Tin–Bromine Bond Lengths and Mössbauer Quadrupole Splittings of Tin(IV) Bromide Complexes. Crystal Structure of Pyridinium Tetrabromodiphenylstannate(IV) ‡

David Tudela *[,a] and **Masood A. Khan** †[,b]
[a] *Departamento de Química, Universidad Autónoma de Madrid, 28049-Madrid, Spain*
[b] *Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA*

Mössbauer and crystallographic data have been obtained for pyridinium tetrabromodiphenylstannate(IV). The Sn atom is six-co-ordinated in the centrosymmetric *trans*-$[SnBr_4Ph_2]^{2-}$ anion with bond distances Sn–Br(1) 2.7592(3), Sn–Br(2) 2.7737(3) and Sn–C(11) 2.158(3) Å. The average Sn–Br distance for five octahedral tin(IV) bromide complexes, $SnBr_4L_2$, is related to the partial quadrupole splitting (p.q.s.) of the ligands by means of the correlation d(Sn–Br)/Å = (−0.048 ± 0.002)(4 p.q.s.) + (2.589 ± 0.003). The relationship rationalises the experimental Sn–Br distances and quadrupole splitting data in terms of the donor properties of the auxiliary ligands (L) in such a way that weak donor ligands give rise to shorter Sn–Br distances. The Mössbauer quadrupole splitting can be useful in the assignment of ν(SnBr) vibrations in the IR and Raman spectra of *trans*-$SnBr_4L_2$ compounds.

Recently we reported a linear relationship [equation (1)]

$$d(\text{Sn–Cl})/\text{Å} = (-0.044 \pm 0.002)(4\ \text{p.q.s.}) + (2.420 \pm 0.003) \quad (1)$$

between the Sn–Cl distance in octahedral tin(IV) chloride complexes $SnCl_4L_2$ and the Mössbauer partial quadrupole splitting (p.q.s.) associated with L.[1] This correlation can yield information about the Sn–L bond strength and the sign of the quadrupole splitting (q.s.), as well as rationalise experimental Sn–Cl distances and q.s. data. A recent example is that of the Mössbauer spectrum of *trans*-$SnCl_4(Ph_2PS_2N_3)_2$,[2] where a single line is observed which is expected[1] on the basis of the average observed Sn–Cl distance of 2.402 Å.[3] Equation (1) can be used to estimate Sn–Cl distances, which are expected to match experimental ones within ±0.02 Å. Additionally discrepancies with the reported Sn–Cl distances for tetrachlorobis(1,3-diethylthiourea)tin(IV)[4] enabled us to detect the incorrectness of the published crystal structure.[5] The calculation of bond distances from the q.s. represents a new structural application of Mössbauer spectroscopy which has been widely used to obtain qualitative information on the stereochemistry of tin compounds,[6,7] but has not so far yielded accurate bond lengths. Quantitative structural predictions from the q.s. have also been obtained for the C–Sn–C angle in diorganotin(IV) compounds,[8] but the calculated values are not very reliable.[9]

It is important to note that equation (1) is empirical and there seems to be no theoretical basis for a linear correlation between interatomic distances and q.s. data. For that reason the validity of equation (1) should be checked for other tin tetrahalide complexes. In the case of octahedral tin(IV) bromide complexes, only a few crystal structures are available in the literature,[4,10–17] and the reported average Sn–Br distances (2.51–2.57 Å) are shorter than in $SnBr_6^{2-}$ (*ca.* 2.60 Å).[18–20] In order to study the relationship between Sn–Br distance and the Mössbauer q.s. a broader range of Sn–Br distances needs to be considered. We were thus interested in $SnBr_4L_2$ complexes in which L was a stronger donor than Br (*i.e.* ligands with a negative p.q.s.) and for which Sn–Br distances > 2.60 Å were expected.[1] We report herein the Mössbauer data and crystal structure of such a complex pyridinium tetrabromodiphenylstannate(IV).

Experimental

The ^{119}Sn Mössbauer spectrum of pyridinium tetrabromodiphenylstannate(IV) was recorded on a Ranger Scientific Inc. MS-1200 constant-acceleration Mössbauer spectrometer. A standard source of $Ca^{119}SnO_3$ was used at room temperature in transmission geometry, and the γ radiation was filtered with a Pd foil. The polycrystalline sample was mounted on a standard copper sample holder with aluminium windows, and cooled to 80 ± 0.5 K by means of a liquid nitrogen cryostat. The isomer shift (i.s.) is relative to $BaSnO_3$ at room temperature, and the reproducibility of the Mössbauer parameters was ±0.05 mm s^{-1}.

