

Redetermination of the Structures of Potassium Sulphate and Potassium Chromate: the Effect of Electrostatic Crystal Forces upon Observed Bond Lengths

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β -Potassium sulphate, K_2SO_4 , and potassium chromate, K_2CrO_4 , are isostructural and crystallize in the orthorhombic space group $Pnam$ ($z=4$) with unit-cell dimensions $a=7.476$ (3), $b=10.071$ (4), $c=5.763$ (2) Å, and $a=7.663$ (3), $b=10.388$ (4), $c=5.922$ (3) Å respectively. X-ray intensity data sets were collected for the two compounds with a 4-circle diffractometer and the atomic parameters were refined by full-matrix least-squares methods, the R values (on F) converging to 5.1 and 3.3% respectively. The shortest contacts between potassium and oxygen in the crystals are in the range 2.68 to 2.79 Å, and amongst the shortest contacts there is one potassium atom approximately collinear with each of the bond axes within the anion. The anions have crystallographically imposed m symmetry. The three independent sulphur–oxygen bond lengths in potassium sulphate are 1.459 (4), 1.473 (4) and 1.472 (5) Å. The three independent chromium–oxygen bond lengths in potassium chromate are 1.636 (3), 1.651 (2), and 1.643 (3) Å. The crystal forces acting upon the atoms in the anions were calculated using an electrostatic model with a range of charges on the atoms. The crystal force tends to compress the bonds within the anions and there was a linear variation of the observed bond lengths with the calculated force for all reasonable values of the assumed charges. In the absence of crystal forces, the bond lengths are calculated to be 1.473 Å for the sulphate anion and 1.653 Å for the chromate anion; applying a thermal motion correction using the riding model yields the best estimate for the sulphur–oxygen bond length in the sulphate anion as 1.486 Å and the chromium–oxygen bond length in the chromate anion as 1.670 Å. A force constant can be derived for the anion bonds and comparison of this with the corresponding force constant derived from infrared spectroscopy indicates that the effective charges upon the atoms in the crystals are approximately 2.0 (for sulphur or chromium), 1.0 (for potassium) and -1.0 (for oxygen). The crystal force calculations were also applied to potassium manganate and potassium selenate using previously reported atomic parameters; the best estimate of the bond lengths in the manganate and selenate anions is 1.675 and 1.650 Å respectively.

Introduction

Many compounds have been shown to be isostructural with β -potassium sulphate and amongst these may be listed potassium chromate, potassium manganate and potassium selenate. Approximate crystal and molecular parameters have been reported for potassium sulphate (Robinson, 1958) and potassium chromate (Zachariasen & Ziegler, 1931); this paper presents more accurate values for these parameters. Accurate crystal and atomic parameters have been reported for potassium manganate (Palenik, 1967) and potassium selenate (Kálmán, Stephens & Cruickshank, 1970).

A topical symposium on *Intermolecular Forces and Packing in Crystals* (1970) provides an excellent summary of earlier work in this field. Hitherto, no attempt to establish a quantitative relationship between crystal forces and observed bond lengths has been reported. This paper describes one such attempt and demonstrates that simply averaging bond lengths which are chemically equivalent in solution is not appropriate, at least in ionic crystals.

Experimental

Crystal data

Potassium sulphate, K_2SO_4 , $M=174.3$. Orthorhombic with $a=7.476$ (3), $b=10.071$ (4), $c=5.763$ (2) Å.

$U=433.9$ Å³. $Z=4$. Space group is $Pnam$ (conditions for reflection are $h0l$, $h=2n$; $0kl$, $k+l=2n$).

Potassium chromate, K_2CrO_4 , $M=194.2$. Isostructural with potassium sulphate. $a=7.663$ (3), $b=10.388$ (4), $c=5.922$ (3) Å. $U=471.3$ Å³.

The cell constants were determined with Mo $K\alpha_1$ radiation ($\lambda=0.70930$ Å) at a temperature of 18 (1) °C, using the setting constants on a 4-circle diffractometer of twelve high angle reflections. The numbers in parentheses following a parameter here and elsewhere in this paper are estimated standard deviations in the least significant figure of the parameter.

