Table 4. *Distances of uranium and pentagon atoms from their least-squares plane*

	Distance $(\text{Å} \times 10^3)$	Error $(\text{Å} \times 10^3)$
U	−36	14
Cl (A), Cl (D)	164	10
Cl (B), Cl (C)	−49	10
O(1) (B)	−195	21

We wish to thank J. H. Levy for technical assistance.

References

ATOJI, M. & MCDERMOTT, M. J. (1970). *Acta Cryst.* B26, 1540–1544.

BAENZIGER, N. & RUNDLE, R. E. (1944). Report CC-1778.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CAGLIOTI, G. (1970). In *Thermal Neutron Diffraction*, Chapter 2. Edited by B. T. M. WILLIS. Oxford Univ. Press.

CARTER, J. M. (1954). U. S. Patent No. 2, 677, 592.

DEBETS, P. C. (1968). *Acta Cryst.* B24, 400–402.

DUNN, H. W. (1956). Report ORNL-2092. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

HALL, D., RAE, A. D. & WATERS, T. N. (1966). *Acta Cryst.* 20, 160–162.

JOHNSON, O. (1944). Report CC-1500.

JOHNSON, O., BUTLER, T., POWELL, J. & NOTTORF, R. (1944). Report CC-1974.

KATZ, J. J. & RABINOWITCH, E. (1951). *The Chemistry of Uranium*, pp. 304–306. Natl. Nuclear Energy Series, Div. VIII-5. New York: McGraw-Hill.

NEUTRON DIFFRACTION COMMISSION (1969). *Acta Cryst.* A25, 391–392.

RIETVELD, H. M. (1967). *Acta Cryst.* 22, 151–152.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* 12, 600–604.

ZACHARIASEN, W. H. (1948). *Acta Cryst.* 1, 285–287.

Alkali Metal Ordering and Hydrogen Bonding in the System KHSO₄–RbHSO₄: the Crystal Structures of $K_xRb_{1-x}HSO_4$ ($0\cdot3 < x < 0\cdot55$) and RbHSO₄

BY W. G. MUMME

Division of Mineral Chemistry, CSIRO, P.O. Box 124, Port Melbourne, Victoria 3207, Australia

The crystal structures of $K_xRb_{1-x}HSO_4$, $x = 0\cdot55$, and of RbHSO₄ have been determined by X-ray single-crystal analysis. $K_xRb_{1-x}HSO_4$, $x = 0\cdot55$, is monoclinic with space group $P2_1/c$ and has the unit-cell dimensions $a = 7\cdot07$, $b = 14\cdot10$, $c = 8\cdot17$ Å, $\beta = 103\cdot9$. As a structure type, $K_xRb_{1-x}HSO_4$ exists for the range $0\cdot30 < x < 0\cdot55$. For $x = 0\cdot55$ all of the Rb⁺ present is ordered into one of the two sites available to the alkali metals. RbHSO₄ is also monoclinic, space group $P2_1/c$, and has unit-cell dimensions $a = 14\cdot29$, $b = 4\cdot61$, $c = 14\cdot76$ Å, $\beta = 120\cdot4°$. The $K_xRb_{1-x}HSO_4$ structure type has a layer structure, and exhibits the same overall arrangement of alkali metals and sulphate groups within each layer as does RbHSO₄ in (010) projection. These layers build into a three-dimensional structure intermediate between that of KHSO₄ and RbHSO₄.

Introduction

The sulphates of potassium, rubidium and caesium all have the orthorhombic K₂SO₄ structure (Wyckoff, 1965). Lithium sulphate (Albright, 1932) has a monoclinic tetramolecular structure (Li is a much smaller ion than K, Rb or Cs), while sodium sulphate is pleomorphic with five different modifications, one of which, Na₂SO₄(III) (Fischmeister, 1954), resembles K₂SO₄. It is noteworthy that many mixed alkali metal–alkaline earth compounds of the stoichiometry ABMO₄, including phosphates, arsenates and vanadates, also have the K₂SO₄ structural arrangement, thus demonstrating an analogy between normal phosphate and sulphate groups.

Except for KHSO₄ (Loopstra & MacGillavry, 1958) the structures of the alkali metal acid sulphates are not

known in any detail. The present paper discusses the structures of two compounds found in the KHSO₄–RbHSO₄ system, $K_{0\cdot55}Rb_{0\cdot45}HSO_4$ and RbHSO₄.

Experimental

Crystals of the acid sulphates were prepared by dissolving Rb₂SO₄ alone, or by mixing in an appropriate molar ratio with K₂SO₄ in sulphuric acid and adding a little water. On cooling to room temperature, well-shaped crystals were formed, most of which were rhombic plates of varying thickness although in the case of RbHSO₄ a few were needle shaped. Rubidium to potassium metal ratios for the single phases crystallized from these solutions were obtained from molecular weights determined by simple acid-base titrations on crystals which had been well washed

in alcohol to remove any acid from the mother liquor.

The approximate existence ranges for the three phases, together with molar volumes, are shown in Fig. 1. Single-phase preparations were formed from

acid solutions having Rb_2SO_4/K_2SO_4 starting concentrations between 0 and 0·25 (KHSO4 type), 0·5 and 0·6 ($K_xRb_{1-x}HSO_4$ type) and 0·9 and 1·0 (RbHSO4 type). At 0·35 and 0·75 two-phase preparations were observed, and their compositions have been estimated by extrapolation of the molar volumes observed for the single phase region.

Unit-cell parameters, listed in Table 1, were derived from a least-squares treatment of powder data (Table 2), which were obtained with a Guinier-type focusing camera using KCl as an internal standard and Cu $K\alpha_{1,2}$ radiation ($\lambda = 1·5418$ Å).

