Potassium Tin(II) Sulphate and Related Tin Apatites: Mössbauer and *X*-Ray Studies

By **R. Alan Howie, Wolf Moser,* Richard G. Starks,** and **Frank W. D. Woodhams,** Departments of Chemistry and Natural Philosophy, University of Aberdeen, Aberdeen AB9 2UE
William Parker, Department of Physics, University of Exeter, Exeter EX4 4QD

Isolation of solid phases containing potassium, tin(II), and sulphate has been attempted from aqueous K–Sn^{II}–SO$_4$ and K–Sn^{II}–SO$_4$–X (X = F, Cl, Br, I, or NO$_3$) systems. The only phases isolated were potassium tin(II) sulphate of composition ranging from $K_2Sn(SO_4)_2$ to $K_2Sn_2(SO_4)_3$, and potassium tin(II) chloride- and bromide-sulphates, $K_3Sn_2(SO_4)_3X$. Single-crystal *X*-ray studies show the former to be essentially similar to the well known $K_2Pb(SO_4)_2$, except for a marked tendency to form solid solutions with the simple Sn^{II} sulphate. The chloro- and bromo-compounds are shown to be closely similar to chlorapatites, with SO_4^{2-} replacing PO_4^{3-}. Mössbauer spectra of these phases are discussed in relation to the proposed structures.

THE chemistry of the alkali-metal tin(II) trihalides $MSn^{II}X_3$ is well established,[1] although new features are still being uncovered.[2] Related phases $MSn^{II}XY$ containing both X and a bi-valent group Y would be of some interest, but so far only one compound, potassium tin(II) sulphate thiocyanate $KSn^{II}SO_4NCS$, has been examined in any detail.[3] More information is available on phases $M_2Sn^{II}Y_2$,[4-6] but the findings partly contradict each other. The present work corrects and extends the date for M = K and Y = SO$_4$, using tin(II) sulphate [7] as a convenient and proven starting material.

EXPERIMENTAL

Preparations.—The crystalline compounds were prepared by mixing an acid solution of tin(II) sulphate, usually 33% w/v in 0·5M-deaerated sulphuric acid, with the appropriate volume of a saturated solution of the potassium salt in deaerated distilled water so that the weights of tin(II) sulphate and potassium salt were (in a typical series of experiments) in the ratios 1 : 1, 1 : 2, or 1 : 4. The mixed solutions were set aside at 5 °C overnight, after which the crystalline precipitate was filtered off under vacuum, washed with a little cold deaerated distilled water, and

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[5] J. C. G. de Marignac, *Ann. Mines* (5), 1857, **22**, 1.

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dried *in vacuo* over potassium hydroxide. Tin(II) sulphate was prepared according to Donaldson and Moser.[7] Potassium fluoride (dihydrate), chloride, bromide, iodide, nitrate, and sulphate were of B.D.H. laboratory grade.

Analyses.—Tin(II) was determined by titration with standard iodate solution. Samples were dissolved in deaerated 8M-HCl; oxygen-free nitrogen was passed through the solution as the sample dissolved and for the duration of the titration. Total tin was determined by reduction to tin metal with aluminium, heating to dissolve the tin metal, and iodate determination of the resulting tin(II). The iodate solution was standardised against resublimed tin(II) acetate.[8] Potassium was determined by flame photometry. Tin(II) sulphate was added to the standard solution of potassium, in comparable amounts to those encountered in the samples, to eliminate interference by tin(II) and sulphate.

Halide was determined potentiometrically with silver(I) nitrate using silver wire as indicator electrode and a platinum wire immersed in the titrant as reference electrode.[9] Nitrate was determined by a standard Devarda's alloy reduction.[10] Sulphate was determined both volumetrically, with barium perchlorate and Sulphonazo-III indicator (B.D.H.)[11] and by a slight modification of the usual gravimetric method, in which the increase in solubility of barium sulphate, in the presence of sufficient hydrochloric acid to prevent hydrolysis and precipitation of tin(II), was allowed for by determining the acid concentration of the solution after filtration and correcting the observed weight of precipitate according to the table in ref. 10 (p. 322).

Instrumental Techniques.—*X*-Ray powder diffraction data were obtained with Cu-K_α filtered radiation and a Philips powder diffractometer. *X*-Ray structure calculations were performed both with programs written by Daly *et al.*,[12] and also with programs written by F. R. Ahmed *et al.* of the National Research Council of Canada, which were adapted by Mr. J. S. Knowles of the Department of Computing, University of Aberdeen.

