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Mössbauer spectra of tin(IV) iodide complexes

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The first examples of compounds containing the $[SnR_2I_3]^-$ anion, *i.e.* $[Bu^n{}_4N][SnR_2I_3]$ (R = Me or Ph), have been prepared and characterized by IR, Raman and ^{119}Sn Mössbauer spectroscopies, and X-ray powder diffraction data. The experimental data are consistent with a trigonal bipyramidal structure, with the R groups in equatorial positions, for the $[SnR_2I_3]^-$ anions. Octahedral $[SnR_2I_4]^{2-}$ anions could not be isolated and it is shown that the previously reported $[Bu^n{}_4N]_2[SnMe_2I_4]$ is actually a 1 : 1 mixture of $Bu^n{}_4NI$ and $[Bu^n{}_4N][SnMe_2I_3]$. The X-ray powder structure of Cs_2SnI_6 has been refined by the Rietveld method. The compound crystallises in the cubic *Fm*3*m* space group with *a* = 11.6410(3) Å and a Sn–I distance of 2.864(1) Å. The Sn–I distances in Cs_2SnI_6, $SnI_4(bipy)$, $SnI_4(Ph_3PO)_2$ and $SnI_4(Ph_2SO)_2$ are related to the Mössbauer quadrupole splitting, showing that ligands that are weaker donors than I^- (*i.e.* have a more positive partial quadrupole splitting) give rise to Sn–I distances that are shorter than for the $[SnI_6]^{2-}$ anion.

Introduction

In recent years there has been an increasing interest in tin-based antitumour drugs.[1] In particular, many octahedral diorganotin dihalide complexes, $SnR_2X_2L_2$, exhibit antitumour activity against P388 lymphocytic leukaemia,[2–4] and recently bis(acetone thiosemicarbazone-*S*)dichlorodiphenyltin(IV) has shown significant cytotoxicity against several tumours.[5] For that reason, several research groups have been interested in the synthesis and structural study of $SnR_2X_2L_2$ complexes.[6–13] Some attempts to correlate structural data and antitumour activity,[4,6] have concluded that active complexes have Sn–N bond lengths ≥2.39 Å. This fact suggests that dissociation of the ligands is an important step in the mechanism of action, and points to the importance of getting information about the tin–ligand bond strength. Therefore, a better understanding of the antitumour activity of octahedral diorganotin dihalide complexes can be obtained with the optimization of spectroscopic techniques that can provide information about the structure of the complexes and the tin–ligand bond strength. Several physical techniques have been used to aid structural elucidation of $SnR_2X_2L_2$ complexes.[9] In the case of Mössbauer spectroscopy the most comprehensive work is that reported by Crowe and Smith[14] in 1982. Although $SnR_2X_2L_2$ complexes usually have both R groups in *trans* positions, Mössbauer spectroscopy has shown the existence of *cis–trans* isomerism,[15,16] as confirmed crystallographically for $Sn(C_6H_4Cl\text{-}4)_2Cl_2\cdot 4,4'\text{-}Me_2bipy$ (4,4′-Me$_2$bipy = 4,4′-dimethyl-2,2′-bipyridine).[17] Furthermore, in the case of monodentate L ligands, the X and L groups can be in *cis* or *trans* positions, and the structure of $SnEt_2Cl_2(OPPh_3)_2$ contains two different isomers in the same unit cell.[18] Therefore, the Mössbauer parameters can be affected by several variables such as the isomer formed (five possible geometrical isomers, one of them optically active), the C–Sn–C angle, and the nature of the R, X, and L groups. In order to understand the effect of the different variables on the Mössbauer parameters it is better to study first related simpler compounds such as SnX_4L_2 or $[SnR_2X_4]^{2-}$. In the case of SnX_4L_2 complexes there is a renewed interest in their structure.[19–24] As far as their Mössbauer parameters are concerned, the isomer shift (IS) is sensitive to the electronegativity of both the halogen X and the donor atom of the ligand L. Indeed, a review of the reference bank of the Mössbauer Effect Data Centre (University of North Carolina, Asheville, USA) has shown that the average IS of $SnCl_4$ complexes with O, N, S, P and As donor ligands are (standard deviations in parentheses) 0.37 (0.08), 0.42 (0.08), 0.66 (0.06), 0.75 (0.10) and 0.78 (0.10) mm s^{-1}, respectively.[25–27] Furthermore, for the same ligands, the IS of SnF_4, $SnBr_4$ and SnI_4 complexes are, respectively, 0.66 (0.02) mm s^{-1} lower, 0.27 (0.07) mm s^{-1} higher, and 0.63 (0.11) mm s^{-1} higher than for $SnCl_4$ complexes.[25] Therefore, IS values can be used to get information about the atoms bonded to tin, and we have shown that some literature IS data that did not agree with our expectations were wrong.[25–27] This information is particularly useful in the case of ambidentate ligands.