Intensity data were collected using a crystal of dimensions $0.20 \times 0.15 \times 0.40$ mm ($0.18 \times 0.13 \times 0.25$ mm).* Initially the c axis of the potassium sulphate crystal (which coincides with the longest crystal dimension) was aligned accurately with the diffractometer ϕ axis but before data collection, this alignment was misset by 4° on one goniometer arc and 7° on the other. The c axis of the potassium chromate crystal was aligned with the diffractometer ϕ axis during data collection. During data collection, crystal-monochromated (zirconium-filtered)* Mo $K\alpha$ radiation was used. The intensities were measured using a Picker (Hilger–Watts)* 4-circle diffractometer scanning in

* Here and elsewhere in this paper, the data quoted first refer to potassium sulphate, those in parentheses marked with an asterisk refer to potassium chromate.

ω-2θ mode at a rate of 1/2°/min (step-scan mode counting for one second at each step)* for a symmetric scan of 1.0° (1.4°)* in 2θ with stationary-crystal, stationary-counter background counts for 40 seconds (10 seconds)* measured at each end of the scan. Intensity data were collected for one octant of the orthorhombic reciprocal lattice out to a Bragg angle of 35°. The intensities of three standard reflections were measured at intervals throughout data collection, but only minor variations were observed. The data were corrected for background, the average changes in the standard reflections and for Lorentz-polarization effects. The individual standard deviations, σ(F²)₀, of the corrected intensities were calculated from counting statistics. The linear absorption coefficient is 24.9 cm⁻¹ (41.4 cm⁻¹)*, but no absorption correction was made. 1152 reflections (1165 reflections)* were measured and

processed; of these, 864 reflections (938 reflections)* had F²₀ ≥ 3 σ(F²)₀. The atomic parameters were refined using only those reflections with F²₀ ≥ 3 σ(F²)₀.

Refinement of the structures

The reported values for the coordinates of all the atoms were used as input to least-squares refinement. The calculations were performed on an IBM 360/67 computer and the programs used included modified versions of Zalkin's FORDAP and Busing, Martin and Levy's ORFLS. The scattering factors for the neutral atoms taken from the tabulations of Cromer & Waber (1965) and the effects of anomalous dispersion were included in Fc using the values for f' and f'' given by Cromer (1965). The function minimized in the refinement is Σw||F₀| - |F|²|² where w = 4F²₀/σ²(F²)₀.

Table 1. Observed and calculated structure factors

(a) Potassium sulphate structure factors (× 100)

Table with multiple columns containing numerical data for structure factors. The columns are grouped under labels like H, K, L, FO, FC, etc., representing different reflections. The rows contain numerical values for each reflection, with some entries marked with asterisks or plus signs. The table is very dense and spans most of the page.

Table 1 (cont.)

(b) Potassium chromate structure factors (×100)

Table with 24 columns labeled H K L FO FC and 24 rows of numerical data representing structure factors for various Miller indices.

Refinement of the scale factor, and positional and isotropic thermal parameters for all atoms led to an *R* value ($R = \sum ||F_o| - |F_c| || / \sum |F_o|$) of 8.7% (8.2%)*. Following the method of Zachariassen (1967), an extinction parameter was refined and anisotropic thermal parameters were refined for all atoms. The *R* value converged to 5.1% (3.3%)* for the reflections with $F_0^2 \geq 3\sigma(F_0^2)$. During the final cycle of refinement, no parameter changed by more than one hundredth of its standard deviation. The final value of the extinction parameter was 7.4 (7) × 10⁻⁶ [2.9 (2) × 10⁻⁶]*. A final difference Fourier synthesis revealed no peaks higher than 1.1 e.Å⁻³ (1.0 e.Å⁻³)*. In neither compound did any of the maxima in the final difference Fourier synthesis appear to correspond with any chemically significant feature.

