SPECTROSCOPIC STUDIES OF HETEROBIMETALLIC ADDUCTS OF TIN WITH Mn(II), Co(II), Cu(II) AND Zn(II)

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Abstract

The reaction of diketones (benzil or 2,4-pentanedione) with primary diamines (diaminoethane or 1,3-diaminopropane) in 1:2 molar ratio in the presence of MCl_2 (M=Mn, Co, Ni, Cu and Zn) and $SnCl_4$ resulted in the formation of heterobimetallic complexes of the type $[Cl_2MLSnCl_2]$ [$L=L_1-L_4$, the respective tetradentate ligand]. These compounds have been characterized on the basis of elemental analyses, IR, ^1H NMR, UV/VIS, EPR and electronic spectral results and by conductivity and magnetic moment measurements. All the compounds are found to be non ionic. An octahedral geometry is assigned for the transition metal ions while a probable tetrahedral geometry is assigned for tin atom.

INTRODUCTION

Several excellent reviews[1,2] have appeared on the studies of transition metal-tin complexes during the past few years. The complexation behaviour of tetradentate transition metal chelates to act as effective bidentate donor ligands to tin(IV) halides, organotin(IV) halides and pseudohalides are well investigated[3-7]. One of the specific interest in 1:1 adducts of tin-transition metal Schiff base complexes lies with the fact that the dioxygen carrying properties of transition metal Schiff base complexes are altered when act as donor ligands to tin[8]. This is in continuation[9-11] of our ongoing work on heterobimetallic complexes of group 14 elements. Here we report the synthesis of a series of tin-transition metal complexes with a view to study the ligating behaviour of the tetradentate ligands towards transition metal and non transition metal ions simultaneously.

EXPERIMENTAL

Materials and method

The metal salts, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $MnCl_2.4H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ were of BDH quality. Benzil, diaminoethane, 1,3-diaminopropane and tin(IV) tetrachloride (all E.Merck) were used as received.

Physical Measurements

Elemental analyses were made by the microanalytical laboratory. ^1H NMR spectra in DMSO-d_6 using a Bruker FX-100 FT NMR Spectrometer with Me_4Si as an internal standard were obtained from IIT, New Delhi. Metals, tin and chlorides were determined volumetrically[12] and gravimetrically[13], respectively. IR spectra (4000-200 cm^{-1}) were recorded as KBr discs on a Perkin Elmer-621 spectrophotometer. Electronic spectra in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. EPR spectra were recorded on a JEOL JES RE 2X EPR spectrometer. Magnetic susceptibility measurements were carried out using a Faraday balance at 25°C. The electrical conductivities of $10^{-3}M$ solutions in DMSO were obtained on a Systronics type 302 conductivity bridge equilibrated at 25°C.

Synthesis of dichloro(1,2-diphenylethane-1,2-dione bis diaminoethane) metal(II) - dichlorotin (IV), [$Cl_2ML_1SnCl_2$] or dichloro (1,2-diphenylethane-1,2-dione bis 1,3 diaminopropane)metal(II) - dichlorotin (IV) [$Cl_2ML_2SnCl_2$] [M=Mn, Co, Ni, Cu, Zn]

A mixture of diaminoethane or 1,3-diaminopropane (0.02 mol) and benzil (0.01 mol) in methanol (~ 50 cm^3) was taken in a round bottomed flask and stirred with gentle heating for about 15 min. Then a hot methanolic solution (~ 50 cm^3) of metal(II) chloride (0.01 mol) was added followed by the addition of tin(IV) tetrachloride (0.01 mol) in methanol. The addition of tin(IV) tetrachloride showed a gradual change in colour of the solution either into more light colour or changed into a new colour. The final mixture was stirred for another 7 h. and the resultant product thus obtained was filtered, washed several times with methanol and dried in vacuo.

