

The Crystal Chemistry of Large Cation Dichromates, Pyrophosphates, and Related Compounds with Stoichiometry $X_2Y_2O_7$

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Crystals of composition $X_2Y_2O_7$ in which the ionic radius of X is greater than 0.97 Å and that of Y is smaller than 0.60 Å crystallize in one of the dozen or so structures whose interrelationships are examined in this paper. A scheme is proposed for classifying the different structures and predicting the possible existence of other structures. It also predicts that the phase transition at 270°C in $K_2Cr_2O_7$ is a displacive transition. The effect of crystal environment on the geometry of the Y_2O_7 group is examined.

Introduction

Crystals of composition $X_2Y_2O_7$ tend to belong to one of a small number of groups of related structures. Crystals for which the ionic radius (I) of the Y atom, generally the more electronegative one, is greater than 0.60 Å crystallize into such structures as pyrochlore (2) and weberite (3) in which the Y atom is octahedrally coordinated. Of the remainder, those in which the ionic radius of X is less than 0.97 Å tend to crystallize in one of the structures related to that of thortveitite (4,5), while those in which X has an ionic radius of greater than 0.97 usually crystallize in one of a series of related structures which, for want of a better name, will be called the dichromate structures, since it is in the alkali metal dichromates that their variety is best displayed. At present, eight of these structures have been identified and it is almost certain that others exist. Potassium dichromate, for example, can be inferred to exist in at least three of these forms under different conditions and the same is probably also true of rubidium dichromate. The existence of so many structures derived from the same basic unit arises from a peculiarity of the packing of this unit. A scheme showing the relationships between these structures will be proposed in this paper.

The Basic Unit

In most of the compounds that crystallize in one of the dichromate structures (see Table I) the X atom is a large alkali metal or alkaline earth such as

K, Rb, Ca, or Sr, while the Y atom is an atom in group V or VI of the periodic table such as P, V, S, or Cr in a high formal oxidation state.

The crystals can therefore be formulated as ionic with X as the cation and Y_2O_7 as the anion. The Y_2O_7 ion consists of two YO_4 tetrahedra sharing an oxygen atom with a $Y-O-Y$ angle of approximately 130°. The thortveitite structures differ from the dichromate structures in that the anion occurs in the former in the staggered configuration (Fig. 1a) and in the latter in the eclipsed configuration (Fig. 1b).

In the eclipsed configuration, the bridging oxygen atom lies almost on the line joining two of the terminal oxygen atoms and for convenience these three atoms will be referred to as the backbone of the ion. The remaining four oxygen atoms, which are nearly co-planar, will be referred to as the feet. The ideal configuration has C_{2v} symmetry, but in practice the ion is usually twisted from this ideal form about the $Y-Y$ axis by a few degrees, an angle that will be referred to as the twist angle (δ).

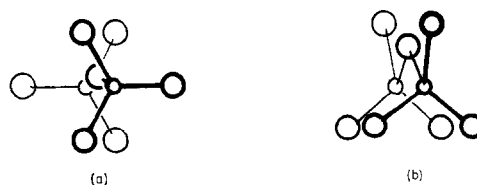


FIG. 1. The configuration of Y_2O_7 groups in (a) thortveitite structures, (in thortveitite itself the ion has D_{3d} symmetry), (b) dichromate structures.

The basic unit in the dichromate structures contains two Y_2O_7 ions related by a center of symmetry, usually in such a way that the oxygen atoms of their backbones are close packed (see, for example, Fig. 5a). The cations lie close to the plane of the feet. Structures in which the basic unit differs from this ideal form will be discussed in a later section.

