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Tin(IV) and organotin(IV) derivatives of bis(pyrazolyl)acetate: Synthesis, spectroscopic characterization and behaviour in solution. X-ray single crystal study of bis(pyrazol-1-yl)acetatotri-iodotin(IV) [SnI_3(bdmpza)]

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Abstract

Novel heteroscorpionate-containing tin and organotin(IV) complexes, [SnR_nX_{3-n}(L)], R = Me, Bu^n, Ph, or cy; X = Cl, Br or I, n = 0, 1, 2 or 3; L = bis(pyrazol-1-yl)acetate (bpza) or bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), have been synthesized and characterized by spectral (IR, ^{1}H, ^{13}C and ^{119}Sn NMR, ^{119m}Sn Mössbauer) and analytical data. In [SnI_3(bdmpza)], the ligand is *fac*-*N*,*N*′,*O*-tridentate, the three iodine atoms thus also *fac* about the six-coordinate tin(IV) atom. Neutral bpzaH reacts with Bu^nSnCl_3, $PhSnCl_3$ and $SnCl_4$ in Et_2O in the absence of base, yielding 1:1 adducts [$XSnCl_3$(bpzaH)] (X = R or Cl).

Keywords: Organotin complexes; Heteroscorpionates; ^{119}Sn NMR; ^{119m}Sn Mössbauer; X-ray study

1. Introduction

Poly(pyrazolyl)borates and poly(pyrazolyl)alkanes constitute a family of stable and flexible polydentate isoelectronic and isosteric ligands discovered by Trofimenko [1]. They represent one of the most widely used classes of ligands in transition and main group metal coordination chemistry [2]. Although the anionic Tp^x (a generic tris(pyrazolyl)borate) are often described as an equivalent to C_5H_5 (Cp) or C_5Me_5 (Cp*), they also exhibit a number of significant differences arising from the lesser π-acceptor and greater σ-donor abilities of pyrazole [2]. It is now accepted that the electronic and steric properties of the Tp^x ligands can strongly influence both the structure and properties of their metal complexes. The poly(pyrazolyl)borate ligands are symmetrical with respect to the nitrogen donors, and are unable to mimic many metalloprotein active sites which lack similar monofunctional, highly organized donor spheres.

Bis(pyrazolyl)acetates are ligands closely related to both neutral tris(pyrazolyl)methane and anionic poly(pyrazolyl)borates in respect of their classical ''pinch and sting'' behaviour (Fig. 1), one of the pyrazolyl groups being replaced by a carboxylate moiety [2]. This change introduces a small degree of steric hindrance and considerable coordinative ligand flexibility. Bis(pyrazolyl)acetates can be easily deprotonated,

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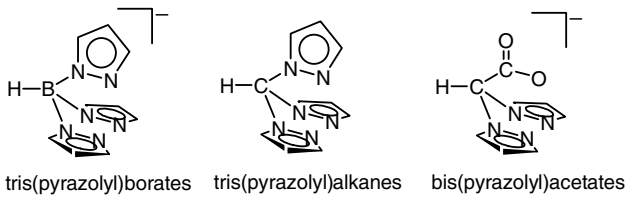


Fig. 1. The three well-known classes of scorpionate ligands.

behaving in the anionic form as *N*,*N*,*O*-tripodal donors, similar to tris(pyrazolyl)borates; alternatively they may react in the neutral form like the tris(pyrazolyl)alkanes. Until now, all metal derivatives reported contain bis(pyrazolyl)acetates in the anionic form [3–13]; only a few organometallic derivatives have been reported, limited to Nb, Re, Mn and Cr carbonyls [14–19] and a short communication on the crystal structure of $Ph_2SnBr(bdmpza)$ (bdmpzaH = bis(3,5-dimethylpyrazol-1-yl)acetic acid) [20].

In the last few years, we have investigated the coordination chemistry of tin(IV) and organotin(IV) acceptors with poly(azolyl)borates [21] and poly(azolyl)alkanes [22]. Here, we report the synthesis and characterization of new tin(IV) and organotin(IV) complexes of the bis(pyrazolyl)acetate ligand in monoanionic and, for the first time, also in the neutral form.

2. Experimental

2.1. Materials and methods

All reagents were purchased from Aldrich (Milwaukee) and used as received. The ligands bpzaH (bpzaH = bis(pyrazol-1-yl)acetic acid) and bdmpzaH were prepared according to literature methods [4,15]. Solvent evaporations were carried out under vacuum using a rotary evaporator. Samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium; dichloromethane was distilled from calcium hydride. All solvents were degassed with dry nitrogen prior to use. Elemental analyses (C, H, N) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental analyzer. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded using a VXR-300 Varian and Bruker AC 200 spectrometers operating at room temperature (respectively at 300 and 200 MHz for ^1H, 75 and 50 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^1H and ^{13}C calibration by internal deuterium solvent lock) and $SnMe_4$ (external). The spectral width is 900 ppm (from +200 to −700 ppm). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. Melting points are uncorrected and were measured using an SMP3 Stuart scientific instrument, and on a capillary apparatus. The electrical conductivity measurements of dichloromethane solutions of complexes **1**–**19** were made with a Crison CDTM 522 conductimeter at room temperature.

^{119}Sn Mössbauer spectra were recorded on solid samples at liquid nitrogen temperature using a conventional constant acceleration spectrometer, coupled with a multi-channel analyzer (a.e.n., Ponteranica (BG), Italy) equipped with a cryostat Cryo (RIAL, Parma, Italy). A $Ca^{119}SnO_3$ Mössbauer source, 10 mCi (Ritverc, St Petersburg, Russia), moving at room temperature with constant acceleration in a triangular waveform was used. The velocity calibration was made using a ^{57}Co Mössbauer source, 10 mCi, and an iron foil as absorber (from Ritverc, St Petersburg, Russia).

2.2. Syntheses of the complexes

2.2.1. Synthesis of [$SnCy_3$(bpza)] (*1*)

A methanol solution (30 ml) containing bpzaH (0.192 g, 1 mmol), KOH (0.056 g, 1 mmol) and Cy_3SnCl (0.219 g, 1 mmol) was stirred for 4 h at room temperature. The solvent was removed and 20 ml chloroform was added. The insoluble precipitate of KCl was removed by filtration, the filtrate reduced to half volume and 40 ml of diethyl ether was added. The resulting colourless precipitate was filtered off, washed with *n*-hexane (10 ml) and dried under vacuum. The compound is soluble in DMSO, acetone, acetonitrile and chlorinated solvents. Yield 54%. Anal. Calcd. for $C_{26}H_{40}N_4O_2Sn$: C, 55.83; H, 7.21; N, 10.02. Found: C, 55.17; H, 7.64; N, 10.01. M.p.: 101–102 °C. IR (nujol, cm^{-1}): 3104w $\nu(C_{arom}–H)$, 1664s, 1640vs $\nu_{asym}(COO)$, 1514m $\nu(C{=}N, C{=}C)$, 1446m $\nu_{sym}(COO)$, 535m, 492m $\nu(Sn–C)$, 417s, 326vs $\nu(Sn–O)$. ^1H NMR (acetone-d_6): δ 1.30, 1.65, 1.89 (m, 33H, Sn–Cy), 6.27 (t, 2H, H_4), 7.03 (s, 1H, C*H*), 7.52 (d, 2H, H_5), 7.78 (d, 2H, H_3). ^{119}Sn NMR (acetone-d_6): 73.3.

