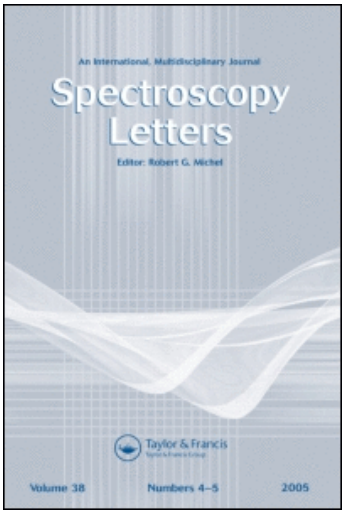

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Studies on some schiff base complexes of Co^{II} , Ni^{II} and Cu^{II} derived from salicylaldehyde and o- nitrobenzaldehyde

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Summary

Schiff bases of the type salicylidene 2-aminobenzothiazole and o-nitrobenzylidene 2-aminobenzothiazole were prepared by condensation of 2-aminobenzothiazole with salicylaldehyde and o-nitrobenzaldehyde. The bases react with cobalt(II) , nickel(II) and copper(II) chlorides to give 1:1 and 1:2 complexes. Electronic spectra , magnetic susceptibility measurements and infrared data are used to infer the structures. The thermal decomposition of the complexes and evaluation of the thermodynamic parameters are also reported.

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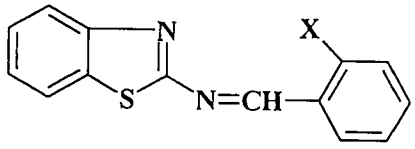
Introduction

Schiff base metal complexes have been a widely studied subject because of their industrial and biological applications[1,2]. In continuation of our work on metal complexes of schiff bases[3], we report here the preparation of Co(II) , Ni(II) and Cu(II) complexes of salicylidene 2-aminobenzothiazole(I) and o-nitrobenzylidene 2-aminobenzothiazole(II). The coordination behaviour of the ligands towards transition metal salts are investigated and the data are correlated with their thermal properties.



(I) X = OH (L)
(II) X = NO_2 (L')

Experimental

The schiff bases were prepared by mixing equimolar amounts of 2-aminobenzothiazole and the aromatic aldehyde in ethamol. The mixture was refluxed for 2-3 h. The crystals of the schiff base that separated on cooling were recrystallised from ethanol.

Preparation of the complexes

A mixture of ethanolic solution of the metal chloride (0.01 mol) and ethanolic solution of the ligand (0.02 mol) was refluxed for 1h and the resulting solid was washed with ethanol, followed by ether and dried in a vaccum desiccator over P_4O_{10}. The analytical data of the ligands and the complexes are collected in Table (1). IR spectra were recorded using a

Table (1) Elemental Analysis and Magnetic Moments of Schiff Bases and Their Metal Complexes.

Species	Colour	Found(Calcd.) %				μ_{eff}
		C	H	Cl	M	(B.M.)
L	Yellow	66.1 (66.1)	3.6 (3.9)			
L^-	Yellow	58.4 (59.4)	4.0 (3.2)			
[CoLCl]	Green	48.0 (48.1)	2.3 (2.3)	10.0 (10.3)	17.5 (17.2)	2.6
[NiLCl]	Yellow	48.2 (48.1)	2.3 (2.3)	10.5 (10.3)	17.3 (17.2)	diam
[CuL]	Pale green	52.7 (52.9)	2.6 (2.8)	11.0 (11.2)	19.8 (20.0)	diam
$[CoL^-_2Cl_2]$	Brown	48.2 (48.3)	3.0 (2.6)	9.9 (10.1)	8.3 (8.6)	4.8
$[NiL^-_2Cl_2]$	Brown	48.3 (48.3)	3.0 (2.6)	10.3 (10.1)	8.6 (8.6)	3.3
$[CuL^-_2Cl_2]$	Brown	47.9 (48.0)	4.0 (2.6)	9.8 (10.0)	9.1 (9.1)	1.93

L , L- denote salicylidene 2-aminobenzothiazole and o-nitrobenzylidene 2-aminobenzothiazole respectively.

