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Adducts of Tin(IV) and Organotin(IV) Derivatives with 2,2′-Azopyridine
II. Crystal and Molecular Structure of $SnMe_2Br_2AZP$ and Further Mössbauer and Photoelectronic Spectroscopic Studies

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Abstract

A series of adducts of tin(IV) derivatives with 2,2′-azopyridine, AZP, has been studied by Mössbauer and X-ray photoelectronic spectroscopies and the crystal and molecular structure of $SnMe_2Br_2$-AZP has been determined. The linear correlation of the Mössbauer parameter isomer shift with partial atomic charge on tin suggests the occurrence of a single homologous series of isostructural adducts. The correlation of the Mössbauer parameter quadrupole splitting and C–Sn–C bond angle permits their calculation in $SnMe_2X_2AZP$ adducts (X = Cl, Br). The N_{1s} binding energies, obtained by XPS data, pointed out two slightly different values for both pyridinic and azo-group nitrogens. The crystallographic study of the $SnMe_2Br_2AZP$ adduct shows a new structure in which the Sn atom is seven-coordinated.

Introduction

A series of adducts of tin(IV) derivatives with 2,2′-azopyridine (AZP), SnR_nhal_{4-n}/AZP ($n = 0$, hal = Cl, Br; $n = 1$, R = Me, hal = Cl, Br; $n = 1$, R = Bu^n, Oct^n, hal = Cl; $n = 2$, R = Me, hal = Cl, Br), has been synthesized and characterized by infrared and Mössbauer spectroscopy, as well as by lattice dynamic studies [1].

Molecular monomeric octahedral structures have been proposed in the solid, with AZP chelated through one heterocyclic and one azo-group nitrogen [1]. We report here the crystal and molecular structure of $SnMe_2Br_2AZP$, and the X-ray photoelectronic spectra of some adducts. The correlations of Mössbauer parameters, the isomer shifts with partial atomic charges on tin [2, 3] and of the quadrupole splittings with the C–Sn–C bond angles [4], are also discussed.

Experimental

The adducts were obtained as described in ref. 1. The Mössbauer spectra were obtained at liquid N_2 temperature [1].

The partial atomic charges on tin values, Q_{Sn}, were calculated by using the CHELEQ program [2, 3] for octahedral structures (see Fig. 4 in ref. 1).

Input formal charge on Sn is taken as 0.00; bond orders, N, and formal charges, F, in the octahedral tin environments (input parameters of the CHELEQ program) have been assigned as follows: (a) all Sn–C bonds: $N = 1.00$, $F_C = 0.00$; (b) $SnMe_2hal_2$: $N_{Sn-N,Sn-hal} = 0.50$, $F_N = +0.50$, $F_{hal} = -0.50$; (c) $SnAlkhal_3AZP$: $N_{Sn-N,Sn-hal} = 0.60$, $F_N = +0.60$, $F_{hal} = -0.40$; (d) $Snhal_4AZP$: $N_{Sn-N,Sn-hal} = 0.667$, $F_N = +0.667$, $F_{hal} = -0.333$. Other parameters in the rest of the molecules were assigned according to the usual valence bond formulation [2].

X-ray photoelectronic spectra were taken with a VG ESCA-3 MK II Spectrometer using Al $K\alpha_{1,2}$ excitation (1486.6 eV) at a residual pressure of 10^{-7} Pa.

Samples were dusted as thin film onto a gold plate to minimize charging effects. Calibration was made by $4f_{7/2}$ gold signal at 83.7 eV and sample charging was corrected by referencing to the C1s line of contaminating oil-carbon, taken at 285.0 eV. The accuracy of the measured binding energies (b.e.) was estimated at ±0.2 eV. Cooling of the

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TABLE 1. Summary of crystal data and intensity measurements

Formula	$C_{12}H_{14}Br_2N_4Sn$
Formula weight	492.78
a (Å)	7.599(2)
b (Å)	14.372(8)
c (Å)	15.394(7)
β (°)	91.52(3)
V (Å^3)	1680.8(12)
Z	4
Space group	$P2_1/c$
Crystal dimension (mm)	0.30 × 0.30 × 0.10
Radiation	Mo Kα
Diffractometer	Nicolet P3
Scan mode	$2\theta-\theta$
Scan range (°)	1.3
Background counts	1/4 of scan time at the end of scan
2θ limits (°)	3–56
No. reflections collected	4828
No. unique data ($I > 3\sigma(I)$)	1831
No variables	172
Final R, R_w	0.069, 0.078

samples to liquid N_2 temperature was performed against possible secondary decomposition effects. Peak deconvolution was performed with a Du Pont 310 curve resolver using a Gaussian shape fit.