The Mössbauer quadrupole splitting (QS) of octahedral SnX_4L_2 complexes can give information, not only about the isomer formed, but also about the Sn–X bond lengths.[28–30] Indeed, we have reported linear relationships between the average tin–halogen distance and the partial quadrupole splitting of the ligands (pqs) for $SnCl_4L_2$[28] and $SnBr_4L_2$ complexes.[29,30] These correlations can yield information about the Sn–L bond strengths and the sign of the quadrupole splitting, as well as rationalize experimental Sn–X distances and QS data in terms of the donor properties of the ligands. Furthermore, these correlations can be used to estimate Sn–X distances, which are expected to agree with experimental values within ±0.02 Å, and discrepancies between calculated and reported distances enabled us to detect the incorrectness of a published crystal structure.[27] It is important to note that the correlations are empirical and there seems to be no theoretical basis for linear correlations between interatomic distances and QS data. For that reason the validity of the correlations should be checked for other tin tetrahalide complexes and, in particular, for SnI_4L_2 complexes, because iodide has a pqs value significantly different from those of the other halides.[31] Furthermore, iodine is the most polarizable of the halogen atoms, and the Sn–I distances could be more variable than the other tin–halogen distances.

Only a few crystal structures of octahedral tin(IV) iodide complexes are available in the literature,[20,32–35] and we have tried to get accurate Mössbauer data for them. Unfortunately, only one or two red-orange crystals of *cis*-$[SnI_4\{MeS(O)(CH_2)_3SMe\}_2]$ could be isolated, and attempts to prepare it in sufficient quantity to enable spectroscopic characterization were not successful,[20] while $SnI_4(PPr^n_3)_2$ [35] was too unstable to run its Mössbauer spectrum.[36] Indeed, it is really a difficult task to obtain pure tin(IV) iodide complexes with phosphine ligands.[37] An important point in the correlation of Sn–I distances with QS data is the perfectly octahedral $[SnI_6]^{2-}$ anion with QS = 0 mm s^{-1}. The X-ray powder crystal structures of cubic Rb_2SnI_6 and Cs_2SnI_6 were reported in 1939 to give Sn–I distances of 2.85 Å.[38] Bearing in mind that the reported standard deviation of 0.05 Å is too high for today's standards, we have refined the X-ray powder structure of Cs_2SnI_6. In order to get a significant correlation between Sn–I distances and Mössbauer QS data, a broad range of Sn–I distances needs to be considered, and the longest Sn–X distances for SnX_4L_2 complexes are obtained for $[SnR_2X_4]^{2-}$ anions.[28,29,39] While Clark and Wilkins[40] could not isolate $[SnMe_2I_3]^-$ nor $[SnMe_2I_4]^{2-}$ salts, the synthesis of $[Bu^n_4N]_2[SnMe_2I_4]$ was reported later by Harrison and coworkers.[41] In order to confirm the existence of $[SnMe_2I_4]^{2-}$ anions, and get X-ray and Mössbauer data for them, we have repeated the synthesis of $[Bu^n_4N]_2[SnMe_2I_4]$, and prepared solids of composition $[Bu^n_4N][SnMe_2I_3]$, $[Bu^n_4N]_2[SnPh_2I_4]$ and $[Bu^n_4N][SnPh_2I_3]$. As it will be demonstrated below, it is concluded that $[SnMe_2I_4]^{2-}$ anions have no real existence.

Experimental

Preparations

All syntheses were carried out under argon by using standard Schlenk techniques. The compounds SnI_4,[42] $SnI_4(Ph_2SO)_2$,[33] $SnI_4(Ph_3PO)_2$,[34] $SnI_4(bipy)$,[32] and Cs_2SnI_6 [38] were prepared by literature methods, $SnMe_2I_2$ and $SnPh_2I_2$ by reaction of aqueous HI solutions (57%) with ethanolic suspensions of $SnMe_2O$ (K&K) or $SnPh_2O$ (M&T), respectively, in 2 : 1 molar ratio. The diorganotin iodides were isolated by vacuum elimination of the solvent and vacuum sublimation, and characterized by elemental analysis, melting point,[43] and IR and ^1H NMR spectroscopies. The Mössbauer spectrum of $SnMe_2I_2$, not previously reported, gave the following parameters: IS = 1.58, QS = 2.79, $\Gamma_1 = 0.91$, $\Gamma_2 = 0.97$ mm s^{-1}. The salts "$[Bu^n_4N]_2[SnR_2I_4]$" and $[Bu^n_4N][SnR_2I_3]$ (R = Me or Ph) were prepared by mixing stoichiometric amounts of SnR_2I_2 and Bu^n_4NI, in CH_2Cl_2 solution, in the absence of light, stirring for *ca.* 30 min, and eliminating the solvent *in vacuo*. Some characterization data are given below.