The observed, and final values of the calculated structure factors are given in Table 1. The final positions and thermal parameters and their standard deviations calculated from the inverse matrix are given

in Table 2. The root-mean-square thermal amplitudes of vibration are given in Table 3.

Description of the structures

The crystal structures are built up by the packing of monomeric anions and potassium cations. There are two crystallographic mirror planes in the unit cell (at $z = \frac{1}{4}$ and $z = \frac{3}{4}$) and in these mirror planes lie all the atoms except the two O(3) atoms of each formula weight which lie approximately midway between the mirror planes. The anions have crystallographically imposed *m* symmetry. The bond angles within the anions are listed in Table 4, as are selected inter-ionic distances and angles. The shortest inter-ionic contacts in general with potassium atoms approximately colinear with the bond axes within the anions.

Fig. 1 shows the sulphate anions and potassium cations at $z = \frac{1}{4}$ (half the contents of the unit cell) projected on to the unit cell outline. The anisotropic vi-

Table 2. Positional and thermal parameters

The form of the anisotropic thermal ellipsoid is $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(1) K ₂ SO ₄									
S	0.23298 (15)	0.41971 (10)	0.25*	0.00554 (16)	0.00281 (9)	0.00866 (27)	-0.00003 (9)	0.0*	0.0*
K(1)	0.67377 (15)	0.41062 (11)	0.25*	0.00820 (18)	0.00472 (10)	0.01273 (29)	-0.00017 (10)	0.0*	0.0*
K(2)	-0.01104 (13)	0.70406 (10)	0.25*	0.00715 (16)	0.00374 (9)	0.01346 (27)	0.00007 (9)	0.0*	0.0*
O(1)	0.0379 (5)	0.4166 (4)	0.25*	0.0064 (5)	0.0067 (4)	0.0199 (12)	-0.0009 (4)	0.0*	0.0*
O(2)	0.2963 (5)	0.582 (3)	0.25*	0.0114 (7)	0.0029 (3)	0.0163 (11)	-0.0018 (4)	0.0*	0.0*
O(3)	0.3009 (4)	0.3522 (3)	0.0412 (4)	0.0134 (5)	0.0055 (2)	0.0111 (6)	0.0013 (3)	0.0020 (5)	-0.0024 (3)
(2) K ₂ CrO ₄									
Cr	0.22900 (6)	0.42059 (5)	0.25*	0.00334 (7)	0.00254 (4)	0.00861 (13)	-0.00008 (4)	0.0*	0.0*
K(1)	0.66544 (10)	0.41449 (8)	0.25*	0.00550 (11)	0.00556 (7)	0.01479 (21)	-0.00054 (7)	0.0*	0.0*
K(2)	-0.01105 (9)	0.69980 (7)	0.25*	0.00509 (10)	0.00334 (6)	0.01428 (19)	0.00012 (6)	0.0*	0.0*
O(1)	0.0155 (4)	0.4200 (3)	0.25*	0.0041 (3)	0.0071 (3)	0.0290 (11)	-0.0007 (2)	0.0*	0.0*
O(2)	0.3024 (4)	0.5700 (2)	0.25*	0.0082 (4)	0.0036 (2)	0.0227 (9)	-0.0017 (2)	0.0*	0.0*
O(3)	0.3022 (3)	0.3471 (2)	0.0233 (3)	0.0123 (3)	0.0068 (2)	0.0128 (5)	0.0026 (2)	0.0009 (3)	-0.0032 (3)

* Parameter fixed by symmetry.