Preparation of Pyridinium Tetrabromodiphenylstannate(IV).—A solution of $SnBr_2Ph_2$ (2.69 g, 6.2 mmol) in $CHCl_3$ (40 cm^3) was added at room temperature to a stirred solution of C_5H_5NHBr (1.99 g, 1.24 mmol) in $CHCl_3$ (80 cm^3), and led to the formation of a white solid. The mixture was heated to boiling and then allowed to cool to room temperature. The white solid was then filtered off, washed with $CHCl_3$ and recrystallized from hot MeCN yielding $[C_5H_5NH]_2[SnBr_4Ph_2]$ (3.83 g, 81.8%) as colourless crystals, m.p. 200–201 °C (decomp.), (lit.,[21] 195 °C) (Found: C, 35.2; H, 3.0; N, 3.8. Calc. for $C_{22}H_{22}Br_4N_2Sn$: C, 35.1; H, 2.95; N, 3.7%). IR (Nujol and hexachlorobutadiene): 3216m, 3156m, 3133w, 3103m, 3087w, 3071m, 3041w, 1637m, 1607s, 1569w, 1533s, 1485s, 1478s, 1429s, 1327m, 1308m, 1239m, 1197m, 1158w, 1060w, 1050m, 1021m, 996m, 873m, 735vs, 697m, 672vs, 560m, 464s and 287m cm^{-1}. Mass spectrum (12 eV, *ca.* 1.92 × 10^{-18} J): *m/z* 432 (0.7, $SnBr_2Ph_2$), 353 (3.5, $SnBrPh_2$), 276 (2.5, SnBrPh), 199 (0.5, SnBr), 197 (0.5, SnPh), 156 (0.7, PhBr), 154 (14.4, Ph_2), 80 (30.9, HBr), 79 (100, C_5H_5N) and 52 (5.3%, C_5H_5N − HCN). Mössbauer (80 K): i.s. = 1.54, q.s. = 3.70, Γ_1 = 1.03 and Γ_2 = 0.97 mm s^{-1}.

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† Author for correspondence on X-ray diffraction results.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic coordinates for the non-hydrogen atoms of pyridinium tetrabromodiphenylstannate(IV)

Atom	*x*	*y*	*z*
Sn	0.500 00(0)	0.500 00(0)	0.500 00(0)
Br(1)	0.442 36(2)	0.341 93(4)	0.232 61(4)
Br(2)	0.593 25(2)	0.674 06(4)	0.303 33(4)
N(1)	0.579 2(3)	0.267 7(8)	−0.063 1(6)
C(11)	0.407 9(2)	0.670 8(4)	0.466 8(3)
C(12)	0.422 9(2)	0.828 3(4)	0.489 4(4)
C(13)	0.365 4(2)	0.938 7(4)	0.459 7(4)
C(14)	0.292 2(2)	0.891 6(5)	0.405 5(5)
C(15)	0.275 8(2)	0.735 2(5)	0.384 7(5)
C(16)	0.333 4(2)	0.624 7(4)	0.415 1(4)
C(22)	0.624 7(4)	0.338 6(7)	0.038 8(9)
C(23)	0.674 1(4)	0.249 9(11)	0.138 5(7)
C(24)	0.669 9(4)	0.091 5(9)	0.120 9(7)
C(25)	0.618 9(4)	0.030 8(6)	0.011 5(7)
C(26)	0.575 3(3)	0.120 1(9)	−0.078 1(6)

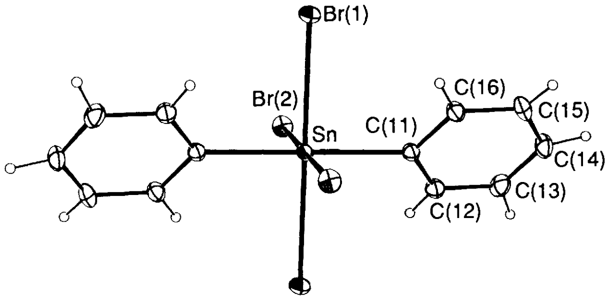

Fig. 1 ORTEP drawing of the centrosymmetric $[SnBr_4Ph_2]^{2-}$ anion in $[C_5H_5NH]_2[SnBr_4Ph_2]$. Selected bond distances (Å) and angles (°): Sn–Br(1) 2.7592(3), Sn–Br(2) 2.7737(3), Sn–C(11) 2.158(3), Br(1)–Sn–Br(2) 88.67(1), Br(1)–Sn–C(11) 89.62(8), Br(2)–Sn–C(11) 89.78(8)

