

Novel Tin(II) Sites in X-Ray Crystal Structures of the Tin(II) Halide Sulphates $K_3Sn_2(SO_4)_3X$ ($X = Br$ or Cl) *

John D. Donaldson and Susan M. Grimes

Department of Chemistry, The City University, Northampton Square, London EC1V 0HB

The crystal structures of $K_3Sn_2(SO_4)_3X$ ($X = Br$ or Cl) have been determined by the heavy-atom method and refined by the full-matrix least-squares method to $R = 0.0564$ for the bromide and 0.0839 for the chloride. The crystals of both compounds are of the hexagonal space group $P6_3(C_6^6, \text{no. } 173)$ with $a = 10.256(2)$, $c = 7.582(4)$ Å, and $Z = 2$ for $K_3Sn_2(SO_4)_3Br$, and $a = 10.183(6)$, $c = 7.540(2)$ Å, and $Z = 2$ for $K_3Sn_2(SO_4)_3Cl$. The structures consist of three-dimensional networks of tin atoms and bridging sulphate groups with discrete potassium and halide ions in holes within the networks. The four tin atoms in the lattices are distributed together with two K^+ ions in a six-fold general position and have three oxygen atoms at unusually long distances of 2.47, 2.57, and 2.63 Å for the bromide and 2.45, 2.55, and 2.56 Å for the chloride. The shortest tin-halogen contacts are 2.97 Å for the chloride and 3.13 Å for the bromide. The halide ion is surrounded in a distorted octahedron by tin(II) or potassium atoms. The arrangement of tin atoms, taken along with ^{119}Sn Mössbauer data and the lengths of the Sn-O bonds in the structures, is consistent with cluster formation in which lone-pair electron density on the tin atoms is delocalised in cluster molecular orbitals.

A number of papers have been published on tin(II) systems in which there is more than one anion present. The majority of these papers describe ternary tin(II) halides.¹⁻⁵ Fewer papers have been concerned with oxyacid or carboxylic acid systems, although it has been shown that the replacement of one, but not both, acetate groups from tin(II) acetate to give compounds of the type $Sn(O_2CMe)(NO_3)$ ⁶ and $Sn(O_2CMe)(C_6H_6NO)$ ⁷ ($C_6H_6NO^- = \text{quinolin-8-olate}$) is possible. There are some reports of the preparation of mixed tin(II) halide-tin(II) oxyacid salts^{8,9} but the exact nature of the materials is not known. The most recent reports on such mixed-anion salts contain details of a potassium tin(II) sulphate thiocyanate¹⁰ and potassium tin(II) halide sulphates¹¹ of the type $K_3Sn_2(SO_4)_3X$ (where $X = Br$ or Cl). Moser and co-workers¹¹ reported the preparation of the halide sulphates from tin(II) sulphate and have described attempts to determine their crystal structures assuming that the chloro- and bromo-complexes had structures closely related to chloroapatites, with SO_4^{2-} replacing PO_4^{3-} . The structure-factor calculations on their predicted model, however, gave R values of about 0.30.

We now report the crystal structure determinations of $K_3Sn_2(SO_4)_3Br$ and $K_3Sn_2(SO_4)_3Cl$ using improved data sets collected for both complexes.

Experimental

The potassium tin(II) halide sulphates $K_3Sn_2(SO_4)_3X$ ($X = Br$ or Cl) were prepared from a mixture of potassium acetate and the appropriate tin(II) halide, in the molar ratio 5 : 1, heated in the minimum amount of sulphuric acid (2 mol dm^{-3}). Colourless acicular crystals formed when the solutions were cooled. The products were filtered off and dried in a desiccator over potassium hydroxide. Crystals from both halide systems were used to obtain cell data and were found to be isostructural.

Crystallography.—The crystal data were obtained from Weissenberg and single-crystal precession data, and refined on the basis of the powder diffraction pattern. Single-crystal intensity data were collected (212 reflections for each compound)

at Queen Mary College, London, using an Enraf-Nonius CAD4 four-circle diffractometer. The complexes are isostructural.

