

Crystal Structure of $\text{Na}_3\text{PCr}_3\text{O}_{13} \cdot 3\text{H}_2\text{O}$: A New Type of Chromophosphoric Anion

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We describe the chemical preparation and crystal structure of a new sodium phosphochromate: $\text{Na}_3\text{PCr}_3\text{O}_{13} \cdot 3\text{H}_2\text{O}$. This salt is orthorhombic with $a = 11.72(3) \text{ \AA}$, $b = 14.89(3) \text{ \AA}$, $c = 16.59(3) \text{ \AA}$, and $Z = 8$, space group $Pbc2_1$. The final R value is 0.063 for 2133 independent reflections. The main feature of this atomic arrangement is the existence of a new type of chromophosphoric anion: $\text{PCr}_3\text{O}_{13}$. Infinite chains of NaO_6 run along the a direction. A survey of some phosphochromates previously described by the authors is given.

Introduction

Several phosphochromic anions have already been described by the authors. A short survey of their main geometrical features will be given at the end of this paper. Most of them, up to now, had a linear conformation, rather similar to that of di- or tripolyphosphate anions. In this paper, we describe the first example of a ramified chromophosphoric group, $\text{PCr}_3\text{O}_{13}$, quite comparable to the hypothetical isopolyphosphate anions imagined by Van Wazer (1).

Chemical Preparation

The first preparation of this salt was accidental, and the right chemical formula was established from the crystal structure determination.

We describe two reproducible ways to prepare this compound:

(a) A solution of a mixture of Na_2HPO_4

and CrO_3 in a 1/3 molar ratio is concentrated by boiling for about 1 hr. The concentration of this solution at the end of this treatment is about 60 g of CrO_3 per 100 cm^3 . After some days of rest at room temperature a seeding of this solution with some small crystals of $\text{Na}_3\text{Cr}_3\text{PO}_{13} \cdot 3\text{H}_2\text{O}$ induces an almost immediate precipitation of the salt, with a rather good yield.

(b) Another possibility is to use a 0.4 M solution of H_3PO_4 and CrO_3 in the molar ratio 1/3 to which Na_2CO_3 is slowly added in stoichiometric proportion. In this solution, left at room temperature, the first crystals appear after 1 or 2 weeks. Crystals of $\text{Na}_3\text{Cr}_3\text{PO}_{13} \cdot 3\text{H}_2\text{O}$ are orange-yellow orthorhombic prisms, very stable in air at room temperature. Large crystals (up to 1.5 mm) can be obtained by the second method.

Crystal Data

This salt is orthorhombic with a unit cell

TABLE I
POWER DIFFRACTION DATA FOR $\text{Na}_3\text{PCr}_3\text{O}_{13} \cdot 3\text{H}_2\text{O}^a$