Table 3. Root-mean-square amplitudes of vibration (Å) along principal axes

(i) K ₂ SO ₄	S	0.120	0.121	0.125
	K(1)	0.146	0.151	0.157
	K(2)	0.138	0.143	0.150
	O(1)	0.132	0.183	0.187
	O(2)	0.112	0.165	0.186
(ii) K ₂ CrO ₄	O(3)	0.116	0.177	0.200
	Cr	0.100	0.118	0.124
	K(1)	0.127	0.162	0.175
	K(2)	0.123	0.135	0.159
	O(1)	0.109	0.198	0.227
	O(2)	0.122	0.171	0.201
	O(3)	0.124	0.180	0.221

brations of all the atoms seem to be chemically reasonable. Each oxygen atom is vibrating principally in a direction normal to the sulphur-oxygen bond. A thermal motion correction to the sulphur-oxygen bond lengths is about 0.013 Å for all three bonds, using the riding model for vibration of the anion. Comparison of the parameters in Table 3 shows that K(1) is vibrating rather more anisotropically in potassium chromate than in potassium sulphate and that all three oxygen atoms in potassium chromate have a higher amplitude of vibration than in potassium sulphate. The thermal motion correction to the chromium-oxygen bond lengths is about 0.017 Å for all three bonds, using the riding model for vibration of the anion.

The cell constants for potassium sulphate are all less than those for potassium chromate ($\Delta a = 0.187$, $\Delta b = 0.317$, $\Delta c = 0.159$ Å). A large proportion of these differences are caused simply by the different bond lengths within the sulphate and chromate anions (sulphur-oxygen bonds are about 0.17 Å shorter than chromium-oxygen bonds in the anions in these crystals). However there are also differences in the shortest contacts between potassium and the oxygen atoms in the anions; those in potassium sulphate are in the range 2.72 to 2.79 Å whereas those in potassium chromate are in the 2.68 to 2.78 Å.

Calculation of crystal forces

The following procedure will specifically mention the case of potassium chromate, but all of the results are directly applicable to potassium sulphate, potassium manganate and potassium selenate. When an anion of the type CrO_4^{2-} is considered as a single isolated species, the four oxygen atoms are equivalent and in a tetrahedral array around chromium with the four chromium-oxygen internuclear distances equal. In the crystal lattice, the anion is subject to anisotropic crystal forces and the three independent chromium-oxygen internuclear distances derived from the diffraction experiments described in this paper are shown in Table 5 along with other known A-O internuclear distances derived for crystals of the type K_2AO_4 , where all of these compounds are isostructural with $\beta\text{-K}_2\text{SO}_4$. All atom nomenclature in Table 5 is consis-

Table 4. Selected internuclear distances and angles

		K ₂ SO ₄ (A = S)	K ₂ CrO ₄ (A = Cr)
(i) Angles within the anion (°)	O(1)–A–O(3)	109.6	109.9
	O(1)–A–O(2)	110.0	110.2
	O(2)–A–O(3)	109.1	108.7
	O(3)–A–O(3)	109.6	109.6
(ii) Shortest contacts between ions (Å)	O(1)–K(1)	2.723 (4)	2.683 (3)
	O(2)–K(2)	2.794 (4)	2.786 (3)
	O(2)–K(2')	2.727 (4)	2.755 (3)
	O(3)–K(2)	2.740 (5)	2.743 (3)
(iii) Angles formed in shortest contacts (°)	A–O(1)–K(1)	180.0	179.0
	A–O(2)–K(2)	167.7	169.1
	A–O(2)–K(2')	103.8	99.4
	A–O(3)–K(2)	161.7	160.2

tent with that in the present paper. The distances quoted in Table 5 have not been corrected for thermal motion, although such corrections are essential for the best absolute values for internuclear distances. The directly derived results were used in the calculation to be described in order that no assumptions be introduced at this point; the corrections calculated using the riding model are very similar for the three independent distances in any one of these structures.

Table 5. Internuclear distances within the anions in compounds of general formula K₂AO₄

A	A–O(1) (Å)	A–O(2) (Å)	A–O(3) (Å)
Cr	1.636 (3)	1.651 (2)	1.643 (3)
S	1.459 (4)	1.473 (4)	1.472 (5)
Mn	1.633 (5)	1.660 (5)	1.648 (5)
Se	1.622 (16)	1.626 (9)	1.628 (6)