2.2.2. Synthesis of [$SnMe_2Cl$(bpza)] (*2*)

Compound **2** was prepared following a procedure similar to that reported for **1**, using Me_2SnCl_2. It is a viscous oil, soluble in DMSO, acetone, acetonitrile and chlorinated solvents. The compound is soluble in DMSO, acetone, acetonitrile and chlorinated solvents. Yield 65%. Anal. Calcd. for $C_{10}H_{13}ClN_4O_2Sn$: C, 32.00; H, 3.49; N, 14.93. Found: C, 33.19; H, 4.08; N, 13.82. M.p.: 194–197 °C. IR (nujol, cm^{-1}): 3164w, 3131w, 3114w $\nu(C_{arom}–H)$, 1666vs $\nu_{asym}(COO)$, 1515m $\nu(C{=}N, C{=}C)$, 1412m $\nu_{sym}(COO)$, 581s, 568m, 526m $\nu(Sn–C)$, 493vs, 377s $\nu(Sn–O)$, 279s, 258sh $\nu(Sn–Cl)$. ^1H NMR (acetone-d_6): δ 1.16 (s, 6H, $^2J(^{119}Sn–^1H)$: 87.5 Hz, $^2J(^{119}Sn–^1H)$: 84.8 Hz, Sn–Me), 6.39 (t, 2H, H_4), 7.16 (s, 1H, C*H*), 7.61 (d, 2H, H_5), 7.76 (d, 2H,

H_3). ^{13}C NMR (acetone-d_6): δ 11.08 (s, Sn–Me), 75.09 (s, *C*H), 106.81 (s, C_4), 130.99 (s, C_5), 140.52 (s, C_3), 167.88 (s, COO). ^{119}Sn NMR (acetone-d_6): −295.6.

2.2.3. Synthesis of [$SnBu^n_2Cl(bpza)$] (3)

Compound **3** was prepared following a procedure similar to that reported for **1**, using $Bu^n_2SnCl_2$. It is a viscous oil, soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 69%. Anal. Calcd. for $C_{16}H_{25}ClN_4O_2Sn$: C, 41.82; H, 5.48; N, 12.19. Found: C, 42.45; H, 6.02; N 11.71. IR (nujol, cm^{-1}): 3118w ν(C_{arom}–H), 1668m, 1615s ν_{asym}(COO), 1516m ν(C=N, C=C), 1411m ν_{sym}(COO), 552m, 535sh ν(Sn–C), 480vs ν(Sn–O), 292vs ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 0.97–1.11, 1.39–1.90 (m, 18H, Sn–Bu^n), 6.44 (sbr, 2H, H_4); 7.22, 7.42 (s, 1H, C*H*); 7.65 (s, 2H, H_5); 8.04, 8.08 (sbr, 2H, H_3). ^{13}C NMR (acetone-d_6): δ 13.98, 26.89, 27.52, 27.76 (s, Sn–Bu^n), 76.25 (d, *C*H), 107.13 (d, C_4), 131.3 (s, C_5), 140.83 (s, C_3), 170.44 (s, COO). ^{119}Sn NMR (acetone-d_6): −195.0, −201.4.

2.2.4. Synthesis of [$SnPh_2Cl(bpza)$] (4)

Compound **4** was prepared following a procedure similar to that reported for **1**, using Ph_2SnCl_2. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 72%. Anal. Calcd. for $C_{20}H_{17}ClN_4O_2Sn$: C, 48.09; H, 3.43; N, 11.22. Found: C, 47.65; H, 3.60; N, 11.04. M.p.: 103–108 °C. IR (nujol, cm^{-1}): 3122w ν(C_{arom}–H), 1664s ν_{asym}(COO), 1557m, 1512m ν(C=N, C=C), 1399m ν_{sym}(COO). ^{1}H NMR ($CDCl_3$): δ 6.34 (t, 2H, H_4), 7.01 (s, 1H, C*H*), 7.68 (d, 2H, H_5), 7.78 (d, 2H, H_3), 7.34, 7.89 (m br, 10H, Sn–Ph). ^{13}C NMR ($CDCl_3$): δ 70.68 (s, *C*H), 107.36 (s, C_4), 128.67, 129.38, 130.71, 136.37 (s, Sn–Ph), 134.80 (s, C_5), 141.38 (s, C_3), 165.74 (s, COO). ^{119}Sn NMR ($CDCl_3$): δ −421.2.

2.2.5. Synthesis of [$SnBu^nCl_2(bpza)$] (5)

Compound **5** was prepared following a procedure similar to that reported for **1**, using Bu^nSnCl_3. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 58%. Anal. Calcd. for $C_{12}H_{16}Cl_2N_4O_2Sn$: C, 32.92; H, 3.68; N, 12.79. Found: C, 32.73; H, 4.05; N, 11.94. M.p.: 211–213 °C. IR (nujol, cm^{-1}): 3112w, 3094w ν(C_{arom}–H), 1694vs ν_{asym}(COO), 1509s ν(C=N, C=C), 1406m ν_{sym}(COO), 411m, 305vs br ν(Sn–O), 229s ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 0.92t, 1.42m, 1.82m (9H, Sn–Bu^n), 6.73 (t, 2H, H_4), 7.73s (1H, C*H*), 8.24 (d, 2H, H_5), 8.41 (d, 2H, H_3). ^{13}C NMR (acetone-d_6): δ 13.88, 26.06, 26.08, 28.21 (s, Sn–Bu^n), 71.68 (s, *C*H), 108.40 (s, C_4), 134.39 (s, C_5), 142.15 (s, C_3), 158.80 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −473.7.

2.2.6. Synthesis of [$SnPhCl_2(bpza)$] (6)

Compound **6** was prepared following a procedure similar to that reported for **1**, by using $PhSnCl_3$. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 58%. Anal. Calcd. for $C_{14}H_{12}Cl_2N_4O_2Sn$: C, 36.73; H, 2.64; N, 12.24. Found: C, 36.53; H, 2.88; N, 11.95. M.p.: 168–170 °C. IR (nujol, cm^{-1}): 3117w ν(C_{arom}–H), 1693vs, 1674s ν_{asym}(COO), 1574m ν(C=C), 1510m ν(C=N, C=C), 1408m ν_{sym}(COO). ^{1}H NMR ($CDCl_3$): δ 6.37, 6.47 (t, 2H, H_4), 7.35, 7.37 (s, 1H, C*H*), 7.55, 7.70, 8.20, 8.32 (m, 9H, H_5, H_3 and Sn–Ph). ^{13}C NMR ($CDCl_3$): δ 70.78 (s, *C*H), 107.90, 108.10 (s, C_4), 129.04, 129.79, 130.39, 131.82, 135.34, 148.09 (s, Sn–Ph), 133.02, 133.65 (s, C_5), 141.52, 141.88 (s, C_3), 164.24 (s, COO). ^{119}Sn NMR ($CDCl_3$): δ 511.7, −522.5.