"$[Bu^n_4N]_2[SnMe_2I_4]$". Yellow solid, mp 99–100 °C; δ_H ($CDCl_3$) 1.00 (24 H, t, *J* = 7.3, $CH_3CH_2CH_2CH_2N$), 1.46 (16 H, sextet, *J* = 7.3, $CH_3CH_2CH_2CH_2N$), 1.68 (16 H, m, $CH_3CH_2CH_2CH_2N$), 1.72 (6 H, s, $J(^{119}SnH) = 65.7$ Hz, $Sn(CH_3)_2$) and 3.35 (16 H, m, $CH_3CH_2CH_2CH_2N$); IR ($\tilde{\nu}_{max}$/cm^{-1}) ν_{asym}(SnC) 554s, lattice Bu^n_4NI (see below) 529m, ν_{sym}(SnC) 502m and ν(SnI) 178s; Raman ($\tilde{\nu}_{max}$/cm^{-1}) ν_{asym}(SnC) 556w, ν_{sym}(SnC) 502vs and ν(SnI) 178vs; Mössbauer (mm s^{-1}) IS = 1.63, QS = 3.33, $\Gamma_1 = 0.74$, $\Gamma_2 = 0.76$; X-ray powder spacings (Cu-Kα, Å) 10.91(32), 9.75(45), 9.39(100), 7.38(30), 6.72(18), 6.30(15), 6.11(23), 5.86(16), 4.92(19), 4.85(21), 4.55(14), 4.37(21), 4.04(25), 3.94(32) and 3.51(21).

$[Bu^n_4N][SnMe_2I_3]$. Yellow solid, mp 119–120 °C; δ_H ($CDCl_3$) 1.02 (12 H, t, *J* = 7.3, $CH_3CH_2CH_2CH_2N$), 1.48 (8 H, sextet, *J* = 7.3, $CH_3CH_2CH_2CH_2N$), 1.69 (8 H, m, $CH_3CH_2CH_2CH_2N$), 1.72 (6 H, s, $J(^{119}SnH) = 65.3$ Hz, $Sn(CH_3)_2$) and 3.36 (8 H, m, $CH_3CH_2CH_2CH_2N$); IR ($\tilde{\nu}_{max}$/cm^{-1}) ν_{asym}(SnC) 554s, ν_{sym}(SnC) 502m and ν(SnI) 178s; Raman ($\tilde{\nu}_{max}$/cm^{-1}) ν_{asym}(SnC) 556w, ν_{sym}(SnC) 503vs and ν(SnI) 178vs; Mössbauer (mm s^{-1}): IS = 1.64, QS = 3.32, $\Gamma_1 = 0.77$, $\Gamma_2 = 0.77$; X-ray powder spacings (Cu-Kα, Å) 10.92(53), 9.73(55), 9.41(100), 7.39(21), 6.71(55), 6.30(22), 6.11(32), 5.87(22), 4.85(38), 4.55(24), 4.38(28), 4.05(51) and 3.52(49).

"$[Bu^n_4N]_2[SnPh_2I_4]$". Orange solid, mp 95–97 °C; δ_H ($CDCl_3$) 1.00 (24 H, t, *J* = 7.3, $CH_3CH_2CH_2CH_2N$), 1.46 (16 H, sextet, *J* = 7.3 Hz, $CH_3CH_2CH_2CH_2N$), 1.68 (16 H, m, $CH_3CH_2CH_2CH_2N$), 3.35 (16 H, m, $CH_3CH_2CH_2CH_2N$) and 7.40–7.78 (10 H, m, $Sn(C_6H_5)_2$); IR ($\tilde{\nu}_{max}$/cm^{-1}) lattice Bu^n_4NI (see below) 530vw, ν_{asym}(SnC) 279s, ν_{sym}(SnC) and/or phenyl *u* 245s, 223m, 200s, ν(SnI) 165s; Raman ($\tilde{\nu}_{max}$/cm^{-1}, decomposes in the laser beam) ν(SnI) 167vs; Mössbauer (mm s^{-1}) IS = 1.49, QS = 2.73, $\Gamma_1 = 0.82$, $\Gamma_2 = 0.81$; X-ray powder spacings (Cu-Kα, Å) 11.20(38), 9.37(62), 9.24(50), 8.74(47), 8.27(100), 7.79(84), 6.63(25), 5.98(33), 5.58(22), 4.92(36), 4.12(21), 4.02(42), 3.94(57), 3.87(34) and 3.59(40).