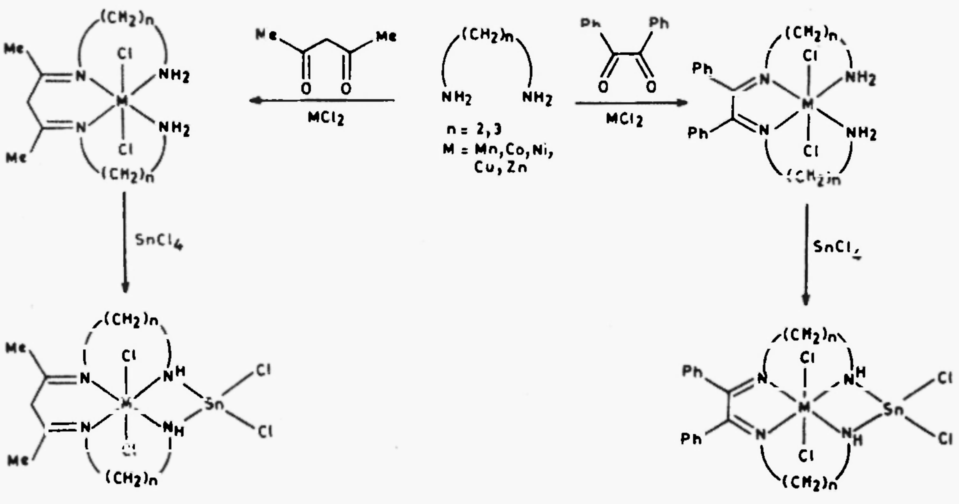
Synthesis of dichloro (1,3-dimethylpropane-1,3-dione bis diaminoethane) metal(II)-dichlorotin(IV), [$Cl_2ML_3SnCl_2$] or dichloro (1,3-dimethylpropane-1,3-dione bis 1,3-diamino propane) metal(II)-dichlorotin(IV), [$Cl_2ML_4SnCl_2$] [M= Mn, Co, Ni, Cu, Zn]

These compounds have been prepared by adopting the same procedure as described above. Here instead of benzil, the diketone 2,4-

pentanedione was employed for the condensation of amine moiety.

RESULTS AND DISCUSSION

The reaction of diaminoethane or 1,3-diaminopropane, with diketones (benzil, 2,4-pentanedione) in presence of transition metal salts and tin(IV) tetrachloride in 2:1:1:1 molar ratio gave a new series of heterobimetallic complexes exhibiting the stoichiometry $[Cl_2M(L_1\text{-}L_4 2)SnCl_2]$ [M=Mn,Co,Ni,Cu and Zn] as shown in Scheme 1. All the complexes are stable to atmosphere at room temperature. These adducts have very low solubility in organic solvents, but are freely soluble in polar solvents such as dimethylformamide, dimethylsulphoxide and acetonitrile. Cobalt complexes are found to give higher yields. The elemental analysis results are acceptable with the proposed stiochiometry of the adducts. The molar conductance values measured for all the compounds are found to be low and are consistent[14] with the non-electrolytic nature of these compounds.



L3, n = 2
L4, n = 3

SCHEME - 1

L1, n = 2
L2, n = 3

The main feature of the IR spectra is the appearance of a band around 1600 cm^{-1} which can be unambiguously assigned to the azomethine linkage ν(C=N) and is consistent[15] with coordinated imine bonds. This information alongwith the absence of bands due to carbonyl groups strongly support that the condensation of primary amine with the carbonyl group has taken place. Another important single strong band appeared around 3170 cm^{-1} assignable to the NH of secondary amino group. The appearance of band around 1125 cm^{-1} for all the complexes may be attributed to ν(C-N) vibration. The appearance of a sharp band around 450 cm^{-1} is attributable[16] to ν(M-N)

Table 3. µeff, electronic spectral data (cm^{1}) and their assignments of the compound

