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SYNTHESIS AND SPECTRAL CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH BENZOTHIAZOLYL-2-HYDRAZONES OF SALICYLIDENE ACETONE AND SALICYLIDENE ACETOPHENONE

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ABSTRACT

A series of complexes of the type [$M_2L_2Cl_2$], where L = 2-(salicylidene acetone–2'-imino) amino benzothiazole (HSAB) and 2-(salicyledene acetophenone-2'-imino) amino benzothiazole (HSPB), M = Cu (II), Co (II), Ni (II) and Zn (II), have been synthesized and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared spectral studies. The results are in consistent with tridentate chelation of ligand with azomethine nitrogen, ring sulphur and oxygen atom.

Key words: Benzothiazolyl-2-hydrazones, Salicylidene acetone, Salicylidene acetophenone and Transition metal complexes.

INTRODUCTION

Schiff base complexes have undergone a phenomenal growth during the recent years because of the versatility offered by these complexes in the field of industries[1,2], catalysis[3] and in biological system[4,5] etc. In this way, the synthesis, structural investigation and reaction of transition metal Schiff bases have received a special attention, because of their biological activities as antitumoral, antifungal and antiviral activities[6]. Thus, Schiff base hydrazones are also interesting from the point of view of pharmacology. Hydrazone derivatives are found to possess antimicrobial[7], antitubercular[8], anticonvulsant[9] and anti-inflammatory[10] activities.

Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands[11-16], we report here the synthesis and structural studies on the complexes of Co (II), Ni (II), Cu (II) and Zn (II) with some hydrazone derivatives containing benzimidazole moiety such as 2-(salicylidene acetone–2'-imino) amino benzothiazole (HSAB) and 2-(salicyledene acetophenone-2'-imino) amino benzothiazole (HSPB).

EXPERIMENTAL

Material and method

Reagent grade chemicals were used in the present study. The solvents were purified before use by standard process.

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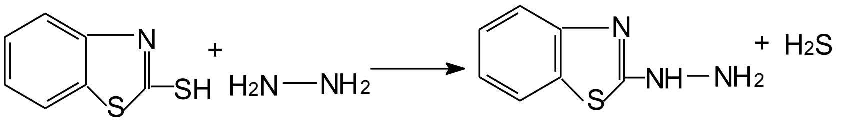
Preparation of ligands

The ligands used in the present investigation were 2-hydrazinobenzothiazole of aldehydes and ketones such as Salicylidene acetone and salicylidene acetophenone have been synthesized by condensing 2-hydrazinobenzothiazole with respective aldehydes and ketone in the following manner.

Synthesis of 2-hydrazinobenzothiazole

To a warm solution of 2-mercepto benzothiazole (1.67 g, 10 m. mole) in absolute alcohol (10 mL), hydrazine hydrate (2 mL) was added and the mixture was refluxed on a water bath for 4 hours or until H_2S gas ceased to evolve. Then it was concentrated and cooled, during which white needle like crystals separated out. It was filtered and recrystallized from ethanol.

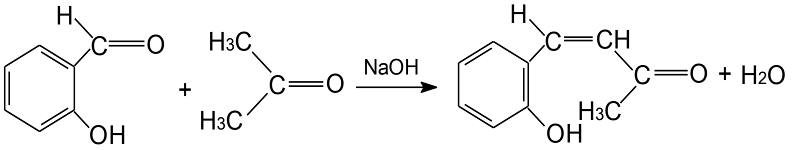


Synthesis of ligands

The ligands 2-hydrazinobenzothiazolyl hydrazones of aldehydes and ketones such as salicyledene acetone and salicyledene acetophenone have been synthesized by condensing 2-hydrazinobenzothiazole with respective aldehyde and ketone in the following manner.