$[Bu^n_4N][SnPh_2I_3]$. Reddish solid, mp 103–104 °C; δ_H ($CDCl_3$) 1.02 (12 H, t, *J* = 7.3, $CH_3CH_2CH_2CH_2N$), 1.48 (8 H, sextet, *J* = 7.3 Hz, $CH_3CH_2CH_2CH_2N$), 1.70 (8 H, m, $CH_3CH_2CH_2CH_2N$), 3.37 (8 H, m, $CH_3CH_2CH_2CH_2N$) and 7.40–7.78 (10 H, m, $Sn(C_6H_5)_2$); IR ($\tilde{\nu}_{max}$/cm^{-1}) ν_{asym}(SnC) 279s, ν_{sym}(SnC) and/or phenyl *u* 245s, 223m, 200s, ν(SnI) 165s; Raman ($\tilde{\nu}_{max}$/cm^{-1}, decomposes in the laser beam) ν(SnI) 167vs; Mössbauer (mm s^{-1}): IS = 1.50, QS = 2.72, $\Gamma_1 = 0.80$, $\Gamma_2 = 0.79$; X-ray powder spacings (Cu-Kα, Å): 11.17(35), 9.25(54), 8.71(79), 8.24(100), 7.77(62), 6.62(25), 5.98(35), 5.57(17), 4.12(21), 4.02(39), 3.95(20), 3.86(23) and 3.59(28).

Physical measurements

The ^1H NMR spectra were recorded on a Bruker AMX-300 instrument, infrared spectra between 4000 and 200 cm^{-1} on a Perkin-Elmer 1650 FT-IR instrument, using Nujol mulls between CsI windows, and between 550 and 50 cm^{-1} on a Bruker IFS 66 V by diffuse reflectance. Raman spectra were measured at room temperature on a Dilor XY spectrophotometer, using the Raman microscope and an argon laser (5145 Å), with the polycrystalline samples sealed in capillary tubes. Mössbauer spectra at liquid N_2 temperature (at room temperature for Cs_2SnI_6) were obtained using the system and conditions described previously.[44] Sample thickness was 11 mg of natural tin per cm^2. The isomer shift is relative to $BaSnO_3$ at room temperature, and the reproducibility of the Mössbauer parameters was ±0.02 mm s^{-1}. Computer fitting of the spectra gave χ^2 values of 0.98–1.20 (with 249–252 degrees of freedom), within the range of statistically satisfactory values (0.80–1.22).[45] X-Ray powder diffraction (XRPD) data were obtained with a Siemens D-5000 diffractometer using Cu-Kα radiation.

Structure refinement of Cs_2SnI_6

The XRPD data were measured with graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å) on a Siemens D-5000 diffractometer equipped with a Si(Li) counter. The generator was operated at 40 kV and 40 mA. The sample was finely ground in an agate mortar and packed on a flat aluminium sample holder. Data were collected in the range $6 \leq 2\theta \leq 100°$ with a step size of 0.02° and a counting time of 10 s per step. Starting from the published unit cell and positional parameters,[38] the structure was refined by the Rietveld method[46] in the cubic *Fm*3*m* space group (no. 225) by using the Young–Sakthivel program (version DBWS-9006PC),[47] with a pseudo-Voigt peak shape, background correction by interpolation between 22 points, asymmetry correction for angles less than 50°, and a correction for preferred orientation.