<i>h k l</i>	d_{cal} (Å)	d_{obs} (Å)	I_{obs}	<i>h k l</i>	d_{cal} (Å)	d_{obs} (Å)	I_{obs}
1 0 0	11.72	—	—	3 1 2	3.440	—	—
1 1 0	9.21	—	—	0 4 2	3.397	—	—
0 0 2	8.30	8.30	22	3 2 1	3.387	} 3.384	} 33
1 1 1	8.05	—	—	2 0 4	3.386		
0 2 0	7.45	—	—	2 1 4	3.302	3.304	5
0 2 1	6.79	} 6.78	} 100	1 4 2	3.263	—	—
1 0 2	6.77			3 2 2	3.194	3.194	4
1 2 0	6.29	6.28	<1	2 4 0	3.143	—	—
1 1 2	6.17	6.17	1	2 3 3	3.126	} 3.123	} 1
1 2 1	5.88	5.88	<1	1 1 5	3.122		
2 0 0	5.86	—	—	3 1 3	3.121	} 3.090	} 7
0 2 2	5.54	—	—	0 4 3	3.089		
2 1 0	5.45	5.46	1	2 4 1	3.088	—	—
2 1 1	5.18	5.18	2	2 2 4	3.083	—	—
1 2 2	5.01	—	—	1 3 4	3.072	—	—
2 0 2	4.79	4.81	15	3 3 0	3.071	—	—
1 1 3	4.74	—	—	0 2 5	3.031	3.031	9
2 2 0	4.61	—	—	3 3 1	3.019	—	—
1 3 0	4.57	} 4.56	} 1	1 4 3	2.987	2.988	1
2 1 2	4.56			2 4 2	2.939	—	—
0 2 3	4.44	} 4.44	} 2	1 2 5	2.935	} 2.933	} 5
2 2 1	4.44			3 2 3	2.934		
1 3 1	4.41	—	—	4 0 0	2.931	—	—
1 2 3	4.15	} 4.15	} 60	1 5 0	2.887	—	—
0 0 4	4.15			3 3 2	2.880	—	—
2 2 2	4.03	4.03	2	4 1 0	2.876	2.875	1
1 3 2	4.00	—	—	3 0 4	2.845	—	—
1 4 0	3.911	} 3.910	} 19	1 5 1	2.844	—	—
3 0 0	3.908			2 1 5	2.835	} 2.837	} 5
2 1 3	3.884	—	—	4 1 1	2.833		
2 3 0	3.788	} 3.787	} 1	2 3 4	2.797	} 2.792	} 1
1 1 4	3.783			3 1 4	2.794		
3 1 0	3.780	—	—	0 4 4	2.771	—	—
0 4 0	3.723	—	—	0 0 6	2.766	} 2.764	} 6
2 3 1	3.693	—	—	4 0 2	2.763		
3 1 1	3.685	—	—	2 4 3	2.733	—	—
0 4 1	3.633	—	—	4 2 0	2.727	—	—
0 2 4	3.624	3.624	2	1 5 2	2.727	—	—
1 4 0	3.549	—	—	4 1 2	2.717	2.713	1
2 2 3	3.539	—	—	1 4 4	2.697	—	—
3 0 2	3.535	} 3.529	} 1	3 4 0	2.696	—	—
1 3 3	3.524			2 2 5	2.693	} 2.689	} 2
1 4 1	3.470	—	—	1 0 6	2.692		
1 2 4	3.462	} 3.458	} 16	4 2 1	2.691	} 2.689	} 2
3 2 0	3.460			1 3 5	2.686		
2 3 2	3.446	—	—	3 3 3	2.685	—	—

^a Measurements were made with a Philips Norelco diffractometer using $\text{CuK}\alpha$ radiation with a low scan speed ($1/8^\circ$ (Θ)/min). Given intensities are peak heights above background.

$$a = 11.72(3) \text{ \AA}, b = 14.89(3) \text{ \AA}, \\ c = 16.59(3) \text{ \AA},$$

and $Z = 8$.

The two possible space groups are *Pbcm* and *Pbc2₁*. The crystal structure determination shows that the right space group is the noncentrosymmetrical *Pbc2₁*.

Table I gives the indexed powder diffraction data of this compound.

Crystal Structure Determination

A small prism fragment approximately cubic (0.12 × 0.12 × 0.12 mm) was used to solve the crystal structure. In a Θ range of 4 to 25°, 2500 independent reflections were collected with an automatic four-circle, Philips PW1100, diffractometer using AgK α radiation (0.5608 Å). All reflections were integrated with an angular scanwidth of 1.20° (Θ) at a speed of 0.02°/sec. Background was measured during 10 sec at each extremity of this domain. An ω scan was used for the collection.