Compound	µeff (B.M.)	Band position (Cm^{1})	Assignments	Molar conductivity ohm^{1} cm^{2} mol^{-1}
[Cl$_2$MnL$_1$SnCl$_2$]	5.79	18600	$^{6}A_{1g}$ -----> $^{4}T_{1g}(P)$	19.7
		22270	$^{6}A_{1g}$ -----> $^{4}T_{2g}(F)$	
[Cl$_2$MnL$_2$SnCl$_2$]	5.77	18900	$^{6}A_{1g}$ -----> $^{4}T_{1g}(P)$	14.5
		21500	$^{6}A_{1g}$ -----> $^{4}T_{2g}(F)$	
[Cl$_2$MnL$_3$SnCl$_2$]	5.80	18550	$^{6}A_{1g}$ -----> $^{4}T_{1g}(P)$	19.5
		21900	$^{6}A_{1g}$ -----> $^{4}T_{2g}(F)$	
[Cl$_2$MnL$_4$SnCl$_2$]	5.77	19100	$^{6}A_{1g}$ -----> $^{4}T_{1g}(P)$	16.1
		21300	$^{6}A_{1g}$ -----> $^{4}T_{2g}(F)$	
[Cl$_2$CoL$_1$SnCl$_2$]	4.54	13700	$^{4}T_{1g}(F)$ -----> $^{4}A_{2g}(F)$	24.6
		21500	$^{4}T_{1g}(F)$ -----> $^{4}T_{1g}(P)$	
[Cl$_2$CoL$_2$SnCl$_2$]	4.56	13500	$^{4}T_{1g}(F)$ -----> $^{4}A_{2g}(F)$	18.6
		21800	$^{4}T_{1g}(F)$ -----> $^{4}T_{1g}(P)$	
[Cl$_2$CoL$_3$SnCl$_2$]	4.57	13900	$^{4}T_{1g}(F)$ -----> $^{4}A_{2g}(F)$	15.5
		21400	$^{4}T_{1g}(F)$ ----> $^{4}T_{1g}(P)$	
[Cl$_2$CoL$_4$SnCl$_2$]	4.58	14250	$^{4}T_{1g}(F)$ -----> $^{4}A_{2g}(F)$	5.4
		21800	$^{4}T_{1g}(F)$ -----> $^{4}T_{1g}(P)$	
[Cl$_2$NiL$_1$SnCl$_2$]	3.14	13500	$^{3}A_{2g}$ -----> $^{3}T_{1g}(F)$	19.9
		17900	$^{3}A_{2g}$ -----> $^{3}T_{1g}(P)$	
[Cl$_2$NiL$_2$SnCl$_2$]	3.15	11600	$^{3}A_{2g}$ -----> $^{3}T_{1g}(F)$	18.5
		17700	$^{3}A_{2g}$ -----> $^{3}T_{1g}(P)$	
[Cl$_2$NiL$_3$SnCl$_2$]	3.15	11300	$^{3}A_{2g}$ -----> $^{3}T_{1g}(F)$	17.5
		17500	$^{3}A_{2g}$ -----> $^{3}T_{1g}(P)$	
[Cl$_2$NiL$_4$SnCl$_2$]	3.13	11700	$^{3}A_{2g}$ -----> $^{3}T_{1g}(F)$	12.9
		17900	$^{3}A_{2g}$ -----> $^{3}T_{1g}(P)$	
[Cl$_2$CuL$_1$SnCl$_2$]	1.78	18700	$^{2}B_{1g}$ -----> $^{2}E_{g}$	8.5
		15800	$^{2}B_{1g}$ -----> $^{2}B_{2g}$	
[Cl$_2$CuL$_2$SnCl$_2$]	1.79	18600	$^{2}B_{1g}$ -----> $^{2}E_{g}$	12.3
		16200	$^{2}B_{1g}$ -----> $^{2}B_{2g}$	
[Cl$_2$CuL$_3$SnCl$_2$]	1.80	19100	$^{2}B_{1g}$ -----> $^{2}E_{g}$	10.4
		16300	$^{2}B_{1g}$ -----> $^{2}B_{2g}$	
[Cl$_2$CuL$_4$SnCl$_2$]	1.80	18900	$^{2}B_{1g}$ -----> $^{2}E_{g}$	11.4
		16400	$^{2}B_{1g}$ -----> $^{2}B_{2g}$	