Perkin- Elemer 1430 spectrophotometer (200-4000cm^{-1}). Electronic spectral measurements were done using a Pye- Unicam SP 1750 spectrophotometer. The molar magnetic susceptibilities were measured on powered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant. $Hg[Co(SCN)_4]$ was used as calibrant. The thermogravimetric analysis (TG) was carried out in dynamic nitrogen atmosphere (20$ml.min^{-1}$) with a heating rate of 10°$C.min^{-1}$ using a Shimadzu TGA-50H thermal analyser. The differential thermal analysis (DTA) was recorded in a nitrogen flow (20$ml.min^{-1}$) with a heating rate of 10°$C.min^{-1}$ using a Shimadzu DTA-50H thermal analyser.

Results and discussion

Infrared spectra

The IR spectrum of the ligand(I) reveals a band at 3200cm^{-1}due to $\nu(OH)$[4] . This band is absent in the Co(II) and Ni(II) complexes, indicating coordination through deprotonated phenolic OH group. The shift of $\nu(CO)$ from 1300 to 1330cm^{-1} supports this[5]. However, the band due to $\nu C{=}N$ (1640-1600cm^{-1}) in the free ligands[6] shifts to negative frequency on complexation suggesting coordination via azomethine group. The negative shift of the band indicates weakening of C-N link. The $\nu C{=}N$ (cyclic) band at ~1526cm^{-1} in the free ligands remains unchanged in the complexes indicating non involvement of the thiazole ring nitrogen atom in the bonding[7]. In addition , the ligands exhibit a band in the region 750-730cm^{-1} due to ν(C-S-C)ring[8] and it remains unchanged on complexation. The ligand N-O band at 1330cm^{-1} is found to be changed indicating participation of the NO_2 group in coordination[9]. In the far IR

spectra of all the complexes, conclusive evidence regarding the bonding of nitrogen and oxygen is provided by the occurrence of bands at 540-500(M-N) and 390-340cm^{-1}(M-O)[10]. The metal complexes of ligand(I) possess chloride bridge structure which is supported by the presence of νM-Cl at 310-290cm^{-1}[11].

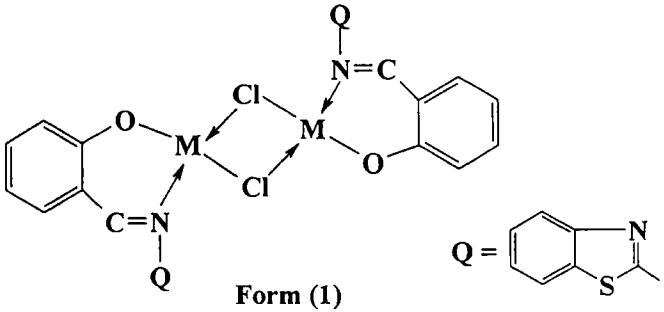
Electronic spectra and magnetic susceptibility measurements

The electronic spectrum of [CuL_2Cl_2] complex shows a broad band centered at 710 nm which may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition in an approximately octahedral environment[12]. The μ_{eff} value is 1.93B.M. which is slightly greater than the spin only value (μ_s 1.73B.M.) suggesting contribution of the orbital moment. However, this higher magnetic moment may be due to lowering of symmetry around Cu(II)[13]. The pale green CuL complex is diamagnetic and shows no d-d bands in the visible region suggesting that it is actually a Cu(I) complex. However , cobalt and nickel complexes of ligand(II) have magnetic moments 4.8 and 3.3B.M. respectively , to confirm octahedral geometry. In addition , the diamagnetic[NiLCl] complex shows two bands at 450 and 650 nm assigned for $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions respectively. These findings suggest square planar geometry for this complex[14] . The μ_{eff} value for [CoLCl] complex is 2.6B.M. consistent with square planar geometry[15].

Thermogravimetric studies

The cobalt and nickel complexes of ligand(I) have nearly identical thermal behaviour leading to believe that the complexes are isostructural.

These complexes begin to lose weight at ~ 180°C in a single step with an exothermic peak in the DTA curve. The weight loss corresponds to the escape of one Cl atom[16]. The exothermic peak in the DTA curve suggests bond breaking. The ligand moiety starts dissociation at ~250°C up to 340°C. The weight decrease amounts 25.28 % due to elemination of C_6H_5OH. The second step of decomposition starts at 340°C and extends up to 550°C corresponding to the loss of rest of the ligand $C_8H_4N_2S$ and formation of metal oxide. The overall weight loss (82.8%) agrees with the proposed struture (form 1).

