Notes

Synthesis, Crystal and Molecular Structure of the Compound Dichlorobis[2-(phenylazo)phenyl-$C^1N^{2'}$]tin(IV) †

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The reaction of chloro[2-(phenylazo)phenyl]mercury(II) with metallic tin leads to dichlorobis-[2-(phenylazo)phenyl]tin(IV) whose structure has been determined by *X*-ray diffraction. The tin atom is six-co-ordinated in a very distorted octahedral fashion with two *cis* chlorine and *cis* nitrogen atoms in the equatorial plane and two carbon atoms of the *ortho*-metallated phenyl groups considerably displaced from the *trans* axial position [C–Sn–C = 149.7(7) °].

Organomercury compounds have widely been used in the synthesis of other organometallic compounds.[1] In particular chloro[2-(phenylazo)phenyl]mercury(II) has been used in the synthesis of some palladium(II), platinum(II), nickel(II), manganese(I), tellurium(IV), and gold(III) 2-(phenylazo)-phenyl complexes.[2]

Results and Discussion

Triaryltin chlorides have been obtained[3] by refluxing in xylene chloro(aryl)mercury(II) compounds with metallic tin according to reactions (1)—(3) (R = aryl).

$$6\,\mathrm{HgRCl} + 3\,\mathrm{Sn} \longrightarrow 3\,\mathrm{SnR_2Cl_2} + 6\,\mathrm{Hg} \qquad (1)$$

$$3\,\mathrm{SnR_2Cl_2} \longrightarrow 2\,\mathrm{SnR_3Cl} + \mathrm{SnCl_4} \qquad (2)$$

$$\mathrm{SnCl_4} + \mathrm{Sn} \longrightarrow 2\,\mathrm{SnCl_2} \qquad (3)$$

When chloro[2-(phenylazo)phenyl]mercury(II) is refluxed in xylene (1 h) with metallic tin (2 : 1.1) an orange solution and a precipitate of metallic mercury (94% yield) are obtained. After filtration the solvent was removed and the yellow solid washed with methanol and recrystallized from diethyl ether–n-hexane (1 : 5). Its analytical data, i.r. spectrum, and non-conductivity in acetone solution point to the formulation of such a compound as dichlorobis[2-(phenylazo)phenyl]tin(IV). The main difference with respect to the similar reported reactions[3] is that only process (1) is observed.

Since several stereoisomers are possible for the title compound its structure was established by *X*-ray diffraction.

The crystal structure consists of discrete molecules separated by normal van der Waals distances (shortest distances: C(10) ··· C(22$^{\mathrm{I}}$) 3.39 (6), and Cl(2$^{\mathrm{I}}$) ··· C(12) 3.60(1) Å, where I = $x - y, x, z + \frac{1}{2}$). The tin atom, as shown in the Figure and Table 1, is six-co-ordinated and surrounded in a strongly distorted octahedral shape by two *cis* chlorine and *cis* nitrogen atoms in the equatorial plane (the sum of the angles being *ca.* 360°) and two carbon atoms of the phenyl rings considerably displaced from the *trans* axial positions [C(1)–Sn–C(13) = 149.7(7)°] that can be explained by the small N–Sn–C angles for both 2-(phenylazo)-phenyl ligands (mean value 69°). In addition in the equatorial plane there are deviations of the angles from their ideal values of 90° the most significant being the N–Sn–N angle [74.2(4)°].