2.2.7. Synthesis of [$SnCl_3(bpza)$] (7)

Compound **7** was prepared following a procedure similar to that reported for **1**, using $SnCl_4$. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 84%. Anal. Calcd. for $C_8H_7Cl_3N_4O_2Sn$: C, 23.09; H, 1.70; N, 13.46. Found: C, 22.99; H, 1.87; N, 12.77. M.p.: 291–292 °C. IR (nujol, cm^{-1}): 3165w, 3156w, 3136w ν(C_{arom}–H), 1723s, 1696s ν_{asym}(COO), 1508m ν(C=N, C=C), 1412s, 1403m ν_{sym}(COO), 421m ν(Sn–O), 335vs br ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 6.99t (2H, H_4); 8.02s (1H, C*H*); 8.48d (2H, H_5); 8.70d (2H, H_3). ^{13}C NMR (acetone-d_6): δ 71.32 (s, *C*H), 109.28 (s, ^3J (Sn–C): 15.9 Hz, C_4), 135.89 (s, C_5), 142.39 (s, C_3), 161.22 (s, COO). ^{119}Sn NMR (acetone): δ −622.31.

2.2.8. Synthesis of [$SnBr_3(bpza)$] (8)

Compound **8** was prepared following a procedure similar to that reported for **1**, using $SnBr_4$. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 68%. Anal. Calcd. for $C_8H_7Br_3N_4O_2Sn$: C, 17.48; H, 1.28; N, 10.19. Found: C, 18.91; H, 1.74; N 9.63. M.p.: 265–268 °C. IR (nujol, cm^{-1}): 3130w, 3111w ν(C_{arom}–H), 1723s, 1695s ν_{asym}(COO), 1516m, 1504m ν(C=N, C=C), 1409m ν_{sym}(COO), 417m, 335m ν(Sn–O), 246vs, 236vs, 224s ν(Sn–Br). ^{1}H NMR (acetone-d_6): δ 6.47 (t, 2H, H_4); 7.57 (s, 1H, C*H*), 7.67 (d, 2H, H_5), 8.07 (d, 2H, H_3). ^{119}Sn NMR (acetone-d_6): δ −739.4.

2.2.9. Synthesis of [$SnI_3(bpza)$] (9)

Compound **9** was prepared following a procedure similar to that reported for **1**, using SnI_4. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 55%. Anal. Calcd. for $C_8H_7I_3N_4O_2Sn$: C, 13.91; H, 1.02; N, 8.11. Found: C, 14.00; H, 0.99; N, 7.93. M.p.: 254–256 °C. IR (nujol, cm^{-1}): 3140w ν(C_{arom}–H), 1664s br ν_{asym}(COO), 1513m ν(C=N, C=C), 1407m ν_{sym}(COO), 410s ν(Sn–O), 212sh, 204vs ν(Sn–I). ^{1}H NMR (acetone-d_6): δ 6.84t (2H, H_4); 7.85s (1H, C*H*); 8.38d (2H, H_5); 8.48d (2H, H_3). ^{13}C NMR (acetone-d_6): δ 71.1 (s, *C*H), 108.1 (s, C_4), 135.5 (s, C_5),

140.3 (s, C_3), 160.8 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −831.9.

2.2.10. Synthesis of [$SnMe_2Cl$(bdmpza)] (10)

Compound **10** was prepared following a procedure similar to that reported for **1**, using Me_2SnCl_2. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 62%. Anal. Calcd. for $C_{14}H_{21}ClN_4O_2Sn$: C, 38.97; H, 4.91; N, 12.98. Found C, 38.61; H, 5.41; N, 11.82. M.p.: 193–195 °C. IR (nujol, cm^{-1}): 3120w ν(C_{arom}–H), 1681s, 1612s ν_{asym}(COO), 1554s ν(C=N, C=C), 1410m ν_{sym}(COO), 584m, 574m, 528m ν(Sn–C), 488s, 349s ν(Sn–O), 277s, 255s ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 1.11 (s, 3H, ^2J(^{119}Sn–^{1}H): 83.3 Hz, ^2J(^{119}Sn–^{1}H): 80.1 Hz, Sn–Me), 1.25, 1.41 (s, 3H, Sn–Me) 2.09, 2.18, 2.19, 2.32 (s, 12H, 3-Me and 5-Me), 5.85, 5.94 (s, 2H, H_4), 6.93, 7.15 (s, 1H, C*H*). ^{1}H NMR ($CDCl_3$): δ 0.98 (s, 3H, ^2J(^{119}Sn–^{1}H): 71.8 Hz, ^2J(^{119}Sn–^{1}H): 67.3 Hz, Sn–Me), 2.32, 2.36 (s, 12H, 3-Me and 5-Me); 5.92 (s, 2H, H_4); 6.56 (s, 1H, C*H*). ^{13}C NMR (acetone-d_6): δ 11.10 (s, Sn–Me), 11.85, 13.50 (s, 3-Me and 5-Me), 71.20 (s, *C*H), 107.71 (s, C_4), 141.93 (s, C_5), 148.84 (s, C_3), COO not observed. ^{119}Sn NMR ($CDCl_3$): δ,−281. ^{119}Sn NMR (acetone-d_6): δ −295.2.

2.2.11. Synthesis of [$SnPh_2Cl$(bdmpza)] (11)

Compound **11** was prepared following a procedure similar to that reported for **5**, using Ph_2SnCl_2. Yield 63%. Anal. Calcd. for $C_{24}H_{25}ClN_4O_2Sn$: C, 51.88; H, 4.54; N, 10.08. Found: C, 51.54; H, 4.70; N, 10.08. M.p.: >350 °C. IR (nujol, cm^{-1}): 3127w, 3064w, 3033w (C_{arom}–H), 1690vs, 1674s ν_{asym}(COO), 1576m, 1557s ν(C=N, C=C), 1429s, 1415m ν_{sym}(COO), 449s ν(Sn–O), 291vs ν(Sn–Cl), 264vs, 246vs ν(Sn–C). ^{1}H NMR (acetone-d_6): δ 1.71br, 2.04, 2.78br, 2.96 (s, 12H, 3-Me and 5-Me), 6.25br, 6.28 (s, 2H, H_4); 7.04s (1H, C*H*); 7.50, 7.76, 7.92 (mbr, 10H, Sn–Ph). ^{13}C NMR (acetone-d_6): δ 13.61, 14.02 (s, 3-Me and 5-Me), 66.28 (s, *C*H), 108.93 (s, C_4), 135.85 (s, C_5), 152.03 (s, C_3), 128.88, 129.35, 135.51, 152.00 (s, Sn–Ph), 162.73 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −451.7, −457.7.