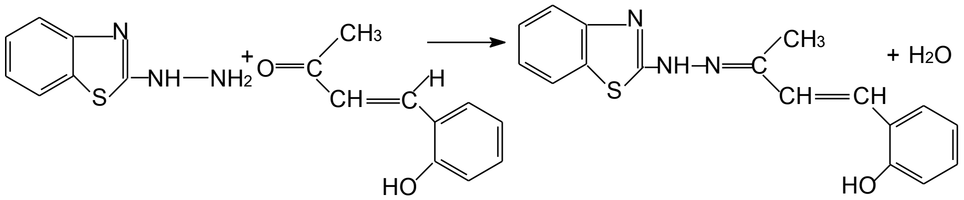
Synthesis of salicylidene acetone

A known method was applied for the synthesis of Salicylidene acetone[2]. A mixture of salicylaldehyde (0.1 mol) and acetone (0.1 mol) in 1 : 1 molar ratio was prepared. Half of the mixture was added to a solution of NaOH (10 g in 100 mL water and 80 mL ethanol), it was maintained at 20-25°C with constant stirring. A red coloured precipitate was formed in 2-3 minutes. The remaining mixture was added and stirring was continued for 30 minutes. The precipitate was filtered at pump and washed with cold water to eliminate unreacted NaOH and was dried at room temperature upon filter paper. It was recrystallized from hot rectified sprit.



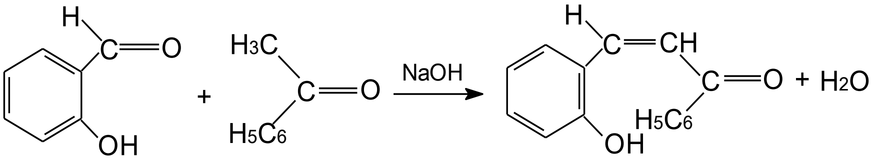
Synthesis of 2-(salicylidene acetone–2'-imino) amino benzothiazole (HSAB)

To a warm ethanolic solution of 2-hydrazinobenzothiazole (0.001 mol in 20 mL) was added an ethanolic solution of salicyledene acetone (0.001 mol in 20 mL) and the mixture was refluxed for about 4 hours on a water bath, when dark brown coloured precipitate was obtained. It was filtered, washed and recrystallized from ethanol.



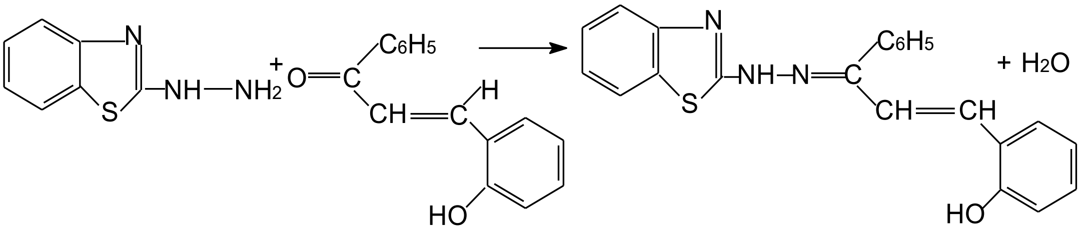
Synthesis of salicyledene acetophenone

Salicyledene acetophenone was synthesized by adopting an identical procedure as in case of synthesized of salicyledene acetone. Here reaction mixture was prepared by mixing salicylaldehyde (0.1 mol) and acetophenone (0.1 mol) half of the mixture was added to a solution of NaOH (10 gm in 100 mL water and 80 mL ethanol), it was maintained at 20-25°C with constant stirring. A deep brown coloured precipitate was formed in 2-3 minutes. The remaining mixture was added stirring was continued for 30 minutes. The precipitate was filtered at pump and washed with cold water to eliminate unreacted NaOH and was dried at room temperature upon filter paper. It was recrystallized from hot rectified sprit.



Synthesis of 2-(salicyledene acetophenone-2'-imino) amino benzothiazole (HSPB)

To a warm ethanolic solution of 2-hydrazinobenzothiazcle (0.001 mol in 20 mL) was added an ethanolic solution of salicyledene acetophenone (0.001 mol in 20 mL) the mixture was refluxed on a water bath for 3-4 hours when a grey coloured precipitate was obtained. It was filtered, washed and recrystallized from ethanol.



Preparation of the complexes

A hot ethanolic solution of the ligand HSAB/ HSPB (0.01 mol in 20 mL) was mixed with an ethanolic solution of respective hydrated metal (II) chloride (0.01 mol in 20 mL) and the mixture was refluxed on a water bath for 3 to 4 hours followed by addition of few drops of conc. NH_3 solution, when coloured precipitates of metal complexes were obtained in each cases. The precipitates were filtered, washed with ethanol followed by ether and finally dried in vacuo over fused $CaCl_2$.