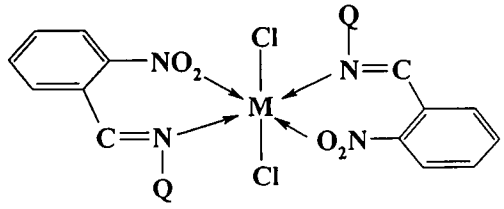


M = Co and Ni **Form (1) (Square planar structure)**

The copper complex of the ligand(I) gives a three stage decomposition pattern. The first stage (61–230°C) represents the loss of cyclopentadiene.The second stage (231-312°C) represents the loss of CO. The weight losses for these temperature ranges are 21.5% and 8.8%, theoretically 20.85% and 8.83% respectively. These fragments are found as a result of the decomposition of C_6H_5OH[17] . There is no distinct transition from the second to the third decomposition stage which begins at 310° up to 650°C due to vaporization of rest of the ligand moiety

$C_8H_4N_2S$ leaving the copper oxide. The infrared spectrum of the complex is highly unresolved which probably suggests it to be a polymeric species. The thermolysis curve of the [CuL_2Cl_2] complex shows weight loss in the temperature range 45-650°C. The decomposition process occurs in different steps and the overall weight loss amounts to 81.16% , theoretically 80.86% due to elemination of the two ligand molecules leaving copper(II) chloride as a residue. The DTA implies that all processes are exothermic. According to the stereochemistry of this complex obtained from electronic spectra and magnetic susceptibility measurements and from the mode of bonding based on the IR spectra , the structure is as shown in (form 2).

The thermogram of [NiL_2Cl_2] complex shows that at a temperature of 116-296°C only one ligand molecule vaporizes , while vaporization of the second molecule occurs at 298-612°C leaving behind the metal chloride. The overall weight loss 79.8% , theoretically 81.3% may be in accordance with the proposed structure of the complex shown in (form 2).



Form (2)
(Octahedral Structure)

M = Cu and Ni

The energies of activation of the decomposition processes of the metal complexes are calculated on Piloyan et al method[18]. In turn , the order

Table (2) Kinetic Data for the Decomposition of some Shiff Base Complexes.

Complex	Peak T (k°)	ΔE kJ / mol	ΔS* kJ/ mol	n
[CoLCl]	523	162.1	-0.206	1.22
	657	137.2	-0.211	0.92
	741	457.3	-0.204	1.13
[NiLCl]	585	159.5	-0.208	1.07
	643	137.9	-0.201	1.09
	664	456.6	-0.199	0.98
[NiL_2Cl_2]	443	207.3	-0.201	1.26
	523	129.9	-0.207	1.20
	702	65.3	-0.218	1.03
[CuL_2Cl_2]	480	51.3	-0.214	0.96
	615	66.5	-0.216	0.98
	853	232.8	-0.212	0.95

values are calculated from the peak symmetry method of Kissinger[19]. The values of Z were calculated by making use of the relation

$$Z = \frac{E}{RT_m} \beta \exp\left(\frac{E}{RT_m^2}\right) \quad (20)$$

and the entropies of activation ΔS* were obtained from the relation

$$Z = \frac{kT_m}{h} \exp\left(\frac{\Delta S^*}{R}\right) \quad (20)$$

where , R represents molar gas constant , β the rate of heating (ks^{-1}) , k the Boltzman constant and h the Blanck's constant. The data are summarized in Table (2). According to the kinetic data obtained from DTA curves, all the complexes have -ve entropy which indicates that activated complexes have more ordered system than reactants. Based on the activation energy values,Co(II) and Ni(II) complexes of ligand (I) have the same thermal stability because they are isostructural. The metal complexes of ligand (I) show higher thermal stabilities than those of ligand(II) due to differences in their structures. Again, the nickel complex of ligand (II) shows a higher thermal stability than those of copper. This can be discussed in terms of repulsions among electron pairs in the valence shell of the central ion. The higher electronegativity of copper than that of nickel leads to a higher repulsion between bonding pairs in the valence shell of copper ion giving a lower stability[21] .

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