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Crystal Structure of $K_3PCr_4O_{16}$: A Second Example of a Quaternary Phosphorus

M. T. AVERBUCH-POUCHOT, A. DURIF, AND J. C. GUITEL

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG 166 X, 38042 Grenoble Cédex, France

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$K_3PCr_4O_{16}$ is monoclinic (Cc) with the following unit cell dimensions: $a = 9.512(6)$, $b = 11.74(2)$, $c = 14.74(2)$ Å, $\beta = 106.13(5)°$, and $Z = 4$. The crystal structure has been solved, with a final R value 0.055. The main feature of this atomic arrangement is the geometrical configuration of the PCr_4O_{16} anion: a central PO_4 tetrahedron sharing its four corners with CrO_4 tetrahedra. This phosphochromic anion provides the second example of a quaternary phosphorus in a finite anion.

Introduction

The first evidence for the existence of a $PCr_4O_{16}^{3-}$ anion was given by the authors in the crystal structure determination of $(NH_4)_3PCr_4O_{16}$ (*1*, *2*). The present study describes the second example of such an anion in the corresponding potassium salt: $K_3PCr_4O_{16}$. This last compound is monoclinic with a unit cell closely related to be rhombohedral unit cell of the ammonium salt. (See "Crystal Chemistry.")

Chemical Preparation

A concentrated solution of tripotassium monophosphate K_3PO_4 and chromic acid with a ratio P/Cr = $\frac{1}{4}$ is kept boiling for some minutes and then left at room temperature. A first precipitation of potassium dichromate occurs some hours later. After elimination of this precipitate, one observes in the remaining solution the formation of orange-red pseudo-rhombohedral crystals of $K_3PCr_4O_{16}$.

Crystal Chemistry

A single-crystal study shows this compound is monoclinic. The following extinction rules

$$h\ k\ l \text{ with } h + k = 2n$$

$$h\ 0\ l \text{ with } h = 2n \text{ and } 1 = 2n$$

lead to two possible space groups: Cc or $C2/c$.

Refinement by a least-squares method of the angular data collected on a powder diffractogram run at a very low scan speed ($\frac{1}{8}°$/min) and operating with Cu$K\alpha$ radiation gives the following cell dimensions: $a = 9.512(6)$, $b = 11.74(2)$, $c = 14.74(2)$ Å, $\beta = 106.13(5)°$, $Z = 4$, and $D_x = 2.59$. Table I reports the indexed powder data.

The rhombohedral unit cell of the corresponding ammonium salt (1) is $a_r = 7.710(5)$ Å, $\alpha_r = 102.59(5)°$.

