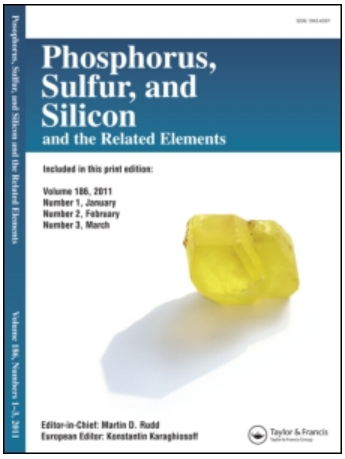

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Crystallographic Studies of Diphenylgermanium, Diphenyltin and Diphenyllead Compounds Containing the Dinegative Ligand Derived from Salicylideneamino-*o*-Hydroxybenzene: $Ph_2M(OC_6H_4CH{=}NC_6H_4O)$

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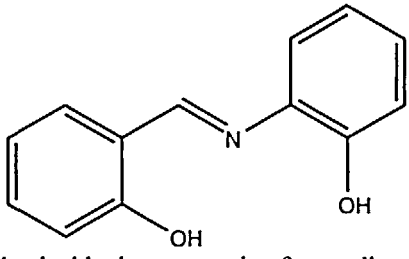
The crystal and molecular structures of $Ph_2M(OC_6H_4CH{=}NC_6H_4O)$ where M = Ge, Sn, Pb and the dinegative ligand is derived from salicylideneamino-*o*-hydroxybenzene have been determined. Monomeric species are found for the Ge(IV) and Sn(IV) compounds in which the metal centre exists in a distorted trigonal bipyramidal geometry with the O atoms occupying axial positions. By contrast, intermolecular association is found in the Pb(IV) analogue, presumably reflecting the desire of the larger lead atom to increase its coordination number. Thus, centrosymmetrically related molecules of $Ph_2Pb(OC_6H_4CH{=}NC_6H_4O)$ are linked via the O-atoms of the azobenzene portion of the molecule giving rise to a central Pb_2O_2 unit and a six-coordinate geometry based on a distorted octahedron.

Keywords: germanium; tin; lead; Schiff base; crystal structure

INTRODUCTION

Condensation of β-diketones or *o*-hydroxy carbonyls with chelating amines can yield tridentate ONO donor Schiff bases which may coordinate to metal centres forming both five- and six-membered rings. As a continuation of an examination of the coordination potential of these and related ligands to transition metal centres such as Ti(IV) and

V(IV)[1], the structures of the title compounds have been investigated. The condensation reaction between salicyaldehyde and *o*-aminophenol yields the Schiff base, salicylideneamino-*o*-hydroxybenzene:



This ligand may be doubly deprotonated to form a dinegative, potentially tridentate ligand. The reaction of this ligand with appropriate organometallic precursors has been shown to yield $Ph_2M(OC_6H_4CH{=}NC_6H_4O)$, hereafter Ph_2M(SalAp), where M = Ge, Sn and Pb, the structures of which have been determined by single-crystal X-ray diffraction methods.

EXPERIMENTAL

Preparation of $SalApH_2$

The ligand was prepared according to the literature method.[2]

Preparation of Ph_2M(SalAp)

M = Ge: Sodium metal (46 mg, 2.0 mmol) was dissolved in dry ethanol (25 ml) and $SalApH_2$ (0.21 g, 0.98 mmol) added thereby forming a yellow solution. After stirring for 10 min at room temperature, the solvent was removed under vacuum leaving the yellow sodium salt of the ligand. A benzene solution (AR, 50 ml) of Ph_2GeCl_2 (0.32 g, 1.1 mmol) was added to the salt under dinitrogen. The yellow solution was refluxed under an atmosphere of dinitrogen for 4 h and allowed to cool to room temperature before further cooling overnight (8 °C). NaCl formed during the reaction and unreacted ligand were removed by filtration. The filtrate was evaporated to dryness yielding a yellow solid. Recrystallisation was from a dichloromethane/hexane solution (1/1) of the compound. Yield 0.19 g (0.43 mmol, 44 %), m. pt 161 - 163 °C. Analysis: Found C, 68.73; H, 4.44; N, 3.21. $C_{25}H_{19}GeNO_2$ requires C, 68.55, H, 4.37, N,