The Dichromate Sheets and Their Packing

Most of the dichromate structures are built out of sheets which are generated from the basic unit by two translation vectors B and C (7). The C vector lies in the plane of the feet and makes an angle of 60° with the backbones of the Y_2O_7 ion (Fig. 2a), while the B vector, which usually is perpendicular to C and of about the same length (7 Å), is almost normal to the plane of the feet. Thus the sheets consist of units of two centrosymmetrically related $X_2Y_2O_7$ molecules lying at the corners of an almost square net (see, for example, Fig. 3b), an arrangement which allows adjacent sheets to be related to each other by rotations of 0° , 90° , 180° and 270° about an axis normal to the sheet, giving rise to four possible stacking operations. In addition, other operations are possible since the two sides of the

sheets are related to each other by a center of inversion and are thus enantiomorphic. One side of each sheet can be considered as right handed and the other as left handed. Therefore, in addition to the four possible relative orientations of adjacent sheets, it is possible for them to be in contact through sides of the same handedness or different handedness. The former will result if adjacent layers are related either by a rotation axis between the sheets or a glide plane perpendicular to them, the latter will result from a screw axis perpendicular to the sheets or a glide plane between them (8). The various possibilities are illustrated schematically in Fig. 4.

For convenience the symbol R can be used to refer to a righthanded face and \bar{A} to a left-handed face. Figures 3a and 3b show that this symbol is defined with the angled stroke of the R pointing roughly in the direction of the backbone of the Y_2O_7 group, the lower end of the stroke nearest the face. The positive A axis points out of the sheet and the B and C directions are taken as defined in the figure. Thus R signifies a right-handed axis system and \bar{A} a left-handed system.

The simplest way in which adjacent sheets can stack (I, see Fig. 4) is that in which adjacent layers are related by a simple translation. The highest possible symmetry is $P\bar{1}$ and this structure has been found in $Cd_2P_2O_7$ (9) and $K_2ON(SO_3)_2$ (10). In the

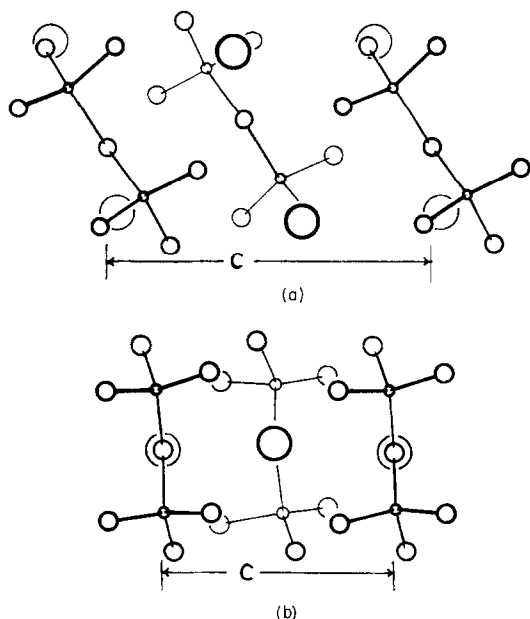


FIG. 2. The arrangement of the basic units of $X_2Y_2O_7$ in (a) the sheet structures (I-X) viewed down the sheet B axis; (b) the row structures (XI-XII). Large circles represent X ions, small circles Y atoms, and the intermediate-sized circles the O atoms.