There is a close relationship between these two unit cells, the rhombohedral one

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TABLE I

Indexed Powder Diffraction Data of $K_3PCr_4O_{16}$

$h\ k\ l$	d_{cal}	d_{obs}	I_{obs}	$h\ k\ l$	d_{cal}	d_{obs}	I_{obs}
1 1 0	7.20	—	—	0 4 0	2.925	2.926	13
$\bar{1}$ 1 1	7.06	7.04	13	1 1 4	2.919		
0 0 2	7.04			$\bar{3}$ 1 3	2.871	2.864	13
1 1 1	5.91	5.90	19	0 4 1	2.864		
0 2 0	5.85	5.84	7	$\bar{2}$ 2 4	2.850	2.851	16
$\bar{1}$ 1 2	5.70	—	—	$\bar{1}$ 1 5	2.843		
0 2 1	5.40	5.40	1	3 1 1	2.742	2.738	4
2 0 0	4.57	4.55	6	1 3 3	2.710	2.706	1
1 1 2	4.56			0 4 2	2.701		
0 2 2	4.50	4.50	6	$\bar{1}$ 3 4	2.662	2.667	1
$\bar{2}$ 0 2	4.44	4.43	9	$\bar{3}$ 1 4	2.639	—	—
$\bar{1}$ 1 3	4.40	4.40		2 2 3	2.595	2.596	2
$\bar{2}$ 2 1	3.69	3.68	3	0 2 5	2.501	—	—
0 2 3	3.66	3.65	4	$\bar{2}$ 4 1	2.492	2.492	2
2 2 0	3.60			3 1 2	2.491		
1 1 3	3.59	3.60	85	0 4 3	2.482	—	—
1 3 0	3.59			2 0 4	2.475	—	—
$\bar{1}$ 3 1	3.57	3.57	38	2 4 0	2.464	—	—
$\bar{2}$ 2 2	3.54	3.53	100	$\bar{3}$ 3 1	2.459	—	—
0 0 4	3.52			1 1 5	2.447	—	—
$\bar{1}$ 1 4	3.48	3.48	1	$\bar{2}$ 4 2	2.443	—	—
2 0 2	3.42	3.42	6	$\bar{3}$ 3 2	2.443	—	—
1 3 7	3.39	3.39	11	3 3 0	2.401	2.401	1
$\bar{1}$ 3 2	3.35	—	—	$\bar{1}$ 1 6	2.391	—	—
2 2 1	3.32	—	—	1 3 4	2.385	—	—
$\bar{2}$ 0 4	3.26	3.26	4	$\bar{3}$ 1 5	2.383	—	—
$\bar{2}$ 2 3	3.22	—	—	$\bar{4}$ 0 2	2.378	—	—
1 3 2	3.06	3.05	3	$\bar{2}$ 0 6	2.374	2.371	4
$\bar{3}$ 1 1	3.06			2 4 1	2.367		
$\bar{3}$ 1 2	3.03	3.02	5	$\bar{3}$ 3 3	2.359	—	—
0 2 4	3.02			0 0 6	2.347	2.350	8
$\bar{1}$ 3 3	3.01			$\bar{1}$ 3 5	2.343	2.341	12
2 2 2	2.954	2.954	37				
3 1 0	2.949						

deriving from the monoclinic one by the transformation matrix

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ -\frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}$$

Structure Determination

An almost regular rhombohedron with edge lengths of about 0.15 mm was used for the data collection. Thirteen hundred ninety-two reflections were collected using a Philips PW 1100 four-circle diffractometer operating with Ag$K\alpha$ radiation (0.5608 Å) monochromatized by a graphite plate. Each reflection was measured at a scan speed of 0.02°/sec in an angular domain of 1.60° using a $\theta/2\theta$ scan. Background was measured for 8 sec at each extremity of this domain. The explored θ range extended from 3 to 20°. The positions of heavy atoms were identified by using the MULTAN program (*3*). Then, successive Fourier syntheses rapidly revealed the complete atomic arrangement and confirmed that the

TABLE II

ATOMIC COORDINATES

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
Cr(1)	0.4447(0)	0.2361(3)	0.1411(0)
Cr(2)	0.3327(4)	0.4351(3)	0.4588(2)
Cr(3)	0.3371(4)	0.0569(3)	0.4359(2)
Cr(4)	0.4491(4)	0.2643(3)	0.7614(2)
P	0.1204(5)	0.2335(4)	0.4801(3)
K(1)	0.2080(6)	0.4622(5)	0.1725(3)
K(2)	0.1462(6)	0.2734(4)	0.8907(3)
K(3)	0.1884(6)	0.0097(5)	0.1606(4)
O(E11)	0.981(2)	0.165(1)	0.718(1)
O(E12)	0.994(2)	0.385(1)	0.688(1)
O(E13)	0.276(2)	0.233(2)	0.090(1)
O(L1)	0.042(3)	0.221(2)	0.567(2)
O(E21)	0.250(3)	0.494(3)	0.365(2)
O(E22)	0.968(3)	0.123(3)	0.950(2)
O(E23)	0.368(3)	0.473(2)	0.038(1)
O(L2)	0.212(2)	0.343(2)	0.495(2)
O(E31)	−0.004(2)	0.431(2)	0.000(1)
O(E32)	0.333(2)	0.125(2)	0.341(1)
O(E33)	0.279(3)	0.065(2)	0.906(2)
O(L3)	0.214(2)	0.128(1)	0.494(1)
O(E41)	0.463(4)	0.383(2)	0.718(2)
O(E42)	0.288(2)	0.251(4)	0.744(2)
O(E43)	0.047(4)	0.311(3)	0.225(2)
O(L4)	0.501(2)	0.264(2)	0.888(1)

TABLE III

ANISOTROPIC THERMAL COEFFICIENTS[a]

