HETEROBIMETALLIC COMPLEXES OF N_2S_2 MACROCYCLIC LIGANDS WITH GROUP IV TETRACHLORIDES AND BIS(TRIMETHYLSILYL)AMINE

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Abstract

Heterobimetallic complexes of the type $[LM(Si_2Me_6N)_2]$ where L = [SS' diethyl(1,3-diaminopropane)dithiocarbamate], or [SS' cyclohexylspiro(1,3-diaminopropane)dithiocarbamate] and M = Ge(IV), Sn(IV), Ti(IV) and Zr(IV) have been synthesized and characterized on the basis of elemental analysis as well as IR, UV-Vis and NMR spectroscopy. All the complexes are covalent in nature and show octahedral geometry.

Introduction

The development of new synthetic approaches in recent years has made a large variety of macrocyclic ligand systems available. Their selectivity for certain metal ions and the stability of resulting metal complexes has also been exploited[1]. Synthetic macrocycles have been used as model in biological systems[2-3]. Here, we report the complexes of N_2S_2 macrocyclic ligands with Group IV tetrachlorides and their heterobimetallic complexes with bis(trimethylsilyl)amine in order to study the nature and stereo chemistry of Group IV atom.

Experimental

Ge(IV), Sn(IV), Ti(IV) and Zr(IV) tetrachlorides, bis(trimethylsilyl)amine (Fluka), 1,3-diaminopropane and dibromoethane (E.Merck), carbon disulphide and cyclohexanone (BDH) were used as received. Elemental analyses were performed on a Perkin Elmer 240-B-Microanalyzer, IR spectra were recorded on a 621 Perkin Elmer Spectrophotometer in Nujol, UV/Vis and ^1H NMR spectra were recorded on a Pye Unicam PU 8800 Spectrophotometer and Bruker WP SY Spectrometer, respectively. Conductances were measured on Elico Conductivity bridge type CMB2T.

Synthesis of [SS' diethyl(1,3-diaminopropane)dithiocarbamate]L [SS' Cyclohexyl spiro 1,3-diaminopropane, dithiocarbamate]L'

Carbondisulphide (0.02 mol, 1.20 ml) was added dropwise with constant stirring to 1,3-diaminopropane (0.01 mol, 0.84 ml) in absolute ethanol (30 cm^3) in alkaline medium at -15°C. The resulting mixture was cooled for 3 hr until a yellow product precipitated. This was further reacted with dibromoethane or cyclohexanone and refluxed for ca. 24 hr. Fine crystals separated on standing overnight. They were washed with diethyl ether and dried under vacuo.

Synthesis of Metal Complexes (ML) or (ML')

To the solution of L(0.001 mol) or L' (0.001 mol) was added Group (IV) chloride in 1:1 ratio. The mixture was cooled to -10°C when coloured crystalline compounds separated out. They were washed with diethyl ether and dried under vacuo.

Synthesis of Heterobimetallic Complexes of L and L'

The complexes (0.001 mol) were treated with bis(trimethylsilyl)amine (0.002 mol) in dry dimethyl formamide (10 ml) in 1:2 ratio at room temperature and cooled to yield a crystalline solid. They were washed with ether and dried under vacuo.

Results and Discussion

The reaction of Group IV metal tetrachlorides with the macrocycles is given in Scheme II. The complexes are soluble in dimethyl sulfoxide and dimethyl formamide.

It is evident that the ligand L and L' react with MCl4 with the deprotonation of the two NH groups and subsequent removal of two moles of HCl, the metal getting coordinated with two nitrogens and two sulphur atoms resulting in the formation of complexes. The low molar conductances (22-25 ohm^{-1} cm^2 mol^{-1}) in anhydrous DMF shows their non-electrolytic nature.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligands L and L' show characteristic -CH_2 proton signals at 2.91, 3.43 and 3.32 ppm respectively. The NH proton signals observed at 7.83 ppm in both L and L' disappear in the (SnL)Cl_2 after the removal of H atom from the N-H group and subsequent coordination of nitrogen to the metal atom. Other signals appearing in 3.32-3.25 ppm range have been assigned to -CH_2 protons in these complexes.

Except for the peak assignable to the methyl protons and appearing at 0.59-1.63 ppm the n.m.r. spectrum of [$SnL(Si_2Me_6N)_2$] is identical with that of the ML and ML'.