Analysis and physical measurements

The metal contents in the complexes were determined gravimetrically following standard procedure[17]. Sulphur was determined as $BaSO_4$. The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (model CL-01-06, cell constant 0.5 cm^{-1}) using 1×10^{-3} M solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined by using a MLW-CHN micro analyser. FTIR spectra in KBr pallets were recorded on a Varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a Perkin-Elmer spectrophotometer. Thermo gravimetric analysis was done by Netzch-429 thermo analyzer.

RESULTS AND DISCUSSION

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (Table 1). The complexes are highly coloured and insoluble in water and common organic solvents but soluble in highly coordinating solvents such as dioxane, DMF and DMSO. They are non hygroscopic, highly stable under normal conditions and all of them decompose above 250°C. The molar conductance data values in DMSO for the complexes indicate them to be non-electrolyte in nature.

Table 1: Analytical and physical data of the complexes

S. No.	Compounds	Cl Found (Calc.)	C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	S Found (Calc.)	M Found (Calc.)
1	HSAB	-	63.11 (63.15)	4.30 (4.33)	17.29 (17.33)	9.86 (9.90)	-
2	HSPB	-	68.53 (68.57)	4.12 (4.15)	14.50 (14.54)	8.27 (8.31)	-
3	$[Co_2(SAB)_2 Cl_2]$	8.49 (8.52)	48.94 (48.98)	3.33 (3.36)	13.41 (13.44)	7.64 (7.68)	14.11 (14.16)
4	$[Ni_2(SAB)_2 Cl_2]$	8.50 (8.53)	48.99 (49.03)	3.32 (3.36)	13.43 (13.46)	7.65 (7.69)	14.02 (14.06)
5	$[Cu_2(SAB)_2 Cl_2]$	8.41 (8.43)	48.41 (48.45)	3.29 (3.32)	13.25 (13.30)	7.55 (7.60)	15.04 (15.08)
6	$[Zn_2(SAB)_2 Cl_2]$	8.35 (8.40)	48.25 (48.28)	3.28 (3.31)	13.21 (13.25)	7.53 (5.57)	15.34 (15.38)
7	$[Co_2(SPB)_2 Cl_2]$	7.39 (7.42)	55.14 (55.17)	3.30 (3.34)	11.65 (11.70)	6.64 (6.68)	12.29 (12.33)
8	$[Ni_2(SPB)_2 Cl_2]$	7.40 (7.42)	55.19 (55.23)	3.31 (3.34)	11.66 (11.71)	6.65 (6.69)	12.20 (12.24)
9	$[Cu_2(SPB)_2 Cl_2]$	7.31 (7.35)	54.61 (54.65)	3.26 (3.31)	11.55 (11.59)	6.58 (6.62)	13.11 (13.14)
10	$[Zn_2(SPB)_2 Cl_2]$	7.28 (7.32)	54.44 (54.49)	3.26 (3.30)	11.52 (11.56)	6.57 (6.60)	13.38 (13.41)

[a] Ohm^{-1} cm^2 $mole^{-1}$

IR spectra

The ligands HSAB and HSPB are formed by condensation of 2-hydrazinobenzothiazole with a condensation product of salicylaldehyde with acetone / acetophenone. Formation of the second precursor by the condensation of salicylaldehyde with acetone/acetophenone is confirmed by remarkable change in IR spectra of salicylaldehyde. The important changes are appearance of an intense band at ~ 1650 cm^{-1} which may be due to $\nu_{C=O}$ carbonyls and a band around ~1675 cm^{-1} which may be due to $\nu_{C=C}$ formed by the condensation of salicylaldehyde with the ketones.

Formation of ligands HSAB and HSPB by the condensation of above precursors with 2-hydrazinobenzothiazole is proved by change in the IR spectra of the starting materials. The most notable change in the IR spectra is the disappearance of the – NH_2 stretching vibration and appearance of an intense band at ~ 1565 cm^{-1} due to $\nu_{C=N}$ (azomethine). The spectra also contains a multiple band system at ~ 1520, ~ 1282 and ~ 860 cm^{-1} attributed to $\nu_{C=N}$ (cyclic) $\nu_{C\text{-}N}$ (cyclic) and $\nu_{C\text{-}S\text{-}C}$ of benzothiazole group respectively.