Atoms	$\beta_{(1.1)}$	$\beta_{(2.2)}$	$\beta_{(3.3)}$	$\beta_{(1.2)}$	$\beta_{(1.3)}$	$\beta_{(2.3)}$
Cr(1)	0.0089(3)	0.0040(2)	0.0025(1)	0.0019(6)	0.0054(3)	0.0010(3)
Cr(2)	0.0087(3)	0.0032(2)	0.0032(1)	−0.0021(6)	0.0040(3)	−0.0013(3)
Cr(3)	0.0076(3)	0.0038(2)	0.0039(2)	0.0019(6)	0.0038(4)	−0.0001(3)
Cr(4)	0.0084(4)	0.0045(2)	0.0027(1)	−0.0002(6)	−0.0002(4)	0.0012(4)
P	0.0064(5)	0.0040(3)	0.0024(2)	−0.0017(8)	0.0039(5)	−0.0017(5)
K(1)	0.0187(7)	0.0120(5)	0.0066(3)	0.0071(10)	0.0069(7)	−0.0028(6)
K(2)	0.0220(7)	0.0094(4)	0.0058(2)	0.0005(10)	0.0092(6)	0.0000(6)
K(3)	0.0225(8)	0.0118(5)	0.0073(3)	−0.0034(11)	0.0109(7)	−0.0051(6)
O(E11)	0.018(2)	0.005(1)	0.0033(7)	−0.007(3)	−0.001(2)	0.002(2)
O(E12)	0.027(3)	0.005(1)	0.0079(9)	−0.010(3)	0.016(2)	−0.007(2)
O(E13)	0.008(2)	0.011(2)	0.007(1)	−0.008(3)	0.003(2)	0.000(2)
O(L1)	0.032(3)	0.013(2)	0.0097(9)	0.013(4)	0.024(2)	−0.003(3)
O(E21)	0.026(4)	0.023(3)	0.006(1)	−0.015(7)	0.001(4)	0.005(4)
O(E22)	0.040(4)	0.018(3)	0.027(2)	−0.027(6)	0.051(4)	−0.020(4)
O(E23)	0.039(4)	0.014(2)	0.007(1)	0.024(5)	0.016(3)	0.016(2)
O(L2)	0.018(3)	0.008(1)	0.014(2)	−0.012(3)	0.010(3)	0.006(3)
O(E31)	0.012(3)	0.016(2)	0.008(1)	−0.004(5)	−0.001(3)	0.006(3)
O(E32)	0.028(3)	0.020(3)	0.0060(9)	0.021(9)	0.018(2)	0.010(3)
O(E33)	0.026(3)	0.008(2)	0.031(3)	0.009(4)	0.037(4)	0.017(4)
O(L3)	0.013(2)	0.007(1)	0.0052(8)	0.012(3)	0.008(2)	0.006(2)
O(E41)	0.081(10)	0.010(2)	0.008(1)	−0.016(8)	0.016(6)	0.005(3)
O(E42)	0.014(3)	0.044(6)	0.011(2)	−0.011(8)	0.007(3)	0.014(6)
O(E43)	0.082(6)	0.046(4)	0.006(1)	−0.104(6)	0.011(5)	−0.010(4)
O(L4)	0.023(3)	0.012(2)	0.0037(9)	−0.017(4)	−0.001(3)	−0.001(2)

[a] The thermal factor used for this calculation is $T = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl$.

TABLE IV

MAIN INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN THE $PCrO_{16}$ GROUP

Cr(1)O_4 Tetrahedron

Cr(1)	O(L1)	O(E11)	O(E12)	O(E13)
O(L1)	1.694(11)	2.54(2)	2.75(1)	2.70(1)
O(E11)	101.1(6)	1.593(8)	2.63(1)	2.60(1)
O(E12)	113.4(6)	111.4(5)	1.594(8)	2.57(1)
O(E13)	111.4(6)	110.7(5)	108.7(6)	1.574(8)

Cr(2)O_4 Tetrahedron

Cr(2)	O(L2)	O(E21)	O(E22)	O(E23)
O(L2)	1.764(9)	2.70(2)	2.73(2)	2.60(1)
O(E21)	109.3(7)	1.548(12)	2.51(2)	2.51(1)
O(E22)	113.4(7)	111.0(9)	1.499(13)	2.53(2)
O(E23)	102.8(6)	108.0(8)	111.9(10)	1.533(9)