I.r. measurements were made on a Perkin-Elmer 237 grating spectrometer. The samples were presented as Nujol mulls and were examined over the range 4000—625 cm^{-1}. Mössbauer spectra were obtained using a conventional constant-acceleration electromechanical drive system and an Intertechnique SA40 B 400-channel multichannel analyser operated in multiscaler mode. Details of the drive system have been reported elsewhere.[13] Velocity calibration was carried out using the ^{57}Fe Mössbauer effect in natural iron. Absorbers were cooled to 80 K with a standard cold-finger cryostat. The source, kept at room temperature, was ^{119}Sn (5 mCi) in $BaSnO_3$, supplied by the Radiochemical Centre, Amersham.

Characterisation of Products from each System.—*Tin*(II) *sulphate and* $KF,2H_2O$. The only products encountered over a range of concentration of both components were identified by *X*-ray powder diffraction as KSn_2F_5[14] and potassium tin(II) sulphate.

Tin(II) *sulphate and* KCl. The only phase encountered over the concentration range studied proved to be $K_3Sn_2(SO_4)_3Cl$ as colourless prisms [Found: Cl, 5·2; K, 17·2; Sn(total), 34·6; Sn^{II}, 33·6; SO_4, 43·2. $K_3Sn_2(SO_4)_3Cl$ requires Cl, 5·2; K, 17·3; Sn(total), 35·0; Sn^{II}, 35·0; SO_4, 42·5%]. M = 678·4, Hexagonal, a = 10·23 (2), c = 7·56 (2) Å (refined by comparison with indexed powder photographs), U = 684·3 Å^3, D_m = 3·30 g cm^{-3} (displacement of benzene), Z = 2, D_c = 3·29 g cm^{-3}, space group $P6_3$ (No. 173) or $P6_3/m$ (No. 176), filtered Cu-K_α radiation, single-crystal oscillation, rotation, and Weissenberg photographs about '*c*' and '*a*'. Indexed powder-diffraction data are given in Table 1.

TABLE 1

X-Ray powder diffraction data for $K_3Sn_2(SO_4)_3X$

X = Cl			X = Br			Index of reflection
$d_{obs.}$ Å	$d_{calc.}$ Å	I/I_m %	$d_{obs.}$ Å	$d_{calc.}$ Å	I/I_m %	
			5·82	5·81	8	101
5·15	5·12	3				110
4·44	4·43	8				200
4·25	4·24	6				111
3·80	3·78	24	3·85	3·84	26	002
3·35	3·35	7	3·37	3·37	10	210
3·06	3·06	100	3·09	3·08	100	211
2·95	2·95	33	2·98	2·97	51	300
2·51	2·51	10	2·52	2·53	15	212
2·46	2·46	4	2·47	2·47	8	310
2·33	2·34	6	2·35	2·35	6	311
	2·33			2·35		302
2·26	2·26	9				113
			2·23	2·23	3	400
2·12	2·12	19	2·14	2·14	25	222
2·06	2·06	9				312
2·01	2·01	21	2·03	2·04	15	213
1·957	1·962	16	1·974	1·974	15	321
1·930	1·933	14	1·947	1·943	9	410
1·907	1·911	7				402
1·889	1·890	4	1·918	1·919	8	004
			1·803	1·803	8	322
			1·779	1·781	8	500
1·722	1·725	4	1·732	1·735	8	501
1·692	1·705	1	1·712	1·714	5	330
1·659	1·660	4				331
1·593	1·592	8				304
			1·599	1·596	9	323
1·556	1·557	11	1·566	1·566	13	511

Tin(II) *sulphate and* KBr. The phase $K_3Sn_2(SO_4)_3Br$ is rather more soluble than the corresponding chloride and the solid was only obtained from more concentrated solutions as colourless prisms [Found: Br, 11·4; K, 16·0; Sn(total), 32·3; Sn^{II}, 31·4; SO_4, 39·8. $K_3Sn_2(SO_4)_3Br$ requires Br, 11·1; K, 16·2; Sn(total), 32·8; Sn^{II}, 32·8; SO_4, 39·9%]. M = 722·8, Hexagonal, a = 10·28(2), c = 7·67(2) Å (refined by comparison with powder-diffraction data), U = 701·9 Å^3, D_m = 3·39 g cm^{-3} (by displacement of benzene), Z = 2, D_c = 3·42 g cm^{-3}, space group $P6_3$ (No. 173) or $P6_3/m$ (No. 176), isostructural with $K_3Sn_2(SO_4)_3Cl$, filtered Cu-K_α radiation, single-crystal rotation, oscillation, and Weissenberg photographs about '*a*' and '*c*'. Indexed powder-diffraction data are given in Table 1.

