

Crystal Structure of the Tetrapolyphosphate $\text{Cr}_2\text{P}_4\text{O}_{13}$

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The structure of the tetrapolyphosphate $\text{Cr}_2\text{P}_4\text{O}_{13}$ was determined from single-crystal X-ray diffraction data. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.097(2)$, $b = 8.787(3)$, $c = 13.098(4)$ Å, $\beta = 105.54(2)^\circ$, $V = 897.8(5)$ Å³, $Z = 4$, and $R = 0.0297$, $R_w = 0.0287$ for 1802 unique reflections. Hexagonal tunnels along the a -axis are formed by the edges of two CrO_6 octahedra and four PO_4 tetrahedra. The framework consists of pairs of edge-sharing CrO_6 octahedra forming Cr_2O_{10} units and unusual tetrapolyphosphate anions $\text{P}_4\text{O}_{13}^{6-}$. The phosphate anion forms a "U" shape and is built up by four corner-sharing PO_4 tetrahedra. The present state of tetrapolyphosphate chemistry is briefly reviewed. © 1989 Academic Press, Inc.

Introduction

The investigation of molybdenum phosphates containing Mo in oxidation states less than +6 has led to a large number of novel structures (1-10). Among these phosphates a few compounds contain unusual Mo(III) O_6 octahedra (6, 8, 10). Trivalent molybdenum appears as a rare species especially in oxides.

While attempting to prepare a chromium analogue of Mo(III) $\text{P}_5\text{SiO}_{19}$ (10), we observed formation of a new phase. Single-crystal X-ray analysis of a green chunk showed that a new chromium phosphate had been formed with a formula $\text{Cr}_2\text{P}_4\text{O}_{13}$. The structure consists of edge-sharing CrO_6 octahedra and a rare tetrapolyphosphate anion, $\text{P}_4\text{O}_{13}^{6-}$.

In this communication we present the crystal structure of the tetrapolyphosphate $\text{Cr}_2\text{P}_4\text{O}_{13}$. The phosphates containing P_4O_{13} groups are briefly reviewed.

Experimental

Small green chunky crystals of $\text{Cr}_2\text{P}_4\text{O}_{13}$ were obtained as a minor product in an attempt to synthesize a chromium analogue of $\text{Mo}_3\text{P}_5\text{SiO}_{19}$ in a sealed fused silica tube containing Cr_2O_3 and P_2O_5 (mole ratio 3 : 5) at 1030°C. However, pure $\text{Cr}_2\text{P}_4\text{O}_{13}$ was never obtained even with appropriate amounts of Cr_2O_3 and P_2O_5 when the composition was known based on X-ray crystal structure analysis.

A green chunk having the dimensions of $0.13 \times 0.09 \times 0.06$ mm was selected for

indexing and intensity data collection on a Nicolet R3/V diffractometer with a Mo X-ray source equipped with a graphite monochromator ($\lambda = 0.71073 \text{ \AA}$). The orientation matrix and unit cell parameters were determined at room temperature by least-squares fit of 15 peak maxima with $15^\circ < 2\theta < 30^\circ$. The intensity data were collected up to $2\theta = 62^\circ$ with a 2θ - θ scan. A periodic check of three standard reflections verified the stability of the sample. A total of 1802 unique reflections with $I > 3.0\sigma(I)$ were corrected for absorption, Lorentz, and polarization effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90° . Crystal data: monoclinic, space group $P2_1/c$, $a = 8.097(2)$, $b = 8.787(3)$, $c = 13.098(4) \text{ \AA}$, $\beta = 105.54(2)^\circ$, $V = 897.8(5) \text{ \AA}^3$, $Z = 4$, $D(\text{calc}) = 3.225 \text{ g/cm}^3$, $F(000) = 848$, $\mu(\text{MoK}\alpha) = 31.49 \text{ cm}^{-1}$.