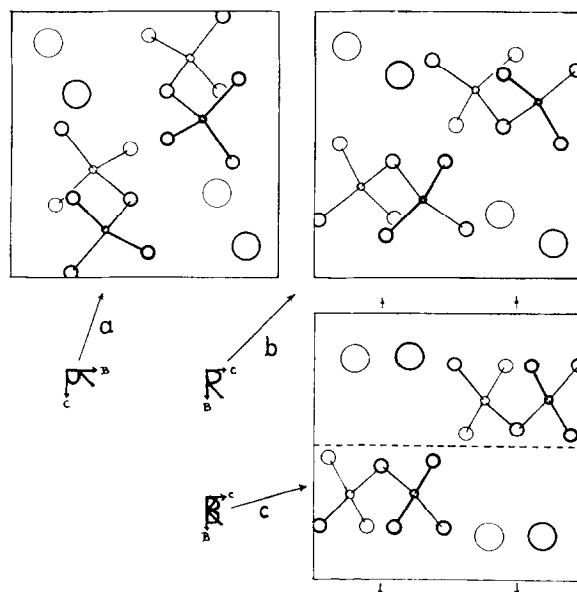


FIG. 3. The basic $X_2Y_2O_7$ unit viewed perpendicularly to the sheets, and the symbol designating the orientation of each sheet. a and b have only a center of symmetry, c has a glide plane and two-fold axis in addition. Transitions for $a \leftrightarrow b \leftrightarrow c$ involve only small changes in the positions of the atoms.

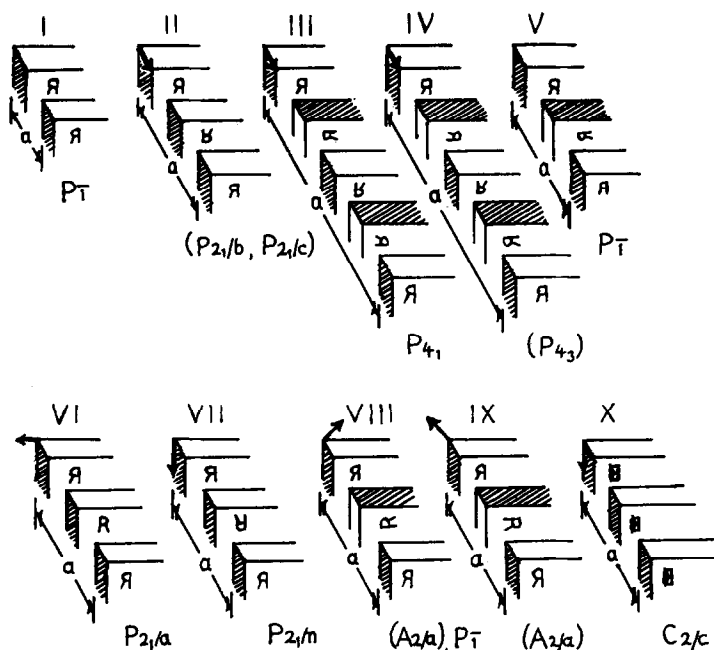


FIG. 4. Some of the possible arrangements of sheets in the dichromate structures. The crystal c axis is directed to the left, b axis to the top, and the a axis out of the paper as shown. The edge of the sheets parallel to the sheet B axis are shaded, those parallel to the sheet C axis are plain. The direction of the unique axis is indicated by an arrow. Structures with space groups given in parentheses have not been observed.

second case (II) adjacent layers are related by a two-fold screw axis along the a direction and a b or c glide perpendicular to this. The resulting crystals have the space group $P2_1/b$ (IIb) or $P2_1/c$ (IIc) (C_{2h}^2). The length of the unique axis, a , is the width of two sheets, approximately 13 Å. No example of either of these structures is at present known. A four-fold screw axis would give rise to the two enantiomorphic structures $P4_1$ (III), and $P4_3$ (IV) in which adjacent layers are related by a 90° (or 270°) rotation. $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (11) is an example of III in which the unique axis, a , covers the width of four sheets. It is interesting to note that in this structure there is no crystallographic center of symmetry found within the sheet although each sheet individually comes close to retaining the center of symmetry.

An alternative structure (V) based on the same packing of adjacent layers has an a axis only two sheets wide. This is achieved by having the first and second sheets related by a 90° rotation and the second and third sheets related by a 270° rotation so that the first and third sheets are related by a simple translation. In this arrangement, which is found in triclinic $\text{K}_2\text{Cr}_2\text{O}_7$ (12,13), there is no crystallographic symmetry that can relate the two sheets and the space group is once again $P\bar{1}$. There is, further, no crystallographic restriction making B

equal to C so that the ratio of $B:C$ in the first sheet is less than one and in the second sheet is greater than one. Consequently, the two sheets will have slightly different structures as discussed below.