For the structure determination a crystal of $K_{0·55}Rb_{0·45}HSO_4$ was obtained from a solution having a K:Rb ratio of 1:1. The crystal measured $0·05 \times 0·1 \times 0·05$ mm, and was mounted along its a axis. Intensity data hkl for the levels $h = 0, 1, 2$ and 3 were collected by

Table 1. *Crystallographic data for* $K_{0·55}Rb_{0·45}HSO_4$ *and* RbHSO4

	(1) $K_{0·55}Rb_{0·45}HSO_4$	(2) RbHSO4
Symmetry	Monoclinic	Monoclinic
Unit-cell dimensions	$a = 7·07\ (\pm 0·01)$ Å	$a = 14·29\ (\pm 0·01)$ Å
	$b = 14·10\ (\pm 0·01)$	$b = 4·61\ (\pm 0·01)$
	$c = 8·17\ (\pm 0·01)$	$c = 14·76\ (\pm 0·01)$
	$\beta = 103·9°\ (\pm 0·1)$	$\beta = 120·4°\ (\pm 0·1)$
Systematically absent reflexions	$h0l,\ l = 2n+1$	$h0l,\ l = 2n+1$
	$0k0,\ k = 2n+1$	$0k0,\ k = 2n+1$
Possible space groups	$P2_1/c$	$P2_1/c$
Z	8	8
D_x	2·63 g cm^{-3}	2·89 g cm^{-3}

Table 2. *X-ray powder diffraction data for* $K_{0·55}Rb_{0·45}H\ SO_4$ *and* RbHSO4

	$K_{0·55}Rb_{0·45}HSO_4$					RbHSO4		
$h\ k\ l$		I	sin²θ_{obs}	sin²θ_{calc}	$h\ k\ l$		I	sin²θ_{obs}	sin²θ_{calc}
0 2 0		w	0·01185	0·01196	3 0 $\bar{2}$		w	0·02751	0·02687
1 0 0	}	w	0·01247	0·01261	0 1 1	}	w	0·03164	0·03158
0 1 1				0·01243	1 1 $\bar{1}$				
1 1 1		s	0·03026	0·03030	1 1 0				
0 0 2		vvs	0·03777	0·03777	1 1 $\bar{2}$				
1 2 1	}	m	0·03926	0·03927	1 1 1	}	ms	0·03943	0·03883
1 3 0				0·03952	2 1 $\bar{1}$				
1 0 $\bar{2}$		m	0·03979	0·3987	2 0 $\bar{4}$				0·04365
1 1 $\bar{2}$		vvs	0·04286	0·04286	2 1 $\bar{2}$	}	vvs	0·04364	0·04289
1 3 $\bar{1}$		vs	0·04690	0·04371	2 1 0				0·04355
0 4 0		s	0·04783	0·04785	1 1 $\bar{3}$	}	m	0·05332	0·05333
0 2 2		ms	0·04961	0·04974	2 1 $\bar{3}$				0·05356
2 0 0		vvs	0·05045	0·05044	2 1 1		m	0·05439	0·05488
1 2 $\bar{2}$	}	vs	0·05234	0·05183	1 1 2				0·05415
2 1 $\bar{1}$				0·05235	3 1 $\bar{2}$	}	m	0·05514	0·05478
1 3 1		s	0·05425	0·05422	3 1 $\bar{1}$				0·05527
0 4 1		vvs	0·05726	0·05729	0 0 4		vs	0·05898	0·05867
1 0 2	}	w	0·06040	0·06090	0 1 $\bar{3}$	}	vs	0·05954	0·06091
1 4 0				0·06046	4 0 $\bar{4}$				0·05992
2 2 $\bar{1}$		m	0·06129	0·06133	3 1 $\bar{3}$		mw	0·06123	0·06162
2 2 0		m	0·06246	0·06240	3 1 0	}	vs	0·06279	0·06310
1 1 2		vs	0·06398	0·06389	4 0 0				0·06255
1 4 $\bar{1}$	}	w	0·06466	0·06464	2 1 $\bar{4}$	}	m	0·07131	0·07157
0 3 2				0·56469	3 0 2				0·07284
1 3 $\bar{2}$		ms	0·06666	0·06678	0 1 $\bar{4}$	}	vvs	0·08701	0·08658
2 0 $\bar{2}$		ms	0·06717	0·06718	4 1 $\bar{4}$				0·08783
2 1 $\bar{2}$		w	0·07006	0·07017	2 1 $\bar{5}$				0·09691
2 1 1		s	0·07349	0·07339	3 0 $\bar{6}$	}	s	0·09789	0·09822
2 3 $\bar{1}$		w	0·07633	0·07628	3 1 $\bar{5}$				0·09730
2 3 0		s	0·07650	0·07735	5 0 0				0·09774
0 5 1	}	m	0·08433	0·08421	3 1 2	}	s	0·10038	0·10076
1 1 $\bar{3}$				0·08482	2 1 3				0·09954
0 4 2		m	0·08569	0·08562	2 0 $\bar{6}$				0·10166
0 1 3	}			0·08798	5 1 $\bar{3}$	}	s	0·10169	0·10118
1 3 2	}	s	0·08797	0·08781	5 1 $\bar{2}$				0·10200
1 4 $\bar{2}$				0·08772	1 1 4	}	s	0·10584	0·10582
1 5 $\bar{1}$		w	0·09175	0·09156	4 1 $\bar{5}$				0·10551
1 2 $\bar{3}$	}	m	0·09409	0·09379	4 1 1	}	m	0·10989	0·10946
2 3 $\bar{2}$				0·09409	5 1 $\bar{1}$				0·11017
0 2 3	}			0·09696	6 0 $\bar{2}$				0·10944
2 3 1	}	s	0·09721	0·09731	0 2 0		m	0·11174	0·11166
2 4 $\bar{1}$				0·09721	1 0 $\bar{6}$		m	0·11257	0·11292
					0 2 1	}			0·11532
					1 2 $\bar{1}$		s	0·11534	0·11540
					1 2 0				0·11557
					5 0 $\bar{6}$				0·11480

the integrated Weissenberg method using film packs together with filtered copper radiation. Exposure times were kept as constant as possible in order that the various levels of data should be closely in scale. The crystal was finally remounted around the b axis and the $h0l$ intensity data also collected: these were used to confirm that the various levels of data collected about a were correctly scaled.