Crystallography.—Crystal data. $C_{22}H_{22}Br_4N_2Sn$, M = 752.74, monoclinic, a = 17.112(3), b = 8.551(2), c = 8.365(2) Å, β = 92.46(2)°, U = 1222.9(6) Å^3 (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (alt. $P2_1/c$, no. 14), D_m = 2.04 g cm^{-3} (by flotation in CCl_4–CH_3I), Z = 2, D_c = 2.044 g cm^{-3}, $F(000)$ = 716. Colourless needles with hexagonal cross-section. Approximate crystal dimensions 0.28 × 0.19 × 0.15 mm, μ(Mo-Kα) = 75.3 cm^{-1}.

Data collection and processing.[22] CAD4 diffractometer, ω–2θ mode with ω scan width 0.75 + 0.35 tan θ, variable scan speed with maximum recording time 90 s, graphite-monochromated Mo-Kα radiation; 2137 unique reflections ($1 \leqslant \theta \leqslant 25°$, $\pm h, k, l$), 1651 reflections with $I > 2\sigma(I)$ were considered as observed. The data were corrected for Lorentz and polarization effects, and a numerical absorption correction was applied (max., min. transmission factors = 0.423, 0.338). No significant crystal decay was observed.

Structure analysis and refinement. Heavy-atom method. Full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms. All the hydrogen atoms were located and refined isotropically. Final R and R' values were 0.019 and 0.021 for 1651 unique observed reflections (number of variables = 177); weighting scheme $w = 1/\sigma^2(F_o)$. No features of chemical significance in final difference map; largest peak 0.3 e Å^{-3}. Programs used and sources of scattering factor data are given in ref. 22. Final positional parameters for the non-hydrogen atoms are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 2 Partial quadrupole splitting[a] of ligands (L) and average Sn–Br distances for octahedral compounds $SnBr_4L_2$

Structure	L	4(p.q.s.)/mm s^{-1}	d(Sn–Br)[b]/Å
cis	Me_2SO	0.86[c]	2.541[d]
trans	$(Me_2N)_3PO$	0.83[e,f]	2.550[g]
trans	Ph_3PO	0.61[e]	2.557[h]
O_h[i]	Br	0[j]	2.600[k]
trans	Ph	−3.70[l]	2.766[l]

[a] 4(p.q.s.) = −q.s. for *trans* compounds; 2 q.s. for *cis* compounds. The sign of the q.s. has been assigned on the basis of chemical considerations and better correlation with the Sn–Br distances. [b] Average value. [c] Ref. 29. [d] Ref. 10. [e] Ref. 30. [f] Ref. 31. [g] Ref. 11. [h] Ref. 12. [i] No $SnBr_6^{2-}$ anion with a perfect octahedral environment about Sn has been reported. Only compounds with Sn–Br distances within 0.005 Å of the mean value, and angles within 0.7° of regular octahedral values have been considered. [j] Required by symmetry. [k] Ref. 18–20. [l] This work.

Results and Discussion

The structure of pyridinium tetrabromodiphenylstannate(IV) consists of pyridinium cations and octahedral *trans*-$[SnBr_4Ph_2]^{2-}$ anions. The shortest N···Br interatomic distance [N(1)···Br(2) 3.533(7) Å] is longer than the sum of the van der Waals radii (3.4 Å).[23] An ORTEP view of the centrosymmetric anion is given in Fig. 1 with the most relevant structural parameters. The average Sn–Br distance is the longest so far reported for a $SnBr_4L_2$ system, as expected from the isovalent rehybridisation concept,[24] since the tin atom will concentrate greater s character into the hybrid orbitals directed toward the less electronegative phenyl groups, and greater p character in the hybrid orbitals directed to Br.

The Mössbauer spectrum of $[C_5H_5NH]_2[SnBr_4Ph_2]$ displays a well resolved doublet with i.s. = 1.54 mm s^{-1} and q.s. = 3.70 mm s^{-1}. The isomer shift is 0.10 mm s^{-1} higher than that reported for $[C_5H_5NH]_2[SnCl_4Ph_2]$,[25] in accord with the higher electronegativity of Cl. The average difference between the i.s. of $SnBr_4L_2$ and $SnCl_4L_2$ complexes is 0.27 mm s^{-1} (standard deviation 0.07 mm s^{-1}),[26] but it is well known that the i.s. of organotin compounds is much less sensitive to change in the electronegativity of the halogen than is the i.s. of inorganic tin compounds.[27] The q.s. value of 3.70 mm s^{-1} {compared to 3.80 mm s^{-1} for $[C_5H_5NH]_2[SnCl_4Ph_2]$[25]} leads to a calculated C–Sn–C angle[8] of 165° reduced by 15° from the experimental value of 180°. Such a difference illustrates the limitations of the structural predictions based on the C–Sn–C angle *vs.* q.s. correlation,[9] for which expected potential errors of ±13° have been reported.[28]