A second group of structures are those in which adjacent sheets have sides of the same handedness in contact. This is achieved in the highest symmetry cases when adjacent sheets are related by a rotation or screw axis lying between them and a glide plane perpendicular to them. Such structures will belong to the monoclinic system with the unique axis lying in the plane of the sheets. The four possible orientations of the unique axis correspond to the four possible relative orientations of adjacent sheets. In structures VI and VII the unique axis lies along the C and B axes of the sheets, respectively. The former is best described by the space group $P2_1/a$, the latter by $P2_1/n$ (14). The former is the structure of chervetite, $\text{Pb}_2\text{V}_2\text{O}_7$ (15). The latter is probably the structure of the $P2_1/n$ phases of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Rb}_2\text{Cr}_2\text{O}_7$ (16). If the unique axis is chosen along the diagonals of the repeat unit in the sheets, structures VIII and IX result, with the highest possible symmetry of $A2/a$. This symmetry would, however, constrain B to be equal to C in both sheets and in practice it is found that the lower symmetry of $P1$ is preferred, at least in $\text{Rb}_2\text{Cr}_2\text{O}_7$, which has

structure VIII (17). As in the case of triclinic $K_2Cr_2O_7$, the ratio of $B:C$ for the first sheet is less than one and for the second sheet is greater than one, resulting in small differences between the two sheets. No example of structure IX is at present known.

One further structure, X, is commonly found. In this structure the sheets, in addition to a center of symmetry, have a two-fold axis along B and a glide plane along C . The two-fold axes run through the bridging oxygen atoms of the Y_2O_7 groups constraining these groups to have C_2 symmetry. In addition, they remove the enantiomorphic relationship between the two sides of the sheet so that both sides are identical. Adjacent layers are related by a simple C centering translation resulting in the space group $C2/c$ with an a axis corresponding to the width of two sheets. This high symmetry structure is the most common of the known structures, having been found in $(NH_4)_2Cr_2O_7$ (18), $K_2S_2O_7$ (19), and a variety of related compounds (20–23), (see Table I). $Rb_2HN(SO_3)_2$ and $(NH_4)_2HN(SO_3)_2$ (24) appear to have a similar structure but with superlattice b translations five and three times, respectively, that of the b translation of X.

In addition to the structures described here, other

possible combinations may appear, particularly those involving more than two sheets in the unit cell (25).

Phase Transitions

A number of the compounds crystallizing with these structures are polymorphic. Vesnin and Khripin (26) report at least four solid state phase transitions in $K_2Cr_2O_7$, and both $K_2Cr_2O_7$ and $Rb_2Cr_2O_7$ can be prepared from solution at room temperature in two different forms (16). Klement and Schwab (16) report that a single crystal of the stable room temperature form of $K_2Cr_2O_7$ -V ($P\bar{1}$) transforms rapidly but irreversibly at about 270° to a single crystal of a monoclinic form ($P2_1/n$ probably Type VII) with an interchange of the b and c axes (27). On cooling, a reversible transition occurs at around $250^\circ C$ but there is some dispute as to whether the phase formed below this transition has the structure of Type V or not (16,26). Under suitable conditions $K_2Cr_2O_7$ can be crystallized from solution with the space group $C2/c$ (probably Type X).

The phase transitions in $Rb_2Cr_2O_7$ are somewhat different from those in $K_2Cr_2O_7$. Two forms of