Cr(3)O_4 Tetrahedron

Cr(3)	O(L3)	O(E31)	O(E32)	O(E33)
O(L3)	1.839(8)	2.75(1)	2.79(1)	2.77(1)
O(E31)	108.1(5)	1.552(10)	2.51(1)	2.66(2)
O(E32)	108.4(5)	105.7(7)	1.601(10)	2.53(2)
O(E33)	109.4(6)	117.8(8)	107.0(9)	1.549(11)

TABLE IV—*Continued*

Cr(4)O_4 Tetrahedron

Cr(4)	O(L4)	O(E41)	O(E42)	O(E43)
O(L4)	1.787(8)	2.79(1)	2.49(2)	2.70(2)
O(E41)	113.5(6)	1.548(13)	2.38(2)	2.40(2)
O(E42)	98.8(6)	103.1(12)	1.488(11)	2.65(3)
O(E43)	110.8(7)	104.4(12)	126.4(15)	1.484(15)

PO_4 Tetrahedron

P	O(L1)	O(L2)	O(L3)	O(L4)
O(L1)	1.657(3)	2.59(2)	2.44(1)	2.57(2)
O(L2)	108.7(7)	1.534(10)	2.52(1)	2.52(2)
O(L3)	101.3(5)	112.4(6)	1.501(8)	2.53(1)
O(L4)	108.2(7)	111.4(7)	114.1(6)	1.513(9)

Other pertinent distances or bond angles

P–Cr(1)	3.281(2)	Cr(1)–O(L1)–P	156.5(8)
P–Cr(2)	3.182(3)	Cr(2)–O(L2)–P	149.4(9)
P–Cr(3)	3.117(3)	Cr(3)–O(L3)–P	137.7(5)
P–Cr(4)	3.182(3)	Cr(4)–O(L4)–P	149.2(7)
Cr(1)–P–Cr(2)	117.1(7)	Cr(1)–P–Cr(3)	136.3(7)
Cr(2)–P–Cr(3)	90.0(7)	Cr(2)–P–Cr(4)	93.1(7)
Cr(1)–P–Cr(4)	120.8(7)	Cr(3)–P–Cr(4)	88.6(7)

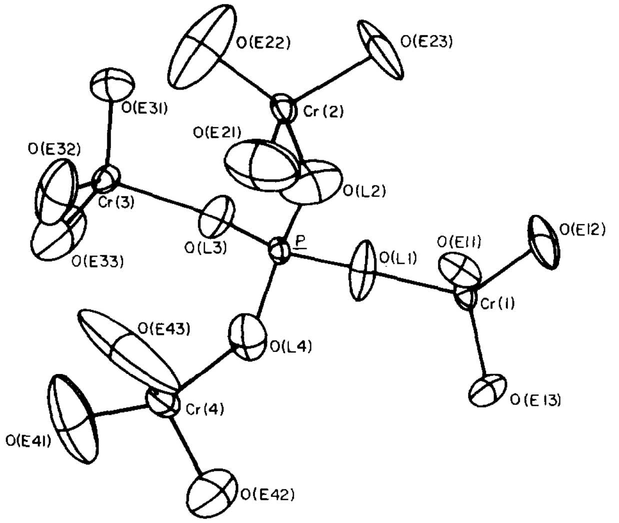

FIG. 1. Perspective view of the PCr_4O_{16} group.