Tin(II) *and Sulphate and* KI. Reactions between these components produced only mixtures of SnI_2 (bright red needles), SnI_2,H_2O (orange needles), $KSnI_3$ (bright yellow needles), and KI from all the solutions studied [Found: I,

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[9] B. R. Chamberlain, Ph.D. Thesis, University of Aberdeen, 1965.

[10] I. M. Kolthoff and C. B. Sandell, 'Textbook of Inorganic Analysis,' 3rd edn., Macmillan, New York, 1959, p. 536.

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[13] P. E. Clark, A. W. Nichol, and J. S. Carlow, *J. Sci. Instr.*, 1967, **44**, 1001.

[14] J. D. Donaldson and J. D. O'Donoghue, *J. Chem. Soc.*, 1964, 271.

68·8; Sn^{II}, 30·3. SnI_2 requires I, 68·1; Sn^{II}, 31·9%. Powder-diffraction pattern identical with that of pure SnI_2 (from Sn + I_2): 4·395vw; 3·620mw; 3·540mw; 3·400vw; *3·370vw;* 3·330mw; 3·274vvs; 3·170vs; 3·090mw; 3·023vw; 2·822vw; 2·745vw; 2·502vw; 2·485vw; 2·292mw; 2·199ms; 2·164mw; 2·159w; and 2·137w. Found: H_2O, 4·5; I, 65·3; Sn^{II}, 30·3. SnI_2,H_2O requires H_2O, 4·6; I, 64·9; Sn^{II}, 30·5%. Powder diffraction pattern: 3·49vs; 3·41vvs; 3·10w; 2·75vw; 2·60w; 2·33m; 2·27m; 1·997w; and 1·808ms. The *X*-ray powder-diffraction pattern of the dehydration product was identical with that of SnI_2 given above. Powder diffraction pattern for $KSnI_3$: 3·77vw; 3·53mw; 3·34vw; 3·22vvs; 2·99vw; 2·92mw; 2·64vw; 2·28vw; and 2·06vw].

Tin(II) *sulphate and* KNO_3. The only crystalline product encountered proved to have an identical powder pattern to that obtained from mixtures of potassium sulphate and tin(II) sulphate. Nitrate was found to be present in small, but irreproducible amounts, stemming from either a slight contamination with potassium nitrate or from a negligible extent of solid solution.

Tin(II) *sulphate and* K_2SO_4. The (homogeneous!) products could all be accounted for by the formula $K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$, where x ranged from 0·0 to 0·42 [Found: Sn(total), 41·6; Sn^{II}, 41·4; SO_4, 47·4. $K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$ (x = 0·42) requires Sn(total), 41·5; Sn^{II}, 41·5; SO_4, 47·3%. Colourless hexagonal crystals showing parallel extinction, M = 406·0, Rhombohedral, a_H = 5·53(1), c_H = 21·30(3) (refined by comparison with powder-diffraction data), a_R = 7·78(1) Å, α_R = 41·5(1)°, U_H = 64·1 Å^3, D_m = 3·69 cm^{-3} (by displacement of benzene), Z = 3 (1 molecule per rhombohedral cell), D_c = 3·59 g cm^{-3}, space group *R*32 (No. 155), *R*3*m* (No. 160), or $R\bar{3}m$ (No. 166), single-crystal oscillation, rotation, and Weissenberg (l = 0—3) photographs about c. Indexed powder-diffraction data are given in Table 2.

TABLE 2

X-Ray powder diffraction data for $K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$ (x = 0·42)

$\frac{d_{obs.}}{Å}$	$\frac{d_{calc.}}{Å}$	$\frac{I/I_m}{\%}$	Index of reflection *
4·70	4·68	19	101
4·39	4·38	30	012
3·19	3·18	100	015
2·77	2·77	65	110
2·58	2·58	31	113
2·19	2·18	32	116
2·09	2·09	16	205
1·949	1·945	15	1,0,10
1·801	1·808	15	211
1·784	1·782	15	208
1·669	1·669	10	125

* Rhombohedral cell referred to non-primitive hexagonal axes.

