

Synthesis and Structural Studies on Some Coordination Complexes of Organotin (IV) with Macrocyclic Crown Ethers

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Three series of hexa-coordinated complexes of organotin (IV) with three different crown ethers have been synthesized having the general formula $\text{Ph}_2\text{Sn}(\text{L}_{1-3})\text{X}_2$ where $\text{X} = \text{Cl}^-$, NO_3^- , ClO_4^- and SCN^- and L_1 , L_2 and L_3 are the crown ether ligands (18—C—6) = 1, 4, 7, 10, 13, 16-hexaoxacycloocta-decane; (15—C—5) = 1,4,7, 10,13-penta-oxacyclopentadecane and (12—C—4)-1,4,7,10-tetraoxacyclododecane. These complexes were characterized by elemental analysis, molar conductance data, IR and ^1H NMR spectra and these results show that only four oxygen atoms of ligands and two phenyl groups are coordinated to tin giving an octahedral structure.

INTRODUCTION

Recently, several metal derivatives of a wide variety of macrocyclic ligands have been synthesized and characterized.¹⁻⁴ The chemistry of macrocyclic polyethers called crown ethers has been studied by Pederson using alkali metals, alkaline earth metals and transition metal cations^{5,6} but almost no work has been done with their organometallic derivatives. The present paper describes the synthesis and spectroscopic studies of several new complexes of organotin (IV) with crown ethers.

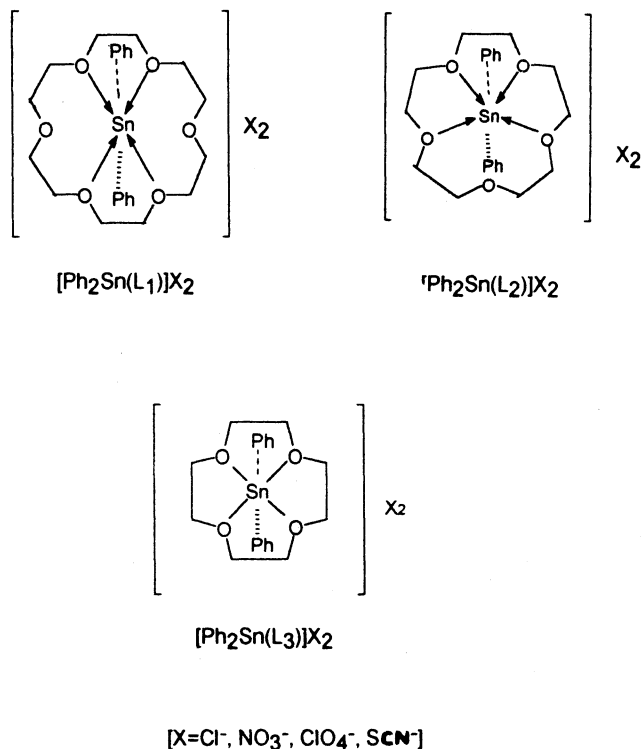
EXPERIMENTAL

SnCl_4 was obtained from M/s Aldrich Chemicals (U.S.A.) and other solvents and reagents from Ranbaxy and purified by standard method.⁷ The solvents were freshly distilled and dried before use and the reactions were carried out under dry nitrogen. Tin was estimated by standard method.⁸ Elemental analysis (C, H and N) were carried out at C.D.R.I., Lucknow. The IR spectra were recorded on CsI on a Perkin-Elmer model 521 spectrophotometer in the range of 4000–200 cm^{-1} . The ^1H NMR spectra were recorded on Perkin-Elmer R-32, 90 MHz spectrometer in DMSO-d_6 with TMS as an internal reference. Molar conductance of the 10^{-3} molar solution in anhydrous DMSO were measured at room temperature by Philips magic-eye conductivity bridge, model PR 9500 using dip type conductivity cell.

