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Research Article

Synthesis & Characterization of Some Diphenyl Metal (III) Cationic Complexes

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ABSTRACT

The present communication deals with interaction of Ph_2MX (X=BPh₄, ClO₄), with 1,10- phenan hroline and ethylenediamine which resulted in the formation of cationic complexes of the formula $[Ph_2M(L)]$ [BPh₄] and $[Ph_2M(L)]$ [ClO₄]rather than molecular adducts with coordination number four. Solid state infrared spectra, molecular weight and conductance measurements have been employed to ascertain the composition and geometry of the complexes

Keywords: Co-ordination, stereochemistry,

INTRODUCTION

The synthesis and stereochemistry of several classes of organometal (III) derivatives and their complexes with unidentate and bidentate ligands have been studied by various workers ¹⁻⁷. These coordination compounds are mainly confined to alkyl -derivatives and relatively less has been reported on aryl metal (III) derivatives. Apart from R₂MXL(X=halide or pseudohalide ^{8,9}, complexes in which X= Cl, BF₄ have also been investigated with a number of ligands in view to obtain coordination number greater than four. Compounds of Ar₂MCI with 1, 10-phenanthroline and 2,2'-bipyridyl 'have been synthesized ().

However the acceptor properties of diphenyl metal (III)-tetraphenyl borate and perchlorate have not yet been reported.

RESULT AND DISCUSSION

The reactions of diphenylmetal chloride with sodium or silver salt of tetraphenylborate or perchlorate were carried out⁵.^t stoichiometric ratio in pyridine- water(1:1) mixture. Products of the type Ph₂MX (Where M=Ga, In, TI and X=BP11₄ orC10₄) have been isolated as a white crystalline substance which interacts with neutral bidentate ligands in refluxing THE or methanol to yield cationic complexes of the types [Ph₂M(L)] [X]

$Ph_2MC1 + M'X \rightarrow Ph_2MX + M'C1$	(i)
$Ph_2MX + L \rightarrow [Ph_2M(L)] [X]$	(ii)

Where M = Ga, In, T1; M' = Na or Ag; $X = BPh_4$ or $C10_4$ and L=1,10 Phenanthroline (phen) and ethylenediamine (en).

The newly synthesized complexes are white crystalline, high melting solids, stable at room temperature and unaffected by moisture. Conductance values for 110-3M solutions in nitrobenzene at room temperature ranges between 25-35 ohm⁻¹ cm² mol⁻¹ which indicate that these complexes existed as 1:1 *electrolyte in solution*.

Molecular weights of the newly sy4hesiied complexes were measured cryoscopically in freezing nitrobenzene and were found to be approximately half of the calculated molecular weight which indicate that the complexes are dissociated in two ions in solution. The calculated value of van't Hoff factor 'i' (i=cal. mol.wt.)/(obs.mol.wt) is thus approximately 2, which supports 1:1 electrolytic behavior of the complexes and is listed in (**Table 3**).

IR Spectra: All the complexes listed in table 1 were characterized in solid state by their I.R. spectra in the region 4000-200cm-1. Important frequencies for the complexes together with their assignment are listed in table 2. These assignments have been made by comparing the spectra in 4000-200cm-1 region in the solid state of the complexes with those of free ligands. For complexes (46) and (10-12) the perchlorate bands were observed around 1095 ± 8 and 615 + 7 cm⁻¹, which are characteristic of a free perchlorate anion. Similarly, for complexes (1-3) and (7-9) IR absorption appearing 1282+3 and 1260+5 cm⁻¹ can be assigned to the free tetraphenyl borate.

In the case of ethylenediamine complexes, v (NH) and v (CN) occurring at 3400cm⁻¹ and 1620+ 10cm⁻¹ in free ligand suffered negative shift and appear at 3250+ 20cm⁻¹ and 1600+ 5cm⁻¹ respectively. This may be attributed to electron donation from nitrogen atom to the metal atom.

The spectrum of 1,10 phenanthroline exhibit three strong absorption associated with C=C, C=N and ring breaking, stretching vibration at 1590,1492 and 1423cm⁻¹ respectively in free ligand. On complexation all these bands show a positive shift which is in conformity with the earlier observations.