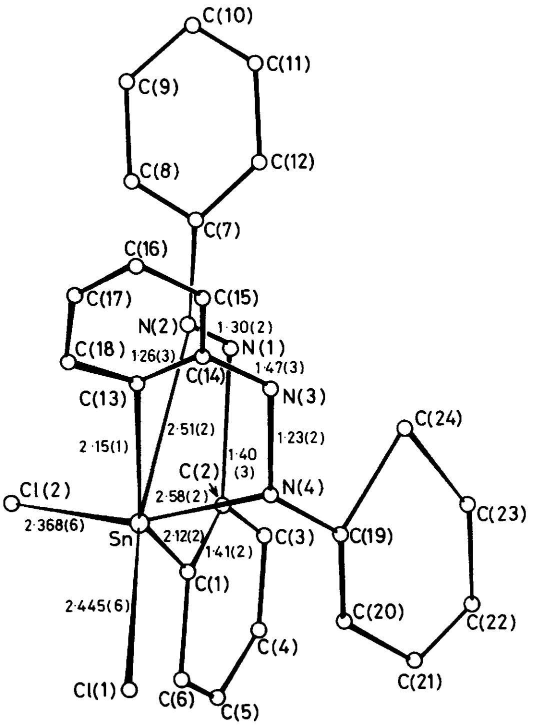

Figure. Molecular structure of dichlorobis[2-(phenylazo)phenyl]-tin(IV) showing atom numbering, Cl–Sn bond lengths, and C–Sn C–C, C–N, and N–N distances in the metallocycles

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† *Supplementary data available* (SUP No. 23399; 9 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Bond lengths (Å) and angles (°)

Sn-Cl(1)	2.445(6)	C(2)-N(1)	1.40(3)	C(16)-C(17)	1.35(4)
Sn-Cl(2)	2.368(6)	N(1)-N(2)	1.30(2)	C(17)-C(18)	1.43(3)
Sn-N(2)	2.51(2)	N(2)-C(7)	1.34(3)	C(18)-C(13)	1.43(3)
Sn-N(4)	2.58(2)	C(7)-C(8)	1.40(3)	C(14)-N(3)	1.47(3)
Sn-C(1)	2.12(2)	C(8)-C(9)	1.40(3)	N(3)-N(4)	1.23(2)
Sn-C(13)	2.15(1)	C(9)-C(10)	1.38(4)	N(4)-C(19)	1.48(3)
C(1)-C(2)	1.41(2)	C(10)-C(11)	1.36(4)	C(19)-C(20)	1.35(3)
C(2)-C(3)	1.37(3)	C(11)-C(12)	1.45(4)	C(20)-C(21)	1.44(3)
C(3)-C(4)	1.45(4)	C(12)-C(7)	1.38(3)	C(21)-C(22)	1.38(3)
C(4)-C(5)	1.39(4)	C(13)-C(14)	1.26(3)	C(22)-C(23)	1.31(3)
C(5)-C(6)	1.47(3)	C(14)-C(15)	1.39(3)	C(23)-C(24)	1.37(4)
C(6)-C(1)	1.47(3)	C(15)-C(16)	1.40(4)	C(24)-C(19)	1.35(3)
Cl(1)-Sn-Cl(2)	97.4(2)	C(3)-C(4)-C(5)	122(2)	C(13)-C(14)-C(15)	126(2)
Cl(1)-Sn-N(2)	163.5(4)	C(4)-C(5)-C(6)	120(2)	C(14)-C(15)-C(16)	117(2)
Cl(1)-Sn-N(4)	94.4(4)	C(5)-C(6)-C(1)	115(2)	C(15)-C(16)-C(17)	120(2)
Cl(1)-Sn-C(1)	97.0(2)	C(1)-C(2)-N(1)	120(1)	C(16)-C(17)-C(18)	121(2)
Cl(1)-Sn-C(13)	98.5(6)	C(3)-C(2)-N(1)	117(2)	C(17)-C(18)-C(13)	118(2)
Cl(2)-Sn-N(2)	95.8(4)	C(2)-N(1)-N(2)	117(2)	C(13)-C(14)-N(3)	122(1)
Cl(2)-Sn-N(4)	165.4(4)	N(1)-N(2)-Sn	111(1)	C(15)-C(14)-N(3)	112(2)
Cl(2)-Sn-C(1)	100.6(4)	C(7)-N(2)-Sn	132(1)	C(14)-N(3)-N(4)	112(2)
Cl(2)-Sn-C(13)	103.0(8)	N(1)-N(2)-C(7)	115(2)	N(3)-N(4)-Sn	114(1)
N(2)-Sn-N(4)	74.2(4)	N(2)-C(7)-C(8)	115(2)	N(3)-N(4)-C(19)	116(2)
N(2)-Sn-C(1)	70.9(6)	N(2)-C(7)-C(12)	126(2)	C(1)-N(4)-Sn	129(1)
N(2)-Sn-C(13)	87.9(6)	C(8)-C(7)-C(12)	119(2)	N(4)-C(19)-C(20)	117(2)
N(4)-Sn-C(1)	86.4(6)	C(7)-C(8)-C(9)	121(2)	N(4)-C(19)-C(24)	120(2)
N(4)-Sn-C(13)	66.6(8)	C(8)-C(9)-C(10)	118(2)	C(20)-C(19)-C(24)	123(2)
C(1)-Sn-C(13)	149.7(7)	C(9)-C(10)-C(11)	123(2)	C(19)-C(20)-C(21)	116(2)
C(2)-C(1)-Sn	119(1)	C(10)-C(11)-C(12)	118(2)	C(20)-C(21)-C(22)	119(2)
C(6)-C(1)-Sn	120(1)	C(11)-C(12)-C(7)	120(2)	C(21)-C(22)-C(23)	123(2)
C(2)-C(1)-C(6)	121(2)	C(14)-C(13)-Sn	124(2)	C(22)-C(23)-C(24)	118(2)
C(1)-C(2)-C(3)	122(2)	C(18)-C(13)-Sn	117(2)	C(23)-C(24)-C(19)	121(2)
C(2)-C(3)-C(4)	118(2)	C(14)-C(13)-C(18)	119(2)		