X-ray Data

Red single crystals of the title compound were grown from ligroin. Preliminary Weissenberg films showed the crystals to be sensitive to X-rays, therefore the crystal specimen was sealed in a thin-walled capillary.

Monitoring of 4 standard reflections, at intervals of 100 reflections, showed no appreciable decay during data collection. A ψ-scan of the reflections 004 and 006, both with χ angle close to 90°, showed absorption phenomena. The data were then corrected by Lorentz and polarization effects and for absorption. A summary of the crystal and intensity data is given in Table 1.

Solution and Refinement of the Structure

The structure was solved by using standard Patterson and Fourier methods to determine the positions of all non-H atoms. The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = a + F_o + cF_o^2$, where a and c are of the order of $2F_o$(min) and $2/F_o$(max) [5]. H atoms were introduced in calculated positions (C–H = 0.96 Å). The calculations were performed on the Eclipse MV/8000 II Data General computer using the Sir-Caos program [6]. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography [7]. See also 'Supplementary Material'.

TABLE 2. Isomer shift, *IS*, and partial atomic charge on tin, Q_{Sn}

Compound	IS^a (mm s^{-1})	$Q_{Sn}{}^b$
$SnCl_4AZP$	0.39	0.413
$SnBr_4AZP$	0.57	0.371
$SnMeCl_3AZP$	1.10	0.318
$SnBu^nCl_3AZP$	1.13	0.319
$SmMeBr_3AZP$	1.18	0.293
$SmMe_2Cl_2AZP$	1.48	0.227
$SnMe_2Br_2AZP$	1.59	0.218

[a] At liquid N_2 temperature with respect to R.T. $Ca^{119}SnO_3$. [b] Q_{Sn} for $SnOct^nCl_3AZP$ corresponds to the $SnBu^nCl_3AZP$ value.

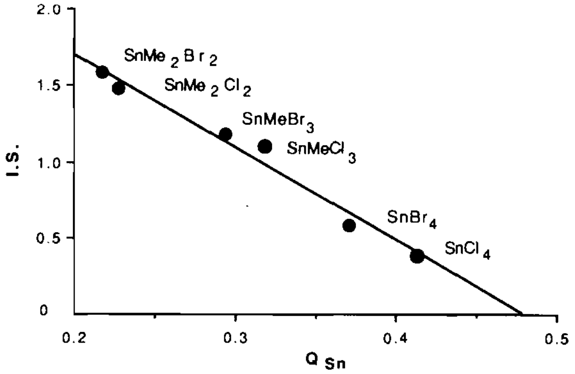

Fig. 1. The correlation IS/Q_{Sn} for the AZP adducts. Full line is the least-squares fit of data points, see Table 2, the related equation and correlation coefficient being: $IS = 2.94 - 6.15\ Q_{Sn}$; $r = 0.983$.

Results and Discussion

Mössbauer Studies

The dependence of the Mössbauer isomer shift values from partial atomic charges on tin (Q_{Sn}), Table 2 and Fig. 1, is linear with a reasonably good correlation coefficient, in agreement with previous results on numerous series of homologous tin(IV) and organotin(IV) compounds [3].

The data points IS/Q_{Sn} for $SnBu^nCl_3$ and $SnOct^nCl_3$ do not match this correlation (see data in Table 2) as expected from previous studies on $SnAlk_n$ derivatives [3], and therefore they have not been taken into account. It is worth noting that this rationalization of the isomer shift data does not distinguish between the bonds to tin by nitrogen atoms of a pyridine and of the azo-group and the bonds to tin by two pyridine nitrogens; in the latter case, a linear correlation is again obtained, as the Q_{Sn} data are constantly decreased by about 0.007. This trend suggests the occurrence of a single homologous series of isostructural AZP adducts.