TABLE I
CRYSTAL DATA FOR COMPOUNDS CRYSTALLIZING WITH DICHROMATE STRUCTURES^a

Structure	Formula	Space group	Unique axis	Unit cell parameters					d_{100} Between sheets	Ref.		
				$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\alpha(^{\circ})$	$\beta(^{\circ})$			$\gamma(^{\circ})$	
I	$Cd_2P_2O_7$	$P\bar{1}$		6.858	6.672	6.623	82.38	95.80	115.38	6.66	9	
	$K_2ON(SO_3)$	$P\bar{1}$		7.14	7.45	7.16	82.0	105.0	113.0	6.90	10	
III	β - $Ca_2P_2O_7$	$P4_1$	a	24.144	6.684	6.684				6.04	11	
V	$K_2Cr_2O_7$	$P\bar{1}$	a	13.367	7.376	7.445	90.75	96.21	97.96	6.57	12,13	
VI	$Pb_2V_2O_7$	$P2_1/a$	c	13.37	7.11	7.16			106°	6.49	15	
VII	* $K_2Cr_2O_7$	$P2_1/n$	b	13.45	7.52	7.55		91.68		6.72	16	
	* $Rb_2Cr_2O_7$	$P2_1/n$	b	13.62	7.62	7.67		93.37		6.79	16	
VIII	$Rb_2Cr_2O_7$	$P\bar{1}$		13.554	7.640	7.735	93.64	98.52	88.80	6.67	17	
X	* $K_2Cr_2O_7$	$C2/c$	b	13.06	7.37	7.43		91.85		6.53	16	
	$(NH_4)_2Cr_2O_7$	$C2/c$	b	13.26	7.54	7.74		93.2		6.62	18	
	$K_2S_2O_7$	$C2/c$	b	12.35	7.31	7.27		92.12		6.17	19	
	$K_2HN(SO_3)_2$	$C2/c$	b	12.430	7.458	7.175		91.18		6.22	20–22	
	$K_2H_2C(SO_3)_2$	$C2/c$	b	12.556	7.773	7.253		90.50		6.28	20,23	
	* $(NH_4)_2H_2C(SO_3)_2$	$C2/c$	b	12.70	7.85	7.65		92.6		6.27	20	
	Xa	* $(NH_4)_2HN(SO_3)_2$		b	12.72	3×7.74	7.49		92.83		6.35	24
	Xb	* $Rb_2HN(SO_3)_2$		b	12.80	5×7.68	7.45		91.90		6.39	24
XI	α - $Ca_2P_2O_7$	$P2_1/n$	b	12.66	8.542	5.315		90.3			28	
XII	α - $Sr_2P_2O_7$	$Pbnn$		13.105	8.910	5.403					29,30	

^a Structures have not yet been determined for those marked with an asterisk.

$\text{Rb}_2\text{Cr}_2\text{O}_7$ can be grown from the same solution ($P\bar{1}$ Type VIII and $P2_1/n$ probably Type VII). Like $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Rb}_2\text{Cr}_2\text{O}_7$ undergoes an irreversible transition to an unknown structure at 318°C (26) but unlike $\text{K}_2\text{Cr}_2\text{O}_7$, this transition takes place slowly and with a well-defined phase boundary (16).

The rapid transition of $\text{K}_2\text{Cr}_2\text{O}_7$ at 270°C can be understood as a displacive transition, that is, one which occurs as a result of comparatively small displacements of the atoms. Figures 3a and 3b show two arrangements of the sheets in which the cations (large circles) are in almost identical positions and the anions are related to each other by a rotation of about 90° around an axis passing through the anion and lying approximately parallel to the line joining the cations on opposite faces. Such a transformation of the first sheet in structure V (Fig. 4) will result in the formation of structure VII but with the c axis of V forming the b axis of VII. A c glide plane and two-fold axis can be introduced into the sheets of VII by a further small rotation of the anions about the c axis followed by small displacements of both the anions and the cations (see Fig. 3c). The result would be a displacive transition from structure VII ($P2_1/n$) to structure X ($C2/c$). On the other hand, if the second sheet rather than the first sheet in structure V were to transform, structure VI ($P2_1/a$) would result with the unique axis again in the direction corresponding to the c axis of V. Thus the series of displacive transitions $\text{VI} \leftrightarrow \text{V} \leftrightarrow \text{VII} \leftrightarrow \text{X}$ is possible.