3.20 %. Crystals for the structure determination were obtained from the slow evaporation of a benzene/hexane solution of the compound.
M = Sn: This compound was prepared and recrystallised using a procedure analogous to that described for the M = Ge compound with sodium metal (13 mg, 0.57 mmol), $SalApH_2$ (0.12 g, 0.56 mmol) and Ph_2SnCl_2 (0.20 g, 0.58 mmol). Yield 0.12 g (0.25 mmol, 44 %), m. pt 208 - 210 °C (lit.[3] 215 - 216 °C). Analysis: Found C, 61.36; H, 3.78; N, 2.91. $C_{25}H_{19}NO_2Sn$ requires C, 62.02, H, 3.96, N, 2.89 %.
M = Pb: Prepared and recrystallised as above using sodium (11 mg, 0.48 mmol), $SalApH_2$ (50 mg, 0.23 mmol) and Ph_2PbCl_2 (0.10 g, 0.23 mmol). Yield 0.12 g (0.21 mmol, 91 %), m. pt 230 - 232 °C (lit.[4] 232 - 235 °C). Analysis: Found C, 54.22; H, 3.42; N, 2.48. $C_{25}H_{19}NO_2Pb$ requires C, 52.44, H, 3.34, N, 2.44 %.

Crystallography

Intensity data sets for each of the crystals were collected at room temperature on an Enraf-Nonius CAD4 diffractometer fitted with graphite monochromatised MoKα radiation, λ = 0.71073 Å, using the ω:2θ scan technique. The data were corrected for Lorentz and polarization effects and in the case of M = Sn and Pb compounds, an analytical absorption correction was applied.[5] Crystallographic data is collected in Table I. The structures were solved by Patterson methods and refinement by a full-matrix least-squares procedure based on F[5] using reflections that satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. In the refinements of the M = Ge(IV) and Sn(IV) compounds, disorder was noted in the positions of the N(1) and C(7) atoms, *i.e.* the backbone of the ligand, such that two conformations were found; these atoms were refined with 55 and 45 % occupancy factors for the M = Ge(IV) compound and 86 and 14 % occupancy for the M = Sn(IV) structure. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the models at their calculated positions but not for the disordered components. A weighting scheme of the form $w = 1/[\sigma^2(F) + |g|F^2]$ was included and each refinement continued until convergence. All calculations were performed using SHELX-76[5] installed on a VAX11/785 computer system. Scattering factors were as incorporated in SHELX-76 or from *International Tables for X-ray Crystallography*.[6] Final refinement details are listed in Table I. The atomic numbering schemes are shown in

Figures 1 - 3 which were drawn with ORTEP[7] at 35 %, 35 % and 50 % probability ellipsoids, respectively. Fractional atomic coordinates, thermal parameters and interatomic parameters have been deposited at the Cambridge Crystallographic Data Centre.

TABLE I Crystallographic data for $Ph_2M(SalAp)$, M = Ge, Sn and Pb

M	Ge	Sn	Pb
Molecular formula	$C_{25}H_{19}GeNO_2$	$C_{25}H_{19}NO_2Sn$	$C_{25}H_{19}NO_2Pb$
Formula weight	438.0	484.1	575.0
Colour	orange	orange	orange
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/c$	$P2_1/n$
a, Å	13.795(3)	9.803(2)	9.980(1)
b, Å	15.060(2)	14.014(1)	17.863(3)
c, Å	19.663(3)	15.151(1)	12.193(2)
β, deg.	90	97.84(1)	112.51(1)
V, Å^3	4085.0	2062.0	2008.1
D_{calc}, g cm^{-3}	1.424	1.559	1.902
Z	8	4	4
μ, cm^{-1}	14.69	11.46	84.54
Max./min transmission factors	na	0.928, 0.850	0.287, 0.136
F(000)	1792	968	1096
Refln meas.	5042	2981	3940
θ_{max}, deg.	25.0	22.5	25.0
Unique reflns	3600	2701	3534
Reflections with $I \geq 2.5\sigma(I)$	1767	1831	2631
R	0.031	0.025	0.032
g	0.006	0.001	0.002
R_w	0.049	0.035	0.032
Residual electron density, e Å^{-3}	0.32	0.49	2.68 / Pb