TABLE 3. Experimental XPS binding energies

Compounds	Binding energies (eV)					
	N_{1s}				$Sn_{3d5/2}$	
	N(1)	N(2)	N(3)	N(4)	Exp.	Corrected
AZP[a]	400.1		398.9			
Pyridine			398.8			
$SnMe_2Br_2AZP$[a]	401.1	400.0	399.4	398.6	486.9	
$SnBr_4AZP$[a]	401.0	400.1	399.5	398.6	486.9	
$SnCl_4pyz$[b]					488.0	
$SnPh_2Cl_2pyz$[b]					487.7	
$SnCl_4DPE$[c]					487.7	498.0
$SnPh_2Cl_2DPE$[c]					487.2	483.0

[a] See Fig. 2 for the identification of N atoms. [b] pyz = pyrazine, see ref. 9. [c] DPE = 1,2-bis(diphenylphosphino)ethane, see ref. 10.

By using the point-charge formalism, the relation between the Mössbauer quadrupole splitting and the C–Sn–C bond angle, crystallographically determined, has been checked for the $SnMe_2Br_2AZP$ adduct [4]. A good agreement has been found between the calculated and experimental values for *QS* and C–Sn–C bond angle: 4.06 mm s^{-1} gives an angle of 169°, while the experimental angle, 162°, gives a splitting of 3.97 mm s^{-1}. Moreover all these data fit very well the calculated curve reported by Parish [4]. The $SnMe_2Cl_2AZP$ adduct presents a *QS* value of 3.80 mm s^{-1} [1] from which a C–Sn–C bond angle of about 153°, smaller than in the bromine derivative, can be calculated. The greater acidity of tin, due to two Sn–Cl bonds, could cause stronger coordination of the nitrogen of the second pyridine: in this way the tin environment becomes approximately seven-coordinated with a consequent C–Sn–C bond angle distortion.

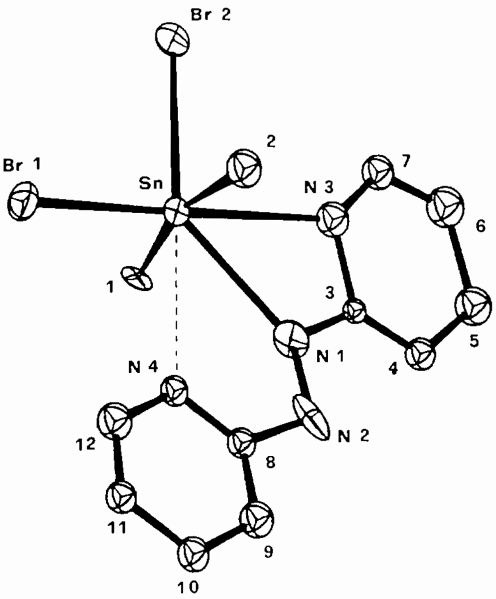

Fig. 2. Perspective view of $SnMe_2Br_2AZP$.

XPS Studies

The core level binding energy (b.e.) values of nitrogen and tin atoms of some compounds of this series have been investigated and evaluated with respect to compounds chosen as references. The results are shown in Table 3.

The N_{1s} photoelectronic signals for the AZP ligand and the $SnMe_2Br_2$ and $SnBr_4AZP$ complexes are very broad (2.7 and 3.5 eV FWHU respectively). This fact suggests the occurrence of different types of nitrogen atoms under our experimental conditions.

Analysis of the N_{1s} spectrum of the AZP ligand, obtained by deconvolution of the photoelectronic peak, shows two b.e. values, 398.9 and 400.1 eV. The 398.9 eV b.e. value is exactly the same as that of the N atom of pyridine [8] and is attributable to the two nitrogen pyridinic atoms N(3) and N(4) of the ligand, whereas the 400.1 eV b.e. value is attributable to the N(1) and N(2) atoms of the azo-groups, see Fig. 2.