RESULTS AND DISCUSSION

The System K–Sn^{II}–SO_4–X (X = F, Cl, Br, I, and NO_3).—In all cases synthesis was attempted by adding slightly acid (sulphuric acid) solutions of tin(II) sulphate [to prevent hydrolysis of tin(II)] to solutions of the appropriate potassium salt. Only the chloride and bromide systems yielded crystalline products containing all four ions in quantity, and only one phase was encountered in each case. Since analytical data indicated the same formula and single-crystal *X*-ray diffraction data showed the two phases to be isostructural, they are discussed together below. A crystalline product from tin(II) sulphate and potassium nitrate proved to be identical with that from $SnSO_4$–K_2SO_4. The same product, and also some KSn_2F_5, was obtained from the fluoride system. Crystalline products of the iodide system were characterised as potassium tri-iodostannate(II) $KSnI_3$,[15] tin(II) iodide,[16] and tin(II) iodide hydrate SnI_2,H_2O, to be described elsewhere.

Analytical data for the chloride and bromide compounds support the formula $K_3Sn_2(SO_4)_3X$ (X = Cl or Br). *X*-Ray crystallographic unit-cell dimensions [refined from *X*-ray powder-diffraction data (Table 1)] and density determinations confirm the analytical formula, and show that the hexagonal unit cell contains two formula units. Marignac[5] described a salt [prepared by the addition of tin(II) chloride solution to potassium sulphate solution] whose morphology appears to be identical with that of the chloride described here. His analytical data differ from ours only in the very low result for chloride, and this can be traced to the method used. The low chloride result prompted Marignac to formulate his compound as $K_8Sn_4(SO_4)_8,SnCl_2$, rather than $K_6Sn_3(SO_4)_6,SnCl_2$ which is the content of our observed crystallographic unit cell. In fact, the second formula fits Marignac's tin analysis results rather better than the first.

X-*Ray crystallography*. The unit-cell contents expressed in the form $M_{10}(SO_4)_6Y_2$, the unit-cell dimensions, and the symmetry are very similar to those encountered in compounds with the apatite structure.[17,18] Definite correlation with this type of structure was established by comparison of a single-crystal rotation photograph (rotation about the hexagonal axis) of the chloro-compound with a similar photograph of the mineral Wilkeite.[19] The distribution of intensities in the two photographs was strikingly similar.

The crystal chemistry of the apatite structure has been reviewed by Cockbain.[18] The general formula $M_{10}(XO_4)_6Y_2$ is subject to considerable variation. In the prototype apatite, cations M are bivalent, anions Y univalent, and X is an element of Group V. The element X may be substituted by those of Groups IV and VI equally, *e.g.* two P by Si and S, without affecting the total charge. Alternatively, substitution of X by elements of other Groups may change the total anion charge, *e.g.* complete substitution of X by Group IV elements only will change the anion charge from −20 to

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[15] P. Freundler and Y. Laurent, *Bull. Soc. chim. France*, 1925, **37**, 1133.

[16] W. Moser and I. C. Trevena, *Chem. Comm.*, 1969, 25; R. A. Howie, W. Moser, and I. C. Trevena, *Acta Cryst.*, 1972, **B28**, 2965.

[17] R. W. G. Wyckoff, 'Crystal Structures,' 2nd edn., Interscience, London, 1965, vol. III, pp. 228—234, 242—245, 168—171.

[18] A. G. Cockbain, *Mineralog. Mag.*, 1967, **36**, 654.

[19] L. Bragg and G. F. Claringbul (ed.), 'The Crystalline State,' Bell, London, 1965, vol. IV, p. 143; Wilkeite is $Ca_5(Si,P,S)_3O_{12}(O,OH,F)$.

—26. In this case, to balance charges, six of the bivalent cations are replaced by trivalent cations. Similarly, anions Y may be substituted or even omitted entirely. In the apatite structure, space group $P6_3/m$, the ten cation sites M divide into two groups, six ' h ' and four ' f '. Nevertheless, the alkaline earth–rare earth silicate and germanate apatites are reported to have their six M^{3+} and four M^{2+} ions distributed randomly over all ten sites.[20]

In the present compounds X is sulphur (total anion charge —14) and six of the bivalent cations M have been replaced by potassium ions. As tin(II) sulphate apatites the compounds raise several points of interest. Only one other pure sulphate apatite has been reported, *viz.* $Na_6Ca_4(SO_4)_6F_2$,[21] which is also listed in refs. 17 and 18. As far as we have been able to ascertain, no full structure determination of this material has been published. However, there is evidence that the distribution of sodium and calcium over the two types of site is essentially ordered. For the present tin(II) sulphate apatites, the crystal chemistry of tin(II) [1,22] would suggest that tin(II) and potassium are even less likely to replace one another fully to produce perfect random occupation of the M sites, *i.e.* with the atom centres in exactly the same positions.