The differences between the three chromium–oxygen internuclear distances are statistically significant; the longest distance is to O(2) and the shortest to O(1). Interestingly this situation is also observed in potas-

sium sulphate and potassium manganate. A systematic crystal effect could cause these deviations from a tetrahedral array, and a computer program has been written to calculate the electrostatic crystal forces acting upon a given anion to change the chromium–oxygen bond lengths. By calculation of the crystal forces and extrapolation to zero crystal force, the bond length in an isolated anion can in principle be derived; this is clearly more valuable than the length obtained by averaging the observed bond lengths because it is crystal-independent. One basic assumption is that the deviations from the ideal tetrahedral array are relatively small and that the electron distribution within the anion is effectively unchanged. The force to be calculated is the net electrostatic force acting upon each oxygen atom in the chromium–oxygen bond direction, relative to the corresponding force upon chromium. It is convenient to define three unit vectors, *p*, *q* and *r* in the internuclear directions Cr–O, Cr–B and O–B respectively, where B is any other chemical species in the lattice. The vector *p* is fixed for any one bond, whereas *q* and *r* vary with B. The electrostatic force (*f*) acting to shorten the bond length is

$$f = \sum_B \left[\frac{c_{(O)}c_{(B)}(\mathbf{p} \cdot \mathbf{r})}{d_{(OB)}^2} - \frac{c_{(Cr)}c_{(B)}(\mathbf{p} \cdot \mathbf{q})}{d_{(CrB)}^2} \right]. \quad (1)$$

In this equation, *d* is the internuclear separation of the atoms specified in the subscript and *c* is the charge assumed for the chemical species specified in the subscript. To calculate the crystal force, the summation should be made over all species B within the crystal, excluding those atoms within the given anion. This summation series is convergent and it proved to be necessary to calculate only those contributions up to a distance of 30 Å; in a few cases, contributions up to a distance of 40 Å were included, but there were only small changes in the results (<0.001 millidyne). A range of charges was assumed for the three chemical species in the compound. Explicit contributions were calculated for oxygen and chromium in all anions, even though, as expected, the contribution from any anion at a distance above 10 Å is effectively that of the appropriate anion charge centred on chromium. As

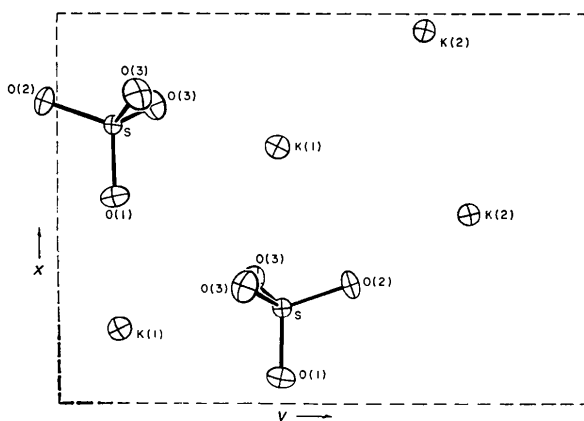


Fig. 1. Potassium sulphate: the contents of the half of the unit cell which is centred at $z = \frac{1}{4}$. The atoms are represented by 50% probability ellipsoids.

Table 6. Results of the force calculation

All forces are in millidynes.

	Charge assumed for potassium	Charge assumed for oxygen	Total force on†			Crystal force on*			Bond length in isolated anion (Å)	Force constant (millidynes/Å)
			O(1)	O(2)	O(3)	O(1)	O(2)	O(3)		
(i) K ₂ CrO ₄	1.0	-1.0	-0.700	0.018	0.053	-0.762	0.034	1.654	4.33	
	0.8	-0.8	-0.448	0.011	0.034	-0.488	0.034	1.654	2.77	
	1.0	-0.8	-0.421	0.014	0.035	-0.486	0.035	1.652	4.57	
(ii) K ₂ SO ₄	1.0	-1.0	-0.835	0.010	0.025	-0.974	0.025	1.473	9.8	
	0.8	-0.8	-0.534	0.006	0.016	-0.623	0.016	1.473	6.3	
	1.0	-0.8	-0.513	0.006	0.017	-0.623	0.017	1.473	7.7	
(iii) K ₂ MnO ₄	1.0	-1.0	-0.701	0.021	0.057	-0.763	0.057	1.661	3.1	
	0.8	-0.8	-0.449	0.013	0.036	-0.488	0.036	1.661	2.0	
	1.0	-0.8	-0.419	0.017	0.038	-0.484	0.038	1.662	2.5	
(iv) K ₂ SeO ₄	1.0	-1.0	-0.711	-0.010	0.012	-0.761	0.012	1.628	15.0	
	0.8	-0.8	-0.455	-0.006	0.008	-0.487	0.008	1.628	9.6	
	1.0	-0.8	-0.433	-0.008	0.006	-0.498	0.006	1.627	14.0	