EXPERIMENTAL

Conductance data were obtained in nitrobenzene with the help of a philips magic eye type PR 950 conductivity cell. IR spectra were recorded on Perkin Elmer 577 spectrophotometer in the range 4000-200cm⁻¹. Diphenyl-gallium, Indium and thallium chloride were prepared by reported methods. Solvents were dried by conventional methods.

Typical experimental details of reactions are described below, other details are listed in table 1-3.

Preparation of Ph₂TI(ClO₄): Diphenylthallium (III) chloride (0.394g, lm mol) and sodium perchlorate (0.122g, 1 m mol) were stirred together at room temperature in pyridine- water (1:1) mixture for about 3hours. A white precipitate appeared, which was filtered, washed with pyridine water (1:1) mixture and dried (found: C=31.63%, H=2.32%; calc. for C1₂H₁₀T1 C10₄: C=31.44%, H=2.18%)

The corresponding Ga and In compounds were prepared by the same method described above for thallium compounds and had satisfactory elemental analysis.

Preparation of Ph₂TI(ClO₄): Diphenylthallium (III) chloride (0.394g, lm mol) and sodium tetraphenyl borate (0.342g, lm mol) were stirred together at room temperature in pyridine-water (1:1) mixture for about 3 hour. A white precipitate appeared, which was filtered, washed with pyridine water (1:1) mixture and dried. (Found: C=63.34%, H=4.41%; calcd. for C36H30T1B: C=63.81%; H=4.43%.

The corresponding Ga and In compounds were prepared by the same method described above for thallium compounds.

Preparation of ph₂TI (ClO₄) Complex: In an oxygen free condition, diphenyl thallium (III) perchlorate (0.457g, lm mol) and 1,10 phenanthroline (0.180g, lm mol) in 1:1 molar ratio were stirred together in refluxing methanol for about 2hours. White precipitate so obtained was filtered and dried in vacuum. Yield: 70 %; M.P.240°c

Preparation of Ph₂TI (ClO₄) Complex: Similarly, reaction of diphenythallium (III) perchlorate (0.457g, lm mol) with ethylene diamine (0.060g, lm mol) yielded white colour adduct. Yield: 72% M.P. 250°c

Preparation of Ph₂TI(ClO₄)Complex: In an oxygen free condition, diphenyl-thallium (III) tetraphenyl borate (0.677g, 1m mol) and 1,10- phenanthroline (0.180g, lm mol) in 1:1 molar ratio were stirred together in refluxing methanol for about 3hour. White precipitate so obtained was filtered and dried in vacuum. Yield: 70 %; M.P.240°c

Preparation of Ph₂TI(ClO₄)IBPh₄I Complex: Ethylenediamine (0.060g, lm mol) and corresponding diphenyithallium (III) tetra phenylborate (0.677g, lm mol) were refluxed in ethanol for about 3hours. The precipitated white solid was filtered and dried in vacuum. Yield:M.P.>250°c

The corresponding Ga and In complexes were prepared by the same method described above for thallium compounds.

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Table 1: Analytical Data of Diphenyl Metal (III) Cationic Complex [Ph₂M(L)] [X]

Com.		Complex		Empirical formula	Solvent	M.P. °C	Analysis found (Calc)		
INO.		$[Pn_2M(L)][X]$					M%	C%	H%
	M	L	X	_					
1	Ga	en	BPh ₄	$C_{38}H_{38}N_2BGa$	THE	>250	11.52	75.45	6.24
							(11.60)	(75.62)	(6.30)
2	In	en	BPh4	C ₃₈ H ₃₈ N ₂ BT1	Methanol	>250	17.63	70.11	5.76
							(17.74)	(70.37)	(5.86)
3	TI	en	BPh ₄	C ₃₈ H ₃₈ N ₂ BT1	Methanol	>250	27.52	61.78	5.12
							(27.67)	(61.87)	(5.15)
4	Ga	en	C1O ₄	C ₃₈ H ₃₈ N ₂ O ₄ Ga	THE	>250	18.17	43.75	4.56
							(18.25)	(43.80)	(4.69)
5	In	en	C1O ₄	C ₃₈ H ₃₈ N ₂ O ₄ G a	Methanol	210d	28.56	39.12	4.02
							(28.83)	(39.20)	(4.20)
6	T1	en	C1O ₄	C ₃₈ H ₃₈ N ₂ O ₄ In	THE	>250	39.37	32.36	3.38
							(39.42)	(32.46)	(3.45)
7	Ga	Phen	BPh ₄	C ₄₈ H ₃₈ N ₂ BGa	THE	>250	9.52	79.48	5.14
							(9.68)	(79.66)	(5.25)
8	In	Phen	BPh ₄	C ₃₈ H ₃₈ N ₂ O ₄ Tl	Methanol	162	14.89	74.92	4.90
							(14.97)	(75.00)	(4.94)