A similar method was used to collect the intensity data from a crystal of $RbHSO_4$. In this case the crystal was needle-shaped measuring $0.02 \times 0.02 \times 0.1$ mm, and since b was both the needle axis of the crystal and the shortest crystallographic axis, the hkl data, $k = 0$, 1, and 2, were collected around this axis. Again, equally timed exposures were used, and $0kl$ data were collected as a check that the b-axis data were well scaled.

Intensities were measured by visual comparison with a standard scale, and their reduction to structure factors and all subsequent computing was made on an Elliott 803 computer with the programming system devised by Daly, Stephens & Wheatley (1963). Although the interlayer scale factors proved to be nearly correct in both cases, they were additionally adjusted after each least-squares cycle. The scattering curves for Rb^+, K^+ and S were taken from *International Tables for X-ray Crystallography* (1962). Suzuki's (1960) data for O^{2-} were used for oxygen.

Determination of the structure

In determining the structure of $K_{0.55}Rb_{0.45}HSO_4$, both a sharpened Patterson projection $P(v,w)$ and a three-

dimensional Patterson synthesis $P(u,v,w)$ were inspected in turn. The three-dimensional Patterson resolved the S(1) and K atom positions, which overlapped in the (100) projection, and the four positions for the potassium, rubidium and two sulphur atoms were obtained. Fourier and structure factor reiteration were used to determine which of these four positions contained the heavier atoms, and finally this method was used to reveal the positions of all the other atoms except hydrogen.
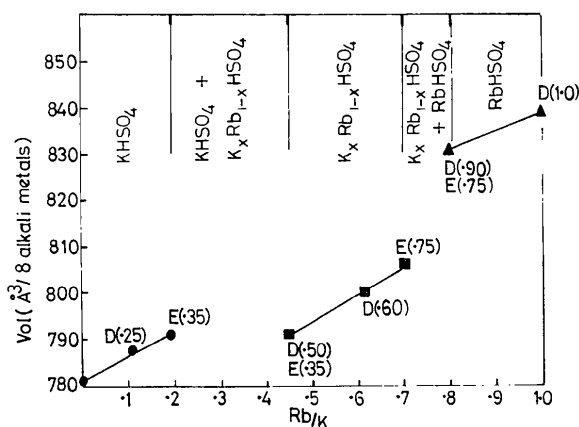

Fig. 1. Approximate existence ranges and plot of molar volumes v. composition for the system $KHSO_4$–$RbHSO_4$. ●, $KHSO_4$ type; ■, $K_xRb_{1-x}HSO_4$ type; ▲, $RbHSO_4$ type; D, composition ($\pm 2\%$) determined by chemical analysis of single-phase preparations; E, compositions inferred for the two-phase region using molar volume slopes of the single-phase regions. For D and E, the numerals in brackets are the Rb_2SO_4/K_2SO_4 starting solution concentration ratios.

Table 3. *Fractional atomic coordinates and temperature factors*

(a) $K_{0.55}Rb_{0.45}HSO_4$

	x	y	z	B
Rb(1)	0.4622 (6)	0.2125 (1)	0.1511 (3)	2.70 (5) Å²
K(1)	0.0926 (9)	0.4562 (2)	0.2799 (4)	0.71 (6)
S(1)	0.4197 (11)	0.9622 (3)	0.2303 (5)	1.10 (8)
S(2)	0.0073 (11)	0.1904 (2)	0.3486 (5)	0.90 (8)
O(1)	0.2529 (34)	0.0094 (10)	0.1214 (20)	2.78 (34)
O(2)	0.4890 (31)	0.3937 (10)	0.3554 (18)	2.34 (32)
O(3)	0.3400 (32)	0.9083 (9)	0.3687 (18)	2.12 (30)
O(4)	0.4339 (31)	0.5304 (10)	0.1798 (17)	1.94 (29)
O(5)	0.1618 (35)	0.7450 (13)	0.0952 (22)	3.49 (40)
O(6)	0.0849 (30)	0.6600 (9)	0.3221 (16)	1.58 (26)
O(7)	0.1589 (35)	0.2581 (12)	0.3514 (21)	3.24 (38)
O(8)	0.0589 (32)	0.1129 (9)	0.4618 (18)	1.92 (29)