Ph_2SnCl_2 was prepared by standard method as reported in literature⁹, while Ph_2SnX_2 ($\text{X} = \text{NO}_3^-$, ClO_4^- and SCN^-) were prepared by simple mathematical reactions of Ph_2SnCl_2 with AgX or NaX in methanol. All the complexes were prepared by non-template method as described below:

Preparation of crown ether complexes of diphenyl tin salt

To a solution of 0.001 mole of Ph_2SnX_2 in absolute ethanol was added 0.001 mole methanolic solution of crown ethers (L_1 – L_3) and the solution was stirred at room temperature under nitrogen for 3 h and then refluxed for 5–6 h. The solvent was distilled off and the residue was recrystallized using petroleum ether or solvent ether and purified by recrystallisation. The compounds were dried over P_4O_{10} , the purity of the compounds was checked by qualitative TLC techniques.



RESULTS AND DISCUSSIONS

The analytical data, yield, melting point and molar conductance values of the complexes are reported in Table-1 and agree with formula assigned.

In the IR spectra of free ligands, a broad band at 2900 cm^{-1} and a peak at 1450 cm^{-1} corresponds to C—H stretching and bending, while a sharp peak at 1350 cm^{-1} is due to O—H bending and the C—O stretching is seen at 1150 – 1100 cm^{-1} .¹⁰ In complexes these peaks show negative shifts which indicates the coordination of crown ether. The peak observed at $290 \pm 5\text{ cm}^{-1}$ in complexes is due to Sn—C(Ph) group in complexes.¹¹ The tin-oxygen stretching vibrations occur over an exceptionally wide range of frequencies depending upon the precise environment of the Sn—O group in the molecule.¹² These are observed in the

spectra of complexes as a weak band at $350 \pm 10 \text{ cm}^{-1}$.¹³ The absorption associated with anions in these complexes are identified at 570 cm^{-1} for chloride¹⁴ at 1360, 810, 230 cm^{-1} for nitrate¹⁵ at 1985, 621, 421 cm^{-1} for chlorate¹⁶ and 484 cm^{-1} for thiocyanate.¹⁷ These positions show the presence of uncoordinated anions.

TABLE-1

Compounds (yield %)	m.p. (°C)	% analysis (found/calcd.)				Molar conductance $\text{ohm}^{-1} \text{ cm}^2$ mole^{-1}
		Sn	C	H	N	
L ₁ 18-C-6	40	—	54.54 (54.53)	9.16 (9.15)	—	—
[Ph ₂ Sn(L ₁)]Cl ₂ (58)	80	19.53 (19.51)	47.41 (47.40)	5.65 (5.63)	—	55
[Ph ₂ Sn(L ₁)](NO ₃) ₂ (51)	280d	18.75 (18.74)	45.53 (45.52)	5.41 (5.42)	4.43 (4.42)	48
[Ph ₂ Sn(L ₁)](ClO ₄) ₂ (47)	165	16.13 (16.12)	39.20 (39.16)	4.67 (4.65)	—	43
[Ph ₂ Sn(L ₁)](SCN) ₂ (48)	240d	18.20 (18.16)	47.81 (47.79)	5.27 (5.24)	4.29 (4.28)	51
L ₂ 15-C-5	100–135 (b.p.)	—	54.54 (54.52)	9.12 (9.15)	—	—
[Ph ₂ Sn(L ₂)]Cl ₂ (51)	85	21.02 (21.04)	46.86 (46.84)	5.32 (5.53)	—	56
[Ph ₂ Sn(L ₂)](NO ₃) ₂ (43)	>300	19.26 (19.23)	42.85 (42.81)	4.86 (4.89)	4.55 (4.53)	49
[Ph ₂ Sn(L ₂)](ClO ₄) ₂ (40)	135–140	17.21 (17.15)	38.16 (38.18)	4.38 (4.36)	—	45
[Ph ₂ Sn(L ₂)](SCN) ₂ (48)	260d	19.51 (19.48)	47.32 (47.30)	4.97 (4.95)	4.62 (4.59)	53
L ₃ 12-C-4	16	—	54.54 (54.53)	9.13 (9.15)	—	—
[Ph ₂ Sn(L ₃)]Cl ₂ (56)	105	22.79 (22.82)	46.24 (46.19)	5.14 (5.03)	—	58
[Ph ₂ Sn(L ₃)](ClO ₄) ₂ (45)	>300	20.76 (20.71)	41.98 (41.91)	4.85 (4.75)	4.68 (4.78)	51
[Ph ₂ Sn(L ₃)](ClO ₄) ₂ (42)	Explosive at 300°C	18.12 (18.31)	37.13 (37.06)	4.19 (4.04)	—	47
[Ph ₂ Sn(L ₃)](SCN) ₂ (51)	200d	21.35 (20.99)	46.78 (46.74)	4.67 (4.63)	4.74 (4.95)	54