The C-Sn, Cl-Sn, and N-Sn bond distances (average values 2.13, 2.40, and 2.54 Å) are respectively, similar, shorter, and longer than those observed in the related octahedral complex $SnPh_2Cl_2$(bipy) (bipy = 2,2′-bipyridine)[4] (average values 2.15, 2.50, and 2.36 Å). As far as we know such long N-Sn bond distances have only been observed in the seven-co-ordinate complex di-isothiocyanatodimethyl(terpyridyl)tin(IV).[5] The longest N_{terpy}-Sn bond distance is 2.57 Å and the average value 2.52 Å.

The two five membered rings containing the 2-(phenylazo)phenyl moieties are different. Bond distances in the N(3), N(4) ligand are similar to those obtained in azobenzene compounds or 2-(phenylazo)phenyl ligands[6] while those in the N(1), N(2) ligand are similar to those observed in the protonated 2,4-diaminoazobenzene hydrochloride dihydrate.[7] It can be observed, for example, that the N(1)-N(2) bond distance is 1.30 Å, which is longer than the average value obtained in other azobenzene structures (1.23 Å) while it is shorter than the N-N single bond distance (1.44 Å). For this ligand N-C_R, N-Sn, and C_R-Sn bond distances in the metallocycle are shorter (although the last one not significantly) than the corresponding in the N(3), N(4) ligand where the N-N and C_R-C_R bond distances are shorter. The C(13)-C(14)-[1.26(3) Å] is shorter than the standard C_R-C_R bond distance (1.39 Å) and the average value (1.38 Å) found in *trans*-azobenzene and even the standard C=C double-bond distance (1.35 Å). The influence of the N(2) and N(4) donor atoms in the equatorial plane is shown by the shortening of Sn-Cl(2) and the elongation of Sn-Cl(1) bond distances.

X-Ray diffraction and ^{119}Sn Mössbauer spectra have shown that many SnR_2L_4 six-co-ordinate tin(IV) complexes with mutually *trans* organic groups have slight or substantial deviations from linearity; the L-Sn-L angles differ substantially from 90° and/or the Sn-L bond lengths differ by a significant amount.[4,5,8]

Experimental

The infrared spectrum was recorded on a Perkin-Elmer 577 spectrophotometer using a Nujol mull between polyethylene sheets. Conductivity was measured in *ca.* 5 × 10^{-4} mol dm^{-3} solution with a Philips PW 9501/01 conductimeter. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer 240 microanalyzer.