Crystal data. $K_3Sn_2(SO_4)_3Br$, $M = 722.3$, $a = 10.256(2)$, $c = 7.582(4)$ Å, $U = 690.67$ Å³, $Z = 2$, $D_c = 3.54$ g cm^{-3} , $F(000) = 672$, Mo- K_α radiation ($\lambda = 0.7093$ Å, $\mu = 75.23$ cm^{-1}).

$K_3Sn_2(SO_4)_3Cl$, $M = 678.2$, $a = 10.183(6)$, $c = 7.540(2)$ Å, $U = 677.17$ Å³, $Z = 2$, $D_c = 3.32$ g cm^{-3} , $F(000) = 636$, Mo- K_α radiation ($\lambda = 0.7093$ Å, $\mu = 49.61$ cm^{-1}).

On the basis of systematic absences, the crystals were assigned to the hexagonal space group $P6_3$ or its centrosymmetric alternative $P6_3/m$ (nos. 173 and 176 respectively). The structures were solved using the non-centrosymmetric space-group positions ($P6_3$), by the use of heavy-atom Patterson and Fourier methods.

Initial refinements by full-matrix least-squares methods were carried out assuming all atoms to be vibrating isotropically and were continued with the introduction of anisotropic thermal parameters for all atoms. Most of the calculations were carried out on a CDC 7600 computer at the University of London Computer Centre using the programs SHELX 76¹² and BONDLA from X-RAY 72.¹³ Stereographic projections of the unit cell were obtained using PLUTO.¹⁴

Structure refinement. The atomic positions were located as a result of heavy-atom Patterson and Fourier syntheses. The vector peaks in the Patterson synthesis can only be fully explained if the Sn atoms are placed in a site at $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ with an occupancy of four-sixths. Attempts to place Sn atoms in two sets of two-fold positions failed.

A three-dimensional Fourier difference map for the bromide, with phasing based on the refined tin positions, located Br at the two-fold site based on 0,0,0, and K atoms on the two-fold sites based on $\frac{2}{3}, \frac{2}{3}, 0$, and $\frac{2}{3}, \frac{2}{3}, \frac{1}{2}$. A Fourier synthesis based on refinement of the Sn, Br, and K positions gave co-ordinates which were assigned to a sulphur atom position and three-dimensional Fourier difference syntheses located the oxygen atoms.

Refinement using four cycles of full-matrix least squares gave a residual of $R = 0.155$. During this refinement a peak on the Fourier difference synthesis map corresponding to about eight electrons appeared at $x = -0.2567$, $y = 0.0140$, $z = 0.2012$, a position 0.62 Å from tin. Since the tin atom lies in a six-fold general position with only two-thirds site

* Supplementary data available (No. SUP 23891, 10 pp.): structure factors and thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Fractional atomic co-ordinates, with estimated standard deviations in parentheses

$K_3Sn_2(SO_4)_3Br$					$K_3Sn_2(SO_4)_3Cl$				
Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	Occupancy	Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	Occupancy
Sn(1)	-0.255 5(6)	0.009 2(5)	0.284 8(14)	0.667 0	Sn(1)	-0.249 5(14)	0.006 0(13)	0.302 1(58)	0.667 0
S(1)	-0.589 4(4)	0.035 5(5)	0.260 1(17)	1.000 0	S(1)	-0.590 0(16)	0.035 2(19)	0.263 7(59)	1.000 0
O(1)	-0.425 5(13)	0.113 5(14)	0.253 4(57)	1.000 0	O(1)	-0.429 9(33)	0.112 6(42)	0.286 8(103)	1.000 0
O(2)	-0.651 2(19)	-0.124 7(16)	0.279 8(64)	1.000 0	O(2)	-0.649 8(46)	-0.124 2(36)	0.263 4(95)	1.000 0
O(3)	-0.648 6(30)	0.080 0(40)	0.416 2(29)	1.000 0	O(3)	-0.643 3(45)	0.085 3(59)	0.428 4(84)	1.000 0
O(4)	-0.621 1(33)	0.089 2(52)	0.096 8(37)	1.000 0	O(4)	-0.621 0(101)	0.093 9(65)	0.085 0(104)	1.000 0
Br(1)	0.000 0	0.000 0	0.500 0	0.333 3	Cl(1)	0.000 0	0.000 0	0.500 0	0.333 3
K(1)	0.666 7	0.333 3	0.008 1(19)	0.333 3	K(1)	0.666 7	0.333 3	0.013 0(64)	0.333 3
K(2)	0.666 7	0.333 3	0.516 0(19)	0.333 3	K(2)	0.666 7	0.333 3	0.518 3(69)	0.333 3
K(3)	-0.258 9(20)	0.021 3(21)	0.206 9(28)	0.333 3	K(3)	-0.244 8(57)	0.029 5(58)	0.222 3(83)	0.333 3

occupancy, it was considered that the remaining potassium must share the general position partially occupied by the tin atom and have an occupancy of one-third.

A refinement on all atoms, with anisotropic thermal parameters for tin and sulphur, gave a residual of 0.062. A final residual of 0.056 was obtained when 27 weak reflections for which $|F_o| > 2 |F_c|$ or $|F_c| > 2 |F_o|$ were omitted, and the thermal parameters for six atoms made anisotropic. The chloride was refined in a similar manner and a final residual of 0.084 was achieved. The final atomic positions for $K_3Sn_2(SO_4)_3Br$ and $K_3Sn_2(SO_4)_3Cl$ are given in Table 1.

Results and Discussion

The structure of $K_3Sn_2(SO_4)_3X$ ($X = Cl$ or Br) consists of a three-dimensional network of tin atoms and bridging sulphate groups, with discrete potassium and halide ions in holes within the tin-sulphate network. Figures 1 and 2 show projections of the network parallel to the *b* and *c* axes respectively.

The tin atoms occupy only four-sixths of the symmetry-related positions available for them in the network, and the remaining two-sixths are taken up by potassium atoms. The remaining potassium and halogen atoms lie in special positions and are discrete ions. Each sulphate group has an almost tetrahedral sulphur environment and forms bonds to the cations Sn/K3 through three of its oxygen atoms with each Sn/K3 atom being bonded to oxygen atoms from three different sulphate groups. The projection in the *c* direction shows the halide ions to be surrounded by six Sn/K3 atoms in an irregular octahedral arrangement. Because of the distribution of ligand atoms around the tin atoms each tin must have its non-bonding lone-pair orbital pointing approximately towards the halogen near the centre of the octahedron of Sn/K3 atoms.

There are three different potassium sites, two of which have K six-co-ordinated by oxygen atoms, with K-O distances of 2.69, 2.70, and 2.84 and 2.79, 2.87, and 3.06 Å for K(1) and K(2), respectively in the bromo-complex, and 2.77, 2.78, and 2.84 and 2.62, 2.76, and 2.97 Å for K(1) and K(2), respectively, in the chloro-complex. The environment of K(3), on the other hand, is unusual in that it is described in terms of partial occupation of the tin(II) site. Each Sn/K3 atom lies in a distorted environment with three unusually long bonds to oxygen atoms of three different sulphate groups, and two longer bonds to halogen atoms, with the shortest (Sn/K)-halogen contact being 2.97 Å for the chloride and 3.13 Å for the bromide. Details of bond distances and angles for the two structures are in Table 2.

In an attempt to assess the nature of the bonding in the tin(II) halide sulphates it is necessary to consider the range of

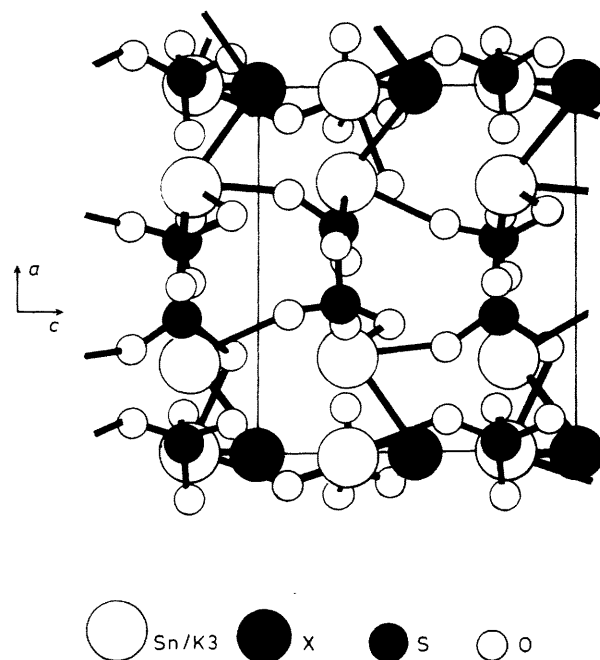


Figure 1. Structure of $K_3Sn_2(SO_4)_3X$ ($X = Cl$ or Br) viewed along the *b* direction. K(1) and K(2) are not included

tin-ligand distances and to compare them with the distances calculated from the appropriate covalent, ionic, and van der Waals radii. Details of the calculated distances are in Table 3 together with some typical tin-ligand distances for comparison. We have examined the extent of bonding between tin and its ligand atoms in a number of compounds.¹⁵ In general we have found that in all compounds with tin in trigonal-pyramidal sites with respect to the nearest-neighbour atoms the shortest distance within the pyramid is always close to or less than the sum of the covalent radii, while the longest distance in the pyramid is generally less than the sum of the ionic radii. This suggests that the bonding in tin(II) compounds is appreciably covalent especially in those compounds that have at least one very short tin-ligand bond. The shortest of the next-nearest-neighbour distances in these compounds are generally much longer than the sum of the appropriate ionic radii and approach the sum of the van der Waals radii. The typical distorted four-pyramidal site has four tin-ligand near-neighbour distances lying between the sums of the appropriate ionic and covalent radii. In most cases two of the bonds are short and approximate to the sum of the covalent

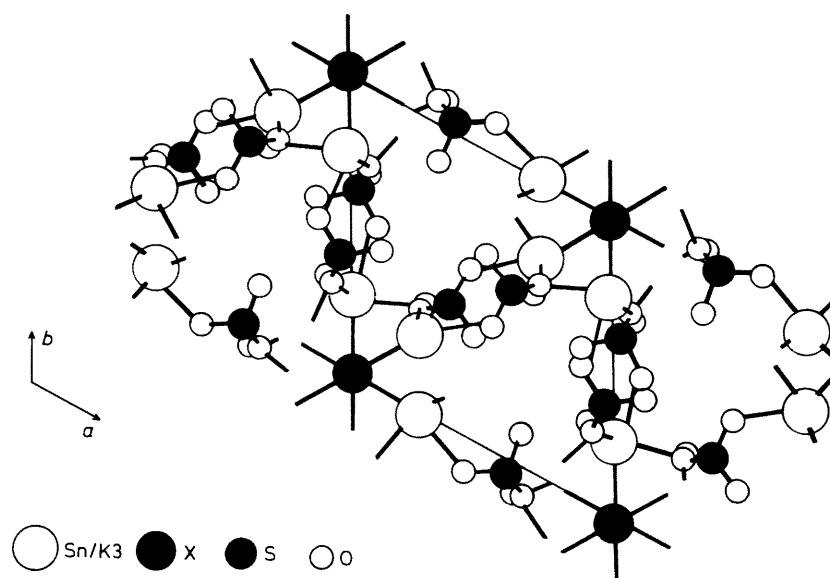


Figure 2. Structure of $K_3Sn_2(SO_4)_3X$ ($X = Cl$ or Br) viewed along the c direction. $K(1)$ and $K(2)$ are not included

Table 2. Bond distances (\AA) and bond angles ($^\circ$) (primed atoms are symmetry related to the unprimed ones)

	$K_3Sn_2(SO_4)_3Br$		$K_3Sn_2(SO_4)_3Cl$	
Tin co-ordination				
Sn(1)—O(1)	2.471	O(1)—Sn(1)—O(3) 82.02	Sn(1)—O(4)	2.446
Sn(1)—O(3)	2.574	O(1)—Sn(1)—O(4) 86.85	Sn(1)—O(3)	2.547
Sn(1)—O(4)	2.634	O(1)—Sn(1)—O(4') 73.38	Sn(1)—O(1)	2.561
Sn(1)—O(4')	2.883	O(1)—Sn(1)—O(3') 81.22	Sn(1)—O(4')	2.961
Sn(1)—O(3')	2.952		Sn(1)—Cl(1)	2.973
Sn(1)—Br(1)	3.128		Sn(1)—O(3')	2.994
Sulphur co-ordination				
S(1)—O(1)	1.457	O(1)—S(1)—O(2) 110.9	S(1)—O(1)	1.425
S(1)—O(2)	1.443	O(1)—S(1)—O(3) 113.0	S(1)—O(2)	1.420
S(1)—O(3)	1.501	O(1)—S(1)—O(4) 100.2	S(1)—O(3)	1.541
S(1)—O(4)	1.456	O(2)—S(1)—O(3) 104.4	S(1)—O(4)	1.568
		O(2)—S(1)—O(4) 117.6		
		O(3)—S(1)—O(4) 110.9		
Potassium co-ordination *				
K(1)—O(1)	2.703	K(2)—O(1) 2.794	K(1)—O(4)	2.771
K(1)—O(1')	2.703	K(2)—O(1') 2.794	K(1)—O(4')	2.771
K(1)—O(2)	2.694	K(2)—O(2) 2.874	K(1)—O(2)	2.783
K(1)—O(2')	2.694	K(2)—O(2') 2.874	K(1)—O(2')	2.783
K(1)—O(3)	2.836	K(2)—O(3) 3.062	K(1)—O(1)	2.840
K(1)—O(3')	2.836	K(2)—O(3') 3.062	K(1)—O(1')	2.840
			K(2)—O(1)	2.618
			K(2)—O(1')	2.618
			K(2)—O(2)	2.759
			K(2)—O(2')	2.759
			K(2)—O(3)	2.972
			K(2)—O(3')	2.972

* The co-ordination about $K(3)$ is unusual, as this atom shares the Sn site.

radii and two are longer and approximate to the sum of the ionic radii. In a few cases there is one very short covalent bond and three longer tin-ligand bonds.

The two $K_3Sn_2(SO_4)_3X$ compounds cannot be described in terms of either of these common types of tin(II) environment. The average Sn—O bond of 2.55 \AA for the bromide and 2.52 \AA for the chloride are unusually long and by comparison with the data in Table 3 are longer than the sum of the ionic radii for tin-oxygen bonds. In the same way the tin-halogen bonds of 3.13 \AA for the bromide and 2.97 \AA for the chloride are also longer than the sums of the appropriate ionic radii, but less than the sum of the van der Waals radii. It must be concluded from the Sn—O and Sn—X bond lengths that the bonding to the ligands is very ionic in nature and that the covalent interactions to O and X are very weak in com-

parison with other known tin(II) compounds. The reasons for these effects have to be explained and in this respect the ^{119}Sn Mössbauer data for tin(II)-oxygen-containing materials have proved useful.