The lack of knowledge about the right chemical formula and the absence of heavy atoms were the main difficulties met during crystal structure determination. So both direct methods (2) and careful examination of the Patterson function were used during this work. After location of chromium and phosphorus atoms successive Fourier syntheses reveal the totality of this atomic arrangement. Introduction of anisotropic thermal parameters for chromium, phosphorus, and sodium atoms leads to a final *R* value of 0.063 for 2133 reflections such that

$$F_o > 20 \text{ (in a scale from 0 to 380)}$$

and

$$\frac{\|F_o\| - \|F_c\|}{\sigma} < 6.$$

Table II gives atomic position parameters for this atomic arrangement while Table III

TABLE II

ATOMIC POSITION PARAMETERS ($\times 10^4$) AND EQUIVALENT THERMAL FACTORS (B_{eq}) FOR P, Cr, AND Na OR ISOTROPIC THERMAL FACTORS FOR THE OXYGEN ATOMS^a

Atom	x (σ)	y (σ)	z (σ)	B_{eq}
P(1)	-17(3)	4465(3)	2085(0)	1.63
Cr(11)	8284(2)	8211(1)	3028(2)	1.53
Cr(12)	705(2)	3248(1)	548(2)	1.61
Cr(13)	8164(2)	3051(2)	2664(2)	1.72
P(2)	4807(3)	1906(3)	4298(2)	1.37
Cr(21)	3073(2)	540(1)	3507(2)	1.70
Cr(22)	6705(2)	665(2)	3520(2)	1.85
Cr(23)	5514(2)	4211(1)	847(2)	1.40
Na(1)	4963(5)	3773(5)	3141(4)	2.07
Na(2)	1777(6)	1170(4)	1693(4)	2.85
Na(3)	3152(5)	3685(4)	4912(4)	2.88
Na(4)	8922(5)	1203(4)	1022(4)	2.55
Na(5)	-184(6)	1308(6)	3295(4)	3.00
Na(6)	6095(5)	1238(4)	192(4)	2.74
O(121)	2000(9)	3442(7)	368(7)	3.47
O(131)	6812(10)	3194(8)	2713(6)	2.68
O(111)	1742(10)	3248(7)	3994(7)	3.52
O(1)	51(8)	460(7)	2047(6)	1.50
O(112)	2961(10)	3366(8)	2693(7)	3.33
O(122)	-7(10)	1568(13)	4761(8)	3.99
O(L11)	784(11)	4133(8)	2794(7)	3.96
O(123)	507(9)	2247(7)	879(7)	2.94
O(113)	1180(8)	2291(6)	2685(6)	1.94
O(132)	8479(9)	2249(7)	2063(7)	3.03
O(L13)	8815(10)	4087(8)	2294(7)	3.41
O(L12)	349(10)	4023(12)	1299(10)	6.35
O(133)	8724(10)	2798(7)	3482(8)	4.06
O(221)	8029(12)	816(9)	3713(8)	4.44
O(2)	4770(8)	2892(8)	4390(6)	1.91
O(211)	3257(9)	423(6)	2565(7)	2.73
O(212)	1761(10)	606(7)	3712(6)	2.74
O(L22)	5969(9)	1619(8)	3923(6)	2.81
O(222)	3744(9)	4774(7)	3925(6)	2.68
O(223)	6476(12)	621(9)	2575(9)	5.04
O(231)	4505(8)	247(6)	636(6)	2.15
O(232)	6825(8)	3826(6)	822(6)	2.95
O(L23)	4721(9)	3555(8)	118(7)	2.75
O(233)	4969(9)	4015(11)	1692(7)	2.98
O(L21)	3795(8)	1594(7)	3757(6)	2.17
O(213)	6350(10)	4721(7)	3975(7)	2.88
W(1)	3294(9)	2027(6)	1179(6)	2.73
W(2)	5647(10)	1921(7)	1510(6)	2.83
W(3)	7741(8)	2181(6)	155(6)	2.02
W(4)	-436(9)	4371(7)	4751(6)	2.97
W(5)	1761(9)	355(6)	467(6)	2.63
W(6)	7288(8)	216(7)	1004(6)	2.64

^a Standard deviations are given in parentheses.