The ¹H NMR spectral data of the complexes are in full accordance with the mode of bonding discussed above. In the ¹H NMR spectra of the ligand L₁, L₂ and L₃ all the CH₂ protons (as these are equivalent) appear as a singlet at δ 3.688 in L₁, δ 3.6859 in L₂ and δ 3.6997 in L₃.

In the ^1H NMR spectra of complexes $[\text{Ph}_2\text{Sn}(\text{L}_1)]\text{X}_2$ mainly three types of methylene protons are observed. One type of protons belongs to the methylene group attached to the free oxygen, *i.e.* which does not participate in coordination and is observed as a singlet at δ 5.844. The other two types of protons belonging to the methylene group attached to oxygen atom merge together and appear at same place at δ 3.661. The downward shift from ligand confirms the coordination of oxygen atom of ligand with the tin metal. The peak of two phenyl groups appears at δ 7.495.

In the ^1H NMR of complexes $[\text{Ph}_2\text{Sn}(\text{L}_3)]\text{X}_2$ only one type of methylene protons are observed because all four oxygens of ligand participate in coordination and these are seen as a singlet at δ 3.668. The downward shift is an indication of coordination. The phenyl group protons appear at δ 7.506.

The molar conductance values of all these complexes in DMSO fall in the range of 40–60 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ corresponding to 1 : 2 electrolyte.

Thus on the basis of the above discussion an octahedral geometry¹⁸ be assigned to all these complexes in which four positions of hexacoordinated tin were satisfied by four oxygen atoms of ligand and remaining two positions by two phenyl groups which lie above and below the coordination sphere or occupy axial positions and anions remain outside the coordination sphere.

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REFERENCES

1. N. Herron, Y.M. Chavan and D.H. Buseh, *J. Chem. Soc., Dalton Trans.*, **8**, 1491 (1984).
2. M.P. Catrol, B. Murphy and J. Nelson, *Inorg. Chim. Acta*, **90**, 169 (1984).
3. V.B. Rana, S.P. Ratra, D.P. Singh and M.P. Teotia, *Trans. Met. Chem.*, **10**, 115 (1985).
4. D.R. Rilay and D.H. Busch, *Inorg. Chem.*, **22**, 4141 (1983).
5. C.J. Pederson, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
6. _____, *J. Am. Chem. Soc.*, **92**, 386, 391 (1970).
7. A.I. Vogel, *A Text Book of Organic Chemistry*, Longman, London (1968).
8. J. Bassett, R.C. Dennev, G.H. Jaffery and J. Mendham, *Text Book of Quantitative Inorganic Analysis*, Longman Group Limited, London Vol. 57A, p. 484 (1978).
9. R.K. Igham, S.D. Rosenburg and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).
10. C.J. Pederson, *J. Am. Chem. Soc.*, **89**, 20 (1967).
11. G.K. Sandhu, R. Gupta and S.S. Sandhu, *Polyhedron*, **4**, 81 (1985).
12. R.C. Pollar, *J. Inorg. Nucl. Chem.*, **24**, 593 (1962).
13. Y. Kawasaki, M. Hori and K. Uenaka, *Bull. Chem. Soc. (Japan)*, **40**, 2463 (1967).
14. H. Poulet and J.P. Matheiss, *J. Chem. Phys. (Paris)*, **9**, 549 (1964).
15. C.C. Addison and B.M. Gatehouse, *J. Chem. Soc.*, 613 (1960).
16. L.G. Moore, R.B. Gayhard and W. Bull, *J. Inorg. Nucl. Chem.*, **26**, 856 (1964).
17. K. Mizokama, H. Hirashima and I. Masuda, *Polyhedron*, **4**, 1891 (1985).
18. D.L. Kepert, *J. Org. Met. Chem.*, **49**, 107 (1976).