RESULTS AND DISCUSSION

The molecular structure of $Ph_2Ge(SalAp)$ is shown in Figure 1 and selected interatomic parameters are listed in Table II. The Ge(IV) atom exists in a distorted trigonal bipyramidal geometry defined by two phenyl substituents and an ONO ligand donor set derived from the dinegative, tridentate ligand. The O atoms define the axial positions; O-Ge-O is 167.6(1)°. The Ge(IV) atom lies 0.1389(5) Å out of the trigonal plane, defined by the N(1) and the phenyl-C atoms, in the direction of the O(1) atom. The trigonal angles range from 114.4(6)° to 121.2(2)° indicating a relatively small distortion from the ideal and the dihedral angle between the two phenyl groups is 66.6°. The chelation of the tridentate ligand results in the formation of both a five- and a six-membered ring each of which show some puckering as seen in the Ge/O(1)/C(1)/C(6) and Ge/O(2)/C(9)/C(8) dihedral angles of 20.6(6)° and 15.7(6)°, respectively. The structure reported here for $Ph_2Ge(SalAp)$ is essentially repeated in that of the Sn(IV) analogue.

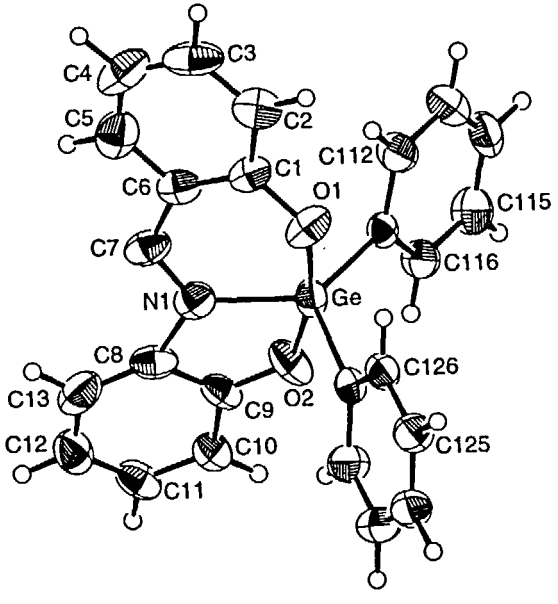


FIGURE 1 Molecular structure of $Ph_2Ge(SalAp)$

TABLE II Selected interatomic parameters (Å, deg.) for $Ph_2M(SalAp)$, M = Ge, Sn and Pb

	Ge[a]	Sn[a]	Pb
M-O(1)	1.921(4)	2.081(3)	2.246(5)
M-O(2)	1.918(4)	2.067(4)	2.326(5)
M-N(1)	2.01(2)	2.220(6)	2.337(5)
M-C(111)	1.945(4)	2.118(5)	2.151(7)
M-C(121)	1.946(4)	2.111(5)	2.166(7)
M-O(1)^{i} [b]			2.767(4)
O(1)-M-O(2)	167.6(1)	159.8(2)	150.5(1)
O(1)-M-N(1)	96.3(6)	74.1(2)	72.8(2)
O(1)-M-C(111)	93.5(2)	95.4(2)	95.7(2)
O(1)-M-C(121)	92.3(2)	93.0(2)	102.7(2)
O(2)-M-N(1)	71.5(6)	86.1(2)	79.0(2)
O(2)-M-C(111)	91.7(2)	96.0(2)	82.2(2)
O(2)-M-C(121)	94.6(2)	95.4(2)	90.7(2)
N(1)-M-C(111)	122.9(6)	113.2(2)	103.6(2)
N(1)-M-C(121)	114.4(6)	125.3(2)	100.0(2)
C(111)-M-C(121)	121.2(2)	120.9(2)	153.5(2)
O(1)-M-O(1)^{i}			65.3(1)
O(2)-M-O(1)^{i}			142.7(1)
N(1)-M-O(1)^{i}			138.1(2)
C(111)-M-O(1)^{i}			84.1(2)
C(121)-M-O(1)^{i}			86.4(2)

a only major component of disordered N(1) site included; *b* symmetry operation *i*: - *x*, - *y*, - *z*.

The molecular structure of $Ph_2Sn(SalAp)$ is shown in Figure 2 and selected interatomic parameters are collected in Table II. The Sn(IV) atom lies 0.0945(3) Å out of the NC_2 plane in the direction of the O(2) atom. Marginally greater distortions are seen in the trigonal plane compared with the Ge(IV) analogue and the dihedral angle between the

phenyl substituents is 114.2°. The M-ligand parameters in the two structures are comparable allowing for the larger size of the Sn(IV) atom with the equivalence of the M-O bond within each of the structures being noteworthy. Similar puckering in the five- and six-membered rings as described above is found. By contrast to the monomeric Ge(IV) and Sn(IV) structures, the structure of the Pb(IV) compound is dimeric.