TABLE III
ANISOTROPIC THERMAL PARAMETERS ($\times 10^5$) FOR PHOSPHORUS, CHROMIUM, AND SODIUM ATOMS^a

	β_{11} (σ)	β_{22} (σ)	β_{33} (σ)	β_{12} (σ)	β_{13} (σ)	β_{23} (σ)
P(1)	313(26)	161(20)	166(13)	-22(18)	-18(20)	35(15)
Cr(11)	267(17)	149(10)	172(7)	19(12)	36(11)	10(9)
Cr(12)	331(17)	161(11)	159(8)	13(11)	-26(11)	-8(8)
Cr(13)	263(17)	163(11)	226(8)	33(12)	53(12)	10(9)
P(2)	285(28)	95(18)	153(13)	-31(18)	-35(16)	5(14)
Cr(21)	304(18)	162(10)	195(9)	-26(12)	-36(12)	-13(9)
Cr(22)	400(19)	181(11)	179(9)	26(13)	56(13)	-17(9)
Cr(23)	292(16)	142(10)	136(8)	-3(11)	10(11)	-14(8)
Na(1)	451(48)	239(33)	134(21)	25(29)	-55(29)	7(22)
Na(2)	426(49)	321(30)	311(25)	-112(36)	7(33)	-47(24)
Na(3)	332(47)	416(33)	278(24)	-7(35)	17(32)	-79(23)
Na(4)	468(50)	295(30)	217(24)	-22(33)	-60(29)	2(22)
Na(5)	411(53)	369(42)	306(30)	-42(33)	115(29)	31(26)
Na(6)	361(49)	310(31)	277(26)	35(33)	-94(30)	2(24)

^a Standard deviations are given in parentheses. $T = \exp - [h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2h k\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.

reports anisotropic thermal parameters for metallic atoms.

All atoms are in the general position of $Pbc2_1$ space group

$$\begin{array}{ccc} x & y & z \\ \bar{x} & \bar{y} & \frac{1}{2} + z \\ x & \frac{1}{2} - y & \frac{1}{2} + z \\ \bar{x} & \frac{1}{2} + y & z \end{array}$$

Description of the Structure

The main feature of this arrangement is the existence of two independent $PCr_3O_{13}^{3-}$ anions. Figure 1 gives the projection of

these two anions along the b axis. Table IV reports interatomic distances and bond angles for these two independent PCr_3O_{13} groups. It is worth noticing that Cr-P-Cr angles depart slightly from 90° (see Table IV). In spite of the close similarity of chemical formula and of bondings the geometry of the previously described (3) $AsCr_3O_{13}$ is quite different, one Cr-As-Cr angle being 147.6° , and other two being close to 90° .

Figure 2 gives a projection of the structure along the b axis; PCr_3O_{13} groups are schematized by the P-Cr bonds only.

All the sodium atoms are in an octahedral coordination. The linkage of these NaO_6

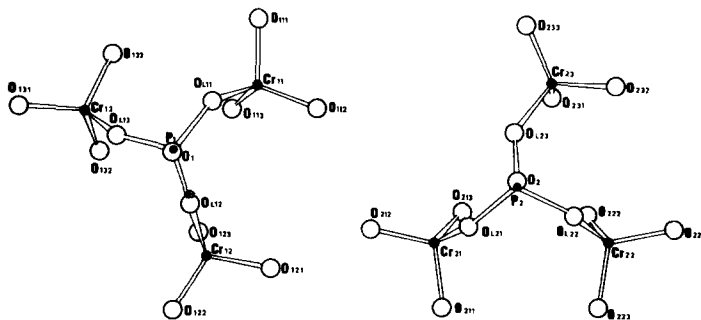


FIG. 1. Projection of the two independent PCr_3O_{13} anions along the b axis.