2.2.12. Synthesis of [$SnMeCl_2$(bdmpza)] (12)

Compound **12** was prepared following a procedure similar to that reported for **1**, using $MeSnCl_3$. The compound is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 53%. Anal. Calcd. for $C_{13}H_{18}Cl_2N_4O_2Sn$: C, 34.55; H, 4.01; N, 12.40. Found: C, 34.03; H, 4.33; N, 11.71. M.p.: 249–250 °C. IR (nujol, cm^{-1}): 3134w, 3091w ν(C_{arom}–H), 1694vs ν_{asym}(COO), 1562s ν(C=N, C=C), 1420m ν_{sym}(COO), 539s ν(Sn–C), 422m ν(Sn–O), 307vsbr ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ, 1.17 (s, 3H, ^2J(^{119}Sn–^{1}H): 121.9 Hz, ^2J(^{119}Sn–^{1}H): 117.5 Hz, Sn–Me), 1.44 (s, 3H, ^2J(^{119}Sn–^{1}H): 126.3 Hz, ^2J(^{119}Sn–^{1}H): 119.4 Hz, Sn–Me), 2.17, 2.35, 2.53, 2.55, 2.65, 2.73 (s, 12H, 3-Me and 5-Me); 6.01s, 6.32s, 7.22s (2H, H_4); 6.84s, 6.88s (1H, C*H*). ^{13}C NMR (acetone-d_6): δ 10.84, 10.88 (s, Sn–Me), 13.58, 14.85, 19.93, 24.17 (s, 3-Me e 5-Me), 65.67 (s, *C*H), 109.30, 109.60 (s, C_4), 143.65, 144.04 (s, C_5), 151.92, 153.05 (s, C_3), 161.50, 162.73 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −472.4, −479.8.

2.2.13. Synthesis of [$SnPhCl_2$(bdmpza)] (13)

Compound **13** was prepared following a procedure similar to that reported for **5**, using $PhSnCl_3$. Yield 59%. Anal. Calcd. $C_{18}H_{20}Cl_2N_4O_2Sn$: C, 42.06; H, 3.92; N, 10.90. Found: C, 41.72; H, 4.01; N, 10.65. M.p.: 252–254 °C. IR (nujol, cm^{-1}): 3138w, 3066w, 3034w ν(C_{arom}–H), 1686vs, 1637m ν_{asym}(COO), 1573w, 1557s ν(C=N, C=C), 1430m, 1418m ν_{sym}(COO), 343vs br ν(Sn–O), 281s ν(Sn–Cl), 246s, 228s ν(Sn–C). ^{1}H NMR (acetone-d_6): δ 1.87, 1.89, 2.68, 2.71, 2.80, 2.83 (s, 12H, 3-Me and 5-Me); 6.24, 6.30, 6.37 (s, 2H, H_4); 6.97, 7.01 (s, 1H, C*H*); 7.45, 7.75 (m, 5H, Sn–Ph). ^{13}C NMR (acetone-d_6): δ 11.00, 11.09, 11.16, 13.31, 13.47, 14.98 (s, 3-Me and 5-Me), 65.93 (s, *C*H), 109.41, 109.52, 109.94 (s, C_4), 144.17, 144.43, 144.67 (s, C_5), 152.77, 153.11, 153.37 (s, C_3), 129.19, 129.52, 130.24, 130.56, 134.00, 134.39, 150.08, 150.20 (s, Sn–Ph), 163.32 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −524.2, −541.1.

2.2.14. Synthesis of [$SnCl_3$(bdmpza)] (14)

Compound **14** was prepared following a procedure similar to that reported for **5**, using $SnCl_4$. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 74%. Anal. Calcd. for $C_{12}H_{15}Cl_3N_4O_2Sn$: C, 30.52; H, 3.20; N, 11.86. Found: C, 30.77; H, 3.41; N, 11.80. M.p.: 292–293 °C. IR (nujol, cm^{-1}): 3144w, 3138w ν(C_{arom}–H), 1724sbr ν_{asym}(COO), 1555s ν(C=N, C=C), 1415s ν_{sym}(COO), 427m ν(Sn–O), 348vs, 333vs, 321vs ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 2.68, 2.71 (s, 12H, 3-Me and 5-Me); 6.42 (s, 2H, H_4); 7.06 (s, 1H, C*H*). ^{13}C NMR (acetone-d_6): δ 11.11, 14.23 (s, 3-Me and 5-Me), 65.49 (s, *C*H), 110.05 (s, C_4), 145.42 (s, C_5), 153.47 (s, C_3), 161.38 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −636.7.

2.2.15. Synthesis of [$SnBr_3$(bdmpza)] (15)

Compound **15** was prepared following a procedure similar to that reported for **5**, using $SnBr_4$. Yield 83%. Anal. Calcd. for $C_{12}H_{15}Br_3N_4O_2Sn$: C, 23.80; H, 2.50; N, 9.25. Found: C, 24.08; H, 2.61; N, 9.18. M.p.: 266–268 °C. IR (nujol, cm^{-1}): 3135w ν(C_{arom}–H), 1697vs br ν_{asym}(COO), 1559s ν(C=N, C=C), 1418m ν_{sym}(COO), 425s ν(Sn–O), 231vsbr, 210sh ν(Sn–Br). ^{1}H NMR (acetone-d_6): δ 2.72, 2.79 (s, 12H, 3-Me and 5-Me), 6.41 (s, 2H, H_4), 7.04 (s, 1H, C*H*). ^{13}C NMR (acetone-d_6): δ 11.52, 15.14 (s, 3-Me and 5-Me), 65.76 (s, *C*H), 110.77 (s, C_4), 145.48 (s, C_5), 153.66 (s, C_3), 161.91 (s, COO). ^{119}Sn NMR (acetone-d_6): δ −770.7.

2.2.16. Synthesis of [SnI_3(bdmpza)] (**16**)

Compound **16** has been prepared following a procedure similar to that reported for **1**. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 67%. Anal. Calcd. for $C_{12}H_{15}N_4O_2I_3Sn$: C, 19.30; H, 2.02; N, 7.50%. Found: C, 18.56; H, 2.17; N, 6.18%. M.p.: 246–247 °C. IR (nujol, cm^{-1}): 3127w $\nu(C_{arom}–H)$, 1715vs br ν_{asym}(COO), 1556s ν(C=N, C=C), 1414m ν_{sym}(COO), 421w ν(Sn–O). ^{1}H NMR (acetone-d_6): δ 2.19s, 2.36s, 2.85s, 3.07s (12H, 3-Me e 5-Me); 6.03s, 6.47s (2H, H_4); 7.10s, 7.33s (1H, C*H*). ^{13}C NMR (acetone-d_6): δ 10.8, 11.1, 13.4, 14.8 (s, 3-Me e 5-Me), 64.9, 72.7 (s, *C*H), 107.3, 110.6 (s, C_4), 129.5, 129.7, 144.1 (s, C_5), 132.7, 133.3, 152.4 (s, C_3), 161.7 (s, *C*OO). ^{119}Sn NMR (acetone-d_6): δ −864.4.