The N_{1s} spectra of $SnMe_2Br_2AZP$ and $SnBr_4AZP$ complexes are very close and their analysis, obtained by deconvolution, gives four b.e. values, see Table 3. The 400.0 and 398.6 eV b.e. values are coincident with the N_{1s} b.e. values of N(1) or N(2) (400.1 eV) and N(3) or N(4) (398.9 eV) respectively of the free AZP ligand. This fact shows that no electronic charge density change with respect to the free ligand occurs for one pyridinic and one azo-group nitrogen and presumably these N atoms do not coordinate or only weakly coordinate to the metal atom.

TABLE 4. Atomic coordinates and isotropic displacement parameters with e.s.d.s in parentheses

	x	y	z	B_{eq}[a]
Sn(1)	0.1943(2)	0.1947(1)	0.7689(1)	4.23(3)
Br(1)	0.1760(3)	0.0210(2)	0.7132(2)	5.7(1)
Br(2)	0.3785(4)	0.2571(2)	0.6373(2)	6.4(1)
C(1)	0.410(3)	0.169(2)	0.856(2)	5.6(7)
C(2)	−0.063(4)	0.239(2)	0.761(2)	7.8(9)
C(3)	0.170(2)	0.370(1)	0.905(1)	4.7(6)
C(4)	0.179(3)	0.435(2)	0.972(1)	4.7(6)
C(5)	0.273(3)	0.515(2)	0.957(2)	6.4(8)
C(6)	0.357(3)	0.522(2)	0.877(2)	6.6(8)
C(7)	0.340(3)	0.454(2)	0.821(1)	7.0(9)
C(8)	−0.093(2)	0.173(1)	0.959(1)	3.0(5)
C(9)	−0.218(2)	0.151(2)	1.018(1)	4.7(6)
C(10)	−0.283(3)	0.063(2)	1.017(1)	5.1(6)
C(11)	−0.233(3)	0.003(2)	0.957(1)	4.9(6)
C(12)	−0.110(3)	0.030(2)	0.895(1)	4.6(5)
N(1)	0.082(2)	0.280(1)	0.905(1)	4.7(5)
N(2)	−0.020(2)	0.267(1)	0.964(1)	4.7(4)
N(3)	0.254(2)	0.376(1)	0.828(1)	5.8(6)
N(4)	−0.039(2)	0.116(1)	0.896(1)	4.7(5)
H(1)	−0.2580	0.1972	1.0581	
H(2)	−0.3645	0.0447	1.0607	
H(3)	−0.2810	−0.0591	0.9551	
H(4)	−0.0751	−0.0136	0.8515	
H(5)	0.1231	0.4237	1.0258	
H(6)	0.2802	0.5635	0.9990	
H(7)	0.4266	0.5758	0.8643	
H(8)	0.3983	0.4263	0.7668	
H(9)	0.4421	0.2251	0.8853	
H(10)	0.3768	0.1225	0.8974	
H(11)	0.5079	0.1464	0.8263	
H(12)	−0.1527	0.2224	0.7559	
H(13)	−0.0627	0.3054	0.7083	
H(14)	−0.0855	0.2092	0.6613	

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j a_i a_j b_{ij}$.

The 399.4 and 401.1 eV b.e. values can be attributed to the couple of nitrogens, pyridinic and azo respectively, which takes place during metal coordination. In fact these higher values, with respect to the free ligand, can be attributed to the electronic density charge decreasing as a consequence of the coordination. The $Sn_{3d_{5/2}}$ experimental b.e. values do not vary in the two compounds examined with respect to other tin adducts previously studied [9, 10]. The uncorrected Sn b.e. values, reported in Table 3, are not related to the partial charges depending on the overall electronegativity of the groups bonded to Sn. Inspection of the b.e. values of Sn, after correction for intramolecular Madelung effects and relaxation processes, indicates a different electronic density charge on the metal atom when halogen atoms are replaced by organic groups according with the different ligand electronegativity.