TABLE IV
BOND LENGTHS (Å) AND BOND ANGLES (°) IN THE TWO INDEPENDENT $\text{PCr}_3\text{O}_{13}$ ANIONS^a

P(1)	O(L11)	O(L13)	O(L12)	O(1)
O(L11)	<u>1.58(1)</u>	2.46(2)	2.54(2)	2.53(2)
O(L13)	104.5(7)	<u>1.52(1)</u>	2.44(2)	2.47(2)
O(L12)	109.5(8)	106.8(8)	<u>1.52(2)</u>	2.52(2)
O(1)	111.0(6)	110.8(6)	113.8(8)	<u>1.49(1)</u>
Cr(11)	O(111)	O(112)	O(113)	O(L11)
O(111)	<u>1.60(1)</u>	2.60(2)	2.68(2)	2.64(2)
O(112)	109.2(6)	<u>1.58(1)</u>	2.63(2)	2.80(2)
O(113)	113.0(6)	111.1(6)	<u>1.61(1)</u>	2.79(2)
O(L11)	101.7(6)	111.9(6)	109.7(5)	<u>1.80(1)</u>
Cr(12)	O(121)	O(122)	O(123)	O(L12)
O(121)	<u>1.57(1)</u>	2.56(2)	2.64(2)	2.62(2)
O(122)	108.8(7)	<u>1.57(1)</u>	2.63(2)	2.73(2)
O(123)	112.0(6)	111.7(7)	<u>1.61(1)</u>	2.74(2)
O(L12)	104.1(7)	110.5(8)	109.6(7)	<u>1.75(2)</u>
Cr(13)	O(131)	O(132)	O(133)	O(L13)
O(131)	<u>1.60(1)</u>	2.62(2)	2.65(2)	2.79(2)
O(132)	111.2(6)	<u>1.57(1)</u>	2.50(2)	2.76(2)
O(133)	114.0(6)	106.1(6)	<u>1.55(1)</u>	2.76(2)
O(L13)	108.6(6)	108.0(6)	108.8(6)	<u>1.52(1)</u>
Cr(11)–P(1)	3.175(5)	Cr(11)–P(1)–Cr(12)	83(1)	
Cr(12)–P(1)	3.244(4)	Cr(11)–P(1)–Cr(13)	84(1)	
Cr(13)–P(1)	3.149(5)	Cr(12)–P(1)–Cr(13)	92(1)	
P(1)–O(L11)–Cr(11)	139.4(8)			
P(1)–O(L12)–Cr(12)	164(1)			
P(1)–O(L13)–Cr(13)	139.9(8)			
P(2)	O(2)	O(L21)	O(L22)	O(L23)
O(2)	<u>1.48(1)</u>	2.48(1)	2.49(2)	2.47(2)
O(L21)	109.5(6)	<u>1.56(1)</u>	2.56(1)	2.52(2)
O(L22)	109.9(6)	110.7(6)	<u>1.56(1)</u>	2.48(2)
O(L23)	110.6(6)	109.2(6)	106.9(6)	<u>1.53(1)</u>
Cr(21)	O(211)	O(212)	O(213)	O(L21)
O(211)	<u>1.59(1)</u>	2.60(2)	2.61(2)	2.71(1)
O(212)	110.6(6)	<u>1.58(1)</u>	2.62(2)	2.81(2)
L(213)	109.7(6)	110.8(6)	<u>1.60(1)</u>	2.82(1)
O(L21)	104.7(5)	110.4(5)	110.4(6)	<u>1.83(1)</u>
Cr(22)	O(221)	O(222)	O(223)	O(L22)
O(221)	<u>1.60(1)</u>	2.62(2)	2.64(2)	2.72(2)
O(222)	110.8(6)	<u>1.58(1)</u>	2.58(2)	2.77(2)
O(223)	111.5(7)	109.2(6)	<u>1.59(1)</u>	2.75(2)
O(L22)	106.3(6)	110.4(5)	108.6(6)	<u>1.79(1)</u>
Cr(23)	O(231)	O(232)	O(233)	O(L23)
O(231)	<u>1.58(1)</u>	2.65(1)	2.61(2)	2.82(1)
O(232)	110.4(5)	<u>1.64(1)</u>	2.63(2)	2.76(1)
O(233)	111.9(6)	109.8(6)	<u>1.57(1)</u>	2.72(2)
O(L23)	111.8(5)	106.0(6)	106.7(6)	<u>1.81(1)</u>
Cr(21)–P(2)	3.163(5)	Cr(21)–P(2)–Cr(22)	85(2)	
Cr(22)–P(2)	3.169(5)	Cr(21)–P(2)–Cr(23)	100(2)	
Cr(23)–P(2)	3.174(5)	Cr(22)–P(2)–Cr(23)	81(2)	
P(2)–O(L21)–Cr(21)	137.6(6)			
P(2)–O(L22)–Cr(22)	141.9(7)			
P(2)–O(L23)–Cr(23)	143.4(8)			