(b) $RbHSO_4$

	x	y	z	B
Rb(1)	0.1247 (2)	0.2981 (11)	0.4609 (2)	2.96 (7) Å²
Rb(2)	0.3764 (2)	0.6381 (11)	0.2918 (2)	2.62 (6)
S(1)	0.1281 (6)	0.2358 (27)	0.2069 (5)	1.89 (17)
S(2)	0.3753 (6)	0.7137 (30)	0.0492 (6)	2.88 (21)
O(1)	0.2773 (19)	0.6957 (79)	0.0527 (18)	3.77 (62)
O(2)	0.4700 (18)	0.6136 (80)	0.1461 (17)	3.62 (39)
O(3)	0.3598 (19)	0.5196 (81)	−0.0423 (18)	3.88 (59)
O(4)	0.4061 (17)	0.9772 (77)	0.0151 (16)	3.55 (54)
O(5)	0.0325 (18)	0.3032 (76)	0.1013 (17)	3.41 (59)
O(6)	0.2141 (18)	0.1148 (76)	0.1951 (17)	3.35 (55)
O(7)	0.0397 (18)	−0.0024 (80)	0.2588 (17)	3.44 (55)
O(8)	0.1656 (18)	0.4755 (80)	0.2350 (17)	3.57 (56)

During the Fourier refinement it was observed that the peak heights of one of the alkali metal sites were consistently greater than those of the other site by a factor of about 1·7, a ratio consistent with most of the rubidium ordering preferentially into this site. Subsequent least-squares refinement was therefore carried out with all the Rb^+ ordered into this site, that is with one of the alkali metal sites having a scattering power of $f(\frac{9}{10}Rb^+ + \frac{1}{10}K^+)$ and the other sites having a scattering power of $f(K^+)$, and this converged to give an R value of 12·0 for the 712 reflexions. This relatively high R value may be due to unavoidable errors of chemical composition and possibly to less than 100% ordering of Rb^+ into the large site. However during the refinement the temperature factors for the ordered alkali metal sites behaved fairly normally, and when refinement had finally converged the average bond lengths calculated for the two alkali metal sites further supported this model (see Section 4).

Thus Rb^+ orders in one site in the structure (together with 9% K^+ to meak up the stoichiometry), and any disordering of Rb^+ into the other site is minimal, though not entirely impossible.

The atomic parameters, the temperature factors and their estimated standard deviations are given in Table 3(a), and interatomic distances in Table 4(a).

Table 4. *Bond lengths*

(a) $K_{0.55}Rb_{0.45}HSO_4$

(i) Rubidium coordination

Rb(1)–O(4′)	2·87 (3) Å
Rb(1)–O(2′)	2·89 (3)
Rb(1)–O(7′)	2·93 (4)
Rb(1)–O(5′)	2·99 (3)
Rb(1)–O(2)	3·03 (3)
Rb(1)–O(3′)	3·06 (3)
Rb(1)–O(6)	3·12 (3)
Rb(1)–O(7)	3·21 (3)
Rb(1)–O(1′)	3·24 (3)
	Av. 3·04

(ii) Potassium coordination

K(1)–O(1″)	2·73 (4) Å
K(1)–O(2)	2·79 (3)
K(1)–O(8′)	2·85 (4)
K(1)–O(1‴)	2·86 (3)
K(1)–O(6)	2·87 (3)
K(1)–O(7)	2·90 (3)
K(1)–O(4)	2·92 (3)
K(1)–O(8″)	2·99 (3)
K(1)–O(3″)	3·08 (3)
	Av. 2·89

(iii) Sulphate groups

S(1)–O(2)	1·43 (2) Å
S(1)–O(4)	1·47 (2)
S(1)–O(1)	1·46 (2)
S(1)–O(3)	1·58 (3)
	Av. 1·48
S(2)–O(7)	1·43 (2) Å
S(2)–O(8)	1·42 (2)
S(2)–O(5)	1·58 (2)
S(2)–O(6)	1·46 (2)
	Av. 1·47

Table 4 (*cont.*)

(iv) Probable hydrogen bonds

O(3)–H–O(4)	2·62 (3) Å
O(5)–H–O(6)	2·55 (3)

(b) $RbHSO_4$

(i) Rubidium coordination

Rb(1)–O(1′)	2·97 (3) Å
Rb(1)–O(5′)	3·00 (3)
Rb(1)–O(1″)	3·01 (3)
Rb(1)–O(5″)	3·04 (3)
Rb(1)–O(6′)	3·05 (3)
Rb(1)–O(8′)	3·05 (3)
Rb(1)–O(5‴)	3·56 (3)
Rb(1)–O(7′)	3·09 (3)
Rb(1)–O(7″)	3·27 (3)
	Av. 3·06
Rb(2)–O(2′)	2·91 (4) Å
Rb(2)–O(6)	2·98 (3)
Rb(2)–O(3′)	3·02 (3)
Rb(2)–O(2)	3·06 (3)
Rb(2)–O(8)	3·06 (3)
Rb(2)–O(4′)	3·06 (3)
Rb(2)–O(1)	3·08 (3)
Rb(2)–O(2′)	3·08 (3)
Rb(2)–O(6)	3·15 (3)
Rb(2)–O(4″)	3·15 (3)
	Av. 3·06

(ii) Sulphate groups

S(1)–O(6)	1·44 (2) Å
S(1)–O(5)	1·46 (2)
S(1)–O(8)	1·49 (2)
S(1)–O(7)	1·59 (2)
	Av. 1·50
S(2)–O(1)	1·43 (2) Å
S(2)–O(2)	1·46 (3)
S(2)–O(4)	1·47 (2)
S(2)–O(3)	1·54 (2)
	Av. 1·48

(iii) Probable hydrogen bonds

O(3)–H–O(4)	2·62 (3) Å
O(7)–H–O(8)	2·59 (3)

In a previous study of $RbHSO_4$, Bengtsson (1941) suggested that it was orthorhombic, unit-cell dimensions $a = 4·60$, $b = 14·75$, $c = 24·6$ Å, space group $Abmm$. Bengtsson indicated a close similarity between the positions of the rubidium atoms in $RbHSO_4$ and the barium atoms in $BaHPO_4$.