A similar transformation applied to $\text{Rb}_2\text{Cr}_2\text{O}_7$ -

VII ($P\bar{1}$) would lead to structure II, probably in the form $P2_1/c$. Such a structure has not been reported and is unlikely to be the high temperature polymorph of $\text{Rb}_2\text{Cr}_2\text{O}_7$ since the phase transition in $\text{Rb}_2\text{Cr}_2\text{O}_7$ involves a slowly moving phase boundary, suggesting that it is different in character from that in $\text{K}_2\text{Cr}_2\text{O}_7$.

A further displacive transformation might also be expected between structures I and IX but no structures of Type IX are yet known.

The existence of metastable polymorphs of $\text{Rb}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$ at room temperature can also be understood. Metastable $\text{K}_2\text{Cr}_2\text{O}_7$ -X ($C2/c$) can only transform by a displacive transition to the stable $\text{K}_2\text{Cr}_2\text{O}_7$ -V ($P\bar{1}$) by passing through the intermediate $\text{K}_2\text{Cr}_2\text{O}_7$ -VII ($P2_1/n$) which is the high temperature form. Similarly there is no way of transforming metastable $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VII ($P2_1/n$) to $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII ($P\bar{1}$) by means of a displacive transition.

Detailed Variations within the Sheets

The previous discussion has concentrated on the mutual arrangements of the sheets and the possible displacive transformations that can occur between them. It has been implicitly assumed that the sheets within any crystal are identical. This is, of course, the case where they are related by symmetry as, for example, in structures III, VI, VII, and X. But in V and VIII, the triclinic $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Rb}_2\text{Cr}_2\text{O}_7$ structures, the sheets are not related by symmetry

TABLE II
BOND LENGTHS AND ANGLES IN VARIOUS Y_2O_7 IONS^a

	Y-OB	Y-OT	OB-Y-OT	OT-Y-OT	Y-OB-Y	Twist
$\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII Sheet 1	1.78(1)	1.61(1)	109(1)	110(1)	123	2(1)
$\text{K}_2\text{Cr}_2\text{O}_7$ -V Sheet 1	1.78(1)	1.61(2)	109(2)	110(1)	124	6(4)
$\text{K}_2\text{Cr}_2\text{O}_7$ -V Sheet 2	1.78(1)	1.62(1)	109(1)	110(1)	128	10(2)
$\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII Sheet 2	1.77(2)	1.60(1)	109(2)	110(1)	138	10(2)
β - $\text{Ca}_2\text{P}_2\text{O}_7$ -III (a)	1.52(2)	1.63(1)	106(3)	112(3)	131	8(5)
$\text{Cd}_2\text{P}_2\text{O}_7$ -I	1.52(4)	1.62(2)	106(3)	113(3)	132	10(3)
β - $\text{Ca}_2\text{P}_2\text{O}_7$ -III (b)	1.52(2)	1.60(2)	106(3)	113(2)	138	17(6)
α - $\text{Ca}_2\text{P}_2\text{O}_7$ -XI	1.51(2)	1.60(2)	108(2)	111(3)	130	18(8)
α - $\text{Sr}_2\text{P}_2\text{O}_7$ -XII	1.50(1)	1.60(2)	107(2)	111(1)	131	0
$\text{K}_2\text{S}_2\text{O}_7$ -X	1.44(1)	1.64	104(3)	113(2)	124	4(2)

^a OT is a terminal oxygen, OB a bridging oxygen. The values given (in Å and degrees) are averages over the ion. The standard deviations are given in parentheses. The standard errors in individual measurements are about 0.01 Å and 1° . For references, see Table I.

and the unit cell is deformed in such a way that they cannot be exactly the same. It is thus interesting to see how the sheets differ and what effect the small changes in environment have on the configuration of the $\text{Cr}_2\text{O}_7^{2-}$ ion.

