

(PCr₄O₁₆)³⁻, a New Zunyite-like Anion in (NH₄)₃PCr₄O₁₆

During a systematic investigation of condensed phosphochromic anions with general formula [PCr_nO_{n+4}]³⁻ (*l*-A) one very often observed when preparing the corresponding ammonium salts the formation of

well-developed orange rhombohedra, later identified as (NH₄)₃PCr₄O₁₆. The symmetry of this compound is trigonal (*R*3*m*) with the unit cell dimensions

$$a_H = 12.033(8) \text{ \AA}, \quad c_H = 10.032(8) \text{ \AA}, \quad Z = 3,$$

$$a_R = 7.710(5) \text{ \AA}, \quad \alpha_R = 102.59(5)^\circ, \quad Z = 1.$$

Crystal structure analysis (*R* = 0.054) shows that the geometry of the anion is that schematically given in Fig. 1. This PCr₄O₁₆ group has a ternary symmetry, Cr(2) and P being located on a threefold axis (Cr₂-O-P = 180°). Detailed geometrical features of this anion will be described later (5) but it is worth noticing the abnormally short P-O average (1.49 Å) in the central tetrahedron and the large difference between the Cr(1)-

O average (1.56 Å) and the same average in the Cr(2)-O₄ tetrahedron (1.66 Å).

This new type of anion, somewhat similar to the Si₅O₁₆ group, observed in zunyite (6) seems, up to now, to be the first example of a quaternary phosphorus in a finite

TABLE I
X-RAY POWDER DATA FOR (NH₄)₃PCr₄O₁₆

<i>h k l</i>	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>I</i>
1 0 1	7.23	7.20	29
1 1 0	6.02	6.02	42
0 2 1	4.62	4.62	57
0 1 2	4.52	4.52	24
2 1 1	3.67	3.67	100
2 0 2	3.61	3.61	87
3 0 0	3.47	3.47	32
0 0 3	3.34	3.34	5
1 2 2	3.10	3.10	6
2 2 0	3.01	3.01	39
1 1 3	2.923	2.923	27
1 3 1	2.777	2.777	1
4 0 1	2.522	—	—
3 1 2	2.504	2.504	1
1 0 4	2.438	—	—
3 0 3	2.409	2.409	11
3 2 1	2.326	—	—
4 0 2	2.312	2.311	1
4 1 0	2.274	2.274	4

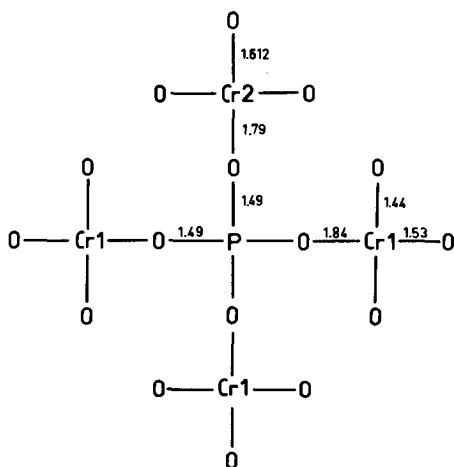


FIG. 1. P and Cr(2) are located on the threefold axis. Cr(1)O₄ tetrahedron has a mirror plane symmetry.

group. Table I gives indexed powder data of this compound which is easily prepared by boiling for some minutes a concentrated solution of ammonium dichromate and phosphoric acid in the ratio $\frac{1}{2}$.

References

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M. T. AVERBUCH-POUCHOT
A. DURIF

*Laboratoire de Cristallographie
CNRS
166 X, 38042 Grenoble Cedex, France*

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