The present study indicated that $RbHSO_4$ is not orthorhombic, but monoclinic, space group $P2_1/c$. A close examination of the Weissenberg data recorded about the 4·6 Å axis reveals that what should be symmetry-related reflexions for an orthorhombic crystal do not have the same intensity. These differences cannot be attributed entirely to absorption effects, and it was concluded that the symmetry was not orthorhombic, but monoclinic with a β angle very close to 120°. Subsequent solution and refinement of the structure showed this to be the correct interpretation of the Weissenberg data.

Approximate parameters for the rubidium and sulphur atoms were determined from the three-dimensional Patterson function, and Fourier and structure factor reiteration were then used to give the positions

of the oxygen atoms. Only the positions of the hydrogen atoms were not determined.

The final R value of 10·6 for 800 reflexions was somewhat high, probably due in part to absorption and anomalous dispersion effects. The atomic parameters, the temperature factors and their estimated standard deviations are given in Table 3(b); and interatomic distances in Table 4(b).

Description of the structures

(i) $K_{0.55}Rb_{0.45}HSO_4$

The structure of $K_{0.55}Rb_{0.45}HSO_4$ is shown projected onto (100) in Fig. 2(a). It consists of discrete SO_4^{2-} tetrahedra and K^+ and Rb^+ ions, the latter coordinated by shells of oxygen atoms. However, the overall structure formed is one of closely packed layers composed of $(K_{0.55}Rb_{0.45}HSO_4)_n$ parallel to (001), which join to each other by alkali metal–oxygen bonds. These bonds, which extend out almost normal to the layers, connect from the K^+ and Rb^+ ions in one layer to the oxygen atoms in adjacent layers so as to complete the coordination shells of the alkali metals. The most likely positions for hydrogen atoms in this structure are O(3)–H–O(4) with an O–O separation of 2·62 Å and O(6)–H–O(5) with O–O separation of 2·55 Å.

Each K^+ and Rb^+ ion is bonded to nine oxygen atoms. For K^+, the bond distances range from 2·73 to 3·08 Å, and for Rb^+ from 2·87 to 3·24 Å. The average bond distance for the Rb^+ site of 3·04 Å is significantly greater than that for the K^+ site, 2·89 Å, and is close to the values found for Rb^+ in $RbHSO_4$.

The system of hydrogen bonding (see Fig. 3) is such that the bonds link tetrahedra in the direction of the c axis. Two S(1) tetrahedra are linked by a double hydrogen bridge on each side of a symmetry centre, forming a double 'molecule' as found in $KHSO_4$ (Loopstra & MacGillavry, 1958). The S(2) tetrahedra are linked by a bridge forming an infinite chain system along c. There is also a significant shortening of the bridge in the S(2) case. These bridges compare with similar bridges found in $KHSO_4$ (Cruickshank, 1964) where the double bridge is 2·62 Å and the single bridge 2·62 Å.

The Rb^+ and K^+ coordination polyhedra are alternatively linked within the layers by the edges O(2)–O(7) and O(4)–O(6) to form zigzag chains along b[Fig. 2(b)]. These chains are then attached to similar chains above and below, not only by direct corner sharing of K^+ and Rb^+ polyhedra, but also by the bridging of Rb^+ polyhedra by S(2) groups and K^+ polyhedra by S(1) groups. Layers are established in a somewhat similar way in $CaHPO_4$ (MacLennan & Beevers, 1955; Dickens, Bowen & Brown, 1972).

(ii) $RbHSO_4$

The structure of $RbHSO_4$ projected onto (010) is shown in Fig. 4. It is composed of discrete SO_4^{2-}

tetrahedra and Rb^+ ions which are coordinated by shells of oxygen atoms. Rb(1) is nine-coordinated with bonds ranging from 2·96 to 3·27 Å, and averaging 3·06 Å. Rb(2) is ten-coordinated, with bonds ranging from 2·91 to 3·15 Å, and averaging 3·05 Å.

Pairs of Rb(1) polyhedra joined by edges at O(5)–O(5′) and pairs of Rb(2) polyhedra joined by edges at
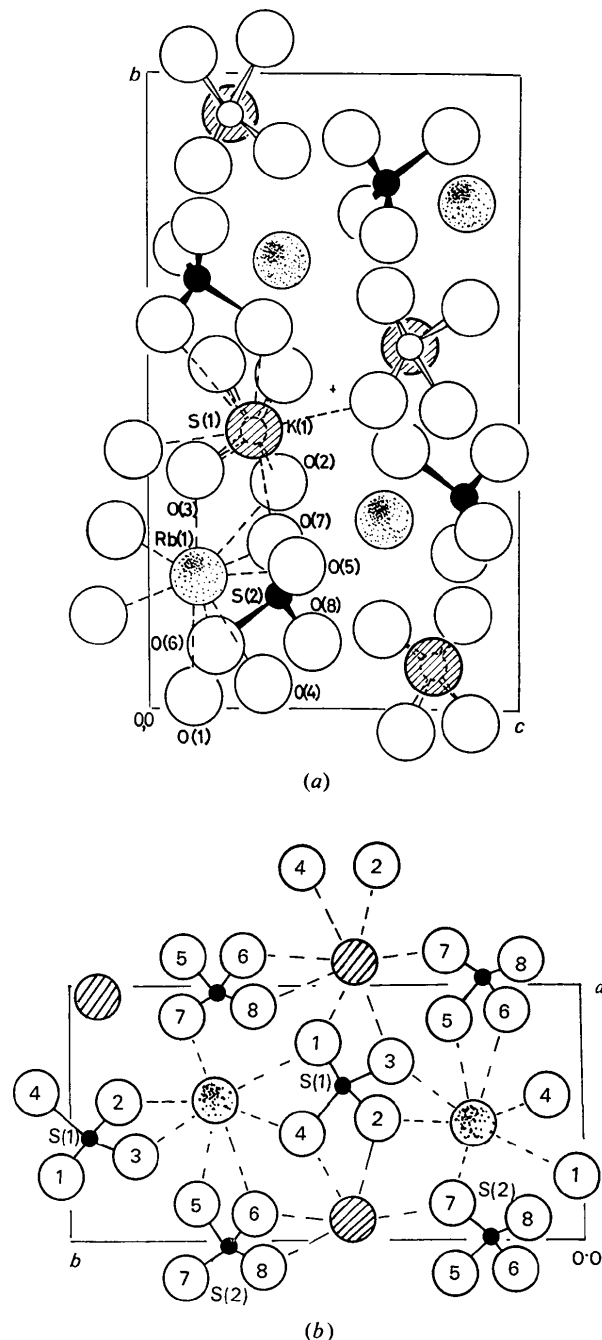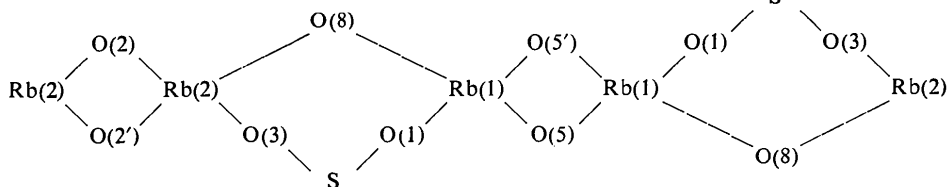