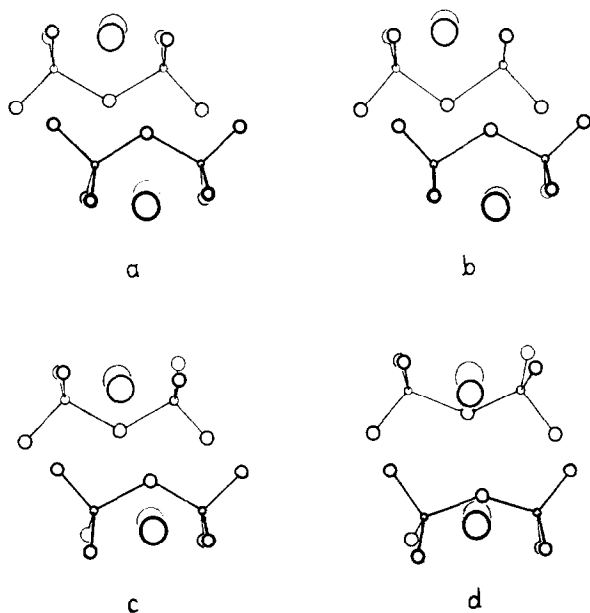


FIG. 5. The basic unit in a series of dichromates (a) $\text{K}_2\text{Cr}_2\text{O}_7$ -V sheet 1; (b) $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII sheet 1; (c) $\text{K}_2\text{Cr}_2\text{O}_7$ -V sheet 2; (d) $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII sheet 2.

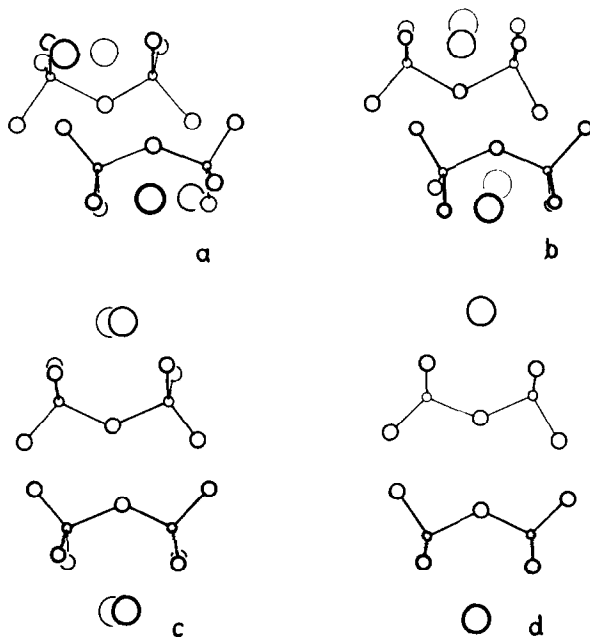


FIG. 6. The basic unit in a series of pyrophosphates (a) $\text{Cd}_2\text{P}_2\text{O}_7$ -I, (b) $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ -III, (c) $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ -XI, (d) $\alpha\text{-Sr}_2\text{P}_2\text{O}_7$ -XII.

Except for the difference in size, the basic unit in the first sheet of $\text{K}_2\text{Cr}_2\text{O}_7$ -V is virtually identical with that in $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII, although their mode of stacking along the crystal b direction (also the sheet B direction) is slightly different. Not surprisingly, the configuration and dimensions of the $\text{Cr}_2\text{O}_7^{2-}$ ions are very similar (see Table II).

The two dichromate groups forming the basic unit of the first sheet in $\text{K}_2\text{Cr}_2\text{O}_7$ -V and $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII are illustrated in a projection perpendicular to the Cr-Cr vector in Figs. 5a and 5b. These figures show well the similarity of these units and the way in which the oxygen atoms of their backbones are close packed. Figures 5c and 5d show the same views of the basic unit in the second sheet of each crystal, respectively. The dichromate groups can be seen to be shifted from the close packed position in a regular progression from the sheet 1 configuration through the $\text{K}_2\text{Cr}_2\text{O}_7$ sheet 2 to the $\text{Rb}_2\text{Cr}_2\text{O}_7$ sheet 2 configuration.