^a Standard deviations are given in parentheses.

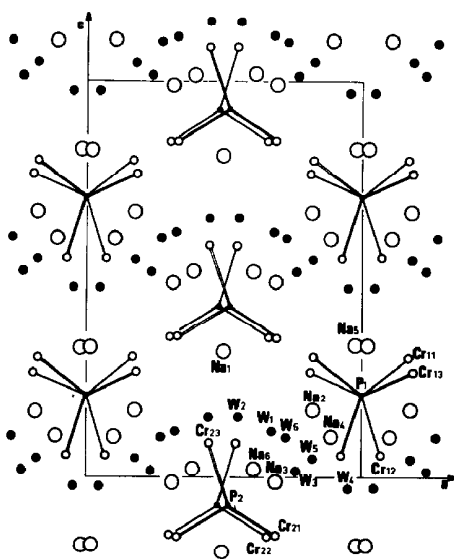


FIG. 2. Projection along the *b* axis of the atomic arrangement of $\text{Na}_3\text{PCr}_3\text{O}_{13} \cdot 3\text{H}_2\text{O}$. $\text{PCr}_3\text{O}_{13}$ anions are schematized by P-Cr bondings only.

octahedra is interesting to examine. All sodium atoms are located in $y = 0.12, 0.38, 0.63,$ or 0.88 . In these planes they associate themselves by groups of three with a common central oxygen atom (O(1) or O(2)). These triangles are themselves connected so as to form monodimensional independent infinite chains running along the *a*

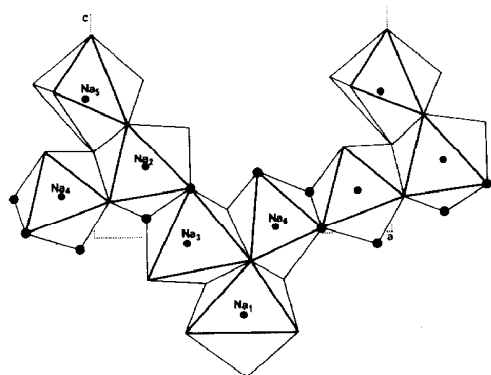


FIG. 3. Projection along the *b* axis of a chain of sodium polyhedra.

TABLE V
BOND LENGTHS (Å) IN NaO_6 OCTAHEDRA^a

Na(1)-O(131) 2.44(1)	Na(2)-O(1) 2.36(1)
-O(112) 2.54(1)	-O(123) 2.57(1)
-O(2) 2.47(1)	-O(113) 2.45(1)
-O(222) 2.44(1)	-O(211) 2.52(1)
-O(233) 2.43(1)	-W(1) 2.35(1)
-O(213) 2.56(1)	-W(5) 2.37(1)
Na(3)-O(111) 2.34(1)	Na(4)-O(1) 2.42(1)
-O(2) 2.40(1)	-O(123) 2.44(1)
-O(222) 2.41(1)	-O(132) 2.41(1)
-O(231) 2.55(1)	-W(3) 2.47(1)
-W(1) 2.36(1)	-W(4) 2.40(1)
-W(5) 2.36(1)	-W(6) 2.42(1)
Na(5)-O(1) 2.44(1)	Na(6)-O(2) 2.42(1)
-O(122) 2.47(1)	-O(231) 2.49(1)
-O(113) 2.40(1)	-O(213) 2.49(1)
-O(133) 2.58(1)	-W(2) 2.47(1)
-O(221) 2.33(2)	-W(3) 2.39(1)
-O(212) 2.60(1)	-W(6) 2.47(1)