Fig. 2. (a) Projection of $K_{0.55}Rb_{0.45}HSO_4$ onto (100) showing layers. (b) Projection of a layer of $K_{0.55}Rb_{0.45}HSO_4$ onto (001).

O(2)–O(2') are further joined to each other by corners at O(8) to form chains thus:

Additional corner sharing of Rb(2) polyhedra *via* O(4) together with edge sharing of Rb(1) and Rb(2) polyhedra along the edge O(1)–O(6) links these chains transversely into corrugated sheets in which the sulphate groups also occupy bridging positions.

Fig. 3. Hydrogen bonding of sulphate groups in $K_{0.55}Rb_{0.45}HSO_4$.

Fig. 4. Projection of $RbHSO_4$ onto (010). Heavy marking, $y \simeq \frac{1}{4}$; light markings, $y \simeq \frac{3}{4}$.

O(3)–O(4) and O(7)–O(8) separations of 2·62 and 2·59 Å. The lengthening of the sulphate ligands S(1)–O(7) and S(2)–O(3) [Table 4(*b*)], caused by these attached hydrogen atoms, is noticeable in this structure as it is in $K_{0.55}Rb_{0.45}HSO_4$.

Alkali metal ordering in $K_{0.55}Rb_{0.45}HSO_4$ and hydrogen bonding in the system $KHSO_4$–$RbHSO_4$

Although the structure of $K_{0.55}Rb_{0.45}HSO_4$ has been conveniently discussed as if it had a K–Rb ratio of unity, at least 9% of the Rb^+ site is occupied by K^+, and there may even be a further small disordering of Rb^+ into the other site.

The results shown in Table 5 indicate that the $K_{0.55}Rb_{0.45}HSO_4$ structure has an existence range around Rb:K ratios close to and greater than unity. Guinier X-ray powder patterns of the material crystallized from an acid solution containing Rb_2SO_4 and K_2SO_4 in a 75:25 mole ratio showed the presence of two coexisting phases having the $RbHSO_4$ and the $K_{0.55}Rb_{0.45}HSO_4$ structures (Table 5, column 5). Although chemical analysis of the individual phases crystallized was not possible owing to the difficulty of separation, the unit-cell volume of the '$RbHSO_4$ structure type' compound formed was considerably lower than that of $RbHSO_4$ itself, indicating the presence of substantial K^+ in the lattice. The unit-cell volume of the '$K_{0.55}Rb_{0.45}HSO_4$ structure type' was greater than that of $K_{0.55}Rb_{0.45}HSO_4$, indicating that the Rb:K ratio in this lattice can be increased well beyond unity.