2.2.17. Synthesis of [$SnBu^nCl_3$(bpzaH)] (**17**)

Bu^nSnCl_3 (0.282 g, 1 mmol) was added to a diethyl ether solution (30 ml) of bpzaH (0.192 g, 1 mmol). The reaction mixture was stirred to room temperature and a colourless precipitate slowly afforded. After 48 h it was filtered off, washed with *n*-hexane (10 ml) and dried to constant weight under reduced pressure. The compound is soluble in dmso acetone, acetonitrile and chlorinated solvents. Yield 54%. Anal. Calcd. for $C_{12}H_{17}Cl_3N_4O_2Sn$: C, 30.39; H, 3.61; N, 11.81. Found: C, 30.58; H, 3.79; N, 11.52%. M.p.: 198–200 °C. IR (nujol, cm^{-1}): 3113s, 3078m $\nu(C_{arom}–H)$, 1692vs, 1669s ν_{asym}(COO), 1509m ν(C=N, C=C), 1406s ν_{sym}(COO), 306vs br ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 0.92t, 1.45m, 1.78m (9H, Sn–Bu^n); 6.35, 6.73, 6.85 (t, 2H, H_4), 7.42, 7.63, 7.88 (s, 1H, C*H*), 7.55, 8.25, 8.35 (d, 2H, H_5), 7.98, 8.40, 8.58 (d, 2H, H_3). ^{13}C NMR (acetone-d_6): δ 13.9, 26.1, 28.2 (s, Sn–Bu^n), 71.7, 74.9, 86.5 (s, *C*H), 107.3, 108.4, 109.1 (s, C_4), 131.3, 140.9 (s, C_5), 134.4, 142.2 (s, C_3), 162.2 (s, *C*OO). ^{119}Sn NMR (acetone-d_6): δ −473.6 br.

2.2.18. Synthesis of [$SnPhCl_3$(bpzaH)] (**18**)

Compound **18** was prepared following a procedure similar to that reported for **17**, using $PhSnCl_3$. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 46%. Anal. Calcd. for $C_{14}H_{13}Cl_3N_4O_2Sn$: C, 34.02; H, 2.65; N, 11.33. Found: C, 34.53; H, 2.72; N, 11.13%. M.p.: 145–150 °C. IR (nujol, cm^{-1}): 3175w, 3091w (C_{arom}–H), 1723s, 1674s ν_{asym}(COO), 1504m ν(C=N, C=C), 1403m ν_{sym}(COO), 310vs br ν(Sn–Cl), 262s, 231m ν(Sn–C). ^{1}H NMR (acetone-d_6): δ 6.33, 6.44 (t, 2H, H_4), 7.19, 7.24 (s, 1H, C*H*), 7.58, 7.66 (d, 2H, H_5), 7.81, 8.04 (d, 2H, H_3), 7.45, 7.84, 8.18 (m, 5H, Sn–Ph). ^{13}C NMR (acetone-d_6): δ 72.2, 79.6 (s, *C*H), 107.9, 108.9, 109.2 (s, C_4), 129.8, 134.9 (s, C_5), 128.4, 129.2, 131.7, 141.5, 142.7, 142.9, 150.2 (s, Sn–Ph), 131.0, 135.4 (s, C_3), 163.2 (s, *C*OO). ^{119}Sn NMR (acetone-d_6): δ −528.9.

Table 1
Selected molecular geometries, [SnI_3(bdmpza)] (**16**)

Atoms	Parameter
Distances (Å)	
Sn–I(1)	2.7521(3)
Sn–I(2)	2.7754(3)
Sn–I(3)	2.7711(3)
C(32)–O(31)	1.302(3)
Sn–N(11)	2.260(2)
Sn–N(21)	2.270(2)
Sn–O(31)	2.087(2)
C(32)–O(32)	1.213(4)
Angles (°)	
I(1)–Sn–I(2)	98.06(1)
I(1)–Sn–I(3)	95.18(1)
I(2)–Sn–I(3)	96.39(1)
N(11)–Sn–N(21)	81.04(8)
N(11)–Sn–O(31)	81.90(8)
N(21)–Sn–O(31)	81.22(8)
I(1)–Sn–O(31)	89.53(5)
I(2)–Sn–O(31)	160.49(6)
Sn–N(11)–N(12)	118.2(1)
Sn–N(11)–N(15)	136.0(2)
C(0)–N(12)–N(11)	119.4(2)
C(0)–N(12)–C(13)	129.1(2)
I(1)–Sn–N(11)	90.49(5)
I(1)–Sn–N(21)	168.22(6)
I(2)–Sn–N(11)	90.74(6)
I(2)–Sn–N(21)	90.26(7)
I(3)–Sn–N(11)	170.18(6)
I(3)–Sn–N(21)	92.15(5)
I(3)–Sn–O(31)	90.11(5)
N(12)–C(0)–N(22)	110.0(2)
Sn–N(21)–N(22)	117.3(2)
Sn–N(21)–N(25)	136.9(2)
C(0)–N(22)–N(21)	120.2(2)
C(0)–N(22)–N(23)	128.1(2)
Sn–O(31)–C(32)	126.0(2)
Torsion angles (°)	
N(21)–Sn–N(11)–N(12)	40.1(2)
Sn–N(11)–N(12)–C(0)	3.9(3)
N(11)–N(12)–C(0)–N(22)	−67.4(3)
Sn–O(31)–C(32)–C(0)	9.1(3)
N(11)–Sn–N(21)–N(22)	−42.2(2)
Sn–N(21)–N(22)–C(0)	0.6(3)
N(21)–N(22)–C(0)–N(12)	64.6(3)

The tin atom lies 0.111(5), 0.082(5) out of the N_2C_3 ring planes (χ^2 9.6, 18.8; interplanar dihedral angle 64.5(1)°) and 0.319(6) Å out of the CO_2 plane, dihedral angles of the latter to the C_3N_2 planes being 64.9(3), 51.1(3)°.

2.2.19. Synthesis of [$SnCl_4$(bpzaH)] (**19**)

Compound **19** was prepared following a procedure similar to that reported for **17**, using $SnCl_4 \cdot 5H_2O$. It is soluble in dmso, acetone, acetonitrile and chlorinated solvents. Yield 68%. Anal. Calcd. for $C_8H_8N_4O_2Cl_4Sn$: C, 21.23; H, 1.78; N, 12.38. Found: C, 21.58; H, 1.92; N, 12.03%. M.p.: 269–271 °C. IR (nujol, cm^{-1}): 3155w, 3126w, 3110w $\nu(C_{arom}–H)$, 1724vs br ν_{asym}(COO), 1510m ν(C=N, C=C), 1410s ν_{sym}(COO), 336vs br ν(Sn–Cl). ^{1}H NMR (acetone-d_6): δ 6.99 (t, 2H, H_4), 8.02s (1H, C*H*), 8.11 (d, 2H, H_5), 8.69 (d,

2H, H_3). ^{13}C NMR (acetone-d_6): δ 71.2 (s, *C*H), 109.1 (s, C_4), 135.6 (s, C_5), 142.2 (s, C_3), 161.0 (s, *C*OO). ^{119}Sn NMR (acetone-d_6): δ −621.5.

2.3. Structure determination

A full sphere of 'low'-temperature CCD area-detector diffractometer data was measured (Bruker AXS instrument, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; ω-scans; $2\theta_{max} = 75°$; T ca. 153 K) yielding 21562 reflections, these merging to 10880 unique (R_{int} 0.026) after 'empirical'/multiscan absorption correction (proprietary software), 10047 with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, (x,y,z, U_{iso})$_H$ constrained at estimates. Difference map residues were modelled in terms of solvate acetonitrile, atom assignment being based on refinement behaviour and location of the hydrogen atoms in difference maps. Conventional residuals on $|F|$ at convergence were $R = 0.031$, $R_w = 0.049$ (reflection weights: $(\sigma^2(F) + 0.0008F^2)^{-1}$). Neutral atom complex scattering factors were employed within the Xtal 3.7 program system [23]. Pertinent results are given below and in Table 1 and Fig. 4, the latter showing non-hydrogen displacement amplitudes at the 50% probability level, hydrogen atoms having arbitrary radii of 0.1 Å. Full details (excluding structure factor amplitudes) are deposited with the Cambridge Structural Database, CCDC **258719**.