^a Standard deviations are given in parentheses.

direction. Figure 3 gives a detailed view of such a chain in projection along the *b* direction. It is also interesting to note that water molecules, which all belong to Na polyhedra, form a chain also waving along the *b* direction with W-W bond lengths ranging from 2.82 to 3.30 Å. Table V gives bond distances in Na polyhedra, and Table VI W-W distances.

TABLE VI
INTERATOMIC DISTANCES (Å)
BETWEEN WATER
MOLECULES^a

W(1)-W(2)	2.82(2)
W(1)-W(5)	3.29(1)
W(2)-W(3)	3.35(1)
W(2)-W(6)	3.30(1)
W(3)-W(4)	3.22(1)
W(3)-W(6)	3.29(1)
W(4)-W(5)	2.87(1)
W(4)-W(6)	3.44(1)

^a Standard deviations are given in parentheses.

TABLE VII
CHEMICAL FORMULA, UNIT CELL, AND SPACE GROUP OF PHOSPHOCHROMATES AND ARSENATOCHROMATES

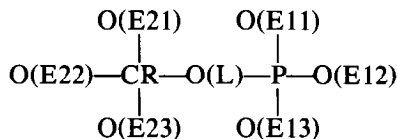
Formula	Unit cell	Space group	References
CuK ₂ H ₂ (CrPO ₇) ₂	$a = 9.559 \text{ \AA}$, $\beta = 93.73^\circ$ $b = 7.196 \text{ \AA}$ $c = 8.983 \text{ \AA}$ $z = 2$	$P2_1/c$	(5)
BaHCr ₂ PO ₁₀ · H ₂ O	$a = 9.333 \text{ \AA}$, $\alpha = 106.28^\circ$ $b = 7.779 \text{ \AA}$, $\beta = 105.37^\circ$ $c = 7.526 \text{ \AA}$, $\gamma = 94.14^\circ$ $z = 2$	$P\bar{1}$	(6)
BaHCr ₂ PO ₁₀ · 3H ₂ O	$a = 10.199 \text{ \AA}$, $\alpha = 108.80^\circ$ $b = 8.207 \text{ \AA}$, $\beta = 107.14^\circ$ $c = 7.749 \text{ \AA}$, $\gamma = 89.04^\circ$ $z = 2$	$P\bar{1}$	(6)
K ₂ HCr ₂ AsO ₁₀	$a = 7.712 \text{ \AA}$ $c = 14.644 \text{ \AA}$ $z = 3$	$P3_1$	(7)
K ₂ HCr ₂ PO ₁₀	$a = 7.572 \text{ \AA}$ $c = 14.460 \text{ \AA}$ $z = 3$	$P3_1$	(7)
BaHCr ₂ AsO ₁₀	$a = 7.418 \text{ \AA}$, $\alpha = 115.85^\circ$ $b = 7.934 \text{ \AA}$, $\beta = 99.37^\circ$ $c = 8.034 \text{ \AA}$, $\gamma = 89.11^\circ$ $z = 2$	$P\bar{1}$	(8)
(NH ₄) ₂ HCr ₃ AsO ₁₃	$a = 14.02 \text{ \AA}$, $\beta = 93.12^\circ$ $b = 9.49 \text{ \AA}$ $c = 9.57 \text{ \AA}$ $z = 4$	$P2_1/c$	(3, 4)
Na ₃ Cr ₃ PO ₁₃ · 3H ₂ O			This work

A Short Survey of the Geometrical Configurations of Phosphochromic and Arsenatochromic Anions

Arsenatochromic anions also exist and very often are quite similar to phosphochromic ions, so we shall include them in this brief survey. This kind of mixed anion can be classified in three groups.