At a ratio of 25 mol% Rb_2SO_4, 75 mol% K_2SO_4, a single phase with the $KHSO_4$ structure was formed having the composition $K_{0.89}Rb_{0.11}HSO_4$. It had a unit-cell volume greater than that of pure $KHSO_4$ (Loopstra & MacGillavry, 1958) consistent with the presence of Rb^+ in the lattice. Extrapolating the molar volume slopes for the denser $K_xRb_{1-x}HSO_4$ type and the $RbHSO_4$ type, it was estimated that for the two-phase preparation the compositions were $K_{0.30}Rb_{0.70}HSO_4$ and $K_{0.20}Rb_{0.80}HSO_4$ respectively (Table 6). This suggests an approximate range of K:Rb ratios from 1·3 to 0·4 for the $K_xRb_{1-x}HSO_4$ structure type. Some degree of isomorphous replacement, therefore, occurs in all three phases formed in the system $RbHSO_4$–$KHSO_4$. Here, however, unlike
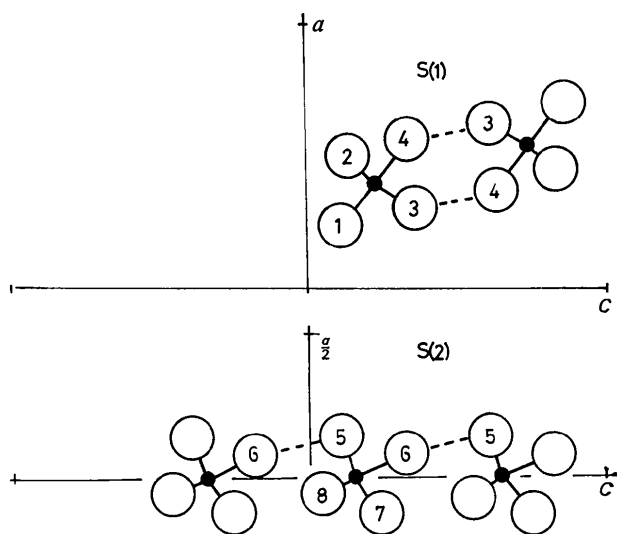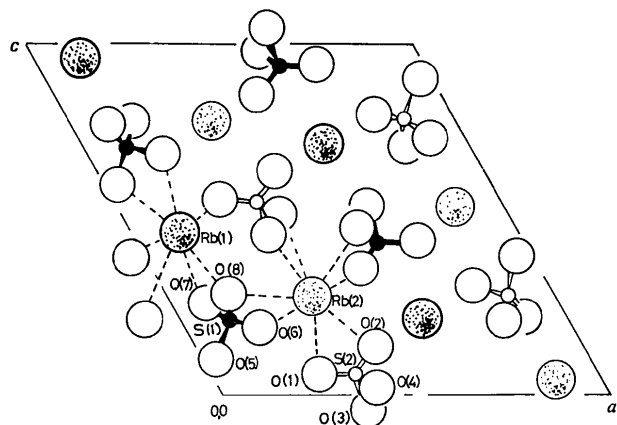
Table 5. *Structure type formation in the system* $KHSO_4$-$RbHSO_4$

Ratio K/Rb*	1:0	0·89:0·11	0·55:0·45	0·3:0·7 0·2:0·8	0:1
Structure type found	$KHSO_4$	$KHSO_4$	$K_xRb_{1-x}HSO_4$	$K_xRb_{1-x}HSO_4$ $RbHSO_4$	$RbHSO_4$
Z	16	8	8	8,8	8
Unit-cell dimensions (and volume)	9·79 Å 18·96 8·41 (1561·0)	9·84 Å 19·06 8·41 (1577·3)	7·07 Å 14·10 8·17 $\beta=103·9°$ (791·2)	7·13 Å 14·19 8·22 $\beta=104·0°$ (806·4) 14·22 Å 4·60 14·69 $\beta=120·5°$ (827·9)	14·29 Å 4·61 14·76 $\beta=120·4°$ (839·5)

* Determined by analysis for single-phase preparations; inferred for the two-phase region by interpolation of molar volumes.

Table 6. *Hydrogen bonding distances* (Å)

Structure	Double molecule	Strings
$KHSO_4$	2·62	2·62
$K_{0.55}Rb_{0.45}HSO_4$	2·62	2·55
$RbHSO_4$		2·62 ⎫ 2·59 ⎭

the Rb_2SO_4-K_2SO_4 system, at a composition between the approximate limits $K_{0.80}Rb_{0.20}HSO_4$ and $K_{0.55}Rb_{0.45}HSO_4$, the $KHSO_4$ structure can no longer tolerate the incorporation of the larger Rb^+ ion in its lattice, and the $K_{0.55}Rb_{0.45}HSO_4$ structure type is formed with a high degree of Rb^+ and K^+ ordering. At still higher concentrations of Rb^+, the $RbHSO_4$ structure type is formed.

A comparison of the hydrogen bond lengths found in compounds in this acid sulphate system $KHSO_4$–$RbHSO_4$ is given in Table 6.

Structural relationships between $KHSO_4$, $K_{0.55}Rb_{0.45}HSO_4$ and $RbHSO_4$

The relationship between the $K_{0.55}Rb_{0.45}HSO_4$ and $RbHSO_4$ structures is seen in Figs. 2(b) and 4. Fig. 2(b) is the (001) projection of a layer of $K_{0.55}Rb_{0.45}HSO_4$, and it shows the same overall arrangement of alkali metals and sulphate groups as $RbHSO_4$. Each alkali metal in the layer of $K_{0.55}Rb_{0.45}HSO_4$ is surrounded by four sulphate tetrahedral groups which are coordinated to it and form the network represented in Fig. 5(a). A similar network is obtained for a unit-cell thickness of $RbHSO_4$ and is represented in (010) projection in Fig. 5(c). The difference between the two structures is that in $RbHSO_4$ each such network falls directly in line with ones above and below to form a three-dimensional structure with continual holes for the alkali metals, while in $K_{0.55}Rb_{0.45}HSO_4$ alternate networks are displaced forming discontinuities in

these holes [Fig. 5(b)]. A similar representation of the $KHSO_4$ structure projected onto (010) shows, in turn, its strong relationship to $K_{0.55}Rb_{0.45}HSO_4$ [Figs. 5(b) and (d)].

