JOURNAL OF SOLID STATE CHEMISTRY **36**, 381–384 (1981)

Crystal Structure of an Ammonium Phospho-chromate: $(NH_4)_3PCr_4O_{16}$

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Received April 28, 1980; in final form July 21, 1980

Ammonium phospho-chromate $(NH_4)_3PCr_4O_{16}$ is trigonal ($R3m$) with the following unit cell dimensions: $a_H = 12.033(8)$, $c_H = 10.032(8)$ Å, and $Z = 3$ for the hexagonal cell, $a_R = 7.710(5)$ Å, $\alpha_R = 102.59(5)°$ and $Z = 1$ for the rhombohedral cell. Crystal structure of this compound has been solved with a final R value 0.054. The main feature of this atomic arrangement is the existence in the anion configuration of a central PO_4 tetrahedron linked to four CrO_4 tetrahedra.

Introduction

Phospho-chromic anions of general formula $[PCr_nO_{3n+4}]^{3-}$ were up to now known for $n = 1$, 2, and 3. $PCrO_7^{3-}$ ($n = 1$) was investigated in $CuK_2H_2(PCrO_7)_2$ (*1*).

$PCr_2O_{10}^{3-}$ ($n = 2$) is known to exist in several compounds: $BaHPCr_2O_{10} \cdot 3H_2O$ for instance (*2*)

$PCr_3O_{13}^{3-}$ ($n = 3$) exists in
$Na_3PCr_3O_{13} \cdot 3H_2O$ (*3*).

$(NH_4)_3PCr_4O_{16}$ is the first structural evidence for the existence of an anion corresponding to the fourth term of this series. Being given the usual behavior of the PO_4 group in condensed anions a linear configuration (Fig. 1a) was expected for the $PCr_4O_{16}^{3-}$ group.

In spite of this assumption crystal structure shows this anion is essentially built from a central PO_4 tetrahedron sharing its four corners with the four CrO_4 tetrahedra (Fig. 1b). This configuration seems to be the first example of a quaternary phosphorus in a finite group.

Crystal Data

Chemical preparation and main crystallo-

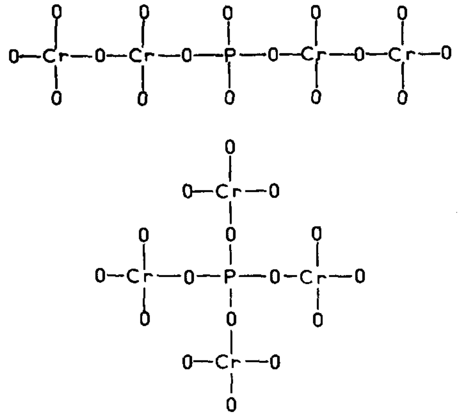

FIG. 1. (a) Possible configuration for a PCr_4O_{16} anion. (b) Observed configuration.

0022-4596/81/030381-04$02.00/0

TABLE I

ATOMIC COORDINATES

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
Cr1	0.8756(0)	−0.8756(2)	0.5075(3)
Cr2	0.0000(0)	0.0000(0)	0.0000(0)
P	0.0000(0)	0.0000(0)	0.3257(4)
OL1	0.9312(0)	−0.9312(10)	0.3646(11)
OE11	−0.0191(10)	0.2260(20)	0.5803(13)
OE12	0.8084(0)	−0.8084(13)	0.4461(17)
OL2	0.0000(0)	0.0000(0)	0.1778(14)
OE2	0.9271(0)	−0.9271(8)	0.9456(9)
N	−0.5152(0)	0.5152(11)	0.4676(9)

graphic features of this salt have already been described by the authors (*4*) so we give here only its unit cell dimensions:

$a_H = 12.033(8) \qquad c_H = 10.032(8)$ Å

$Z = 3$

for the hexagonal description;

$a_R = 7.710(5)$ Å $\qquad \alpha = 102.59(5)°$

$Z = 1$

for the rhombohedral cell.

The space group is $R3m$. $D_x = 2.17$ g/cm³. It is worth noticing this compound has been prepared for the first time as early as 1894 by Friedheim and Moskin (*5*).