Results and discussion

Diorganotin iodide anions

While octahedral $[SnR_2X_4]^{2-}$ (R = Me, Et, Ph or vinyl; X = F, Cl or Br) anions are well known, and several crystal structures have been reported,[29,39,48–59] the only report on the analogous $[SnR_2I_4]^{2-}$ anions deals with the synthesis and IR spectrum of $[Bu^n{}_4N]_2[SnMe_2I_4]$.[41] On the other hand, Clark and Wilkins[40] concluded that the capacity to form both $[SnMe_2X_3]^-$ and $[SnMe_2X_4]^{2-}$ ions extends over the fluoride, chloride and bromide, but neither type of iodo-complex could be isolated. In order to clarify the situation, we have repeated the synthesis of $[Bu^n{}_4N]_2[SnMe_2I_4]$. While only one *ν*(SnC) would be IR active for octahedral $[SnMe_2I_4]^{2-}$, the IR spectrum shows three bands (at 554, 529 and 502 cm^{-1}) between 500 and 600 cm^{-1}. Furthermore, the concordance of activities between IR and Raman spectra precludes a centrosymmetric octahedral structure. In order to check whether the composition $[Bu^n{}_4N]_2[SnMe_2I_4]$ corresponds actually to a 1 : 1 mixture of $Bu^n{}_4NI$ and $[Bu^n{}_4N][SnMe_2I_3]$, we have prepared this last compound. Indeed, both $[Bu^n{}_4N]_2[SnMe_2I_4]$ and $[Bu^n{}_4N][SnMe_2I_3]$ have essentially the same Mössbauer parameters, and the IR spectrum of $[Bu^n{}_4N]_2[SnMe_2I_4]$ agrees with the sum of the spectra corresponding to $Bu^n{}_4NI$ and $[Bu^n{}_4N][SnMe_2I_3]$ (a finely ground 1 : 1 mixture of $Bu^n{}_4NI$ and $[Bu^n{}_4N][SnMe_2I_3]$ has the same melting point and IR spectra as those of $[Bu^n{}_4N]_2[SnMe_2I_4]$). The IR spectrum of $Bu^n{}_4NI$ shows a band at 529 cm^{-1} that does not appear in the spectra of other $Bu^n{}_4N^+$ salts, and could correspond to a lattice band, thus leaving the bands at 554 and 502 cm^{-1} as the antisymmetric and symmetric, respectively, tin–carbon stretching vibrations of a bent $SnMe_2$ arrangement. The non-existence of $[Bu^n{}_4N]_2[SnMe_2I_4]$ is unambiguously confirmed by the X-ray powder diffraction patterns because all the peaks corresponding to $[Bu^n{}_4N][SnMe_2I_3]$ are present in the pattern of $[Bu^n{}_4N]_2[SnMe_2I_4]$, that also shows the peaks corresponding to $Bu^n{}_4NI$. Anions $[SnMe_2I_4]^{2-}$ are not formed either in $CDCl_3$ solutions because even 7 : 1 mixtures of $Bu^n{}_4NI$ and $SnMe_2I_2$ gave a $J(^{119}SnH)$ coupling constant as low as 76.5 Hz, that corresponds to a C–Sn–C angle of about 127°.[60] In order to check whether other $[SnR_2I_4]^{2-}$ anions can be isolated in the solid state we have prepared solids of composition $[Bu^n{}_4N]_2[SnPh_2I_4]$ and $[Bu^n{}_4N][SnPh_2I_3]$. Again, melting point, vibrational and Mössbauer spectra, and X-ray powder diffraction data confirm that the solid of composition $[Bu^n{}_4N]_2[SnPh_2I_4]$ is actually a 1 : 1 mixture of $Bu^n{}_4NI$ and $[Bu^n{}_4N][SnPh_2I_3]$. Therefore, we have disproven previous claims on the existence of $[SnR_2I_4]^{2-}$ anions,[41] and characterized the first examples of compounds containing $[SnR_2I_3]^-$ anions, *i.e.* $[Bu^n{}_4N][SnR_2I_3]$ (R = Me or Ph). The Mössbauer parameters of $[Bu^n{}_4N][SnMe_2I_3]$ and $[Bu^n{}_4N][SnPh_2I_3]$ are reasonable. So, the IS of $[Bu^n{}_4N][SnPh_2I_3]$ (IS = 1.50 mm s^{-1}) is lower than that of $[Bu^n{}_4N][SnMe_2I_3]$ (IS = 1.64 mm s^{-1}), in agreement with the higher electronegativity of the Ph group as compared with Me. Furthermore, a comparison of the Mössbauer parameters of $[Bu^n{}_4N][SnMe_2I_3]$ (IS = 1.64, QS = 3.32 mm s^{-1}) with those corresponding to $[Et_4N][SnMe_2Br_3]$ (IS = 1.52, QS = 3.41 mm mm s^{-1})[61] and $[Bu^n{}_4N][SnMe_2Cl_3]$ (IS = 1.39, QS = 3.40 mm s^{-1})[62] shows similar QS values, and IS values increasing as the electronegativity of the halogen diminishes. A similar trend is observed when comparing the Mössbauer parameters of $[Bu^n{}_4N][SnPh_2I_3]$ (IS = 1.50, QS = 2.72 mm s^{-1}) and $[Bu^n{}_4N][SnPh_2Cl_3]$ (IS = 1.20, QS = 2.56 mm s^{-1}).[62] Finally, on going from $SnMe_2I_2$ (IS = 1.58, QS = 2.79 mm s^{-1}) and $SnPh_2I_2$ (IS = 1.51, QS = 2.38 mm s^{-1})[61] to $[Bu^n{}_4N][SnR_2I_3]$ (R = Me or Ph) the IS remains essentially unchanged and the QS increases by *ca.* 0.3–0.5 mm s^{-1}. It is surprising that the Mössbauer parameters of such a simple compound as $SnMe_2I_2$ had not been reported previously. While the crystal structures reported for $[SnPh_2Cl_3]^-$ anions show isolated ions with the phenyl groups in the equatorial positions of a trigonal bipyramidal structure,[59,63] $[SnMe_2Cl_3]^-$ anions are usually associated into dimers through more or less strong chlorine bridges.[50,64–68] Nevertheless, the structure of $[SnMe_2Cl(terpy)][SnMe_2Cl_3]$ contains isolated $[SnMe_2Cl_3]^-$ anions.[69] Bearing in mind that iodine should have a weaker tendency than chlorine to form bridges, it would be reasonable to expect monomeric trigonal bipyramidal structures for the $[SnR_2I_3]^-$ anions. Indeed, the C–Sn–C angles calculated from the Mössbauer QS values[31] are 137° for $[Bu^n{}_4N][SnMe_2I_3]$ (compare with 140(2)° for $[SnMe_2Cl(terpy)][SnMe_2Cl_3]$[69]) and 127° for $[Bu^n{}_4N][SnPh_2I_3]$ (compare with 127.51(8)° for $[Et_4N][SnPh_2Cl_3]$[63] and 135.78(8)° for $[C_{10}H_9ON{\cdot}H{\cdot}NOH_9C_{10}][SnPh_2Cl_3]$[59]). The fact that the C–Sn–C angles are larger than the ideal value of 120°, and larger for $[SnMe_2X_3]^-$ than for $[SnPh_2X_3]^-$ anions, is in agreement with Bent's isovalent rehybridization principle.[70] The tin atom concentrates greater s character in the orbitals directed to the less electronegative Me groups, thus increasing the C–Sn–C angle. The electronegativity considerations also agree with the bond angles according to the VSEPR model.[71] The absence of data for compounds containing $[SnR_2I_4]^{2-}$ anions will severely restrict the range for any possible corrrelation between Sn–I distances and Mössbauer QS data for SnI_4L_2 complexes, but it is shown below that a significant trend can still be observed.