The first group, with up to now only one known example is also the simplest and can

be schematized by



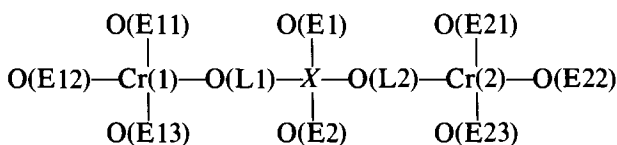
Main geometrical features of this anion are summarized in Tables VII and VIII.

The second group with many more representatives can be schematized by

TABLE VIII
INTERESTING INTERATOMIC BOND LENGTHS (Å) AND ANGLES (°) IN PHOSPHOCHROMATES AND ARSENATOCHROMATES^a

Formula	P(As)-Cr(1)	Cr(1)-O(L1)-P(As)	P(As)-O(L1)	Cr(1)-O(L1)	$\frac{\overline{\text{P(As)-O}}}{\overline{\text{Cr-O}}}$
	-Cr(2)	Cr(2)-O(L2)-P(As)	P(As)-O(L2)	Cr(2)-O(L2)	
	-Cr(3)	Cr(3)-O(L3)-P(As)	P(As)-O(L3)	Cr(3)-O(L3)	
CuK ₂ H ₂ (CrPO ₇) ₂	2.988	122.8	1.550	1.849	1.539 1.671
BaHCr ₂ PO ₁₀ · H ₂ O	3.142 3.078	138.0 131.2	1.538 1.549	1.826 1.828	1.536 1.662
BaHCr ₂ PO ₁₀ · 3H ₂ O	3.064 3.116	129.1 134.7	1.547 1.538	1.843 1.836	1.534 1.663
K ₂ HCr ₂ AsO ₁₀	3.193 3.189	127.9 129.4	1.72 1.70	1.84 1.83	1.67 1.67
K ₂ HCr ₂ PO ₁₀	Isotypic with the last one (not refined)				
BaHCr ₂ AsO ₁₀	3.229 3.145	132.7 121.4	1.692 1.72	1.83 1.89	1.68 1.68
(NH ₄) ₂ HCr ₃ AsO ₁₃	3.130 3.133 3.216	123.2 124.1 131.3	1.682 1.685 1.677	1.875 1.861 1.853	1.684 1.669
Na ₃ Cr ₃ PO ₁₃ · 3H ₂ O (two independent anions)	3.175 3.244 3.149	139.4 164.3 139.9	1.585 1.524 1.520	1.799 1.750 1.831	1.529 1.636
	3.163 3.169 3.174	137.5 141.9 143.4	1.559 1.528 1.558	1.833 1.793 1.813	1.531 1.648

^a The last column of this table gives average P-O, As-O, or Cr-O distances in the corresponding anion.

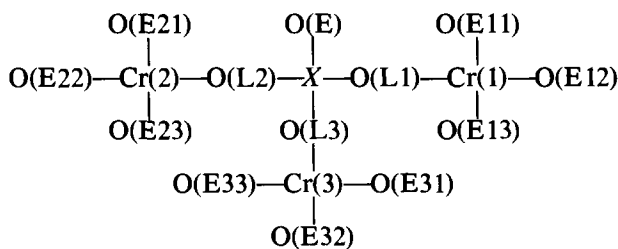


where $X = \text{P}$ or As .

Geometric details for most of them are given in Tables VII and VIII.

The third group corresponds to a ramified

anion with the global formula $X\text{Cr}_3\text{O}_{13}$, where $X = \text{P}$ or As , and can be schematized as follows:



Tables VII and VIII summarize the most interesting characteristics of the two examples known in this group.

Atomic notations used in three schematic drawings are used in tables VII and VIII.

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