* The crystal force acting upon a given oxygen atom is the sum of interactions external to the specified anion acting to shorten the bond.

† The total force is the crystal force plus the intra-anion forces.

defined in equation (1), a net positive force upon the chromium-oxygen bond tends to compress that bond and, for all reasonable values of the assumed charges, the crystal force is positive. Since the crystal has overall electrical neutrality, only two of the charges can be selected and calculations were made using charges upon potassium ranging from 0.4 to 1.0 and charges upon oxygen ranging from -0.2 to -1.0. Some of the results of the calculation are shown in Table 6 in the columns headed *Crystal force*.

Extrapolation to zero crystal force would yield an estimate of the bond length in an isolated anion. However, this procedure does not make allowance for changes in the forces acting within the ion under consideration. For example if there was a net electrostatic crystal force acting to compress only one bond, then that oxygen atom would be brought closer to the other three, thereby experiencing an increased repulsive force from these three oxygen atoms. This increased repulsive force is tending to minimize the effect of the crystal force. Thus it is necessary to extend the sum in equation (1) to include the intra-anion forces (O-O and Cr-O) and thereby derive the total applied electrostatic force (*i.e.* the sum of the crystal force and the forces acting within the distorted anion). These results are listed as *Total force* in Table 6 and plotted in Figs. 2 and 3. Comparison of these results with an equation expressing the expectation value for the internal repulsive forces in a perfect tetrahedral array will lead to the best estimate of the bond length in an isolated anion.

By assuming that the change in bond length is proportional to the force acting upon that bond (this assumption is analogous to the assumption of simple harmonic motion for the vibration of two atoms bonded together, this latter assumption being widely used in interpreting infrared spectra of molecules), the following equation can be used,

$$d = -kf + d_0; \quad (2)$$

d is the observed chromium-oxygen internuclear distance, k is the reciprocal of the force constant for the bond, f is the total applied electrostatic force acting upon the bond and d_0 is the chromium-oxygen internuclear distance in the absence of any force (*i.e.* in the hypothetical species Cr-O⁴⁺ in which the electronic configuration in the chromium-oxygen bond is the same as in the chromate anion). Using the three chromium-oxygen internuclear distances observed in the crystal and the total applied electrostatic forces, a least-squares fit leads to values for k and d_0 for every set of assumed charges. These are the slopes and intercepts in Figs. 2 and 3. The reciprocal of k is listed as the calculated *Force constant* in Table 6.

In an isolated chromate anion, there are no net forces acting upon chromium because it has T_d symmetry and consequently the electrostatic force acting to change the internuclear chromium-oxygen distance is simply,

$$f = -\frac{lc_{(o)}^2}{d_1^2} \quad (3)$$

d_1 is the chromium–oxygen internuclear distance in an isolated chromate anion. l is a constant to allow for the geometry of the anion; when $c_{(o)}$ is in electron charge units and d_1 in Ångstroms, then l equals 2.119 to give f in millidynes. To calculate d_1 , equation (3) is used to substitute for f in equation (2) along with the values of k and d_0 obtained as above; the resulting cubic equation can be solved in the usual way. Two roots of

the cubic equation are imaginary when the force constant for the bond is positive, and the real root provides a unique value for d_1 . The results are listed in Table 6 as the *Bond length in isolated anion*.

