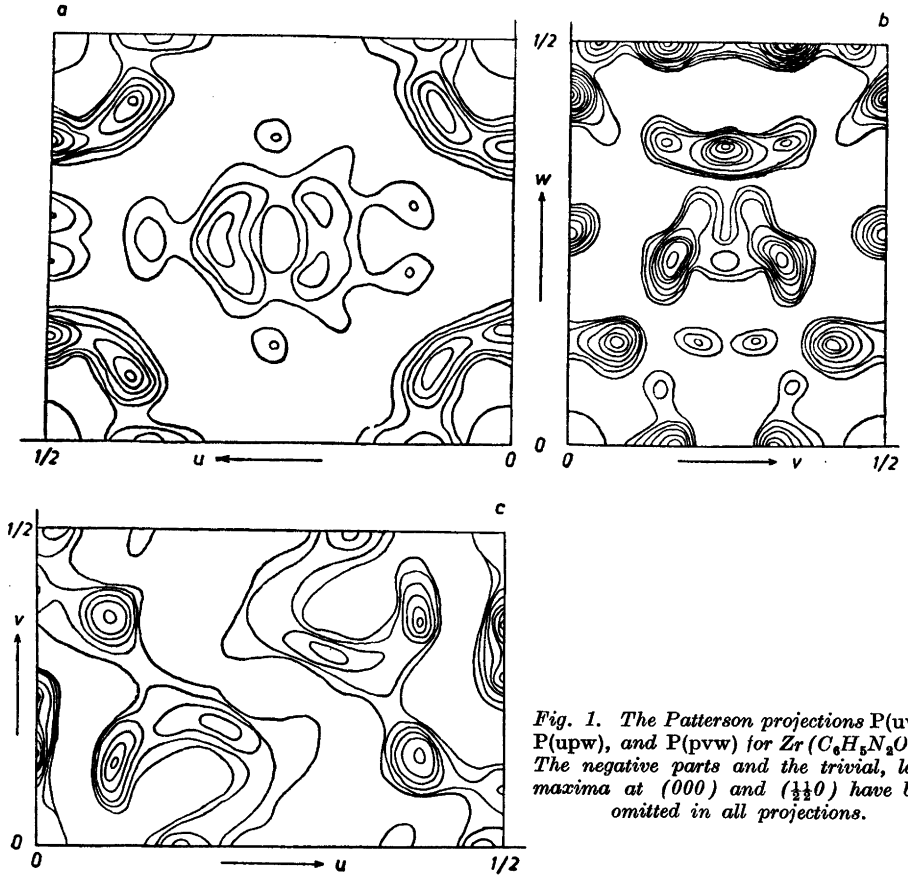

Fig. 1. The Patterson projections P(uvp), P(upw), *and* P(pvw) *for* $Zr(C_6H_5N_2O_2)_4$. *The negative parts and the trivial, large maxima at (000) and* $(\frac{1}{2}\frac{1}{2}0)$ *have been omitted in all projections.*

atomic ratio 1:1. These compounds had been prepared by precipitating water solutions of Me^{4+} perchlorates with the equivalent of "cupferron" (= $NH_4C_6H_5N_2O_2$), dissolving the compounds obtained, preferably in chloroform, and slowly evaporating the solutions. The crystals were light yellow for Me = Zr^{4+}, light yellowish brown for Me = $(Zr, Hf)^{4+}$ and light brown for Me = Hf^{4+}. They were all rather long rods with a rhombic cross-section.

From single crystal photographs of $Zr(C_6H_5N_2O_2)_4$ ($hk0$-$hk7$, $h0l$-$h5l$, $0kl$-$8kl$) taken in Weissenberg cameras with CuK radiation, it was concluded that it is orthorhombic with the following dimensions:

$$a = 16.7 \pm 0.2 \text{ Å}$$
$$b = 11.2 \pm 0.1 \text{ Å}$$
$$c = 14.4 \pm 0.2 \text{ Å}$$
$$V = 2.69 \cdot 10^3 \text{ Å}^3$$

From a few Weissenberg photographs of the (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 ± 0.002 g/ml as determined by flotation methods, the cell content was found to be $3.99 \approx 4$ formula units $Me(C_6H_5N_2O_2)_4$.

The following reflections are systematically absent:

$hk0$ with $h + k$ = odd
$h0l$ with l = odd
$0kl$ with k = odd

which is characteristic for the space group No. 60 *Pbcn* [2].

The positions of the metal atoms were determined from the three Patterson projections *P (upw)*, *P (pvw)*, and *P (uvp)* of the zirconium compound (*cf.* Fig. 1). Their parameters were found to be:

4 Zr in *Pbcn* 4(*e*): $\pm(0, y, \frac{1}{4})$;
$\pm(\frac{1}{2}, \frac{1}{2} + y, \frac{1}{4})$ with $y = 0.074$

They are thus situated on the twofold axes in the unit cell and consequently have the special extinction: hkl absent for $h+k$ = 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.

The determination of the O, N, and C parameters has also been begun. It was possible to determine the majority of the signs of F_{hk0} and F_{0kl}, whereas, because of the special extinctions for the Me atoms, only half of the signs of F_{h0l} could be determined. In this way, reliable electron density maps $\varrho(xyp)$ and $\varrho(pyz)$ could be obtained. The work to interpret these projections and to find out the arrangement of the oxygen, nitrogen, and carbon atoms is continuing.

1. Dyrssen, D. *Svensk Kem. Tidskr.* **68** (1956) 212.
2. *International Tables for X-ray Crystallography*, Birmingham 1952, Vol. I, p. 149.

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Chromatographic Separation of Aliphatic Monocarbonyl Compounds

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In work on the chromatographic separation of the 2,4-dinitrophenylhydrazones 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-