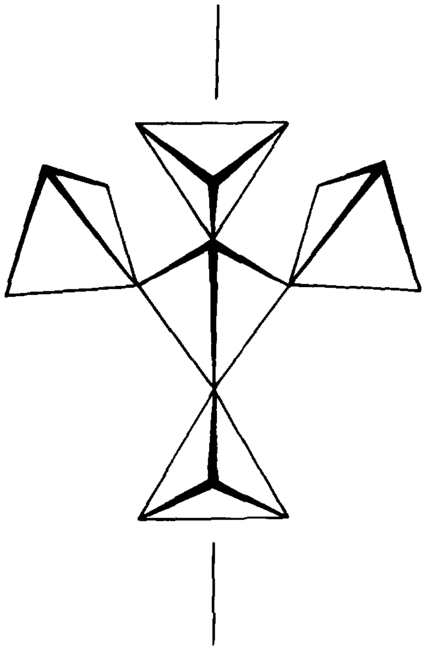

FIG. 2. Perspective view of the PCr_4O_{16} anion. The threefold axis is schematized by the vertical line.

Crystal Structure

The crystal used for the structure determination was an almost equant rhombohedron (0.34 × 0.30 × 0.30 mm). A set of 3132 reflections was collected with a Philips PW 1100 four circle diffractometer using silver radiation, monochromatized with a graphite plate. From these data a set of 674 independent reflections was obtained after averaging equivalent reflections. Internal

TABLE II

ANISOTROPIC TEMPERATURE FACTORS[a]

Atoms	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Cr1	0.0096(0)	0.0096(1)	0.0095(1)	0.0128(1)	0.0014(0)	−0.0014(3)
Cr2	0.0073(0)	0.0073(2)	0.0063(2)	0.0073(0)	0.0000(0)	0.0000(0)
P	0.0064(0)	0.0064(3)	0.0048(3)	0.0064(0)	0.0000(0)	0.0000(0)
OL1	0.0173(0)	0.0173(9)	0.016(1)	0.0258(10)	0.003(0)	−0.003(2)
OE11	0.028(1)	0.130(3)	0.051(1)	0.087(3)	−0.053(3)	−0.138(3)
OE12	0.060(0)	0.060(1)	0.032(3)	0.113(1)	−0.001(0)	0.001(4)
OL2	0.022(0)	0.022(3)	0.004(1)	0.022(0)	0.000(0)	0.000(0)
OE2	0.0112(0)	0.0112(7)	0.015(1)	0.0165(8)	−0.001(0)	0.001(2)
N	0.0132(0)	0.0132(9)	0.0091(9)	0.017(1)	0.003(0)	−0.003(2)

[a] The formula used here is: $T = (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + hl\beta_{23})$.

consistency for equivalent reflections was 1.2%.

Measurements were run with an ω-scan in a range of 3 to 30°(θ) at a speed of 0.02°/sec. Scanwidth was 1.60°(θ) and the background was measured during 10 sec at each end of this domain.

Crystal structure determination was normally run by using the classical Patterson function followed by successive Fourier syntheses.

As suggested by the examination of the Patterson map space group $R3m$ was used for the final refinements. Throughout this work unitary ponderation has been used. The final R value is 0.054 for 516 reflections such that $F > 3\sigma(F)$ and 0.063 for the whole set of 674 reflections.

Atomic coordinates and anisotropic thermal parameters are reported in Tables I and II.

Final difference-Fourier map being strictly flat no attempt has been made for hydrogen atoms location.

Description of the Structure

The main feature of this atomic arrangement is the geometrical configuration of the $PCr_4O_{16}^{3-}$. The central phosphorus and the chromium atom Cr_2 are both located on a threefold axis. PO_4 and CrO_4 tetrahedra share OL_2 oxygen atom, itself on the same threefold axis ($P-OL2-Cr_2$ = 180°). The three remaining chromium atoms (Cr1) are connected to the central phosphorus by the OL1 oxygen atoms with bond angles P-OL1-Cr1 = 144.1°. Figure 2 gives a perspective view of the arrangement of this five tetrahedra. Three unusual features are to be noticed in the geometry of this PCr_4O_{16} group.

(a) The abnormally short average of the P-O bond lengths in the central PO_4 tetrahedron (1.49 Å).

(b) Thermal factors are all larger than those usually observed in other phosphochromic anions (see Table II). In spite of this fact the compound is stable for years at room temperature.