A set of *X*-ray diffraction intensity data was collected for the layers *hk*0—5, using a Hilger and Watts Y-190 linear diffractometer with Mo-K_α radiation and a zirconia filter. The Patterson (vector) map, calculated on the basis of these intensities (corrected in the usual way for Lorentz and polarisation effects), was used to find the distribution of tin and potassium over the available ' M ' sites. If the complex had indeed belonged to the space group $P6_3/m$, the occupancy of the 4f sites should have been clearly represented by four peaks of identical intensity in the vector map at 1/3, 2/3, 0; 1/3, 2/3, 1/2; 2/3, 1/3,0; and 2/3, 1/3, 1/2. (The size of these peaks relative to that of the origin would have depended on whether the 4f positions were occupied exclusively by tin, or at random by tin and potassium.) Instead, we observed very large peaks at 1/3, 2/3, 1/2 and 2/3, 1/3, 1/2, and much smaller peaks (about one third the size) at 1/3, 2/3, 0 and 2/3, 1/3, 0. This result indicates that tin and potassium alternate regularly in the direction of ' *c* ' in the 1/3, 2/3 and 2/3, 1/3 lattice rows, and that the two rows in the unit cell are related by a two-fold screw axis. The remaining peaks of the vector map of the tin–potassium compound are consistent with the apatite structure, the remaining two tin and four potassium atoms seemingly occupying the 6h positions at random. The distribution of tin and potassium over the 4f sites is not consistent with the presence of a mirror plane, and the compounds must therefore be allocated to space group $P6_3$ rather than $P6_3/m$. The atom co-ordinates in $P6_3$, compared with those of the chlorapatite structure ($P6_3/m$),[17] would be approximately as follows:

Sn(1) in (2b) 1/3, 2/3, z; 2/3, 1/3, $1/2 + z$ with $z = 0{\cdot}00$
K(1) in (2b) 1/3, 2/3, z; 2/3, 1/3, $1/2 + z$ with $z = 0{\cdot}50$

[equivalent to the positions of Ca(1) in (4f) of chlorapatite]

$$\left.\begin{array}{r} 2/3\ \mathrm{Sn(2)} \\ 1/3\ \mathrm{K(2)} \end{array}\right\} \text{ in (6c) with } x = 0{\cdot}25,\ y = 0{\cdot}00, \text{ and } z = 0{\cdot}25$$

[equivalent to the positions of Ca(2) in (6h) of chlorapatite]

$$\left.\begin{array}{r} \mathrm{S\ in\ (6c)} \\ \mathrm{O\ in\ (6c)} \\ \mathrm{Cl\ in\ (2a)} \end{array}\right\} \begin{array}{l} \text{with co-ordinates} \\ \text{equivalent to} \\ \text{those of} \end{array} \left\{\begin{array}{l} \mathrm{P\ in\ (6h)} \\ \mathrm{O\ in\ (12i)} \\ \mathrm{Cl\ in\ (2b)} \end{array}\right\} \text{ of chlorapatite}$$

The random distribution of the Sn(2)–K(2) atoms in 6c follows from the overall six-fold symmetry of the structure. The alternation of Sn(1)–K(1) in 2b also avoids the placing of pairs of tin atoms only *c*/2 (3·79 Å) apart. This distance would be similar to the Sn–Sn distance in blue-black SnO (3·70 Å),[23] whose colour and other properties suggestive of Sn–Sn bonding are however entirely unlike those of the present chloride and bromide sulphates. Structure-factor calculations on the above model give an *R* value of 30%. Although this is disappointingly high, it suggests that the general features of the structure are correct. Electron-density and difference maps prepared at this stage show all the atoms very close to the expected positions with the expected electron densities. The most striking feature of the difference map is large positive lobes in directions plus and minus ' *c* ' relative to the M cation positions. While this may be partially due to genuine anisotropic thermal vibrations, it is more probable that it arises from splitting of each of the cation positions, when occupied by tin, into two equivalent positions symmetrically displaced from the apparent atomic centre along the positive and negative directions of ' *c* '. In this way the tin atoms would achieve a distorted environment consistent with the i.r. spectra of these compounds which suggest co-ordination of tin by sulphate groups (Table 3).