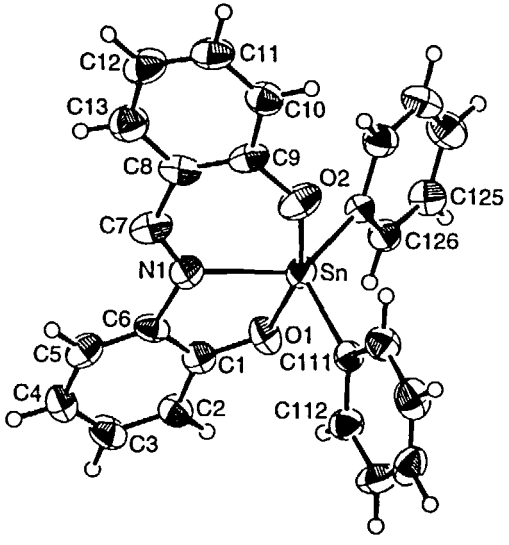


FIGURE 2 Molecular structure of $Ph_2Sn(SalAp)$

The molecular structure of $Ph_2Pb(SalAp)$ is shown in Figure 3 and geometric parameters are given in Table II. The Pb(IV) atom is coordinated as for the monomeric compounds, *i.e.* by two phenyl groups and the ONO donor set and to a first approximation may be described a distorted trigonal bipyramidal as above. The difference between the structures is the presence of an additional, albeit weaker, Pb-$O(1)^i$ interaction where the $O(1)^i$ atom is derived from a centrosymmetrically related molecule; symmetry operation *i*: - *x*, - *y*, - *z*. The $O(1)^i$ atom approaches the Pb(IV) atom in a position approximately between the two phenyl groups and opposite the N(1) atom resulting in the C-Pb-C angle opening to 153.6(2)°. Thus, in the case of $Ph_2Pb(SalAp)$ the

dinegative ligand is tetradentate, a coordination mode that leads to the formation of a dimeric unit. The six-coordinate Pb(IV) atom exists in a grossly distorted octahedral geometry with the phenyl substituents (dihedral angle: 65.3°) occupying positions approximately *trans* to each other. Distortions arise, in part, as a result of the restricted bite angles of the chelate rings, a feature that also precludes the closer approach of the $O(1)^{i}$ atom.

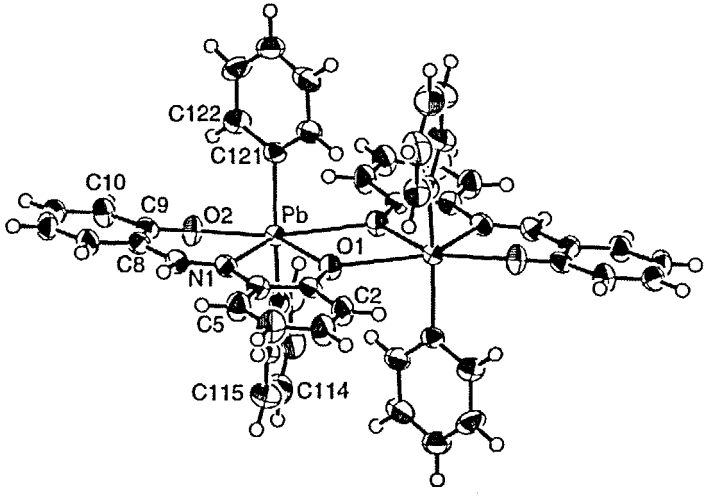


FIGURE 3 Molecular structure of $Ph_2Pb(SalAp)$

The structure reported here for $Ph_2Pb(SalAp)$ is similar to that found in another diphenyllead compound, *i.e.* [Ph_2Pb(2,6-pyridine-dicarboxylate) hydrate]$_2$,[8] with the exception that an additional coordination site is occupied by a water molecule leading to a distorted pentagonal bipyramidal geometry. Similarly, such dinuclear structures may be found for related $R_2Sn(IV)$ systems.[9] Indeed, the structure of $Me_2Sn(SalAp)$ is available in the literature which shows the presence of dimers in the solid state.[10] Such differences in coordination motif are often encountered in organotin structures[11] but the difference here may

simply related to the greater steric bulk of the phenyl groups in $Ph_2Sn(SalAp)$, compared with methyl groups in $Me_2Sn(SalAp)$, that preclude association. The difference between the three structures with the general formula $Ph_2M(SalAp)$ is likely to be related to the propensity of the metal centre to increase its coordination number as it increases in size.

ACKNOWLEDGMENTS

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