Where Phen = 1,10-phenanthroline, en = ethylene diamine

Com		Complex		Empirical formula	Solvent	M.P. °C	Analysis found (Cale)		Cale)
No.		[Ph2M(L)][X]					M%	C%	H%
NO.				_					
	M	L	X						
9	T1	Phen	BPh ₄	$C_{48}H_{38}N_2BT1$	Methanol	210	23.72	67.08	4.39
							(23.90)	(67.28)	(4.43)
10	Ga	Phen	C1O ₄	$C_{24}H_{18}C1NO_4Ga$	THF	210d	14.85	57.04	3.48
							(13.90)	(57.19)	(3.57)
11	In	Phen	C1O4	$C_{24}H_{18}C1N_2O_4In$	Methanol	>250	21.31	52.43	3.22
							(20.80)	(52.50)	(3.28)
12	T1	Phen	C1O ₄	$C_{24}H_{18}C1N_2O_4T1$	THF	240d	32.08	45.03	2.78
							(32.00)	(45.17)	(2.82)

Synthesis...

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Complex No.	v(N-H)	v(C-N)	v(C=C)	v(C=N)	Ring breathing complexes	Ring Anion freque breathing complexes	
(1)	3270	1600s				1285s	1258
(2)	3260	1598s				1284s	1264
(3)	3260	1590s				1281s	1262
(4)	3250	1590s				1088s	622m
(5)	3230	1591s				1085s	620m
(6)	3240	1595s				1090s	620m
(7)			1598m	1500	1425	1285	1255
(8)			1600	1502	1432	1283	1265
(9)			1605	1500	1430	1279	1262
(10)			1608	1505	1428	1095s	615m
(11)			1605	1:498	1435	1103	618m
(11)			1595	1495	1430	1100	622m

Table 2: IR Spectra data of the Diphenyl Metal (III) Cationic Complexes

where s = strong. m = medium

Comp. No.			Complex [Ph ₂ M(L)][X	[]	Molar Conductance	Molecular weight		Van't Hoff 'i'
				ohm ⁻ cm ² mol ^{-⊥}		Calc.		
	М		L	Empirical				
1	Ga	en	BPh ₄	C ₃₈ H ₃₈ N ₂ BGa	28.00	310	603	1.95
2	In	en	BPh4	$C_{38}H_{38}N_2BTl$	31.00	327	684	.98
3	TI	en	BPh4	$C_{38}H_{38}N_2BT1$	29.00	380	737.	.93
4	Ga	en	C1O4	C38H38N2O4Ga	30.00	205	383.5	87
5	In	en	C1O4	C38H38N2O 4 G a	34.00	222	428.5	.93
6	T1	en	C1O4	C ₃₈ H ₃₈ N ₂ O ₄ In	26.00	280	517.5	.84
7	Ga	Phen	BPh ₄	C48H38N2BGa	30.00	365	723	98
8	In	Phen	BPh ₄	C ₃₈ H ₃₈ N ₂ O ₄ Tl	33.00	400	768	.92
9	TI	Phen	BPh ₄	C ₄₈ H ₃₈ N ₂ BTI	29.00	432	857	.98*
10	Ga	Phen	C1O4	$C_{24}H_{18}CINO_4Ga$	32.00	280	503.5	80
11	In	Phen	C1O4	$C_{24}H_{18}C1N_2O_4In$	28.00	290	548.5	89
12	T1	Phen	C1O4	C ₂₄ H ₁₈ C1N ₂ O ₄ T1	34.00	325	637.5	.96

Table 3: Molar Conductance and Molecular Weight of Diphenyl Metal (III) Cationic Complexes (Nitrobenzene)

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