1-Ethoxy-3-phenylthiourea. A solution of phenyl isothiocyanate (0.1 mol) in ether (25 ml) was added to another solution of ethoxyamine (0.1 mol) in ether (25 ml). A slightly exothermic reaction occurred on mixing. The solution was allowed to stand for 24 h. The colourless, crystalline precipitate was filtered off and washed with a small amount of ether. The crude product (yield 60 %; m.p. 98–99°C) was submitted to elemental analysis without further purification. (Found: C 54.90; H 6.14; N 14.27. Calc. for $C_9H_{12}N_2OS$: C 55.09; H 6.16; N 14.28).

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Note on the Structures of $M^{IV}P_2O_7$ (M^{IV} = Ge, Zr, and U)

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In connection with studies on the geometry of anions of B_2X_7 stoichiometry, such as diphosphates, several members of the extensive series of $M^{IV}P_2O_7$ compounds have been synthesized and characterized by X-ray techniques. This family of compounds was first investigated by Levi and Peyronel [1,2] who reported the structure to be cubic (space-group $Pa3$). The structure determination was performed on the basis of X-ray powder data of ZrP_2O_7. The symmetry requires the P–O–P bridge of the P_2O_7 group to be linear.

While the existence of the linear P–O–P bridge has been questioned from several quarters as being not very likely from a theoretical point of view the first experimental evidence of deviations from the structure given by Levi and Peyronel was reported in 1963 by Völlenke, Wittmann and Novotny,[3] who found from single-crystal data of GeP_2O_7 that the actual cube axis of this compound is three times the one previously reported.

The compounds prepared within the present investigation include SiP_2O_7, GeP_2O_7, TiP_2O_7, ZrP_2O_7, SnP_2O_7, ThP_2O_7. Single crystals suitable for X-ray examinations have been obtained of the Ge, Zr, and U compounds.

X-Ray powder patterns of the various compounds were taken with a Guinier-Hägg camera using strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å) and with potassium chloride ($a = 6.2923$ Å at 25°C)[4] added to the specimen as an internal standard. The photographs of SiP_2O_7 and GeP_2O_7 were found to contain a large number of very weak lines not accounted for by the unit cells reported by Levi and Peyronel. Such lines were not observed in the patterns of the other specimens. All the extra lines could be indexed when the unit cell reported by Novotny and coworkers [3] was assumed. This type of superstructure was also revealed by single-crystal rotation and Weissenberg photographs of GeP_2O_7, ZrP_2O_7, and UP_2O_7. The dimensions of the super-

Table 2. The subcell structure of ZrP_2O_7.

Space group: No. 205, $Pa3$
Unit-cell dimensions: $a = 8.2474 \pm 0.0004$ Å

Cell content: 4 ZrP_2O_7
4 Zr in 4(a); 8 P in 8(c); 24 O_1 in 24(d) and
4 O_2 in 4(b)

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
Zr	0	0	0	2.3 ± 0.1
P	0.395 ± 0.001 (0.39) [a]	0.395 ± 0.001 (0.39) [a]	0.395 ± 0.001 (0.39) [a]	2.0 ± 0.2
O_1	0.446 ± 0.004 (0.394) [a]	0.229 ± 0.004 (0.218) [a]	0.427 ± 0.004 (0.458) [a]	6.5 ± 0.6
O_2	1/2	1/2	1/2	5.2 ± 1.4

[a] Coordinates according to Levi and Peyronel.[1]

structure cells deduced from the three powder photographs are listed in Table 1.

Table 1. Unit cell dimensions.

GeP_2O_7	a	$= 22.823 \pm 0.002$ Å
ZrP_2O_7	$a/3$	$= 8.2474 \pm 0.0004$ Å
UP_2O_7	$a/3$	$= 8.6274 \pm 0.0004$ Å

The intensities of the superstructure reflections are very much lower than those of the substructure in the single crystal photographs. The best set of data was the one of ZrP_2O_7. In order to get an idea of the significance of the structure reported for the subcell a lest-squares refinement was performed on the basis of the subcell intensities of ZrP_2O_7 with the positional parameters reported by Levi and Peyronel as starting parameters. The Weissenberg data which had been registered with CuK radiation were corrected for absorption and Lorentz-polarization effects. The positional and thermal parameters thus obtained are given in Table 2 together with the starting parameters. The final R value is 12.8 %.

The refinement process did not give very large shifts from the original atomic positions (the maximum shift being 0.25 Å for the O_1 atom). However, it is felt that the refinement has not given an accurate picture of the structural details — the P—O distances deviate considerably from those observed for other diphosphate compounds and the thermal parameters obtained for the oxygen atoms are rather high. Further information about the atomic arrangement can only be obtained by a full superstructure investigation. Complete three-dimensional single-crystal data have accordingly been collected for ZrP_2O_7 by means of an automatic diffractometer. The analysis of this material is in progress.

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