Preparation of the Complex.—A suspension of chloro[2-(phenylazo)phenyl]mercury(II)[9] (0.20 g, 0.47 mmol) and powdered metallic tin (0.03 g, 0.025 mmol) were refluxed in xylene (6 cm^3). After 1 h the suspension was filtered and the solvent removed under vacuum. The crude complex (85 mg, 65% yield) was obtained by washing with methanol (2 cm^3) and refiltering. Afterwards it was recrystallized from diethyl ether by slow addition of n-hexane (Found: C, 51.0; H, 3.2; N, 9.9. $C_{24}H_{18}Cl_2N_4Sn$ requires C, 52.2; H, 3.3; N, 10.1%), m.p. 222 °C, $\Lambda = 0\ \Omega^{-1}\ cm^2\ mol^{-1}$, $\nu_{max.}$ (Nujol) at 1 585w, 1 310w, 1 300m, 1 263w, 1 220m, 1 170w, 1 155w, 1 105m, 1 070w, 1 015w, 965w, 950w, 910w, 830w, 775s, 767vs, 760vs, 710vs, 705s, 685vs, 675m, 563w, 540m, 433w, 320w, and 295s cm^{-1}.

X-Ray Data Collection, Structure Determination, and Refinement.—Crystal data. $C_{24}H_{18}Cl_2N_4Sn$, M = 553.7, hexagonal, a = 9.723(3), c = 43.343(5) Å, U = 3 548(2) Å^3, space group $P6_1$, Z = 6, D = 2.32 Mg m^{-3}, $F(000)$ = 1 656, Mo-K_α radiation λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 8.56 cm^{-1}.

A small crystal was selected for crystallographic measurements on a Philips PW-1100 four-circle diffractometer. The

Table 2. Final fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	9 469(1)	−6(3)	3 403(0)
Cl(1)	10 767(7)	−692(7)	3 809(2)
Cl(2)	11 444(7)	695(6)	3 019(2)
C(7)	6 725(21)	317(23)	2 910(5)
C(8)	6 957(22)	−559(24)	2 679(5)
C(9)	5 852(31)	−1 282(27)	2 440(6)
C(10)	4 503(32)	−1 165(33)	2 443(6)
C(11)	4 176(31)	−410(33)	2 670(6)
C(12)	5 331(27)	371(25)	2 912(5)
N(2)	7 908(20)	1 001(18)	3 117(4)
N(1)	8 037(21)	2 267(17)	3 247(4)
C(2)	9 239(21)	3 030(20)	3 468(4)
C(3)	9 503(31)	4 459(28)	3 578(5)
C(4)	10 851(45)	5 346(31)	3 779(6)
C(5)	11 725(26)	4 688(24)	3 900(7)
C(6)	11 317(29)	3 063(28)	3 815(6)
C(1)	10 082(19)	2 299(18)	3 577(3)
C(19)	6 425(21)	−262(21)	3 949(4)
C(20)	7 555(27)	580(24)	4 158(4)
C(21)	7 148(28)	1 352(26)	4 394(5)
C(22)	5 662(33)	1 229(31)	4 383(5)
C(23)	4 595(25)	386(31)	4 174(6)
C(24)	4 987(24)	−359(29)	3 950(6)
N(4)	6 841(20)	−1 046(20)	3 703(4)
N(3)	5 745(21)	−2 275(18)	3 596(4)
C(14)	6 293(18)	−3 008(20)	3 368(4)
C(15)	5 089(28)	−4 509(30)	3 284(7)
C(16)	5 471(27)	−5 335(24)	3 065(6)
C(17)	6 977(31)	−4 676(29)	2 958(5)
C(18)	8 154(22)	- 3 123(23)	3 050(5)
C(13)	7 717(25)	−2 333(19)	3 275(6)

unit cell was measured by centring 25 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. 2 055 Independent reflections were measured in the range 2θ = 0—45°, 1 581 of which were considered as 'observed' applying the condition $I \geqslant 2.5\ \sigma(I)$. Lorentz polarization, but no absorption, corrections were made.

The structure was solved by direct methods, using the MULTAN system of computer programs.[10] An electron-density map computed from the set of phases with highest combined figure of merit revealed peaks for all non-hydrogen atoms. Isotropic and anisotropic refinements were carried out by the full-matrix least-squares method, using the SHELX76 program.[11] Anomalous dispersion corrections were applied for all atoms. The function minimized was $w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0143|F|^2]^{-1}$. Refinements were terminated at *R* equal to 0.073 for all observed reflections. Final co-ordinates are given in Table 2, bond lengths and angles in Table 1.

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