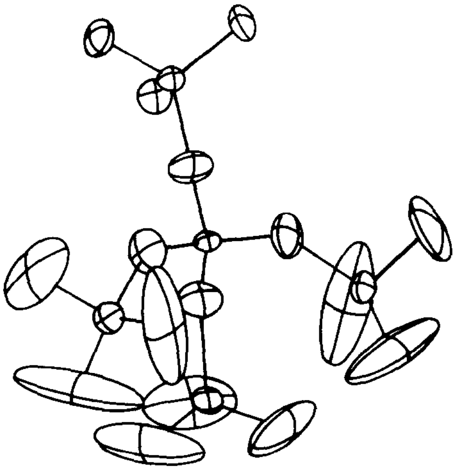

FIG. 3. Perspective view of the PCr_4O_{16} anion showing the large thermal anisotropy of the external tetrahedra.

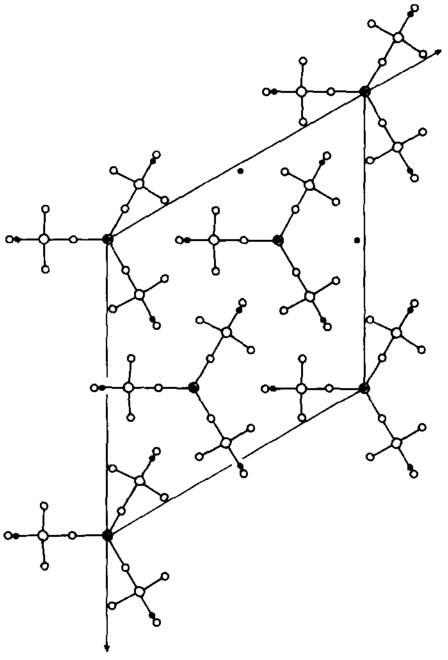

FIG. 4. Projection along the c axis of a unit cell of $(NH_4)_3PCr_4O_{16}$. $Cr(2)O_4$ tetrahedron and PO_4 tetrahedron have a common projection.

TABLE III

MAIN INTERATOMIC BOND LENGTHS AND ANGLES IN $(NH_4)_3PCr_4O_{16}$[a]

		Cr1–OL1	1.84(1)		
		2 × Cr1–OE11	1.44(1)		
		Cr1–OE12	1.53(1)		
2 × OL1–Cr1–OE11	112.2(7)			2 × OL1–OE11	2.74(2)
OL1–Cr1–OE12	105.1(5)			OL1–OE12	2.69(2)
OE11–Cr1–OE11	119.1(9)			OE11–OE11	2.49(3)
2 × OE11–Cr1–OE12	103.2(8)			2 × OE11–OE12	2.33(2)
		3 × P–OL1	1.49(1)		
		P–OL2	1.49(1)		
3 × OL1–P–OL2	105.2(4)			3 × OL1–OL1	2.49(2)
3 × OL1–P–OL1	113.4(5)			3 × OL1–OL2	2.36(2)
		3 × Cr2–OE2	1.612(9)		
		Cr2–OL2	1.79(1)		
3 × OL2–Cr2–OE2	109.5(3)			3 × OL2–OE2	2.78(1)
3 × OE2–Cr2–OE2	109.5(3)			3 × OE2–OE2	2.63(1)
				Cr1–OL1–P	144.1(5)
3 × Cr1–P	3.172(3)			Cr2–OL2–P	180.0
P–Cr2	3.272(4)			Cr1–P–Cr2	125.2(5)
				Cr1–P–Cr1	90.2(5)
(2×)N–OE11	2.84(2)			N–OL1	3.30(2)
N–OE2	2.95(2)			(2×)N–OE11	3.42(2)
(2×)N–OE2	3.10(2)			N–OE12	3.46(2)
N–OE12	3.14(2)				

[a] These calculations have been made by using the unit cell dimensions given by the four circle diffractomer and used for the structure determination: $a = 12.037(8)$, $c = 10.045(8)$ Å. These dimensions are slightly different of those obtained by powder data refinement and given in this paper.

(c) The external oxygen atoms of the Cr1 O_4 tetrahedra [OE12 and OE11 × 2] have very large thermal factors. Figure 3 gives an idea of thermal ellipsoids in this PCr_4O_{16} group and suggests these very large thermal factors are to be interpreted as a rotation of these tetrahedra around the Cr1–OL1 direction. It is rather evident that the harmonic approximation used here is not the most appropriate to describe accurately this rotation phenomenon.

Table III reports bond lengths and angles in this arrangement.

The ammonium ions have a 10-fold coordination with NH_4–O distances ranging from 2.84 to 3.46 Å (Table III).

This new type of anion is to be compared with the Si_5O_{16} group as observed in zunyite (*5*).

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