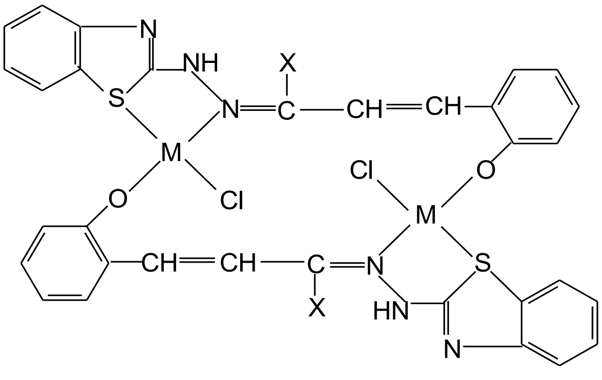
In the IR spectra of all the metal complexes, the position of bands due to $\nu_{C=N}$ (cyclic) and $\nu_{C\text{-}N}$ (cyclic) remain unchanged there by indicating non-participation of the ring nitrogen atom in coordination. However, the position of $\nu_{C\text{-}S\text{-}C}$ band shifts to lower frequency by 10-20 cm^{-1}. This indicates involvement of ring sulphur atom in coordination. In the entire complexes band at 3300 cm^{-1} due to phenol -OH disappears implying its coordination to metal center after deprotonation. This is further confirmed by the up field shift of phenol $\nu_{C\text{-}O}$ mode 10-20 cm^{-1} in complexes.

The position of band due to $\nu_{N\text{-}H}$ (imino) and $\nu_{C\text{-}N}$ (imino) remain practically unchanged in complexes, showing non-involvement of imino nitrogen in coordination. However, the bands due to $\nu_{C=N}$ (azomethine) and $\nu_{N\text{-}N}$ vibration change their position in all complexes. The former band shows blue shift, there by implying coordination of azomethine nitrogen atom to the metal centers.

All the metal complexes show a pair of sharp band in their IR spectra around ~ 560 and ~ 450 cm^{-1} which may be due to $\nu_{M\text{-}N}$ and $\nu_{M\text{-}O}$ vibrations respectively. This proves involvement of phenolic oxygen and azomethine nitrogen in coordination. Due to instrumental limitation $\nu_{M\text{-}S}$ and ν_{Cl} could not be studied in this case but insolubility of the complexes in water and their non-electrolytic nature provide sufficient evidence for the co-valency of the counter ion Cl^-.

Here it is proposed that the ligand moiety satisfies 3-coordination numbers of the metal center and the fourth coordination number is satisfied by Cl^- ion. As the metal center is unable coordinate with phenolic oxygen of the same ligand with which it is coordinating through azomethine nitrogen and ring sulphur as this involves formation of highly strained 8-membered ring and coordinates with phenolic oxygen of another ligand. This indicates involvement of two metal centers as evidenced by elemental analysis. Absence of any band around ~3500 cm^{-1} indicates that neither coordinated nor lattice water is present in these complexes which is further supported by thermal analysis.

Basing on the result of IR spectral study we come to know that the ligand behaves as a tridentate mono basic donor coordinating through azomethine nitrogen, ring sulphur and phenolic oxygen and we tentatively propose the following structure (Fig. 1) for the metal complexes, which is further confirmed by electronic spectral and magnetic moment data.



M = Co (II), Ni (II), Cu (II), Zn (II),

X = -CH_3 or C_6H_5

Fig. 1

Thermal analysis

The complexes formed using ligands HSAB and HSPB follow similar thermal decomposition pattern. The complexes remain stable up to ~300°C indicating absence of coordinated or lattice water molecules. The complexes do not adhere to constant weight and decompose due to decomposition of organic constituents up to ~ 800°C and give rise to their stable oxide. Thermal data of there complexes are recorded in Table 2. Relative stability of these complexes can be represented as below,

HSAB complexes: Cu (II) < Ni (II) < Co (II) < Zn (II)

HSPB complexes: Co (II) < Ni (II) < