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## The Crystal Chemistry of Divalent Tin<sup>1</sup>

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Received August 22, 1963

Recent crystal structure studies of divalent tin compounds have revealed formerly obscure similarities within these structures. A fairly simple interpretation of tin(II) crystal chemistry is given. Expectations for tin(II) compounds are: (1) Ionic compounds with typical symmetrical ionic lattices. None is known. (2) Covalent compounds with (a) threefold coordination and bond angles *ca.* 90° (this type is found in SnS, orthorhombic SnSe, SnCl<sub>2</sub>, SnCl<sub>2</sub>·2H<sub>2</sub>O, K<sub>2</sub>SnCl<sub>4</sub>·H<sub>2</sub>O, and SnSO<sub>4</sub>) and with (b) sixfold octahedral coordination (this type is found in SnTe and cubic SnSe). From the available data, a radius is found for tin(II), 1.63 Å. Extensions to other lower valence states are discussed. Most R<sub>2</sub>Sn compounds are compounds of tetravalent tin and contain Sn–Sn bonds.

### Introduction

Surprisingly few structure determinations of tin(II) compounds have been made. In the past there has been found no simple generalization or common factors which can be said to characterize tin(II) crystal chemistry. More recently a few new structures have been examined which do have common features. We show below that if tin(II) compounds are defined as those in which a tin atom uses only two electrons in any type of bonding, ionic, covalent, or in forming Sn–Sn bonds, then a fairly simple interpretation of tin(II) compounds can be made, a tin(II) covalent radius can be found, the primary coordination number can be found, etc. It will be clear from the above definition of tin(II) compounds that composition alone will not be the final criterion for the valence of tin.

### Expectations for Tin(II) Compounds

(1) **Ionic Compounds.**—With very electronegative elements tin(II) should behave as Sn<sup>+2</sup> with a spherically symmetrical 5s<sup>2</sup> configuration. In such ionic compounds tin(II) salts should resemble salts of other spherically symmetrical, divalent cations of about the same size.

Evidence for such salts is completely lacking. A recent X-ray study of SnF<sub>2</sub>, the compound most likely to form an ionic structure, has shown that the structure is complex, but it has failed to reveal the fluorine positions in the presence of the heavy tin atoms.<sup>4</sup> The complexity of the structure is evidence against completely ionic character for this compound.

SnO has the PbO structure.<sup>5</sup> Each tin atom sits at the apex of a square pyramid with four oxygen atoms in the base positions, and each oxygen atom is tetrahedrally coordinated to four tin atoms. The Sn–O distance is 2.21 Å. In addition, there are adjacent layers of tin atoms with Sn–Sn distances of 3.70 Å.

(1) Contribution No. 1352. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) The entire community of inorganic and physical chemists was sorrowed by the death of Dr. Robert E. Rundle of Iowa State University on Oct. 9, 1963. He was a productive and imaginative scholar and his contributions to the field of inorganic chemistry will be sorely missed.

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(4) G. Bergerhoff, *Acta Cryst.*, **15**, 509 (1962).

(5) W. J. Moore and L. Pauling, *J. Am. Chem. Soc.*, **63**, 1392 (1941).

These distances may indicate some degree of Sn–Sn bonding so that SnO may not be a true tin(II) compound; the nature of the bonding in this compound is not yet clear. In any case, this structure is not typical of ionic compounds, MX.

SnS, SnCl<sub>2</sub>, and the orthorhombic form of SnSe, all below, have structures more characteristic of covalent compounds, though the bonds must have considerable ionic character. The cubic forms of SnSe and SnTe have the rock salt structure but must also be mainly covalent, since according to Pauling's electronegativity scale the electronegativities of Sn, Se, and Te are 1.8, 2.4, and 2.1, respectively.<sup>6</sup> Undoubtedly tin(II) should be more electropositive than tin(IV), but a completely ionic interpretation is not justified. These compounds are discussed below.

(2) **Covalent Compounds.**—In forming covalent compounds, again it is to be expected that tin(II) will have a 5s<sup>2</sup> core. There will be two valence electrons and three valence orbitals for forming bonds so that tin(II) is like a true metal in the sense that it has more valence orbitals than valence electrons.<sup>7</sup> Since all valence orbitals are expected to be used in forming bonds,<sup>7</sup> and since the valence orbitals are the three 5p-orbitals, bond angles are expected to be ~90°. In the usual case, three bonds at right angles are to be anticipated. The only alternative which seems likely is coordination number of six using both lobes of the p-orbitals in delocalized bonding. Actually, there appear to be compounds of tin(II) of both types.

(2a) **Coordination Number Three for Tin(II) Compounds.**—The known compounds where tin(II) forms three short bonds include SnCl<sub>2</sub>, SnS, orthorhombic SnSe, SnCl<sub>2</sub>·2H<sub>2</sub>O, K<sub>2</sub>SnCl<sub>4</sub>·H<sub>2</sub>O, and SnSO<sub>4</sub>. These structures will be reviewed briefly here to show the extent to which it is possible and reasonable to interpret these structures in terms of a primary coordination number of three.

In SnCl<sub>2</sub>·2H<sub>2</sub>O, Fig. 1a, the tin atom sits at the apex of a trigonal pyramid with two chlorine atoms and one water oxygen in the base positions.<sup>8</sup> Distances Sn–Cl

(6) L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 93, 98.

(7) R. E. Rundle, *J. Am. Chem. Soc.*, **69**, 1327 (1947); *J. Chem. Phys.*, **17**, 67 (1949); *Record Chem. Progr.*, **23**, 195 (1962).

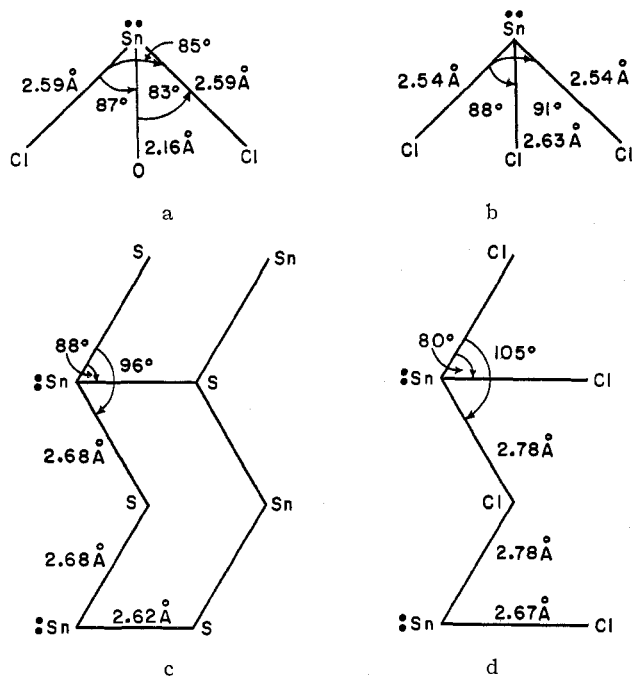


Fig. 1.—Three-coordinate tin(II) in: (a)  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , (b)  $\text{K}_2\text{SnCl}_4 \cdot \text{H}_2\text{O}$ , (c)  $\text{SnS}$ , (d)  $\text{SnCl}_2$ .

are 2.59 Å., while Sn-O is 2.16 Å. Pertinent angles are  $\text{Cl-Sn-Cl} = 85^\circ$ ,  $\text{Cl-Sn-O} = 87$  and  $83^\circ$ , consistent with the use of three p-orbitals of tin(II) in forming bonds. All other distances are very much longer ( $\text{Sn-Cl} > 3.29$  Å.). The second water molecule in  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is not bonded to tin(II), but forms hydrogen bonds to the water molecules bound to tin(II). The structure does not seem to be one in which ionic bonding determines the configuration. At present, bond distances are known for this structure to  $\pm 0.02$ – $0.04$  Å.

In  $\text{K}_2\text{SnCl}_4 \cdot \text{H}_2\text{O}$ , Fig. 1b, despite the composition, there are three short Sn-Cl bonds, two of 2.54 Å. and one of 2.63 Å.<sup>9</sup> Within the  $\text{SnCl}_3^-$  ions, the angles Cl-Sn-Cl are 88 and  $91^\circ$ . All other Sn-Cl distances are very much longer. The water molecule is not in the primary coordination sphere of tin(II), but rather in the polyhedron about potassium(I). Again, the structure does not seem to be determined by ionic bonding. The estimated errors are in the same range as those of the previous structures.

In Sn-S, there are zig-zag  $-\text{S-Sn-S-Sn}-$  chains with  $\text{Sn-S} = 2.68$  Å.<sup>10</sup> Each tin atom makes one other short bond to the sulfur of a neighboring chain, with  $\text{Sn-S} = 2.62$  Å. The next nearest Sn-S distance is 3.27 Å. For the three short bonds to tin(II), the angles S-Sn-S are  $88^\circ$  (2) and  $96^\circ$  as shown in Fig. 1c.

Orthorhombic SnSe has been reported more recently.<sup>11</sup> It is isomorphous with SnS. The corresponding Sn-Se distances are 2.77 and 2.82 Å., with Se-Sn-Se angles of 96 and  $89^\circ$  (2).

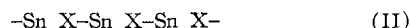
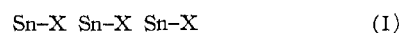
The structure of  $\text{SnCl}_2$  was determined independently in our laboratories<sup>12</sup> and by Van den Berg.<sup>13</sup> In this

structure, there are  $-\text{Sn-Cl-Sn-Cl}-$  chains, with  $\text{Sn-Cl} = 2.78$  Å. To each tin(II), there is also bonded a chlorine atom at 2.67 Å., Fig. 1d. This tin atom and the three chlorine ligands form a trigonal pyramid with the tin atom at the apex. Bond angles Cl-Sn-Cl within the pyramid are 80 and  $105^\circ$ . All other Sn-Cl distances are  $\geq 3.06$  Å.

The structure of  $\text{SnSO}_4$  has been determined recently by powder methods.<sup>14</sup> In this structure there are twelve oxygen atoms located about the tin atom at distances ranging from 2.34 to 3.29 Å. The three shortest Sn-O distances are 2.33 and 2.40 Å. (2) with the next shortest Sn-O distance 2.92 Å. The three O-Sn-O angles associated with these three short distances are 74 and  $76^\circ$  (2). The agreement between calculated and observed intensities is very good, but because the structure was determined from a minimum amount of data using trial and error techniques, it is difficult to assign standard errors to the bond lengths and angles.

(2b) **Tin(II) Compounds with Coordination Number Six.**—It has been noted that SnTe and one form of SnSe have the rock salt structure. There is no reason to suppose that these are especially ionic compounds, so it seems necessary to assume that they are essentially covalent compounds in which both lobes of the three p-orbitals of tin(II) bond equally with six neighbors.

Starting with  $\text{Sn}^{+2}$  and  $\text{Se}^{+4}$  or  $\text{Te}^{+4}$ , there will be three empty valence p-orbitals on each atom directed along the three cube directions. In an MO scheme, the bond orbitals will be just filled by the six electrons per SnSe (or SnTe) pair. (The s-orbitals could be brought into this scheme, but bonding and antibonding orbitals would both be filled.) In a valence bond description, there will be resonance among the forms



in all three cube directions. Such a resonating system of covalent bonds would place a formal charge of  $-1$  on tin and  $+1$  on the chalcogen. Hence, we may expect more than 33% ionic character in each bond to redistribute the charge, making the charge on tin somewhat positive in view of its slightly lower electro-negativity.

In these crystals, the Sn-Se and Sn-Te bond distances are 3.00 and 3.14 Å., respectively, too long for single bonds, but quite in keeping with bond number one-half (see below). This bonding is similar to that in interstitial compounds.<sup>15</sup>

### The Covalent Radius of Tin(II)

In  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{K}_2\text{SnCl}_4 \cdot \text{H}_2\text{O}$  all Sn-Cl bonds appear to be normal electron pair bonds. The Sn-OH<sub>2</sub>

(12) Submitted as a Communication to the Editor to *J. Am. Chem. Soc.* in 1960 but not accepted as a Communication to the Editor. Withdrawn when published as a communication in *Acta Cryst.* by Van den Berg. The importance of coordination number three was noted in this paper and in *Record Chem. Progr.* **23**, 195 (1962).

(13) J. M. Van den Berg, *Acta Cryst.*, **14**, 1002 (1961).

(14) P. J. Rentzeperis, *Z. Krist.*, **117**, 431 (1962).

(15) R. E. Rundle, *Acta Cryst.*, **1**, 180 (1948). For an MO treatment of this type of bonding see H. Bilz, *Z. Physik*, **158**, 338 (1958).

(8) D. Kamenar and B. Grdenic, *J. Chem. Soc.*, 3954 (1961).

(9) D. Kamenar and B. Grdenic, *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962).

(10) W. Hofmann, *Z. Krist.*, **92**, 161 (1935).

(11) A. Okazaki and I. Ueda, *J. Phys. Soc. Japan*, **11**, 470 (1956).

bond is also an electron pair bond, but of the semipolar double bond type in Sidgwick's nomenclature; that is, the electron pair is "donated" by the water molecule, and the bond must have considerable ionic character, probably shortening it. Indeed frequently such bonds have appeared to be so short as to cause some authors to assign them double bond character.