2.3.1. Crystal data

$C_{12}H_{15}I_3N_4O_2Sn.CH_3CN$, $M_r = 787.8$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 7.9048(6)$, $b = 10.4369(8)$, $c = 13.719(1)$ Å, $\alpha = 99.751(2)$, $\beta = 103.508(2)$, $\gamma = 95.395(2)°$, $V = 1074$ Å^3. D_c ($Z = 4$) $= 2.43_6$ g cm^{-3}. $\mu_{Mo} = 5.5$ mm^{-1}; specimen: $0.45 \times 0.37 \times 0.24$ mm; $'T'_{min/max} = 0.59$.

3. Results and discussion

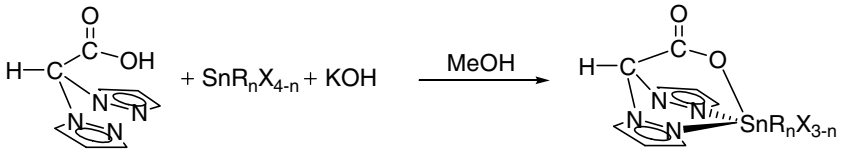
3.1. Syntheses

The tin complexes **1**–**16** were prepared by reaction of the bis(pyrazolyl)acetate ligand with the appropriate tin(IV) or organotin(IV) acceptor in methanol in the presence of potassium hydroxide (Schemes 1 and 2).

The derivatives **1**–**16** are reasonably stable in air, and in acetonitrile, acetone, and chlorinated solvents, where they are non-electrolytes, as well as in the solid state. However, prolonged warming and/or storage under reduced pressure appears to induce some decomposition process via decarbonylation, with the release of CO_2 and the formation of a mixture of pyrazole-containing metal complexes and other unidentified products.

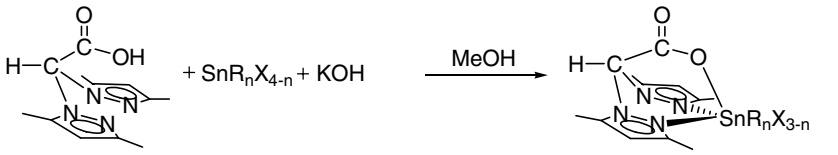
3.2. Spectroscopy

Infrared spectra, measured on the solid samples (nujol, mull), showed all the expected bands for the ligand and the tin moieties: weak absorptions near 3100 cm^{-1} are due to the pz ring C_{arom}–H stretching, and medium to strong absorptions in the range 1500–1560 cm^{-1} are related to ring "breathing" vibrations. The presence of the COO moiety is indicated by strong ν_{asym}(COO) bands in the range 1610–1770 cm^{-1}, a red shift relative to the free neutral ligands being observed upon complex formation [3–20]. This is in keeping with an electron flow from the ligand toward the tin moiety, with consequent decreasing C=O bond order. Further, the presence of a ν_{sym}(COO) in the range 1400–1450 cm^{-1} was always detected. The difference $\Delta\nu = \nu_{asym}$(COO) –



1, R = Cy,n = 3, X = Cl
2, R = Me,n = 2, X = Cl
3, R = Bu^n,n = 2,X = Cl
4, R = Ph, n = 2, X = Cl
5, R = Bu^n,n = 1,X = Cl
6, R = Ph,n = 1, X = Cl
7, n = 0, X = Cl
8, n = 0, X = Br
9, n = 0, X = I

Scheme 1.



10, R = Me, n = 2, X = Cl
11, R = Ph, n = 2, X = Cl
12, R = Me, n = 3, X = Cl
13, R = Ph, n = 3, X = Cl
14, n = 0, X = Cl
15, n = 0, X = Br
16, n = 0, X = I

Scheme 2.

ν_{sym}(COO) is always higher than 200 cm^{-1}, in accordance with a unidentate COO moiety [24]. In the far-IR region medium to strong absorptions appear upon coordination, arising from the stretching modes of Sn–O [24], Sn–R [25–29] and Sn-halide components [24]. In the IR spectra of **1**–**16**, single absorptions assigned to Sn–O have been detected between 350 and 430 cm^{-1}. Trends have been found for the ν(Sn–O) mode, the replacement of R groups with chlorine increasing its absorption frequency. Moreover, ν(Sn–O) decreases in the order: Cl > Br > I, respectively. These trends can be easily explained on the basis of the higher inductive effect of the electron-withdrawing chlorine relative to alkyls and other halides, with concomitant strengthening of the Sn–O bond [24].

The proton NMR spectra show all the expected resonances for the tripodal ligands and the tin moieties. A unique set of signals is found in the ^{1}H NMR spectra of **1**, **7**–**9** and **14**–**16**, only one geometrical isomer being possible. When both R and X groups are bonded to the metal atom, as alkyls and chlorine, two different geometrical isomers are possible in solution (Fig. 2). In fact, in the ^{1}H NMR spectra of derivatives **3**, **6**, **11**, **12** and **13**, two or three sets of signals are generally observed for the protons of bpza and bdmpza and two sets for the protons of alkyl groups bonded to the tin, in accordance with the existence of the complexes in both the isomeric forms. By contrast in the ^{1}H NMR spectra of **2**, **4**, **5** and **10**, only one set of resonances has been observed, all ascribable to the *trans* isomer. In all cases the resonances of the ligand protons are deshielded upon coordination.

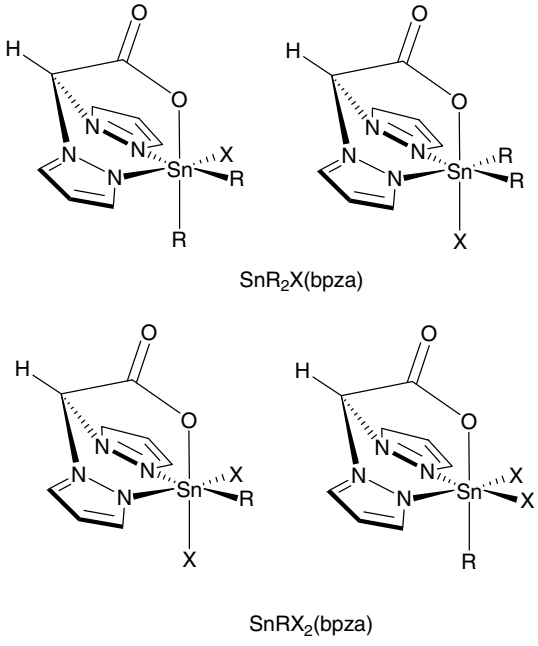
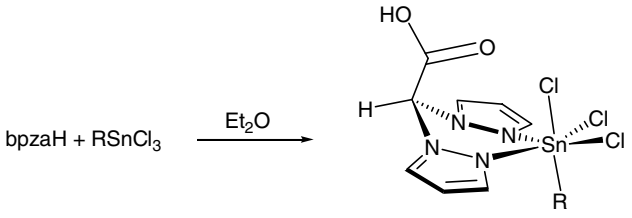


Fig. 2. Possible isomers for [$SnR_2X(L)$] and [$SnRX_2(L)$] complexes.