I.R. Spectra

The IR of the ligands (Table II) show characteristic vibrations in the region (1067-1092 cm^{-1}) and (769-772 cm^{-1}) due to νC=S and νC-S respectively. While the C=S remains unchanged in all the complexes. The (C-S) undergoes a shift to lower wave number (730-740 cm^{-1}) region indicating unsymmetrical coordination through the dithiocarbamate group. Tautomerization of the thiono form of ligand to the thiole moiety has been ruled out since no band appears at ca. 2570 cm^{-1} confirming absence of S-H group. A broad band at 3250 cm^{-1} has been ascribed to NH. This band disappears in the complexes indicating the removal of a hydrogen atom from the N-H group. In the complexes, a doublet appears at 1320 cm^{-1} and 1300 cm^{-1} assignable to C-N indicating that nitrogen is involved in bond formation[6-7].

In the far IR region the occurrence of M-Cl, M-S and M-N vibrational modes are expected. However, we have observed a shoulder at 280 cm^{-1} and a strong band at 260^{-1} assignable to (M-Cl) vibration[8,9]. When ML and ML' were treated with bis(trimethylsilyl)amine, they yielded the heterobimetallic complex [$MLSi_2Me_6N_2$] or

$ML'Si_2Me_6N_2]$. The M-Cl band disappeared due to replacement of chloride ions by $(SiMe_3)_2N$ and an additional band (Si-C) at 650 cm^{-1} and Si-N at 580 cm^{-1} appeared. The IR data suggest that the complexes [ML/ML'] are formed by coordination of the metal ions through N_2S_2 groups of the macrocycles. It was concluded that the octahedral geometry of the metal ions is maintained throughout.