We have previously studied the relationship between ^{119}Sn Mössbauer chemical shift parameters and bond lengths. We have found that for a number of tin(II) compounds with Sn—L bonds to the same type of ligand atom there is a close relationship between the Mössbauer chemical shift and the average Sn—L bond distances; *viz.*, an increase in average bond length results in an increase in shift. The shift data for the two compounds $K_3Sn_2(SO_4)_3X$ ($X = Br$ or Cl) are compared with those of the parent material, tin(II) sulphate, in Table 4. The considerable increase in the average Sn—O bond length in the halide sulphates is not reflected in an

Table 3. Sn-L interatomic distances (Å)¹⁵

Bond	Typical Sn-L bond	Sum of covalent radii *	Sum of ionic radii *	Sum of van der Waals radii *
Sn-O	2.14	2.06	2.40	3.40
Sn-Cl	2.54	2.39	2.81	3.80
Sn-Br	2.83	2.51	2.95	3.95

* Values quoted for tin(II).

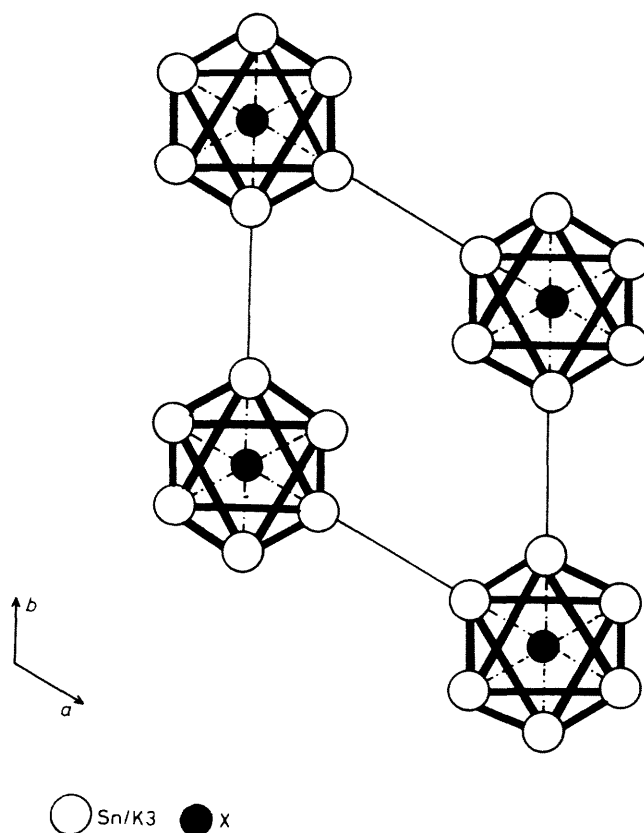
Table 4. ¹¹⁹Sn Mössbauer parameters

Compound	Average Sn-O bond length/Å	δ/mm s ⁻¹	Ref.
K ₃ Sn ₂ (SO ₄) ₃ Br	2.55	3.86	*
K ₃ Sn ₂ (SO ₄) ₃ Cl	2.52	3.76	*
SnSO ₄	2.26	3.95	15
SnHPO ₃	2.17	3.15	15
KSn(O ₂ CH) ₃	2.16	3.08	15
Ca[Sn(O ₂ CMe) ₃] ₂	2.14	2.90	15

* This work.

expected increase in chemical shift, but instead a significant decrease is observed. We would not expect the longer than ionic tin-halogen bond to have much effect on the shift and so this loss of *s*-electron density must be explained in terms of solid-state effects rather than tin-ligand interactions.