TABLE 3

I.r. absorption maxima (cm^{-1}) (sulphate only) of potassium tin(II) sulphates and tin(II) sulphate

$K_3Sn_2(SO_4)_3Cl$	1184	1117	1000	930
$K_3Sn_2(SO_4)_3Br$	1185	1120	1000	930
$K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$	1170	1110	1025	940
$SnSO_4$	1170		1035	972

The System K–Sn^{II}–SO_4.—Marignac [5] and Rammelsberg [6] described potassium tin(II) sulphate compounds of identical appearance but obtained different analytical results. Both proposed formulae between $K_2Sn(SO_4)_2$ and $K_2Sn_2(SO_4)_3$. Blaize *et al.*[4] found $K_2Sn(SO_4)_2$, but noted that their tin analyses were consistently low. Our own early analyses of the same phase were equally variable and inconclusive. Detailed investigation showed that the composition is a function of the tin(II) concentration in the solution before precipitation. In terms of the general formula $K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$, Table 4 gives values of x for the various suggested

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[21] R. Klement, *Naturwiss.*, 1939, **27**, 568; P. Dihn and R. Klement, *Z. Elektrochem.*, 1942, **48**, 331.

[22] R. E. Rundle and D. E. Olson, *Inorg. Chem.*, 1964, **3**, 596.

[23] W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392.

formulae and for precipitates obtained from solutions of various concentrations. It can be seen that x reaches a limiting value independent of the Sn : K mole ratio. In contrast to Blaize *et al.*,[4] we did not find compositions poorer in tin than that of $K_2Sn(SO_4)_2$, but our experiments, unlike theirs, precluded partial hydrolysis.

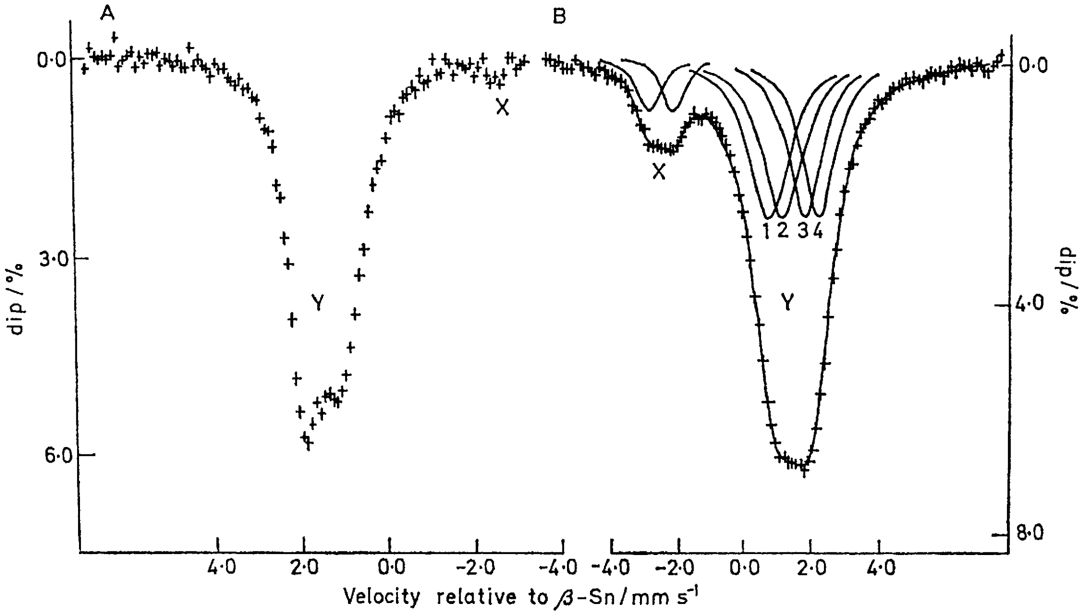
TABLE 4

Composition of potassium tin(II) sulphates $K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$ deposited from solutions of various tin(II) and potassium concentrations