In the spectra of the dimethyltin-derivatives **2** and **10** and the methyltin derivative **12** it has been possible to detect $^2J_{Sn-H}$ coupling constants; they lie in the ranges 80–90 and 117–121 Hz, respectively, somewhat higher than those observed for the analogous methyltin-tris(pyrazolyl)borates [21].

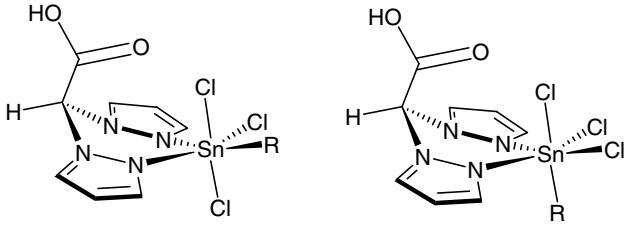
^{119}Sn NMR data fall in the range typical for octahedral tin species, showing more resonances in the case of derivatives **3**, **6**, **11**, **12** and **13**, in accordance with the presence of a mixture of isomers in solution [30,31], indicating further some progressive decomposition process to be operating in solution. After some days the initial resonances decrease in intensity, with new signals appearing in the range of −200/−350 ppm, presumably due to the dissociation of the ligand and the formation of solvated tin species such as $(acetone)_3SnR_nCl_{3-n}$.

We have also studied the direct interaction of bpzaH with some tin acceptors as Bu^nSnCl_3, $PhSnCl_3$ and $SnCl_4$ in Et_2O, in the absence of base; the 1:1 adducts **17**–**19** have been isolated (Scheme 3). They are air stable solids soluble in acetone, acetonitrile and dmso. Their IR spectra indicate that the carboxylate is not coordinated to the tin, as the ν_{asym}(COO) is not shifted with respect to free neutral bpzaH ligand. Moreover, no ν(Sn–O) has been detected in the far-IR region. The proton NMR spectra of derivatives **17** and **18** show three and two sets of resonances, respectively, due to the presence of two isomers in solution (Scheme 4).



17, R = Bu^n
18, R = Ph
19, R = Cl

Scheme 3.

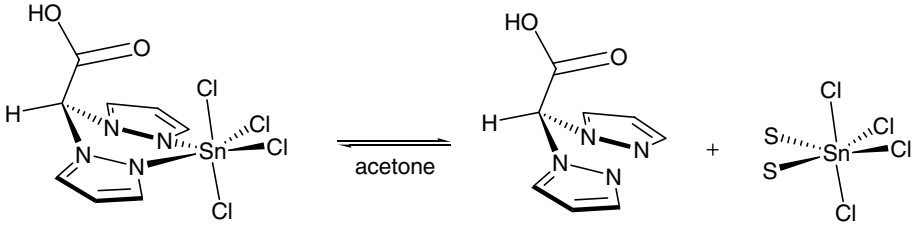


17, R = Bu^n
18, R = Ph

Scheme 4.

However, in the ^{119}Sn NMR spectra only broad resonances have been detected. In acetone solution derivative **19** slowly undergoes partial dissociation with the formation of the initial neutral free bpzaH and solvated $(acetone)_2SnCl_4$ (Scheme 5). In fact, the ^{1}H NMR spectrum in deuteroacetone shows two sets of resonances, one of which is due to free bpzaH and the other assignable to coordinated bpzaH, a downfield shift being observed both for the pz protons and for the bridging CH.

The experimental ^{119}Sn Mössbauer spectra are of three distinct types (Fig. 3): (i) a single absorption in each of the complexes SnX_3-ligand **7**, **9**, **14**, **15** **16**; or (ii) a well resolved doublet in each of the $SnRX_2$-ligand and SnR_2X-ligand **3**, **5**, **6**, **10**, **11**, **13** complexes; or (iii) a spectrum with two asymmetric absorptions in each of $[SnCy_3(bpza)]$ (**1**) and $[SnPh_2Cl(bpza)]$ (**4**). In these latter complexes the fits of the spectra are consistent with the presence of two doublets with different parameters and resonant area. The ^{1}H and ^{119}Sn NMR results indicate the presence of only one octahedral geometry in **1**, but the Mössbauer data, in the solid, point to two different Sn(IV) sites: the doublet with larger δ, Δ, Γ and A% parameters, Table 2, can be associated with an octahedral geometry, unusual in R_3Sn complexes, while the 2.87 mm/s quadrupole splitting value should be



S = acetone

Scheme 5.

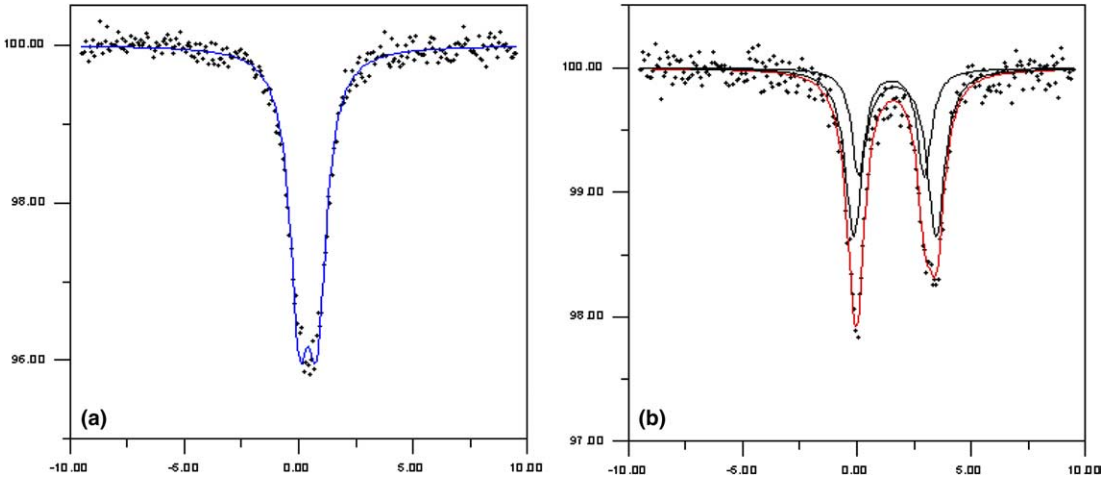


Fig. 3. The Mössbauer spectra of (a): $[SnI_3(bdmpza)]$ (**16**) and (b): $[SnCy_3(bpza)]$ (**1**).