Vertical displacements of the atoms in $KHSO_4$ are required to bring them into positions where the more distinct layers of the $K_{0.55}Rb_{0.45}HSO_4$ structure are formed. Horizontal displacement of alternate layers
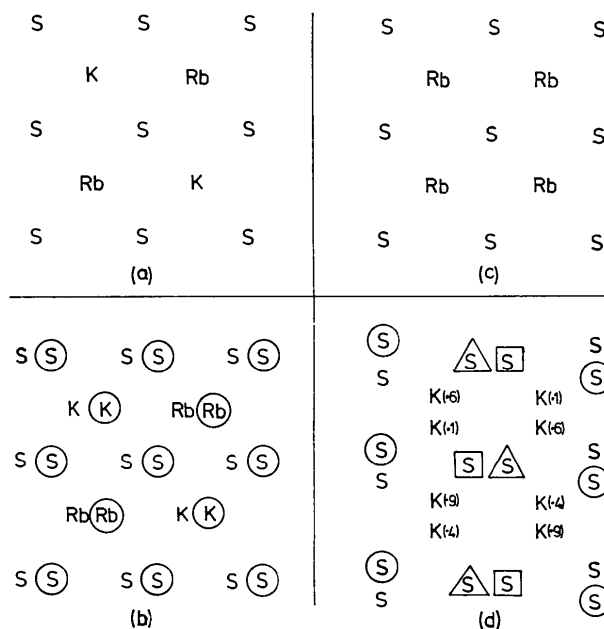

Fig. 5. Structural representation of (a) single layer of $K_{0.55}Rb_{0.45}HSO_4$ projected onto (001); (b) multiple layers of $K_{0.55}Rb_{0.45}HSO_4$ projected onto (001), atoms in alternate layers; (c) $RbHSO_4$ structure projected onto (010); (d) $KHSO_4$ structure projected onto (100); △ atoms at zero, unlabelled at ¼, □ at ½, ○ at ¾; oxygen atoms omitted.

of atoms in $K_{0.55}Rb_{0.45}HSO_4$ is then necessary for the alignment of sulphate groups and alkali metals which is found in $RbHSO_4$.

Comparable structure dissimilarities have been observed previously between such compounds as $BaSO_4$ and $BaHPO_4$ (Bengtsson, 1941). These differences may derive from the influence of the hydrogen atom on the mutual orientation and distances in the sulphate (and phosphate) tetrahedral groupings in these compounds.

References

ALBRIGHT, J. G. (1932). Z. Kristallogr. 84, 150–155.
BENGTSSON, E. (1941). Ark. Kem. 15B, 1–8.

CRUICKSHANK, D. W. J. (1964). Acta Cryst. 17, 682–683.
DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Monsanto Research S. A., Final Report No. 52.
DICKENS, B., BOWEN, J. S. & BROWN, W. E. (1972). Acta Cryst. B28, 797–806.
FISCHMEISTER, H. (1954). Acta Cryst. 7, 776–777.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201 et seq. Birmingham: Kynoch Press.
LOOPSTRA, L. H. & MACGILLAVRY, C. H. (1958). Acta Cryst. 11, 349–354.
MACLENNAN, G. & BEEVERS, C. A. (1955). Acta Cryst. 8, 579–583.
SUZUKI, T. (1960). Acta Cryst. 13, 279–279.
WYCKOFF, R. W. G. (1965). Crystal Structures. Vol. III, 2nd ed. New York: Interscience.

The Crystal and Molecular Structure of Bis-(N-benzyldiphenylphosphinic amide)-dichlorocobalt(II)

BY R. M. ROY* AND J. W. JEFFERY

Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E7HX, England

The crystal and molecular structure of bis-(N-benzyldiphenylphosphinic amide)dichlorocobalt(II), $[(C_6H_5)_2PONHCH_2C_6H_5]_2CoCl_2$, has been elucidated by single-crystal X-ray diffraction. The crystals are monoclinic, space group Cc or $C2/c$, with unit-cell dimensions $a=12.767$ (4), $b=14.038$ (3), $c=20.811$ (6) Å, $\beta=101.7$ (1)°, and $Z=4$. The conventional discrepancy index is 0.119 for 1669 visually estimated reflexions. The molecule contains a cobalt atom which is bonded in almost regular tetrahedral directions to two chlorine atoms and two oxygen atoms, one each from the N-benzyldiphenylphosphinic amide ligands.

Introduction

The reflux reaction between p,p-diphenyl-N-benzyl-phosphinothioic amide and a large excess of cyclohexene (Ibrahim, 1968) gives a number of products, one of which, a viscous colourless liquid, can be extracted by thin layer chromatography from the residue obtained by distilling off the excess cyclohexene. Treatment of an ethereal solution of this liquid with anhydrous cobalt chloride in alcohol, followed by evaporation of the solvents and extraction of the residue with anhydrous ether, yields a blue solution from which deep blue crystals of a cobalt complex can be obtained. On the basis of the above method of preparation and the partial chemical analysis figures for batch (1) shown in Table 1, a chemical formula of $[(C_6H_5)_2PNHCH_2C_6H_5]CoCl$ was assigned to the complex. An approximate molecular weight, measured in 1,2-dichloroethane using a vapour pressure osmometer, was found to be 668; the above formula requires a molecular weight of 385. It was suggested that the

molecule could be a dimer (molecular weight = 770) containing two cobalt atoms with the additional possibility of chlorine bridging between these two atoms.

The crystal structure analysis of this cobalt complex was undertaken in order to determine the atomic arrangement and the molecular geometry. In the course of this investigation the original formula was found to be incorrect and the correct formula, $[(C_6H_5)_2PONHCH_2C_6H_5]_2CoCl_2$, obtained. The corrected formula was checked by repreparing the complex by the reaction of pure crystalline $(C_6H_5)_2PONH.CH_2.C_6H_5$ directly with anhydrous cobalt chloride; the blue crystals obtained (m.p. 164·5–165·5°C, Thakur, 1970) were shown to have identical X-ray diffraction spectra to the initial batch. An analysis of these crystals [Table 1, batch (2)] confirmed the new formula.

Experimental

Crystal data

All crystallographic observations were made at 20 ± 5°C and are recorded according to the recom-

---

* Present address: Department of Physics, C.M. College, Darbanga, India.