Table 1 Crystallographic data for Cs_2SnI_6

Empirical formula	Cs_2I_6Sn
M	1145.95
Crystal system	cubic
Space group	*Fm*3*m* (no. 225)
a/Å	11.6410(3)
Z	4
D_c/g cm^{-3}	4.825
Preferred orientation, G(111)	0.103(2)
No. data points	4700
No. contributing reflections	128 (64 Kα doublets)
No. refined variables	14
R_{exp}	0.085
R_p	0.087
R_{wp}	0.114
R_{Bragg}	0.050
χ^2	1.80

$R_p = \Sigma|y_{i,o} - y_{i,c}|/\Sigma y_{i,o}$, $R_{wp} = [\Sigma w_i(y_{i,o} - y_{i,c})^2/\Sigma w_i y_{i,o}{}^2]^{1/2}$, $R_{Bragg} = \Sigma|I_{i,o} - I_{i,c}|/\Sigma I_{i,o}$, $R_{exp} = R_{wp}/(\chi^2)^{1/2}$, $\chi^2 = \Sigma w_i(y_{i,o} - y_{i,c})^2/(N_{obs} - N_{var})$, where y_i and I_i are the (observed or calculated) *profile* and *integrated* intensities, respectively, w_i is a weighting factor (taken as $1/y_{i,o}$), and N_{obs} and N_{var} are the number of observations and variables, respectively.