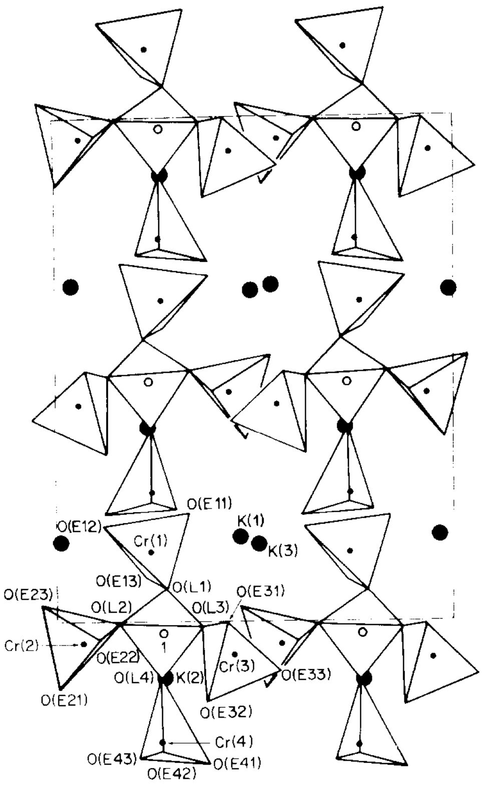

FIG. 2. Projection of the $K_3PCr_4O_{16}$ arrangement along the a axis.

right space group is the noncentrosymmetrical *Cc*.

After some least-squares refinement cycles using anisotropic thermal factors the final *R* value is 0.055 for 1011 reflections such that

$$F_0 > 2\sigma.$$

The same factor is 0.061 for the complete set of reflections. Table II gives the atomic coordinates for this arrangement, while Table III reports the anisotropic thermal coefficients. Throughout this structure determination a unitary weighting scheme was used.

Structure Description

The main feature of this atomic arrangement rests in the geometrical configuration of the PCr_4O_{16} groups, essentially built from a central PO_4 tetrahedron sharing its four corners with CrO_4 tetrahedra. Main interatomic bond lengths and angles in this group are given in Table IV.

If the average P–O distance (1.551 Å) in the central PO_4 tetrahedron is much larger than those observed for the same anion in the corresponding ammonium salt (1.49 Å), (*1*, *2*), the Cr–O terminal bond lengths ranging from 1.484 to 1.601 Å are quite comparable with those observed in the ammonium salt (1.44–1.612 Å). Bridging Cr–O bond distances are also quite similar for the two salts: (1.694–1.839 Å) for the potassium salt and (1.79–1.84 Å) for the ammonium salt.

As can be seen from Cr_i–P–Cr_j bond

TABLE V

POTASSIUM–OXYGEN DISTANCES (Å) IN THE KO_n POLYHEDRA

K(1)–O(E43)	2.60(1)	K(2)–O(E33)	2.74(1)	K(3)–O(E41)	2.81(2)
K(1)–O(E12)	2.77(1)	K(2)–O(E22)	2.75(1)	K(3)–O(E32)	2.96(1)
K(1)–O(E21)	2.78(1)	K(2)–O(E42)	2.86(1)	K(3)–O(L3)	3.004(8)
K(1)–O(E31)	2.79(1)	K(2)–O(E13)	2.889(9)	K(3)–O(E13)	3.02(1)
K(1)–O(E23)	2.82(1)	K(2)–O(E11)	2.890(8)	K(3)–O(E12)	3.08(1)
K(1)–O(E11)	2.907(9)	K(2)–O(E21)	2.96(2)	K(3)–O(E23)	3.11(1)
K(1)–O(E41)	2.96(2)	K(2)–O(E31)	3.06(1)	K(3)–O(E11)	3.12(1)
K(1)–O(L2)	3.10(1)	K(2)–O(E32)	3.10(1)	K(3)–O(L1)	3.18(1)
		K(2)–O(E12)	3.22(1)	K(3)–O(E42)	3.33(2)
		K(2)–O(L4)	3.39(1)	K(3)–O(E22)	3.50(2)
		K(2)–O(E23)	3.48(1)		

angles given in Table IV, the PCr_4O_{16} group has a pseudo-threefold symmetry around the P–Cr_1 direction, and so, as suggested by the close relationship between the unit cells, has a geometry almost similar to those observed in the corresponding ammonium salt (*1*, *2*). Figure 1 gives a perspective view of the anion, while Fig. 2 gives a projection of the atomic arrangement along the **a** axis. Bond distances in potassium–oxygen polyhedra are given in Table V.

$M^I_3XCr_4O_{16}$ Compounds

$M^I_3XCrO_{16}$ compounds have been investigated for M^I = K, NH_4, and Rb, and X = P, As. With the exception of the rhombohedral $(NH_4)_3PCr_4O_{16}$ all of them are monoclinic and isotypic with $K_3PCr_4O_{16}$ (*4*, *5*).

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