TABLE I
FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\text{\AA}^2 \times 10^3$) FOR $\text{Cr}_2\text{P}_4\text{O}_{13}$

Atom	x	y	z	$U(\text{eq})^a$
Cr(1)	9579(1)	-26(1)	2788(1)	4.2(2)
Cr(2)	5623(1)	33(1)	2613(1)	4.6(2)
P(1)	5016(1)	2523(1)	-671(1)	5.4(3)
P(2)	1330(1)	2428(1)	-690(1)	5.4(3)
P(3)	7140(1)	2767(1)	1580(1)	4.6(2)
P(4)	2146(1)	1988(1)	1610(1)	4.3(2)
O(1)	1185(3)	1723(3)	397(2)	7.6(8)
O(2)	3261(4)	3050(3)	-440(2)	9.2(8)
O(3)	6178(3)	2077(3)	451(2)	9.1(8)
O(4)	7485(3)	1294(3)	2255(2)	5.9(7)
O(5)	7771(3)	-1242(3)	3245(2)	6.0(8)
O(6)	5827(4)	1173(3)	3929(2)	11.1(8)
O(7)	5325(4)	-1106(3)	1302(2)	10.4(8)
O(8)	11235(3)	-1508(3)	3517(2)	8.0(8)
O(9)	8962(4)	-1133(3)	1441(2)	9.0(8)
O(10)	3929(3)	1935(3)	1798(2)	9.1(8)
O(11)	10169(3)	1231(3)	4067(2)	7.8(8)
O(12)	3997(4)	-1184(3)	3045(2)	12.1(9)
O(13)	11131(3)	1217(3)	2249(2)	8.4(8)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE II
ANISOTROPIC THERMAL PARAMETERS ($\text{\AA}^2 \times 10^3$) FOR $\text{Cr}_2\text{P}_4\text{O}_{13}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	3.4(3)	4.7(2)	4.8(2)	0.2(2)	1.4(2)	-0.1(2)
Cr(2)	3.5(3)	4.4(2)	5.9(2)	0.3(2)	1.5(2)	0.2(2)
P(1)	4.7(5)	7.0(4)	4.5(3)	-0.2(3)	0.9(3)	-0.5(4)
P(2)	5.2(5)	6.5(4)	4.0(4)	-0.2(3)	0.6(3)	-0.1(4)
P(3)	4.3(5)	4.4(4)	5.1(3)	0.5(3)	1.3(3)	0.1(3)
P(4)	4.1(5)	4.6(4)	4.1(3)	-0.2(3)	1.0(3)	-0.1(3)
O(1)	10(1)	6(1)	6(1)	1.3(9)	1(1)	-2(1)
O(2)	6(1)	10(1)	13(1)	-3(1)	4(1)	-1(1)
O(3)	11(1)	9(1)	6(1)	0.4(9)	-1(1)	-1(1)
O(4)	4(1)	6(1)	8(1)	2.3(9)	0.9(9)	0(1)
O(5)	6(1)	4(1)	9(1)	0.9(9)	3(1)	-1(1)
O(6)	12(2)	12(1)	10(1)	-3(1)	5(1)	4(1)
O(7)	12(2)	9(1)	10(1)	-5(1)	3(1)	-1(1)
O(8)	6(1)	7(1)	11(1)	2(1)	3(1)	2(1)
O(9)	11(2)	10(1)	6(1)	-3.1(9)	3(1)	-2(1)
O(10)	5(1)	9(1)	12(1)	3(1)	1(1)	4(1)
O(11)	8(1)	8(1)	7(1)	-2.4(9)	2(1)	-3(1)
O(12)	10(2)	8(1)	21(1)	2(1)	9(1)	-2(1)
O(13)	10(2)	7(1)	10(1)	0(1)	6(1)	-1(1)

Note. The anisotropic displacement exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12})$.

The structure was solved by direct methods using SHELXTL PLUS programs and refined by full-matrix least-squares based on F values. The refinement of 173 parameters with the weighting scheme $1/w = \sigma^2(F_0) + 0.0002(F_0^2)$ converged at $R = 0.0297$, $R_w = 0.0287$, goodness of fit = 1.24. In the final difference Fourier map the deepest hole was -0.60 e/\AA^3 , and the highest peak 0.56 e/\AA^3 . The final atomic coordinates and thermal parameters are given in Tables I and II. Selected bond distances and angles are listed in Table III. Tables of observed and calculated structure factor amplitudes are available on request from the authors.