Figure 6 depicts the corresponding views of the basic unit in a series of pyrophosphate structures. These show the same progression that is found in the dichromate series. At the one extreme are the basic units with close packed backbones, $\text{Cd}_2\text{P}_2\text{O}_7$ (Figure 6a) and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (Fig. 6b). At the other extreme (Figs. 6c and 6d) are the pyrophosphate ions whose basic units are even further shifted from the close packed configuration than are the dichromate ions in the second sheet of $\text{Rb}_2\text{Cr}_2\text{O}_7$. In crystals where these extreme shifts are found, the basic units do not form sheets of the kind discussed above,

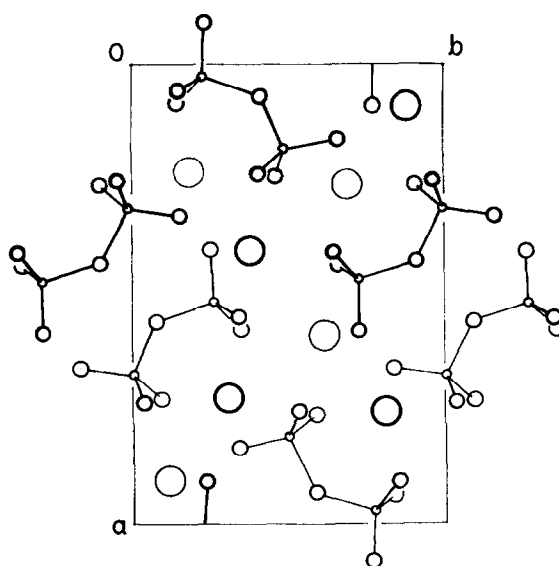


FIG. 7. $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ -XI projected down the row (c) direction.

but rows whose translation vector, like the C vector of the sheets, lies in the plane of the feet but makes an angle of nearly 90° rather than 60° to the backbones (Fig. 2b). The structures based on these rows (Fig. 7) are, of course, quite different from those based on the sheets, although in both structures, cations are found between the front and back feet on either side of the anion. At present, two such row structures are known, α - $\text{Ca}_2\text{P}_2\text{O}_7$ ($P2_1/n$ Type XI) (28) and α - $\text{Sr}_2\text{P}_2\text{O}_7$ ($Pbnm$, Type XII) (29,30), and these differ principally by the presence in the latter structure of a mirror plane passing through the backbone and phosphorous atoms of the P_2O_7 group.

Table II lists the bond lengths and angles in various Y_2O_7 groups. Apart from the twist angle and the angle at the bridging oxygen atom, all the dichromate ions are virtually identical as are the pyrophosphate ions. Furthermore, there is a close correlation between the angle at the bridging oxygen atom and the twist angle, the difference between them being about 120° for all ions except for those found in $\text{Rb}_2\text{Cr}_2\text{O}_7$ -VIII (sheet 2), α - $\text{Ca}_2\text{P}_2\text{O}_7$ -XI, and α - $\text{Sr}_2\text{P}_2\text{O}_7$ -XII. These latter three, which are the ions whose backbones do not close pack, show other small differences in their configurations, all of which must be attributed to the effects of their environment.

Note added in proof: Since this paper was submitted for publication, $\text{Ag}_2\text{Cr}_2\text{O}_7$ has been reported as having a structure of Type I. (R. G. HAZELL, *Acta Cryst.* 25A, S116 (1969), and private communication.)

Acknowledgments

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6. This angle is calculated by taking the average of the three smallest angles occurring between the projections of opposite YO bonds onto the plane perpendicular to YY' .
7. Capital letters will be used to refer to translations within a single sheet. Small letters will be used to refer to the crystal translations.
8. The possibility of the sheets being related by a mirror plane can be ignored, since this would bring into contact ions of the same charge on the two sheets.
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