Table 2
Mössbauer data

Compounds	δ[a,b] (mm/s)	Δ[b] (mm/s)	$\Gamma\pm$[c] (mm/s)	A%[d]
$[SnCy_3(bpza)]$ (**1**)	1.52	2.87	0.74	35
	1.67	3.61	0.90	65
$[SnBu^n_2Cl(bpza)]$ (**3**)	1.41	3.32	0.85	100
$[SnPh_2Cl(bpza)]$ (**4**)	0.68	1.68	0.80	13
	0.93	2.35	0.94	87
$[SnBu^nCl_2(bpza)]$ (**5**)	0.89	1.77	0.97	100
$[SnPhCl_2(bpza)]$ (**6**)	0.78	1.63	0.94	100
$[SnCl_3(bpza)]$ (**7**)	0.32	Singlet	1.05	100
$[SnI_3(bpza)]$ (**9**)	0.89	Singlet	1.03	100
$[SnMe_2Cl(bdmpza)]$ (**10**)	1.36	3.57	1.04	100
$[SnPh_2Cl(bdmpza)]$ (**11**)	0.89	2.13	0.87	100
$[SnPhCl_2(bdmpza)]$ (**13**)	0.76	1.71	1.04	100
$[SnCl_3(bdmpza)]$ (**14**)	0.23	0.51	1.22	100
$[SnBr_3(bdmpza)]$ (**15**)	0.53	Singlet	0.98	100
$[SnI_3(bdmpza)]$ (**16**)	0.42	0.78	1.00	100

[a] With respect to R.T. spectrum of $CaSnO_3$.
[b] ± 0.01 mm s^{-1}.
[c] Full-width at half-maximum.
[d] Percentage area.

preferably associated with the *mer*-R_3TBP structure [21,32]. In complex **4** the two doublets highlight the presence of a pair of octahedral *cis*-R_2 isomers in a ratio of about 7:1, as showed in Fig. 2. In the compounds **3**, **5**, **6**, **10**, **11**, and **13**, in each, a single doublet, with $\Gamma \pm$ values in the range 0.85–1.04 mm/s, is consistent with an octahedral arrangement for all the derivatives, but a very large C–Sn–C angle respect to a regular geometry can be inferred from the high Δ value in Alk_2–SnCl moieties. The spectra of $[SnX_3(bdmpza)]$ **14** and **16** may be fitted as two line spectra with quadrupole splitting values 0.51 and 0.78 mm/s, respectively. The observed Δ values can arise from a distortion from ideal O_h symmetry arising from the steric demand of the ligand or a different electron withdrawal of the N,N′,O ligand atoms respect to the halides. In the compounds **7**, **9**, and **15**, single absorption lines indicate a minor degree of distortion respect to regular octahedral geometry.

3.3. X-ray single crystal study

The results of the 'low'-temperature single crystal X-ray study of **16**, crystallized from acetonitrile solution, are consistent with its formulation in terms of stoichiometry and connectivity as **16.CH$_3$CN**, one such formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. The solvent molecule is well-defined (C–N, C(H_3) 1.148(7), 1.454(7) Å, C–$\hat{C}$–N 177.6(6)°), but appears to have no intimate interactions with the **16** substrate. Within the molecule of **16** (Fig. 4) the ligand is *fac*-*N*,*N*′,*O*-tridentate, the three iodine atoms thus also *fac* about the six-coordinate tin(IV) atom. Despite the six-membered rings formed by the tridentate, the angles subtended by it at the tin are diminished well below 90°, and

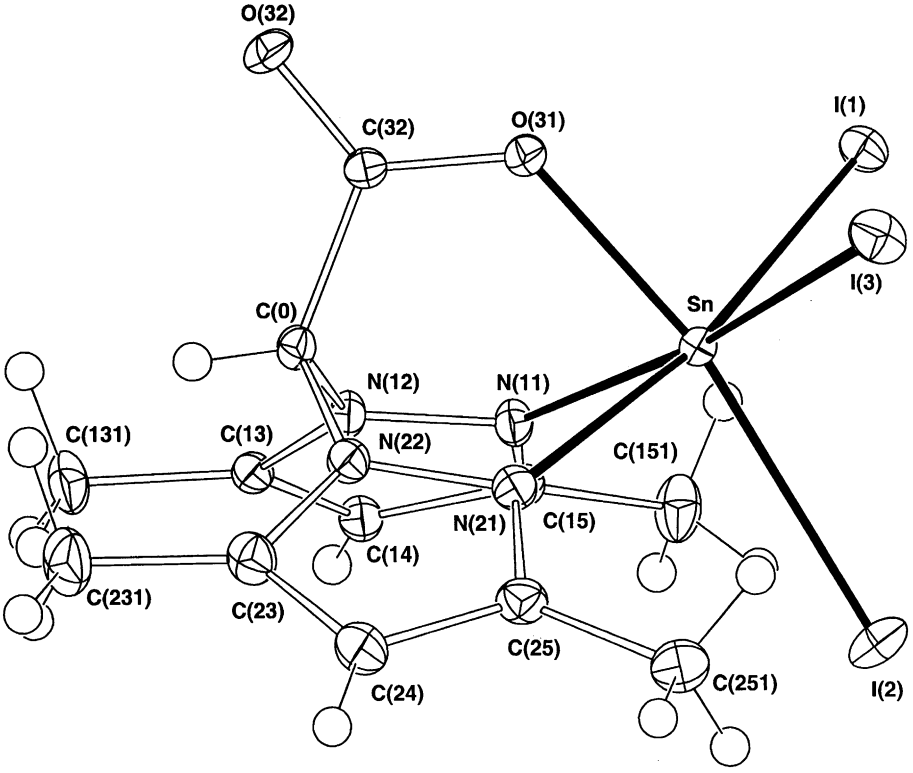


Fig. 4. A single molecule of $[SnI_3(bdmpza)]$ (**16**).

remarkably similar (81.04(8)–81.90(8)°), despite a substantial difference in the interactions of the two nitrogen atoms, cf. the oxygen at the tin, the latter difference also showing no appreciable *trans*-effect within the associated Sn–I distances.

The present appears to be the second structurally characterized bis(pyrazolyl)acetato (tridentate) complex of a tetravalent group 14 species, the other being [Ph_2SnBr(bdmpza)] [20], mononuclear with six-coordinate tin, with the pair of phenyl groups *cis*, and Cl *trans* to O (Sn–O, N_2 2.137(3); 2.314(4), 2.399(3) Å). Numerous *fac*-SnI_3 systems have been defined, a number oligonuclear with bridging associations which essentially constitute a tripod ligand; a number of tris(pyrazolyl)-N_3 complexes of the form $\{N_3\}SnX_3$ have been defined for X = Cl [21,33–36], only one example for X = Br [22], and seemingly no other iodides. Of relevance also is the complex of a highly hindered *N*,*N*′-disubstituted bis-imino-acetylacetonate N_2SnI_3, which, with a planar *N*,*N*′-donor six-membered chelate, is five-coordinate [37].

4. Conclusions

In this work, we have prepared and characterized, through a variety of techniques, 16 new heteroscorpionate-containing tin and organotin(IV) complexes, [SnR_nX_{3-n}(L)]. Three 1:1 adducts [$RSnCl_3$(bpzaH)] were also obtained when the reaction between the ligand and the organotin(IV) acceptors was carried out in diethyl ether in the absence of base. The X-ray single crystal study of [SnI_3(bdmpza)] show the ligand to coordinate to the tin in a *fac*-*N*,*N*′,*O*-tridentate form, in that complex.

^{119}Sn Mössbauer data confirm six-coordinate octahedral tin sites in all the examined complexes studied save the complex [$SnCy_3$(bpza)] (**1**), where the presence of two different geometries is suggested: one with a six-coordinated tin atom, and the other with *mer*-R_3 TBP structure.

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