This entire discussion has been limited to the effect of crystal forces upon bond extension and contraction. The bending of bonds is in general more facile than stretching and clearly a similar treatment can be developed to allow for this. Until this is done, bond angles observed in the solid state must be considered to have large systematic errors.

Discussion of the results of the force calculation

In principle there are four useful results that can be derived from calculations of this type.

(i) There is an independent check upon the accuracy of bond lengths calculated from diffraction experiments. Fig. 2 shows the variation of observed bond length with calculated force for potassium chromate, and Fig. 3 shows an expanded scale graph of this same variation for potassium sulphate. Pleasingly, the three points deviate but little from the best straight line drawn through them for all values of the charges assumed for the chemical species in the crystal. Gross deviations from linearity would indicate poor data quality and systematic errors would be suspected if the deviations were much greater than the estimated standard deviations of the bond length. At the present level of accuracy of parameters derived from diffraction results, the assumptions inherent in the use of equation (2) are probably valid, especially for small distortions. However, it may prove possible, with highly accurate experimental work, to derive a more accurate equation.

(ii) A value can be calculated for the bond length (d_1) in an isolated anion and this should be crystal independent. Examination of the results given in Table 6 show the derived value for d_1 to vary but little with the assumed charges. Consequently, some considerable faith can be placed in this value. Since no correction for thermal motion was made to the original bond lengths, a correction should be made now. After adding the average correction, calculated using the riding model, the best estimate of the anion bond lengths are 1.670 (K₂CrO₄), 1.486 (K₂SO₄), 1.675 (K₂MnO₄) and 1.650 Å (K₂SeO₄). A proper estimate of the standard deviation in these bond lengths can be made but the method has not as yet been developed; this standard deviation should be rather less than the standard deviations quoted in Table 5, provided the results follow equation (2) closely, as they do for potassium sulphate and potassium chromate. An isolated anion is one upon which no external forces are acting and this can only be achieved in practice in the vapor phase; in solution, the powerful solvation forces would result in a changed mean bond length (probably shorter than in the isolated anion).

(iii) The reciprocal of k [from equation (2)] is equal to the stretching force constant for the bond and the

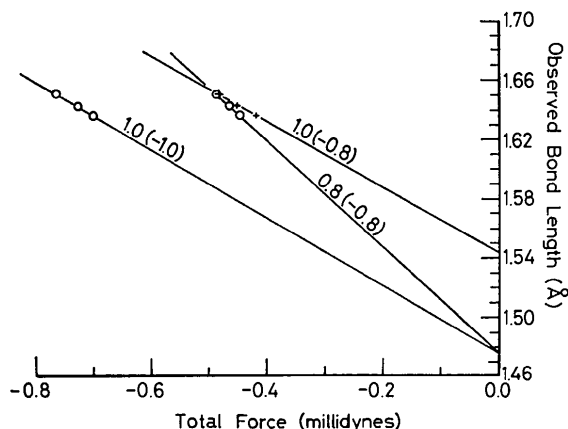


Fig. 2. Potassium chromate: the variation of observed bond length with total force. This force is the sum of the crystal force and the intra-anion force. Each set of three points is obtained by assuming different charges upon the chemical species. The charge upon potassium is indicated on each line with the charge upon oxygen in parentheses. The two sets of points marked with the symbol \circ are bound to have a common intercept since the charges are all changed by a constant factor. The intercepts are equal to the bond length in a hypothetical species Cr–O⁴⁺. The slopes are equal in magnitude to the reciprocal of the force constant for the bond.