Description of the Structure and Discussion

The crystal structure of $\text{Cr}_2\text{P}_4\text{O}_{13}$, viewed along the a -axis, is shown in Fig. 1 and has two basic types of tunnels. Each of the hexagonal tunnels results from the stacking of rings formed by the edges of two CrO_6 octa-

TABLE III
SELECTED BOND DISTANCES (Å) AND ANGLES (°)
FOR $\text{Cr}_2\text{P}_4\text{O}_{13}$

Distances			
Cr(1)–Cr(2)	3.150(1)	Cr(1)–O(4)	2.019(3)
Cr(1)–O(5)	2.028(3)	Cr(1)–O(8)	1.928(3)
Cr(1)–O(9)	1.958(3)	Cr(1)–O(11)	1.956(3)
Cr(1)–O(13)	1.936(3)	Cr(2)–O(4)	2.025(3)
Cr(2)–O(5)	2.048(3)	Cr(2)–O(6)	1.962(3)
Cr(2)–O(7)	1.946(3)	Cr(2)–O(10)	1.915(3)
Cr(2)–O(12)	1.896(3)	P(1)–O(2)	1.598(3)
P(1)–O(3)	1.567(2)	P(1)–O(6)	1.485(3)
P(1)–O(7)	1.478(3)	P(2)–O(1)	1.585(3)
P(2)–O(2)	1.606(3)	P(2)–O(9)	1.481(3)
P(2)–O(11)	1.488(3)	P(3)–O(3)	1.596(2)
P(3)–O(4)	1.550(3)	P(3)–O(8)	1.497(3)
P(3)–O(12)	1.477(3)	P(4)–O(1)	1.588(2)
P(4)–O(10)	1.493(3)	P(4)–O(5)	1.565(3)
P(4)–O(13)	1.484(3)		
Angles			
O(4)–Cr(1)–O(5)	78.4(1)	O(5)–Cr(1)–O(8)	87.7(1)
O(4)–Cr(1)–O(13)	96.7(1)	O(8)–Cr(1)–O(13)	97.4(1)
O(4)–Cr(2)–O(5)	77.8(1)	O(5)–Cr(2)–O(12)	98.8(1)
O(4)–Cr(2)–O(10)	89.7(1)	O(10)–Cr(2)–O(12)	93.9(1)
Cr(1)–O(4)–Cr(2)	102.3(1)	Cr(1)–O(5)–Cr(2)	101.2(1)
P(1)–O(2)–P(2)	136.8(2)	P(2)–O(1)–P(4)	135.0(2)
P(1)–O(3)–P(3)	142.7(2)		

hedra and four PO_4 tetrahedra. The tetragonal tunnels are each formed by the edges of two CrO_6 octahedra and two PO_4 tetrahedra. The framework consists of tetrapolyphosphate groups and pairs of edge-sharing CrO_6 octahedra forming Cr_2O_{10} units. The Cr_2O_{10} units, connected by PO_4 tetrahedra, form strings along the a -axis which are linked to each other by the same PO_4 tetrahedra, resulting in the formation of sheets in the ab -plane. Adjacent sheets are linked through Cr–O–P–O–P–O–Cr bonds to form a three-dimensional framework. Each Cr_2O_{10} unit shares its 10 corners with seven different P_4O_{13} groups (Fig. 2). Four P_4O_{13} groups are each coordinated to a Cr_2O_{10} unit as a monodentate ligand, and the other three P_4O_{13} groups each as a bidentate ligand to the same Cr_2O_{10} unit. Whereas $\text{Cr}(1)\text{O}_6$ octahedron is bonded to six different P_4O_{13} groups, $\text{Cr}(2)\text{O}_6$ octahedron is bonded to only four P_4O_{13} groups, of which two are each coordinated to $\text{Cr}(2)\text{O}_6$ as a bidentate ligand, one forms a bridge

between $\text{Cr}(1)$ and $\text{Cr}(2)$, and the other is a monodentate ligand. Therefore, the strain on $\text{Cr}(1)\text{O}_6$ is expected to be smaller in comparison with $\text{Cr}(2)\text{O}_6$.

As indicated by the O–O distances (2.558–2.923 Å for $\text{Cr}(1)$; 2.558–2.993 Å for