$[SnSO_4]$ / mol l^{-1}	$[K_2SO_4]$ / mol l^{-1}	$[Sn^{2+}]/[K^+]$ in solution	x	Ideal stoicheiometric composition
0·12	0·59	0·10	0·00	$K_2Sn(SO_4)_2$
0·19	0·48	0·20	0·16	
			0·20	$K_4Sn_3(SO_4)_5$
0·25	0·30	0·41	0·29	
			0·33	$K_2Sn_2(SO_4)_3$
0·36	0·45	0·40	0·42	
0·36	0·89	0·20	0·42	
0·36	1·77	0·10	0·42	
			0·50	$K_2Sn_3(SO_4)_4$
			1·00	$SnSO_4$

X-*Ray crystallography*. X-Ray powder-diffraction patterns of products with different values of x were found to be very similar (Table 2), suggesting a series of solid solutions. The patterns also closely resembled that of $K_2Pb(SO_4)_2$.[24] A crystal from a sample with $x = 0{\cdot}42$ was examined by single-crystal techniques and the symmetry and unit cell determined. The cell dimensions were found to be only slightly larger than those deduced by Blaize *et al.*[4] from the powder pattern of a sample with $x = 0$, again indicating solid solution. All the evidence points to the conclusion that the characteristic phase isolated from the system K–Sn^{II}–SO$_4$ consists of a range of solid solutions of $SnSO_4$ in $K_2Sn(SO_4)_2$. The space group of these solutions could be *R*32, *R*3*m*, or *R*$\bar{3}$*m*. While a close structural relation with $K_2Pb(SO_4)_2$ (palmierite, *R*$\bar{3}$*m*)[17] is indicated, the identity of the two structure types cannot be regarded as established.

Mössbauer Spectroscopy.—Mössbauer spectra of potassium tin(II) sulphate and the chloride and bromide sulphates were all very similar in appearance. Typical spectra, those of $K_3Sn_2(SO_4)_3Br$, are shown in the Figure. The small resonance absorption dip X arises from an SnO_2 impurity in the sample whilst the major dip Y is due to Sn^{II}. This resonance dip is asymmetric at room temperature; at 80 K, although the asymmetry has disappeared, the dip is still clearly non-Lorentzian in shape indicating that it must be composed of two or more overlapping lines. Such a situation would arise if there were Sn atoms in (*a*) a single site with quadrupole splitting, (*b*) two (or more) sites having different isomer shifts but zero quadrupole splitting, or (*c*) two (or more) sites with different isomer shifts and quadrupole splittings giving rise to a number of overlapping lines. These three possibilities were investigated, (*a*) and (*b*) by fitting the spectra to a two-line model, and (*c*), assuming two sites, to a four-line model.



Mössbauer spectra of $K_3Sn_2(SO_4)_3Br$ at room temperature (A) and 80 K (B). The small dip X is due to SnO_2 impurity. The component lines in the tin(II) portion of spectrum B are numbered 1—4 in order of increasing velocity

Two-line model. Spectra were computer-fitted to two single Lorentzian lines by a standard iterative least-squares technique. The program minimised *F*, the sum of the squares of the deviations of the channel counts from the best-fit model divided by the variance at a single channel, and gave the best estimate of the line parameters together with their standard deviations.

[24] H. Schwarz, *Z. anorg. Chem.*, 1966, **344**, 54.

No constraints were placed on the line parameters. It was found, however, that these fits were not statistically acceptable on the basis of a χ^2 test. In any case, there are also good physical grounds for rejecting this model. Model (*a*) (single site with quadrupole splitting) is unrealistic, as the *X*-ray studies show that the tin atoms occupy two non-equivalent crystallographic sites. This model would only be realistic if the two sites had essentially the same isomer shifts and quadrupole splittings, but structural evidence suggests that this is improbable.

Model (*b*) (two sites with different isomer shifts but zero quadrupole splittings) is at least reasonable on the crystallographic evidence (of two non-equivalent sites) but meets with the following objections.

TABLE 5

^{119}Sn Mössbauer parameters of potassium tin(II) sulphates (fitted to *four-line* model [a])

Compound	T/K	Paired lines [b]	Site [c]	Isomer shift [d] mm s^{-1}	Quadrupole splitting mm s^{-1}	Area ratio site B : site A
$K_3Sn_2(SO_4)_3Cl$	80	1, 3	A	1·25(1)	1·17(2)	1·00(4)
		2, 4	B	1·64(1)	1·18(2)	
$K_3Sn_2(SO_4)_3Br$	Room temp.	1, 3	A	1·26(2)	0·92(4)	1·00 [e]
		2, 4	B	1·45(2)	0·78(4)	
	80	1, 3	A	1·23(3)	1·04(5)	1·00(4)
		2, 4	B	1·48(3)	1·03(5)	
$K_{(2-2x)}Sn_{(1+x)}(SO_4)_2$ ($x = 0{\cdot}42$)	Room temp.	2, 3	A	1·46(4)	0·91(8)	1·00(8)
		1, 4	B	1·24(3)	1·58(5)	
	80	2, 3	A	1·21(2)	0·88(4)	0·42(6)
		1, 4	B	1·12(2)	2·09(4)	