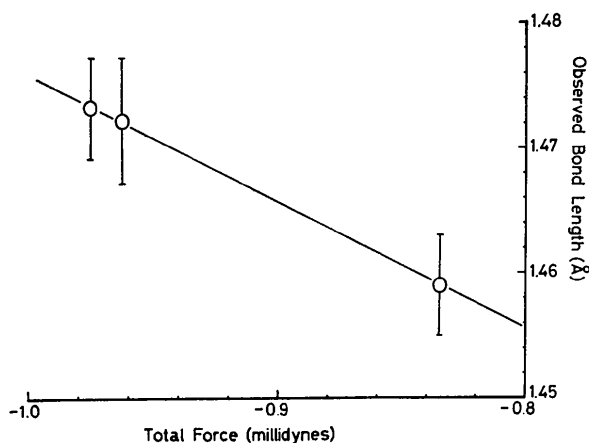


Fig. 3. Potassium sulphate: the variation of observed bond length with total charge. The assumed charges are 2.0 (S), 1.0 (K) and -1.0 (O). The vertical error bars represent one estimated standard deviation in the bond length.

force constants derived in this way are given in Table 6. A totally independent derivation of bond force constants is possible by means of vibrational spectroscopy. Infrared stretching-force constants can be calculated accurately by complete assignment of the whole spectrum of the compound or approximately from the position of the symmetric stretching frequency of the anion in the compound (preferably in the solid state, although force constants have proved to be characteristic of the bond and fairly independent of the compound). For the compounds under discussion, the infrared force constants are 5.48 (K_2CrO_4 ; Stammreich, Bassi & Sala, 1958), 10.26 (K_2SO_4 ; Rosenthal, 1934), 5.2 (K_2MnO_4 ; from the infrared results of Rocchiccioli, 1963), and 6.1 millidynes/Å (K_2SeO_4 ; from the infrared results of Tarte & Nizet, 1964). Comparison of the force constants derived in these two ways enables the effective charges upon the chemical species in the crystal lattice to be estimated. For potassium chromate, potassium sulphate and possibly potassium manganate, the charges upon A (=Cr, S, Mn respectively), K and O appear to be close to 2.0, 1.0 and -1.0. For the purposes of this calculation, the structure of potassium selenate needs to be redetermined. Force constants derived from the crystallographic results with these values for the charges are rather smaller than those derived from vibrational spectroscopy, but they do show the right trend in going from potassium chromate to potassium sulphate. Closer agreement can be achieved by increasing the charge separation within the anions. However, forces other than electrostatic are important in the solid state and at least the short-range repulsive forces should be included before accurate force constants can be expected. However, several approximations must be

made before these short-range forces can be estimated and much of the value of the electrostatic calculation detailed above would be obscured.

It should be noted that, whilst there are significant differences in the chromium-oxygen bond lengths observed in potassium chromate, there will not necessarily be three observable infrared bands corresponding to the stretching modes. Since equation (2) appears to be valid, the absorption frequency for all three bonds would be expected to be nearly equal. The mere fact that a 'symmetric' stretching frequency is observable in the infrared spectrum is indicative of the fact that the anion is distorted in the solid state.

(iv) If this procedure is valid then any observed deviations must be assigned to specific causes. For example, in ammonium sulphate there should be extra forces due to hydrogen bonding, and calculations on this compound are in progress.

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The Crystal and Molecular Structure of *cis*-1,3,5-Trichlorocyclohexane

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The crystal and molecular structure of *cis*-1,3,5-trichlorocyclohexane, a cyclic form of polyvinyl chloride, has been determined from X-ray data by direct methods and confirmed by Patterson techniques. The structure was refined by block-diagonal least-squares methods using three-dimensional data. The unit cell is monoclinic, space group $C2/c$ with $a=22.131$, $b=8.803$, $c=9.033$ Å, $\beta=101.3^\circ$ and $Z=8$. The final R value based on 1399 independent observed reflexions is 6.3%.

Introduction

The crystal and molecular structure of *cis*-1,3,5-trichlorocyclohexane, a cyclic trimer model of polyvinyl chloride, was determined as part of a systematic study of the conformational structure of polyvinyl chloride model compounds (Obereigner, Doskočilová & Štokr, 1968). Colourless crystals, purified in the final stage

by vacuum sublimation, were prepared by Dr B. Obereigner of the Institute of Macromolecular Chemistry, ČSAV, Prague.

Experimental

The elementary cell parameters were derived by the least-squares technique from rotation and Weissen-