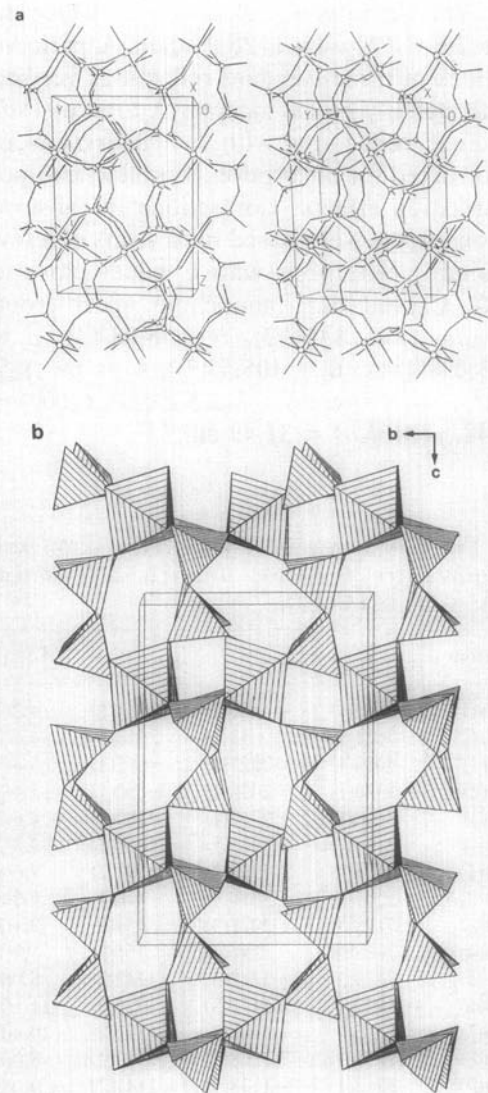


FIG. 1. (a) A stereoscopic view of the $\text{Cr}_2\text{P}_4\text{O}_{13}$ structure along the a -axis. The Cr and P atoms are represented by larger and smaller open circles, respectively. For clarity, the radii for oxygen atoms are set equal to zero. (b) STRUPLO84 drawing of the $\text{Cr}_2\text{P}_4\text{O}_{13}$ structure along the a -axis.

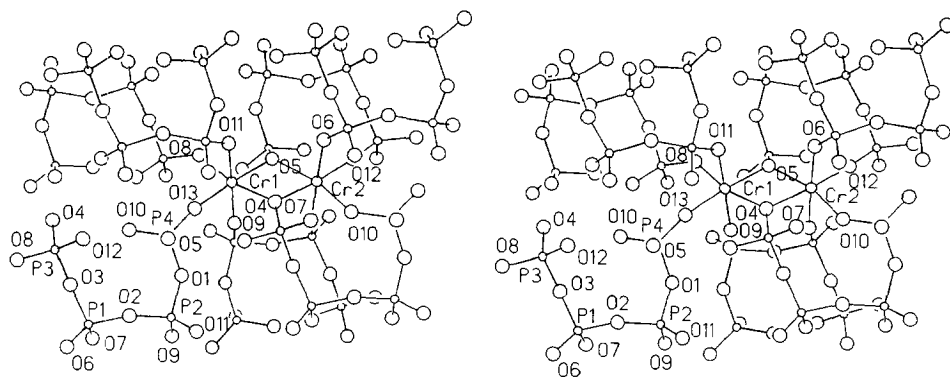


FIG. 2. A stereoscopic view of the coordination of P_4O_{13} ligands around a Cr_2O_{10} unit in $Cr_2P_4O_{13}$. The Cr, P, and O atoms are represented by medium, small, and large open circles, respectively.

Cr(2)), both CrO_6 octahedra are markedly distorted primarily due to the connection through their common edges, although the $3d^3$ electronic configuration of the Cr^{3+} ion favors regular octahedral coordination. Both CrO_6 exhibit two longer Cr–O distances and four shorter ones. The longer distances correspond to those from Cr to the common oxygen atoms. The Cr^{3+} ions are 3.15 Å apart, being actually displaced in their CrO_6 octahedra away from each other and indicating the absence of Cr–Cr bonding. For the same reason, the O(4)–Cr(1)–O(5) and O(4)–Cr(2)–O(5) bond angles are considerably smaller than the corresponding angles *trans* to them. The octahedral distortion can be quantitatively estimated by using the equation $\Delta = (\frac{1}{6})\sum((R_i - \bar{R})/\bar{R})^2$, where R_i is an individual bond length and \bar{R} is the average bond length (11). The calculation results show that the distortion for Cr(1) O_6 ($\Delta \times 10^4 = 3.87$) is smaller than that for Cr(2) O_6 ($\Delta \times 10^4 = 7.82$). The greater distortion for Cr(2) O_6 can be correlated with more bidentate ligands bonded to Cr(2) (*vide supra*).

One of the major interests of the structure of $Cr_2P_4O_{13}$ rests on the presence of a tetrapolyphosphate anion $P_4O_{13}^{6-}$. The anions are rare and up to now only six crystal structures containing $P_4O_{13}^{6-}$ anions were well determined. Drawings of the tetra-

meric anions are collected in Fig. 3. $(NH_4)_2SiP_4O_{13}$ was reported in 1976 and its two-dimensional framework is built up from linear P_4O_{13} groups connected by Si atoms in an octahedral coordination (12).