TABLE 5. Selected bond distances and angles in $SnMe_2Br_2AZP$ with e.s.d.s in parentheses

Distances (Å)		Angles (°)	
Sn–C(1)	2.12(2)	C(1)–Sn–C(2)	162.1(9)
Sn–C(2)	2.19(3)	C(1)–Sn–Br(1)	94.0(6)
Sn–Br(1)	2.643(3)	C(1)–Sn–Br(2)	97.3(6)
Sn–Br(2)	2.650(3)	C(1)–Sn–N(1)	80.9(7)
Sn–N(1)	2.585(17)	C(1)–Sn–N(3)	81.0(7)
Sn–N(3)	2.793(18)	C(1)–Sn–N(4)	89.0(7)
Sn–N(4)	2.899(17)	C(2)–Sn–Br(1)	96.7(7)
C(3)–C(4)	1.38(3)	C(2)–Sn–Br(2)	95.8(7)
C(3)–N(1)	1.461(26)	C(2)–Sn–N(1)	81.4(7)
C(3)–N(3)	1.36(3)	C(2)–Sn–N(3)	89.0(8)
C(4)–C(5)	1.38(3)	C(2)–Sn–N(4)	79.0(8)
C(5)–C(6)	1.40(4)	Br(1)–Sn–Br(2)	95.50(9)
C(6)–C(7)	1.32(4)	Br(1)–Sn–N(1)	134.0(4)
C(7)–N(3)	1.30(3)	Br(1)–Sn–N(3)	173.7(4)
C(8)–C(9)	1.36(3)	Br(1)–Sn–N(4)	79.7(4)
C(8)–N(2)	1.47(3)	Br(2)–Sn–N(1)	130.5(4)
C(8)–N(4)	1.34(2)	Br(2)–Sn–N(3)	81.3(4)
C(9)–C(10)	1.36(3)	Br(2)–Sn–N(4)	172.4(3)
C(10)–C(11)	1.34(3)	N(1)–Sn–N(3)	49.4(6)
C(11)–C(12)	1.41(3)	N(1)–Sn–N(4)	54.6(5)
N(1)–N(2)	1.229(22)	N(3)–Sn–N(4)	104.0(6)
		C(3)–N(1)–N(2)	115.5(7)
		C(8)–N(2)–N(1)	109.9(16)
		C(4)–C(3)–N(1)	127.4(19)
		C(4)–C(3)–N(3)	126.2(19)
		N(1)–C(3)–N(3)	106.2(17)
		C(9)–C(8)–N(2)	115.8(17)
		C(9)–C(8)–N(4)	125.5(18)
		N(2)–C(8)–N(4)	118.7(16)
		C(3)–N(3)–C(7)	112(2)
		C(8)–N(4)–C(12)	115(2)

Crystallographic Study

Figure 2 shows a stereoview of the complex without H atoms. Atomic coordinates and selected bond distances and angles are given in Tables 4 and 5.

The metal atom can be considered ‘quasi’ seven-coordinated being directly bonded to the methyl groups (approximately *trans* to each other), to three nitrogen atoms from the AZP ligand and two bromine atoms.

Coordination number seven is probably due to a combination of several factors: (i) increased ligand–ligand repulsion; (ii) weaker bonds; (iii) reduced crystal field stabilization energy. The three coordination geometries known are: (1) the pentagonal bipyramid; (2) the capped octahedron to which a seventh ligand has been added to a triangular face; (3) the capped trigonal prism to which a seventh ligand has been added to a rectangular face. These geometries are considered to have approximately equal a priori probabilities [11].

Many of these seven-coordinated compounds contain polydentate ligands. Two exceptions are IF_7, which belongs to the first type of arrangement [12], and K_2NbF_7, where the anion is of the third type [13].

We can consider our molecule as belonging to the first group because five atoms surrounding the metal lie approximately in a plane [Br(1), Br(2), N(1), N(3), N(4)]. The distances of these atoms from the plane are within 0.2 Å, and the metal lies on the plane. In addition, four atoms [Br(1), Br(2), N(3) and N(4)] occupy almost regular octahedral positions. Thus, the *trans*-angles Br(1)–Sn–N(3) and Br(2)–Sn–N(4) are 174 and 172° respectively, and the *cis*-angles are not far from 90° (see Table 5). Then we can consider the fifth ligand, N(1), as being inserted in between two atoms [N(3), N(4)] of the equatorial plane [Br(1), Br(2), N(3), N(4)] in this pseudo-octahedron, The Sn–N(1) bond lies close to the diagonal of the angle N(3)–Sn–N(4).

The two methyl groups occupy the apical postions with a C(1)–Sn–C(2) angle of 162°. This appears to be noteworthy.