The unique Sn-Cl bond in SnCl<sub>2</sub> is a normal electron pair bond, but the Sn-Cl-Sn-Cl bonds in the chains are cases in which, by donating a pair, chlorine forms two bonds, and these bonds are longer than normal in other cases. They will have more ionic character than the single Sn-Cl bond by the same argument as given above for the bonding in SnSe, etc. For Sn-Cl bonds we should then average the normal single bond distances. The Sn-Cl distances in SnCl<sub>2</sub>·2H<sub>2</sub>O and K<sub>2</sub>SnCl<sub>4</sub>·H<sub>2</sub>O have relatively large errors ( $\pm 0.03$ ) since the structures were derived from a minimum of data. The distance in SnCl<sub>2</sub> ( $2.67 \pm 0.01$  Å.) is known with more accuracy since, in our laboratory, it came from a complete three-dimensional refinement of all the X-ray data obtainable from Mo K $\alpha$  radiation. We have weighted this value with double weight in getting an averaged Sn(II)-Cl distance of  $2.62$  Å. Using the normal covalent radius of Cl ( $0.99$  Å.), the tin(II) radius is  $1.63$  Å.<sup>16</sup> This radius can now be tested to see how well it predicts other Sn(II)-X distances. Thus  $\Sigma r$  for Sn-O in SnCl<sub>2</sub>·2H<sub>2</sub>O =  $2.29$  vs.  $2.16 \pm 0.04$  Å. (obsd.).<sup>17</sup> In SnS  $\Sigma r$  for Sn-S =  $2.66$  vs.  $2.68$  (2) and  $2.62$  (1) observed and  $\Sigma r$  for Sn-Se =  $2.80$  vs.  $2.82$  (2) and  $2.77$  (1) observed in orthorhombic SnSe.<sup>18</sup>

This tin(II) radius can also be tested for the SnSe and SnTe cubic structures where Sn-Se bonds have bond number one-half. Thus the predicted distances are  $\Sigma r$  Sn-Se =  $2.80$  Å,<sup>16</sup> but this is to be increased by  $0.18$  to  $2.98$  Å. by Pauling's rule for fractional bonds.<sup>19</sup> The observed distance is  $3.00$  Å. Similarly the Sn-Te distance in SnTe is predicted to be  $3.18$  vs.  $3.14$  Å.

The tin(II) radius of  $1.63$  Å. reported here seems to be roughly correct. The uncertainty in the radius is due in part to the data from which it has been derived. Possibly better data will permit evaluation of other details not yet clear. In any case, the tin(II) radius is very significantly greater than the radius for tin(IV), where the accepted value is  $1.40$  Å.

(16) The single bond covalent radius has been used; see ref. 6, p. 224.

(17) There is a large probable error in the experimental length, and if there is a discrepancy one expects the Sn-O bond here to be abnormally short (see above).

(18) The observed distances are shorter than expected for both S and Se coordinated to three tin atoms.

(19) Reference 6, p. 255.

### Extension to Other Low Valence States

Clearly the present type of treatment should be extendible to other lower valence states, notably germanium(II) and lead(II), and to the valence state I for the third row elements, gallium, indium, and thallium. At present good structural data are very limited for lower valence states for most of these elements. Considerable information exists for lead(II) and this is reviewed below briefly. (1) PbF<sub>2</sub> has the rutile structure, more typical of ionic compounds. (2) PbCl<sub>2</sub> and PbBr<sub>2</sub> are isomorphous with SnCl<sub>2</sub>. Using recent structural data for PbBr<sub>2</sub>,<sup>20</sup> the bridge Pb-Br bonds are  $3.015 \pm 0.006$  Å. and the short Pb-Br bonds are  $2.964 \pm 0.006$  Å., while the similar distances in PbCl<sub>2</sub> are  $2.90$  and  $2.86$  Å.<sup>21</sup> From the single bonds, we find  $r_{\text{Pb(II)}} = 1.82$ - $1.87$  Å. The Pb-Br distances seem more reliable and therefore we take  $1.84$  Å. as the weighted average. This radius seems too large to account for the distances in PbS, PbSe, and PbTe, all of which have the rock salt structure as shown in Table I.

TABLE I

	PbS	PbSe	PbTe
$r$ (calcd.), Å.	3.06	3.19	3.39
$r$ (obsd.), Å.	2.97	3.06	3.22

Several bits of evidence point toward considerably more ionic character in lead(II) than in tin(II) compounds. For example, the PbF<sub>2</sub> structure, above, and the fact that PbS has the rock salt structure rather than the more complex SnS structure. It may be that most of the salts of lead(II) are too ionic to correspond well with this proposal which emphasizes the covalent character of tin(II).

A further consideration of lower valence states is deferred until a greater quantity of more reliable structural data can be collected.

### Organometallic Compounds, R<sub>2</sub>Sn

It might at first be supposed that R<sub>2</sub>Sn compounds are compounds of tin(II). Some monomeric R<sub>2</sub>Sn species have been reported, but all polymerize through the formation of Sn-Sn bonds. This is supported by both chemical<sup>22</sup> and X-ray evidence.<sup>23</sup> These bonds have length  $2.8$  Å. as in gray (diamond form) tin. Thus stable R<sub>2</sub>Sn compounds are really tin(IV) compounds according to the previous definition.

(20) A redetermination in this laboratory by H. D. McBride.

(21) K. Sahl and J. Zemann, *Naturwiss.*, **48**, 651 (1961).

(22) W. P. Neumann, *Angew. Chem.*, **75**, 225 (1963).

(23) D. H. Olson and R. E. Rundle, *Inorg. Chem.*, **2**, 1310 (1963).