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Synthesis, Characterisation and Reactions of Some Coordination Complexes of α, α′-Bipyridyl Involving Organotin Derivatives as Lewis Acids

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Some coordination complexes were prepared using α, α′-bipyridyl as Lewis bases and the organotin derivatives as Lewis acids. Some replacement reactions were also done using ethylenediamine, 1,10-phenanthroline and α, α′-bipyridyl as secondary ligands. These secondary ligands being better donors were found to replace the anion in order to coordinate with the Lewis acid. All these complexes were characterized on the basis of elemental analysis, IR and ^{1}H NMR studies.

A number of coordination complexes involving organometallic derivatives as Lewis acids and simple Schiffs bases or macrocyclic amines as ligands have been reported from this laboratory[1-3]. In the present communication we give the preparation, characterisation and reactions of some complexes of α, α′-bipyridyl with diphenyltin derivatives. The complexes have been assigned octahedral or tetrahedral geometries on the basis of analytical data, conductance measurements and IR spectra.

All the chemicals used were AR grade and the solvents were chemically pure. The diphenyl tin derivatives used for the reactions were prepared as follows:

The diphenyltin dichloride was obtained commercially from E. Merck whereas the diphenyltin diperchlorate and diphenyltin dipernitrate were prepared by stirring silver perchlorate or silver nitrate with diphenyltin dichloride in dry methanol for two hours in a 2 : 1 molar ratio and filtering off the resulting silver chloride. The filtrate was used as such for further reactions.

The complexes were prepared as follows:

α-α′ bipyridyl (0.01 mol) was dissolved in 5 ml of absolute methanol and the appropriate diphenyltin derivative (0.01 mole) also in methanol was added to it with constant stirring. The stirring was continued for about 12 hrs by a magnetic stirrer. The solvent was distilled off and the complexes were crystallized using petroleum ether. The complexes

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were purified by running over TLC plates, separated quantitatively with suitable solvents, recrystallized with acetone-petroleum ether and analysed.

The replacement reactions were studied with the diphenyltindichloride complex [ϕ_2 SnCl$_2$·(bpy)]. The complex [ϕ_2 SnCl$_2$·(bpy)](0.01 mol) was refluxed with the ethylenediamine or 1,10-phenanthroline or α–α′ bipyridyl (0.01 mole) in methanol for about 10 hours. The solvent was filtered off, the compounds were crystallized using pet. ether-acetone mixure and analysed.

The molar conductance values of the complexes were measured in DMSO by a Toshniwal direct reading conductivity bridge, the molecular weights were determined by depression in freezing point method using Beckman thermometer, the IR spectra were recorded in a Perkin Elmer 157 spectrophotometer in the range 4000–200 cm^{-1}, and the ^{1}H NMR studies were done on Perkin Elmer R–32 spectrometer.

TABLE 1

ANALYTICAL AND MOLAR CONDUCTANCE DATA OF THE COMPLEXES

Complex	Mol. wt.	Sn	% Found (Calcd.)		N	Molar conductance in DMSO (ohm^{-1} cm^{2}mol^{-1}
			C	H		
[ϕ_2Sn(bpy)Cl$_2$]	490	22.90	51.96	3.24	5.98	14.50
	(500)	(23.89)	(52.80)	(3.60)	(5.60)	
[ϕ_2Sn(bpy)](ClO$_2$)$_2$	602	18.19	42.80	2.64	4.14	41.23
	(628)	(18.95)	(42.04)	(2.87)	(4.46)	
[ϕ_2Sn(bpy)](NO$_3$)$_2$	516	21.14	47.80	3.96	10.32	46.14
	(553)	(21.52)	(47.47)	(3.26)	(10.13)	
[ϕ_2Sn(bpy)(en)]Cl$_2$	580	21.19	51.82	4.81	10.24	51.21
	(560)	(21.25)	(51.43)	(4.64)	(10.00)	
[ϕ_2Sn(bpy)(phen)]Cl$_2$	691	17.18	59.12	3.18	8.91	54.30
	(680)	(17.50)	(60.00)	(3.82)	(8.24)	
[ϕ_2Sn(bpy)$_2$]Cl$_2$	642	18.94	59.27	3:82	8.62	50.00
	(656)	(18.14)	(58.54)	(3.96)	(8.53)	

where bpy = α–α′ bipyridyl ($C_{10}H_8N_2$), en = ethylenediamine ($C_2H_8N_2$) and phen = 1, 10-phenanthroline ($C_{12}H_8N_2$).

All the complexes obtained were found to be soluble in aprotic solvents DMSO and DMF; they however showed little or not solubility in methanol and acetone.