The q.s. of octahedral *cis*- and *trans*-$SnBr_4L_2$ species is related to the p.q.s. of the ligands by means of the point-charge expressions: q.s. = 2 p.q.s. (L) − 2 p.q.s. (Br) for *cis* complexes, and q.s. = 4 p.q.s. (Br) − 4 p.q.s. (L)* for *trans* complexes. Bearing in mind that the octahedral p.q.s. of Br is close to zero,[6] p.q.s. data can be calculated for ligands L, and are collected in Table 2 alongside average Sn–Br distances for those octahedral tin(IV) bromide complexes for which both data are available. The sign of the q.s. has not been experimentally measured for the compounds included in Table 2, but there is little doubt that the reported signs are correct for the following reasons. (*i*) They agree with those accepted in the literature,[1,6,32] and (*ii*) they are consistent with the idea that weaker donors than Br$^-$ have a positive p.q.s.,[6] and should give rise to shorter Sn–Br distances than in the anion $SnBr_6^{2-}$.[1] The p.q.s. value for a ligand L is somewhat dependent on the nature of the other ligands in the compound[33] and on their geometric arrangement.[34] For that reason, p.q.s. values for L in Table 2 have been obtained from

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* These expressions give the sign of the q.s., and differ from expressions giving the sign of the electric field gradient because the quadrupole moment of the excited state is negative for ^{119}Sn.

Table 3 Vibrational Sn–Br stretching frequencies and Mössbauer quadrupole splitting for *trans*-$SnBr_4L_2$ complexes

L	E_u/cm^{-1}	A_{1g}/cm^{-1}	B_{1g}/cm^{-1}	Ref.	q.s.*/mm s^{-1}	Ref.
PBu_3	197	166	141	35	1.01	35
$AsEt_3$	203	168	149	35	0.83	35
C_4H_8S	230	181	152,149	43	−0.41	44
$(Me_2N)_3PO$	240	187	145	43	−0.83	30,31
dmf	243	198	150	45	−0.83	34
thf	248	202	159	43	−1.31	38,46

* Sign assigned by chemical considerations (see ref. 34) and better correlation with the ν(SnBr) modes.

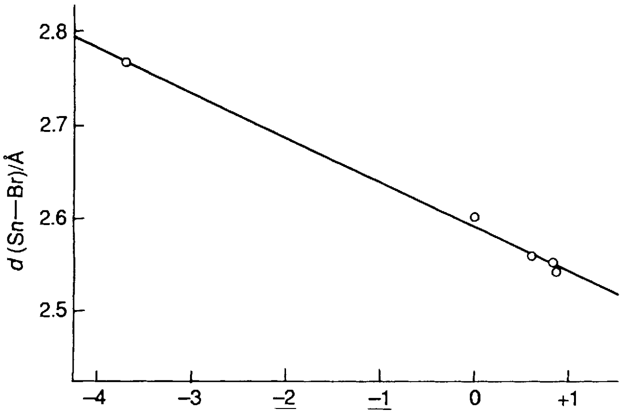

Fig. 2 Plot of $\bar{d}$(Sn–Br) *vs.* 4(p.q.s.)

the experimental q.s. of $SnBr_4L_2$ rather than using tabulated values.[6,32]

The data in Table 2 show that the Sn–Br bond length increases as the p.q.s. of the ligands L becomes more negative. This is the same trend as observed for the Sn–Cl bond lengths in tin(IV) chloride complexes,[1] and is expected because as the donor strength of the ligand L increases, the Sn–L bond becomes stronger and the Sn–Br bond becomes weaker, while the p.q.s. of the L decreases. This trend can also be rationalised in terms of the concept of isovalent rehybridisation.[1] Having established a relationship between the Sn–Br distance and p.q.s. data, we can determine whether this relationship is essentially linear for practical purposes, as in the case of tin(IV) chloride complexes. A least-squares linear regression of the data in Table 2 gives equation (2) (correlation coefficient $r = 0.998$, for

$$d(\text{Sn–Br})/\text{Å} = (-0.048 \pm 0.002)\,(4\,\text{p.q.s.}) + (2.589 \pm 0.003) \quad (2)$$