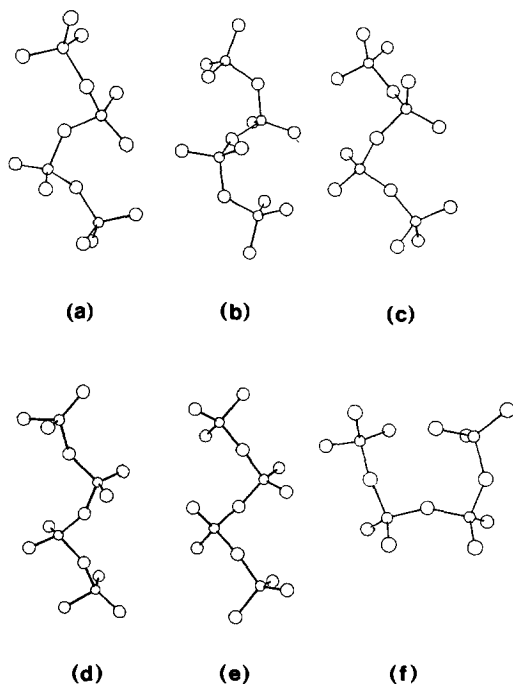


FIG. 3. The tetrapolyphosphate anion $P_4O_{13}^{6-}$ in (a) $(NH_4)_2SiP_4O_{13}$, (b) $Pb_3P_4O_{13}$, (c) $Bi_2P_4O_{13}$, (d) $(NbO)_2P_4O_{13}$, (e) $CaNb_2O(P_4O_{13})(P_2O_7)$, and (f) $Cr_2P_4O_{13}$.

An isotopic germanium compound was also synthesized (13). The other four tetrapolyphosphates were reported in recent years. In $\text{Pb}_3\text{P}_4\text{O}_{13}$ a three-dimensional network is built up by linear P_4O_{13} groups and Pb atoms with a seven- or eightfold oxygen coordination (14). The crystal structure of $\text{Bi}_2\text{P}_4\text{O}_{13}$ was determined and the anion is really a P_4O_{13} group as proposed in the literature (15). The interesting feature of $\text{CaNb}_2\text{O}(\text{P}_4\text{O}_{13})(\text{P}_2\text{O}_7)$ rests on the coexistence of a tetrameric linear phosphate anion and a dimeric one (16). In $(\text{NbO})_2\text{P}_4\text{O}_{13}$ an analogous tetrameric phosphate anion was also observed (17).

The geometry of the P_4O_{13} group in $\text{Cr}_2\text{P}_4\text{O}_{13}$ is rather different from those in the above-mentioned tetrapolyphosphates. It forms a "U" shape with P-O $_{\mu}$ bond distances 1.567–1.606 Å, P-O $_t$ 1.477–1.497, 1.550, 1.565 Å, P-O $_{\mu}$ -P bond angles 135.0–142.7°, and O $_t$ -P-O $_t$ 103.7–119.1°, where O $_{\mu}$ and O $_t$ represent bridging and terminal oxygen atoms, respectively. The P(3)-O(4) (1.550 Å) and P(4)-O(5) (1.565 Å) distances are considerably longer than the other P-O $_t$ distances. Because O(4) and O(5) are each simultaneously bonded to two Cr atoms, the P-O(4) and P-O(5) bonds must be weaker in order to make the bond strength sums at the oxygen atoms equal to their valence. The average P-O bond lengths are quite comparable: P(1)O $_4$ (1.532 Å), P(2)O $_4$ (1.540 Å), P(3)O $_4$ (1.530 Å), P(4)O $_4$ (1.532 Å). The tetrahedral distortion can be estimated by using the equation $\Delta = \frac{1}{4}\sum((R_i - \bar{R})/\bar{R})^2$, and the calculation results show that the distortions for P(1)O $_4$ ($\Delta \times 10^3 = 1.14$) and P(2)O $_4$ ($\Delta \times 10^3 = 1.32$) are greater than those for P(3)O $_4$ ($\Delta \times 10^3 = 0.92$) and P(4)O $_4$ ($\Delta \times 10^3 = 0.86$). The greater distortions for the central two PO $_4$

tetrahedra can also be explained by Pauling's electrostatic valence rule.

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