The analytical data of the complexes correspond to 1 : 1 stoichiometry while the molar conductance data correspond to non-electrolyte value for $[\phi_2 SnCl_2 \cdot (bpy)]$ complexes and 1 : 2 electrolyte for all the other complexes. Thus the molecular formulae of the complex are $[\phi_2 Sn(bpy)Cl_2]$, $[\phi_2 Sn(bpy)]X_2$ or $[\phi_2 Sn(bpy)(SL)]Cl_2$ where $X = ClO_4^-$ or NO_3^- and SL = ethylenediamine, 1, 10-phenanthroline or α-α′ bipyridyl.

The IR spectra of the complexes show a band at *ca.* 280 cm^{-1} corresponding to Sn–C bond[4] whereas a weak band at *ca.* 365 can be attributed to Sn–Cl[5,6]. The bands at 940 cm^{-1} and 470 cm^{-1} are attributed to the uncoordinated uninegative perchlorate[7] whereas the bonds at 1360 cm^{-1} and 820 cm^{-1} are due to the ionic nitrate group[8]. The coordination of ethylenediamine is confirmed by the lowering of ν_{NH} frequency to 3400 cm^{-1} [9,10] in the case of $[\phi_2Sn(bpy)(en)]Cl_2$. The coordination of the ligand α–α′ bipyridyl is confirmed by the lowering of C–N ring stretch to 1580 cm^{-1} [11].

The ^1H NMR spectra of the complexes show the following pattern for the complexes—

Compounds	*NMR shifts* (δ)
$[\phi_2Sn(bpy)Cl_2]$	7.14–7.20(m); 7.30–7.36(m)
$[\phi_2Sn(bpy)](ClO_4)_2$	7.10–7.20(m); 7.30–7.36(m)
$[\phi_2Sn(bpy)](NO_3)_2$	7.14–7.24(m); 7.30–7.34(m)
$[\phi_2Sn(bpy)(en)]Cl_2$	1.42(t); 3.10–3.12(t), 7.10–7.30(m)
$[\phi_2Sn(bpy)(phen)]Cl_2$	7.10–7.38 (brm)
$[\phi_2Sn(bpy)_2]Cl_2$	7.12–7.20 (brm)

m = multiplet, t = triplet, brm = broad multiplet

Thus on the basis of the analytical data, conductance measurements, IR & ^1H NMR spectral studies the compound $[\phi_2Sn(bpy)Cl_2]$ is proposed to have an octahedral structure in which the two positions of the octahedron are occupied by two uninegative chlorine atoms, two by nitrogen atoms of α-α′ bipyridyl and the remaining two positions are occupied by phenyl groups of ϕ_2Sn derivative. The complexes $||\phi_2Sn(bpy)||X_2$ were found to have a tetrahedral structure, the anions remaining outside the coordination sphere whereas the complexes $[\phi_2Sn(bpy)(SL)]Cl_2$ were assigned to have octahedral structures in which the chloride remains outside the coordination sphere and the octahedral geometry is achieved by the coordination of α, α′-bipyridyl and the ligand (SL) to the tin atom which is bonded to two phenyl groups. In all the above complexes the tin atom behaves as central metal atom.

REFERENCES

1. P. R. Shukla, M. Bhatt, and N. Ahmad, *Curr. Sci.* (*India*), **58**, 562 (1989).
2. P. R. Shukla, M. C. Sharma, and G. Narain, *Synth. React. Inorg. Org. Met. Chem.*
3. P. R. Shukla, M. C. Sharma, M. Bhatt, N. Ahmad and S. K. Srivastava, *Indian J. Chem.* (*A*) (in press).
4. R. C. Polar, J.R.R. Ruddick, M. Theraras and W. R. Mcwhinnie, *J. Chem. Soc.* (*A*), 2327 (1969).
5. N. Rama Rao and N. K. M. Prasad, *Ind. J. Chem. Sci.*, **2**, 17 (1988).
6. T. M. Aminabhavi, N. S. Biradar, R. H. Raythatha and M. D. Patil, *Indian J. Chem.*, **25A**, 250 (1986).
7. K. Nakamato, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York (1963).
8. C. C. Addison and B. M. Gatihouse, *J. Chem. Soc.*, 613 (1960).
9. D. W. Powell and N. J. Sheppard, *Chem. Soc.*, **79** (1959).
10. P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 966 (1969).
11. M. R. Silverstein, G. C. Bassler, and T. C. Morril, Sepectrometric Identification of Organic Compounds, John Wiley & Sons (1974).

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