five data points). In spite of the satisfactory correlation, Fig. 2 shows that to be sure of a linear behaviour over the whole range of *d*(Sn–Br) and 4 p.q.s., more data points would be needed for compounds with *d*(Sn–Br) in the range 2.60–2.76 Å. According to equation (2), Sn–Br distances of *ca.* 2.64 Å are expected for some *trans*-$SnBr_4L_2$ complexes with L = phosphine whose reported q.s. values are 1 mm s^{-1}.[35,36] Unfortunately, attempts to obtain crystals suitable for X-ray analyses for this class of compound have been unsuccessful.[37] Nevertheless, the similarity of the slope in equations (1) and (2) suggests a very similar behaviour for complexes $SnCl_4L_2$ and $SnBr_4L_2$, and it is reasonable to assume that equation (2) can be used for quantitative purposes, though some caution should be applied.

By means of equation (2) we can estimate the shortest possible average Sn–Br distance for an $SnBr_4L_2$ compound. Acetonitrile and diethyl ether form stable complexes with $SnCl_4$, but not with the weaker Lewis acid $SnBr_4$.[38] By comparison with the q.s. of $SnCl_4L_2$ and $SnBr_2Cl_2$ (L = MeCN or OEt_2)[38] we can estimate a q.s. of *ca.* 1 mm s^{-1} for *cis*-$SnBr_4(MeCN)_2$ and *ca.* 1.4 mm s^{-1} for *trans*-$SnBr_4(OEt_2)_2$ which correspond to Sn–Br distances of 2.49 and 2.52 (±0.02) Å, respectively; and we can expect that the shortest average Sn–Br distance should be *ca.* 2.50–2.51 Å. Shorter distances would only be expected for weaker donor ligands which probably would not form stable complexes with $SnBr_4$. The shortest average Sn–Br distance so far reported for an octahedral $SnBr_4L_2$ complex is 2.514 Å (near the lowest possible limit) for the chelate $SnBr_4(Bu^tNHCOCONHBu^t)$,[16] while the average Sn–Br distance for $SnBr_4$ itself is 2.41 Å.[39]

It was previously thought that for tin(IV) halide complexes with Group 15 and 16 donor atom ligands only the *trans* isomers yield resolvable doublets,[7] but we have shown that both *cis* and *trans* complexes SnX_4L_2 can yield resolved doublets or single lines according to the donor properties of the ligands L.[1,40,41] Whether Mössbauer doublets can be resolved depends not only on the q.s. but also upon experimental conditions such as source, sample thickness or quality of the spectrum. Although in particular cases q.s. values smaller than 0.6 mm s^{-1} can appear as partially resolved doublets,[41] normally only for q.s. values higher than *ca.* 0.6–0.7 mm s^{-1} can doublets be observed even in good quality ^{119}Sn Mössbauer spectra. We can use equation (2) to estimate that for octahedral $SnBr_4L_2$ complexes with *d*(Sn–Br) longer than *ca.* 2.65 Å or shorter than *ca.* 2.53 Å, both *cis* and *trans* isomers should display a resolved quadrupole doublet, while a single line spectrum will be obtained for both isomers for *d*(Sn–Br) in the range 2.56–2.62 Å. Resolved doublets would be obtained only for *trans* isomers if *d*(Sn–Br) is in the ranges *ca.* 2.53–2.56 or *ca.* 2.62–2.65 Å. For example a single line has been reported in the Mössbauer spectrum of *cis*-$SnBr_4(Ph_2SO)_2$,[42] in which the average Sn–Br distance is 2.542 Å.[17]

The weakening of the Sn–Br bonds in compounds $SnBr_4L_2$ as the ligand L becomes a stronger donor (*i.e.* has a more negative p.q.s.) should also be reflected in the IR and Raman Sn–Br stretching frequencies.[34] Table 3 shows data for six octahedral *trans*-$SnBr_4L_2$ complexes from which it can be seen that ν(Sn–Br) bands shift to higher wavenumbers as the q.s. values become more negative (positive p.q.s. values). Although the Raman active B_{1g} mode is not very sensitive to the L, the IR active E_u and the Raman active A_{1g} modes show a marked dependence on the q.s., and least-squares linear regressions give the relations E_u/cm^{-1} [(−23 ± 1) q.s. + (221 ± 1)] ($r = 0.996$), and A_{1g}/cm^{-1} [(−15 ± 2) q.s. + (180 ± 2)] ($r = 0.96$). These equations can be useful for band assignments in IR and Raman spectra, but predictions can fail for some compounds if ν(Sn–Br) modes are strongly coupled to other vibrations.

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