The ¹¹⁹Sn Mössbauer data and the long Sn-O and Sn-X bonds provide evidence that the unusual distorted-octahedral arrangement of Sn/K3 atoms around the halogens in the structures actually results in cluster formation (Figure 3). The non-bonding lone-pair tin orbitals that are pointing approximately into the centre of the octahedron must overlap empty *d* orbitals of adjacent Sn atoms giving rise to weak Sn-Sn cluster interactions. The Sn-Sn distances in the clusters are in the range 4.62–4.64 Å for K₃Sn₂(SO₄)₃Br and 4.45–4.56 Å for K₃Sn₂(SO₄)₃Cl. The fact that the non-bonding electron pairs are all directed towards the centre of an octahedron must, even if they are being delocalised into cluster orbitals, lead to a build-up of electron density. In this respect it is interesting that the clusters contain only four Sn atoms with the remaining two atoms being K. The effect of the potassium atoms and possibly the central halogen atom must be to reduce the electron build-up within the octahedron and to stabilise the cluster. The effects of the cluster electron-delocalisation interactions would be three-fold: *viz.*, (1) to remove the distorting effects of lone-pair orbitals pointing towards a halide ion, (2) to delocalise the tin electron density into cluster orbitals giving rise to its anomalous ¹¹⁹Sn Mössbauer chemical shift, and (3) to weaken the tin-ligand bonds outside the cluster. Cluster formation of metal atoms around the halogens therefore provides an explanation for all the apparent anomalous structural and Mössbauer data for the K₃Sn₂(SO₄)₃X compounds. Cluster formation involving tin(II) atoms is a novel example of the Sn-Sn interactions that have important consequences in certain tin(II) compounds. The types of Sn-Sn interactions range from dimer formation in Sn[CH(SiMe₃)₂]₂,¹⁶ where the stability and structure of the material arise from interactions between the lone pair of one Sn atom with the empty orbital on the other Sn atom in the dimer, to the interactions that account for the optical and electrical properties of compounds such as CsSnBr₃¹⁷ and SnO¹⁸ where the non-bonding orbitals are delocalised into three-dimensional and adjacent-layer tin bands respectively. The Sn-Sn interactions in the K₃Sn₂(SO₄)₃X clusters must be

**Figure 3.** Cluster arrangements of Sn/K3 atoms around the halogen atoms in the K₃Sn₂(SO₄)₃X structures.

intermediate in nature between those of Sn[CH(SiMe₃)₂]₂ and the fully delocalised systems.

Acknowledgements

We thank the S.E.R.C. and the International Tin Research Institute for a C.A.S.E. studentship (to S. M. G.).

References

- 1 T. Karantassis, *C.R. Acad. Sci.*, 1926, **182**, 134.
- 2 W. H. Nebergall, G. Baseggio, and J. C. Muhler, *J. Am. Chem. Soc.*, 1954, **76**, 5353.
- 3 P. Pascal, 'Nouveau Traite de Chimie Minerale,' Masson et Cie, Paris, 1963, vol. 8.
- 4 J. D. Donaldson, D. R. Laughlin, and D. C. Puxley, *J. Chem. Soc., Dalton Trans.*, 1977, 865.
- 5 J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, 1969, 2358.
- 6 C. C. Addison and W. B. Simpson, unpublished work.
- 7 J. S. Morrison, Ph.D. Thesis, University of New Hampshire, 1965.
- 8 D. A. Everest, *J. Chem. Soc.*, 1951, 2903.
- 9 R. Klement and H. Haselback, *Chem. Ber.*, 1963, **96**, 1022.
- 10 B. R. Chamberlain and W. Moser, *J. Chem. Soc. A*, 1969, 354.
- 11 R. A. Howie, W. Moser, R. G. Starts, F. W. D. Woodhams, and W. Parker, *J. Chem. Soc., Dalton Trans.*, 1973, 1478.
- 12 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determinations, University of Cambridge, 1975.
- 13 The X-RAY system, Version of June 1972, J. M. Stewart, Technical Report TR-192, Computer Science Centre, University of Maryland, U.S.A.

- 14 W. D. S. Motherwell, *PLUTO: Plotting Molecular and Crystal Structures*, University of Cambridge, 1979.
- 15 J. D. Donaldson and S. M. Grimes, *Rev. Silicon, Germanium, Tin Lead Comp.*, in the press.
- 16 J. D. Cotton, P. J. Davidson, M. F. Lappert, J. D. Donaldson, and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1976, 2286.
- 17 S. J. Clark, C. D. Flint, and J. D. Donaldson, *J. Phys. Chem. Solids*, 1981, **42**, 133.
- 18 J. D. Donaldson, J. Silver, S. Hadjiminolis, and S. D. Ross, *J. Chem. Soc., Dalton Trans.*, 1975, 1500.

Received 4th July 1983; Paper 3/1148