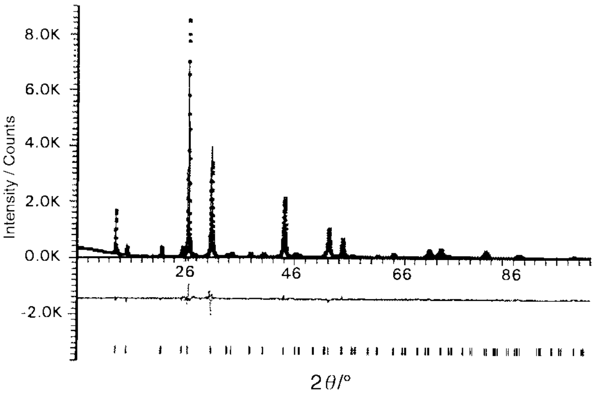

Fig. 1 Rietveld refinement plot for polycrystalline Cs_2SnI_6. Reflection markers and the difference plot are also included.

Powder structure of Cs_2SnI_6 and Mössbauer spectra of SnI_4L_2 complexes

Crystal data and refined values for the structural parameters of Cs_2SnI_6 are given in Table 1. A plot of the experimental X-ray diffraction pattern and difference data after Rietveld refinement are shown in Fig. 1, and final positional and thermal parameters are collected in Table 2. The $[SnI_6]^{2-}$ ion has a crystallographically imposed regular octahedral structure (and, hence, a zero value for the Mössbauer QS) with a Sn–I distance of 2.864(1) Å. That distance is longer than the average distances

Table 2 Atomic coordinates and isotropic thermal parameters for Cs_2SnI_6 with estimated standard deviations in parentheses

	X/*a*	*Y*/*b*	*Z*/*c*	*B*/Å^2
Sn	0	0	0	2.00(7)
Cs	0.25	0.25	0.25	4.51(7)
I	0.2460(1)	0	0	3.96(4)

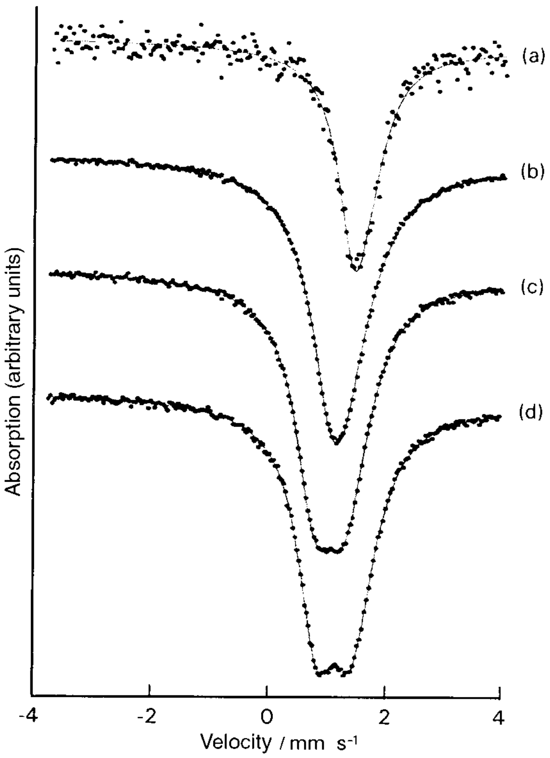

Fig. 2 Mössbauer spectra of Cs_2SnI_6 at room temperature (a), and $SnI_4(bipy)$ (b), $SnI_4(Ph_3PO)_2$ (c) and $SnI_4(Ph_2SO)_2$ (d) at liquid N_2 temperature.

Table 3 Mössbauer data (mm s^{-1}) and crystallographic average Sn–I distances (Å) for SnI_4L_2 complexes

	Cs_2SnI_6 [a]	SnI_4(bipy)	$SnI_4(Ph_3PO)_2$	$SnI_4(Ph_2SO)_2$
IS	1.37	1.09	1.02	1.15
QS	0	0.28	0.55	0.62
Γ_1	0.80	1.01	0.94	0.89
Γ_2	—	1.01 [b]	0.84	0.85
% effect	4	23	19	17
4 Δpqs [c]	0	0.56	1.10	1.24
d(Sn–I)	2.864(1)	2.802(2)	2.798(2)	2.784(1)

[a] At room temperature. [b] The two lines were constrained to have identical width. [c] Δpqs = pqs(L) − pqs(I$^-$).