UV Spectral data : 280, 340, 381 nm

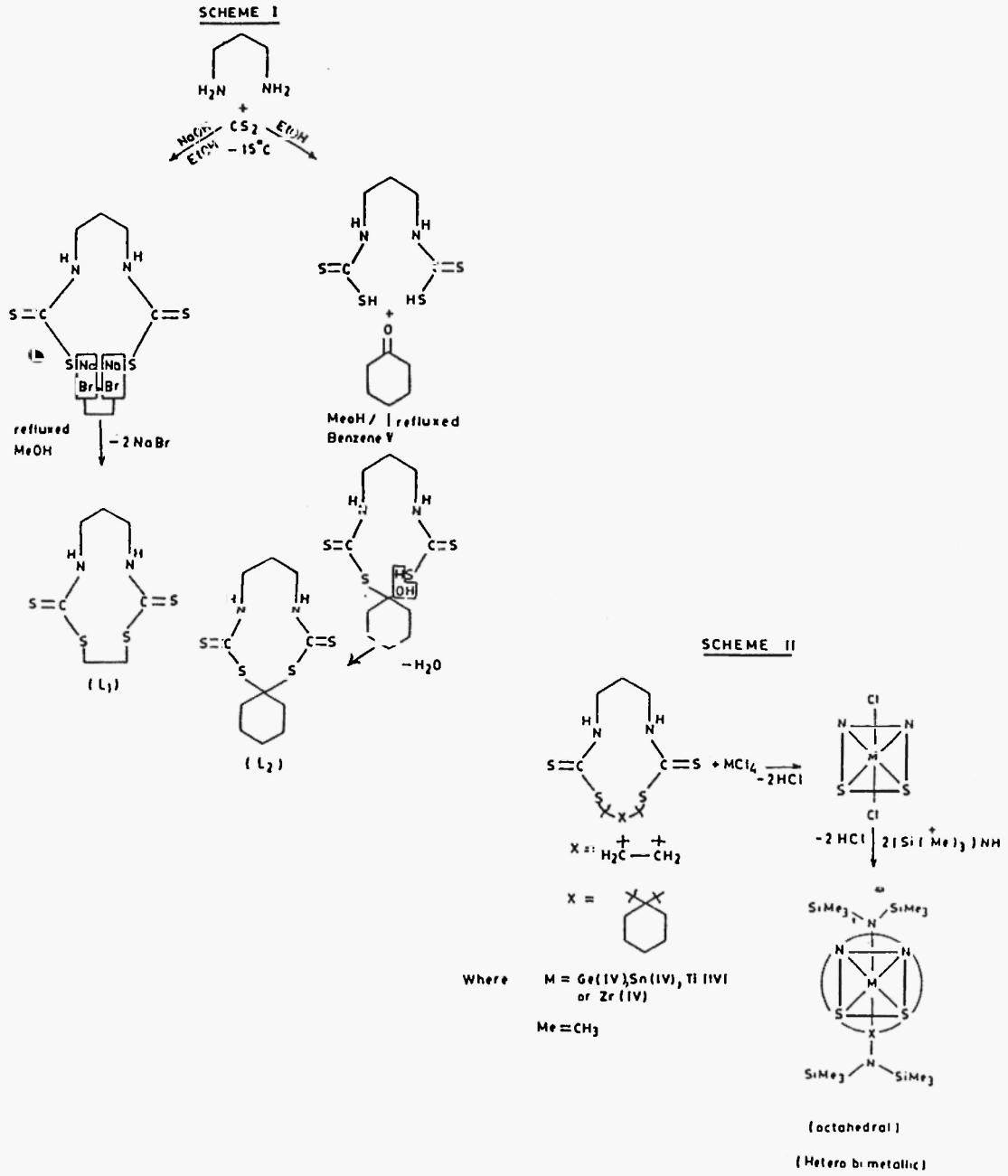

Table I

Analytical data of the ligands L,L' and their complexes

Complex	M.P.	Colour	Yield	%Analytical Calcd. (Found)				
	°C		%	C	H	N	S	Cl
$C_7H_{12}N_2S_2$ (L) - H_2	195	L. yellow	70	33.33(33.54)	4.76(4.78)	11.11(11.22)	50.79(51.00)	
[L $GeCl_2$]	238	Cream	58	21.87(22.02)	2.60(2.63)	7.29(7.33)	33.33(33.67)	18.61(18.82)
[L $SnCl_2$]	225	Yellow	60	19.11(19.23)	2.27(2.39)	6.37(6.49)	29.10(29.45)	16.26(16.86)
[L $TiCl_2$]	228	Orange	53	22.74(22.96)	2.70(2.81)	7.58(7.69)	34.66(34.99)	16.26(16.86)
[L $ZrCl_2$]	228	Orange	48	20.35(20.48)	2.42(2.53)	6.78(6.87)	31.01(31.33)	19.36(19.50)
[L $Ge(Si_2Me_6N)_2$]	185	Yellow	58	35.46(35.69)	7.15(7.26)	8.71(8.83)	19.91(20.23)	
[L $Sn(Si_2Me_6N)_2$]	180	Brown	62	33.13(33.34)	6.68(6.79)	8.13(8.24)	18.60(18.73)	
[L $Ti(Si_2Me_6N)_2$]	183	Orange	63	34.90(34.23)	7.44(7.56)	9.06(9.15)	20.71(20.98)	
[L $Zr(Si_2Me_6N)_2$]	178	Orange	65	34.48(34.68)	6.95(7.68)	8.46(9.57)	19.35(19.56)	
$C_{11}H_{18}N_2S_4$ (L') - H_2	218	L. Brown	75	43.13(43.38)	5.88(6.98)	9.15(9.28)	41.83(42.20)	
[L' $GeCl_2$]	230	Brown	57	29.46(29.78)	3.66(3.78)	6.25(6.36)	28.57(28.87)	15.95(16.00)
[L' $SnCl_2$]	233	Yellow	63	26.74(24.98)	3.24(3.330	5.69(5.71)	25.93(26.03)	
[L' $TiCl_2$]	236	Orange	68	31.20(31.39)	3.71(3.82)	6.61(6.73)	30.23(30.48)	16.77(16.98)
[L' $ZrCl_2$]	238	Orange	53	28.31(28.44)	3.43(3.54)	6.00(6.12)	28.31(28.56)	
[L' $Ge(Si_2Me_6N)_2$]	195	Orange	58	39.65(39.97)	7.47(7.58)	8.04(8.13)	18.39(18.42)	
[L' $Sn(Si_2Me_6N)_2$]	188	Orange	62	37.19(37.20)	7.00(7.11)	7.54(7.63)	17.25(17.45)	
[L' $Ti(Si_2Me_6N)_2$]	198	Orange	63	41.10(41.43)	7.74(7.85)	8.33(8.44)	19.06(19.20)	
[L' $Zr(Si_2Me_6N)_2$]	193	Orange	59	38.59(38.88)	7.27(7.32)	7.82(7.91)	17.89(17.99)	

Table II

Important IR Absorption (cm^{-1}) of the ligand L,L' and their representative complexes

Complexes	vNH	vC-S	vC-N	vC=S	vM-S	vM-N	vM-Cl
$C_7H_{12}N_2S_2$ (L)	3250	769	1380	1067	-	-	-
[L $GeCl_2$]	-	730	1320	1066	340	545	346
$C_{11}H_{18}N_2S_2$ (L')	3250	772	1390	1092	-	-	-
[L' $GeCl_2$]	-	735	1320	1090	370	540	342
[L $Ge(Si_2Me_4N)_2$]	-	740	0110	1067	368	530	-
[L' $Ge(Si_2Me_4N)_2$]	-	735	1320	1092	370	425	-

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