vibration. All of the tin(IV) chloride adducts exhibit a broad intense band in the 300-350 cm^{-1} region may probably be associated with the ν(Sn-Cl) frequencies. In the 750-900 cm^{-1} region of the spectra, there are adsorption bands which should arise from methylene and methyl rocking vibration together with symmetric C-N streching. A weak intensity absorption band in all the complexes identified around 380 cm^{-1} probably be due to ν(Sn-N) vibration[17].

The ^{1}H NMR spectra of $[Cl_2Zn(L_1\text{-}L_4)SnCl_2]$ adducts appear to be more complex and do not show any bands assignable to primary amino protons. All the compounds gave two multiplets between 6.08 and 6.20 ppm and between 3.18 and 3.21 ppm which can be assigned[18-19] to the secondary amino (C-NH, 2H) and the methylene (CH_2-N,4H) protons of amine moiety respectively. The spectra of $[Cl_2ZnL_2SnCl_2]$ and $[Cl_2ZnL_4SnCl_2]$ showed a multiplet between 2.03 and 2.11 ppm which may be ascribed[19] to the central methylene (C-CH_2-C,4H) protons of 1,3-diaminopropane portion. A multiplet appeared for the complexes $[Cl_2ZnL_1SnCl_2]$ and $[Cl_2ZnL_2SnCl_2]$ between 7.47 and 7.52 ppm and a sharp singlet observed for the complexes $[Cl_2ZnL_3SnCl_2]$ and $[Cl_2ZnL_4SnCl_2]$ between 2.38 and 2.43 ppm may, correspond[20] to the phenyl ring protons (C-C_6H_5, 10H) and imine methyls (CH_3-C=N,6H), respectively. However, the broadness of the band in 2.38 ppm for the complex $[Cl_2ZnL_4SnCl_2]$ may be due to the overlapping of middle methylene protons of 2,4-pentanedione and 1,3-diaminopropane.

The powder sample EPR spectra of $[Cl_2Cu(L_1\text{-}L_4)SnCl_2]$ have been recorded at room temperature which showed a single broad signal with two g values. The absence of hyperfine splitting in these complexes indicate that the paramagnetic centres are not diluted. It has been reported that the values of $g_{\parallel}$ and $g_{\perp}$ have been used to distinguish unambiguously[21] between $d_{x^2-y^2}$ and the d_{z^2} ground states. The heterobimetallic complexes exhibit $g_{\parallel}$ and $g_{\perp}$ values in the range 2.23-2.28 and 2.10-2.14, respectively which suggest an axially distorted octahedral copper(II) complexes where the unpaired electron is present in the $d_{x^2-y^2}$ orbital with $^2B_{1g}$ as a ground state term. The existance of $g_{\parallel}$ values below 2.3 range suggest[22] the considerable covalent character of these complexes. The axial symmetry parameter, G is obtained by the relation $(g_{\parallel}-2)/(g_{\perp}-2)$ appeared in the range 1.66-2.66 indicating[23] the possibility of considerable exchange interaction present in the complexes.

The electronic spectra (Table 1) of all the complexes are consistent with their octarhectral geometry around the metal ions. All the spectra show very strong intense bands in the ultraviolet region in 37100-39000 cm^{-1} region which are probably due to the ligand to metal charge transfer transitions. Another broad band maxima around 33000 cm^{-1} may be assigned to n ⟶ π^* transition of the ligand.

The observed magnetic moment values (Table 1) for all the complexes $[Cl_2M(L_1\text{-}L_4)SnCl_2]$ [M=Mn(II), Co(II), Ni(II) and Cu(II)] also support their octahedral structures.

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