Slighter deviations from linearity are seen in several cases. In the seven-coordinated complex Sn(DAPT)(ethyl)$_2$, the Sn–ethyl bonds form the bipyramidal axis and the related bond angle C–Sn–C is 172.4° [14]. In the similar complexes Sn(DAPS)(propyl)$_2$ and Sn(DAPA)L_aL_b [L_a = Cl, L_b = n-butyl] the axis angle C–Sn–C and Cl–Sn–C are 170.4 [15] and 173.1° [16] respectively and for L_a = L_b = phenyl, the axis angle C–Sn–C is 176.4° [16]. In Sn(TROP)$_3$X [X = Cl or OH, TROP = tropolonato anion = $C_7H_5O_2^-$], the bipyramidal axis angle Cl–Sn–O is 175.7 [11]. A larger deviation from linearity is observed in $SnPh_2(NO_3)_2(Ph_3AsO)$, where the angle Ph–Sn–Ph is 156° [17].

According to Drew the halogens Cl, Br and I exhibit a preference for capped octahedral coordination when all seven ligands are monomers [18]. Instead, if polydentate ligands are used, only chlorine complexes of the pentagonal bipyramidal type are described [18]. The values of the *cis*-angles in the equatorial plane can be close to 72°, as in the case of IF_7 [12]. The geometry of the chelating ligands can exert a great influence on these angles. In Sn(TROP)$_3$X complexes, little variation is present: the angles range from 71.5 to 73° (X = Cl) and from 71.3 to 73.4° (X = OH) [11]. A greater range is observed in several other examples: Sn(DAPT)(ethyl)$_2$ (67.1–89.0) [14]; Sn(DAPA)Cl(butyl) (67.4–82.5°) [16]; Sn(DAPA)Ph$_2$ (67.5–85.8°) [16]; Sn(DAPS)(propyl)$_2$ (66.7–89.3°) [15]. In our complex the *cis*-angles range from 49.4° [N(1)-SnN(3)] to 95.5° [Br(1)SnBr(2)]. This large variation is also seen in $SnPh_2(NO_3)_2(Ph_3AsO)$, where the angles range from 50.6 to 97° [17].

Another fact to note is the bending of the methyls. As shown in Table 5 the smallest angles of C(1) and C(2) with the equatorial ligands are with N(1). In this complex, the Sn–N bond distances are very different, that with the azo-group nitrogen being the shortest one, [2.585(17) Å]. Curiously, when compared with similar equatorial ligands in other tin complexes, it is found to be longer. For instance, in Sn(DAPT)(ethyl)$_2$ the Sn–N bonds are 2.300(16), 2.306(17) and 2.356(16) Å [14], in Sn(DAPA)Ph$_2$ 2.266(9), 2.308(9) and 2.324(9) Å [16], in Sn(DAPA)ClBu, 2.278(5), 2.318(9) and 2.278(5) Å [16], in Sn(DAPS)(propyl)$_2$, 2.326(8), 2.337(8) and 2.315(9) Å [15]. The other two Sn–N bonds are very long [(2.793(18) and 2.899(17) Å)]. These values can be compared with those in octahedral complexes of tin. For instance, in $SnMe_2Cl_2$(pyridine)$_2$, the Sn–N bond lengths are 2.39 Å [19]; in $SnPh_2Cl_2$(2,2′-bipyridil) they are 2.34 and 2.38 Å [20] and in $Sn(CHCH_2)_2(CO_2CF_3)_2$-(2,2′-bipyridil) they are 2.34 Å [21]. Other complexes where the nitrogens are pyridine-like show similar Sn–N bond distances. Thus, in $SnMe_2Cl_2$(NMiz)$_2$, [NMiz = *N*-methyl imidazole], they are 2.33 Å [22] and in $SnMe_2Cl_2$(dmp)$_2$, [dmp = dimethylpyrazole], they are 2.38 Å [23]. Given that Sn–N bonds do not vary much, it appears that no appreciable expansion of the covalent radii of Sn and N occurs on going from six to seven coordination. Coordination number seven has been reviewed [18, 24]. The only tin complex described among a series of twelve structural studies of monomers containing tridentate ligands that have been reported by Drew [18], is $SnMe_2$(terpyridyl)(NCS)$_2$ [25]. This compound has a coordination sphere reminiscent of that in the present study: the axial bond angle C–Sn–C (173.7°); the *cis*-angles at the girdle that range from 64.5 to 78.5°; the Sn–N bonds to the terpyridyl ligand that are 2.48, 2.50 and 2.57 Å; and the Sn–N bonds of the thiocyanato anions which are significantly shorter (2.280 and 2.285 Å). It is apparent that this complex shows normal bond angles for a pentagonal bipyramidal geometry when compared to the complexes of DAPT, DAPS, DAPA and TROP ligands. Nevertheless the Sn–N(terpyridyl) bonds are longer (see above). Because the corresponding bonds in the present compound are even longer than those in the terpyridyl complex, we can conclude that the ligand AZP, on the whole, is weakly coordinated to the metal.