[a] Values in parentheses are standard deviations associated with the least significant digit of each entry. [b] See the Figure. [c] Site A is that in which tin is co-ordinated to the sulphate group only (in the chloro- and bromo-compounds) or that fully occupied by tin [in potassium tin(II) sulphate]. [d] Relative to β-Sn at room temperature. [e] Areas constrained to be equal in the fitting process.

(i) While for the chloro- and bromo-compounds the small peak-area differences at room temperature (and their disappearance at 80 K) could be attributed to slight differences in the recoil-free fractions at the two sites, the potassium tin(II) sulphate peak-area ratios obtained from this model (0·7 at room temperature and 1·05 at 80 K, for tin sites in a ratio of 1 : 2·4) would require very different *f* factors at the two sites. This seems unlikely, especially at 80 K, since the oxidation state of tin is the same in each site, and in each case the co-ordination is to sulphate.

(ii) The changes in the isomer shifts with temperature are not those expected from the second-order Doppler effect, *e.g.* in the chloro-compound the isomer shift of the lower-velocity line falls by 0·3 mm s^{-1}, whereas the second-order Doppler effect predicts an increase of the order of 0·08 mm s^{-1} between room temperature and 80 K.

(iii) Those tin sites in the chloro- and bromo-compounds which are co-ordinated only to sulphate groups, and the more regular tin sites in potassium tin(II) sulphate, appear from the proposed structure and i.r. spectroscopic data to be similar to the tin site in tin(II) sulphate. Thus it might be expected that one of the lines of each spectrum would have an isomer shift close to that of tin(II) sulphate,[25,26] namely 1·2 mm s^{-1} relative to β-Sn. This is not observed.

(iv) Interpretation in terms of model (*b*) also runs counter to the results for most other tin(II) compounds,[1] where quadrupole splittings are usually observed.

We conclude then that the two-line models are not capable of explaining our Mössbauer data.

Four-line model. Spectra were then fitted to a two-site model, each site giving rise to a two-line quadrupole spectrum. It was found necessary to constrain the widths and areas of the component lines of each quadrupole doublet to be equal, in order that the fitting program should converge with sensible results. The results are given in Table 5. The problem remains of assigning the lines in pairs to specific absorptions, and in turn assigning the absorptions to particular tin sites in the proposed structures. We have made the assignment as follows. As stated earlier, we would expect one of the absorptions of all three spectra to be reasonably similar to that of tin(II) sulphate. In view of this we have made the assignment (see the Figure) that lines **1**—**3** and **2**—**4** are pairs for the chloride and bromide sulphates, and **1**—**4** and **2**—**3** for potassium tin(II) sulphate. On this assignment the isomer shift of the tin atoms co-ordinated both to the halide and sulphate groups decreases on going from the chloro- to the bromo-compound (*cf.* $SnBr_2$ and $SnCl_2$[1]). In the case of potassium tin(II) sulphate, the smaller quadrupole splitting then corresponds to the more regular tin site and the larger quadrupole splitting to the randomly occupied sites, which are normally occupied by potassium. If the structure of potassium tin(II) sulphate is indeed like that of $K_2Pb(SO_4)_2$, then the potassium sites are of lower symmetry than the lead sites. Hence tin atoms in potassium sites would be expected to show a greater quadrupole splitting than those in the regularly occupied (lead) sites. Assuming that the recoil-free fractions of

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[25] M. Cordey-Hayes, *J. Inorg. Nuclear Chem.*, 1964, **26**, 915.

[26] J. D. Donaldson and B. J. Senior, *J. Inorg. Nuclear Chem.*, 1969, **31**, 881.

the two sites are equal, the 80 K potassium tin(II) sulphate fit gives the relative number of tin atoms in the two sites as 0·42 : 1, in excellent agreement with the chemical analysis figure of 0·42! Nevertheless, the above interpretation must be regarded as tentative, in view of the fact that peaks from the two sites are virtually unresolved from each other.

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