reported for SnI_4(bipy) (2.802 Å),[32] $SnI_4(Ph_3PO)_2$ (2.798 Å),[34] and $SnI_4(Ph_2SO)_2$ (2.784 Å).[33] According to the relationship between crystallographic and Mössbauer data reported for SnX_4L_2 (X = Cl or Br),[28–30] ligands that are stronger donors than X$^-$ (*i.e.* have a negative pqs) weaken the Sn–X bond and give rise to longer Sn–X distances, while ligands that are weaker donors than X$^-$ (*i.e.* have a positive pqs) give rise to shorter Sn–X distances. In both cases the more positive or negative the pqs is, the more different the Sn–X distances from those found in the $[SnX_6]^{2-}$ anion. If a similar relationship also holds for SnI_4L_2 complexes, the ligands bipy, Ph_3PO and Ph_2SO are weaker donors than I$^-$, have a more positive pqs, and the QS should increase in the order $Cs_2SnI_6 < SnI_4(bipy) < SnI_4(Ph_3PO)_2 < SnI_4(Ph_2SO)_2$ (all three complexes have a *cis* structure). The four Mössbauer spectra are displayed in Fig. 2, where it is shown that the linewidth increases from Cs_2SnI_6 to SnI_4(bipy), while an incipient doublet is starting to be resolved for $SnI_4(Ph_3PO)_2$, and it is clearly seen for $SnI_4(Ph_2SO)_2$. Bearing in mind that the average Sn–I bond length for SnI_4(bipy) (2.802 Å)[32] is significantly shorter than for Cs_2SnI_6 (2.864 Å), the QS for the former complex should not be exactly zero. Indeed, going from a single line fit to a doublet fit reduces the linewidth from 1.11 to 1.01 mm s^{-1}, and χ^2 from 1.68 (with 252 degrees of freedom) to 0.98 (with 250 degrees of freedom), while the statistically acceptable values of χ^2 are in the range 0.80–1.22.[45] Therefore, although the computed QS value of 0.28 mm s^{-1} is probably subject to a higher error than for the other compounds reported in this paper, it is certainly more accurate than a QS value of 0 mm s^{-1}. The spectra of SnI_4(bipy)[72,73] and $SnI_4(Ph_3PO)_2$[74] have been previously reported as single lines and the IS values are in reasonable agreement with ours. While the spectra of the SnI_4L_2 complexes were collected at liquid N_2 temperature, the spectrum of Cs_2SnI_6 was registered at room temperature because we know from the XRPD data that it is cubic at that temperature and, therefore, its Mössbauer QS is exactly zero (we do not know if it may have a phase transition at lower temperatures). The lower percent effect in the room temperature spectrum of Cs_2SnI_6 is reflected in the appearance of the spectrum (see Fig. 2). The Mössbauer parameters are collected in Table 3 with the Sn–I distances. The IS values of the SnI_4L_2 complexes are consistent with those expected for octahedral SnI_4 complexes with N and O donor ligands,[25] while the QS and pqs data† can be related to the Sn–I distances by means of the correlation $d(\text{Sn–I}) = -0.058\ (4\ \Delta\text{pqs}) + 2.854$ Å. Although, the range of Sn–I distances in Table 3 is very narrow, the range for SnI_4L_2 complexes that can be obtained in the future is not much broader for the following reasons. (a) If complexes containing $[SnR_2I_4]^{2-}$ anions cannot be obtained (see above), the next type of ligands that give rise to long Sn–X distances are phosphines,[28] and the average Sn–I distance in $SnI_4(PPr^n{}_3)_2$ is 2.867 Å,[35] only 0.003 Å longer than for Cs_2SnI_6. (b) The shortest Sn–I distances for SnI_4L_2 complexes will be obtained for the weakest donor ligands that can form isolable complexes with SnI_4. The crystal structures of $SnX_4(thf)_2$ (X = Cl or Br) have been reported recently,[75] but no complex between SnI_4 and thf could be isolated. Bearing in mind that the average Sn–Br distances for $SnBr_4(thf)_2$[75] and $SnBr_4(Ph_2SO)_2$[76] are quite similar, we may conclude that $SnI_4(Ph_2SO)_2$ is close to the limit of shortest Sn–I distances that can be obtained for SnI_4L_2 complexes.‡ Therefore, although the correlation is probably not very significant, it can be a useful guide to relate Mössbauer and crystallographic data within the short range of Sn–I distances expected for SnI_4L_2 complexes. In any case, the principal point is that SnI_4L_2 complexes follow the same trend as SnX_4L_2 (X = Cl or Br), showing that ligands that are weaker donors than I$^-$ (*i.e.* have a more positive pqs) give rise to Sn–I distances that are shorter than for the $[SnI_6]^{2-}$ anion.

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† Δpqs = pqs(L) − pqs(I$^-$). QS = 2 Δpqs for *cis* complexes, and −4 Δpqs for *trans* complexes.

‡ *Note added at proof*: quite recently, the structures of three octahedral tin(IV) iodide complexes with O amd As donor ligands have been reported.[77] Average Sn–I distances range from 2.784 to 2.814 Å.

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