The intramolecular distance between the bromines (3.91 Å) is equal to the related van der Waals distance (3.90 Å) [26]. In addition, the distance between Br(1) and the methyl groups are 3.50 Å, [C(1)], and 3.60 Å, [C(2)], whereas for Br(2) these values are 3.60 and 3.59 Å, respectively. These parameters are shorter than the related van der Waals distance of 3.95 Å [26]. Also, the methyls show intramolecular contacts with some nitrogens. Thus, the distances C(1)–N(1) (3.06 Å) and C(1)–N(3) (3.23 Å) are shorter than the corresponding van der Waals distance of 3.50 Å, while for C(1)–N(4) it is of the same order [3.54 Å] [26]; and the distances C(2)–N(1) [3.13 Å] and C(2)–N(4) [3.28 Å] are also shorter, whereas for C(2)–N(3) the distance is of the same order [3.51 Å]. In addition, the distances Br(1)–N(4) and Br(2)–N(3) are 3.55 Å, that is close to the Br–N van der Waals distances of 3.45 Å [26]. Thus the environment of the metal is very crowded.

We may conclude that the large size of bromine is responsible for the opening of the bond angle Br(1)–Sn–Br(2) and the bending of the methyls in the bipyramidal axis Me–Sn–Me.

In octahedral complexes of tin, made up of heterocyclic nitrogen containing ligands, the Sn–N bonds are considered as having a low degree of covalent character since they are much longer than the sum of the atomic radii of tin and nitrogen (2.10 Å) [27] and that they are similar for both *cis* or *trans*-complexes [28]. The low covalent character of the Sn–N bond makes the AZP ligand further away in the coordination sphere, resulting in the long Sn–N bond distances.

It is interesting to note that in this structure the AZP ligand prefers to form a higher energy four-atom ring [Sn–N(3)–C(3)–N(1)] instead of a five-atom ring as previously described on the basis of Mössbauer and IR spectra [1].

Calculations show that the entire ligand (AZP) is essentially planar, the angle between the pyridine planes being 15° only. In addition, molecular models indicate that in the five-atom ring, previously proposed, a short contact [Br(1)–N(4)] could be present.

In conclusion we may observe that: (i) the resonance energy of the AZP ligand is maintained (due to its quasi planarity); (ii) there is a higher energy four-atom ring instead of a five-atom ring; (iii) the system saves energy by avoiding a putative Br(1)–N(4) contact on formation of a four-atom ring; (iv) the balance of these items favours in the solid the formation of a seven-coordinated complex with the tridentate ligand weakly coordinated, in spite of the ligand–ligand repulsion.

Conclusions

The AZP ligand has four possible coordinating sites deriving from two pyridinic and two azo-nitrogens. The N_{1s} b.e. values suggest the occurrence of nitrogen atoms differently bonded. An isostructural series is suggested by the linear correlation of the Mössbauer parameter isomer shift with a partial atomic charge on tin. The crystallographic study of the $SnMe_2Br_2AZP$ adduct formulates a new structure with the tin atom seven-coordinated, where the AZP ligand, assuming a *cis*-configuration and maintaining the quasi planarity of the molecule, coordinates with one nitrogen of the azo-group and more weakly with two pyridinic nitrogens giving rise to a distorted bipyramidal pentagonal arrangement.

Supplementary Material

Observed and calculated structure factors are available from one of the authors (F.C.).

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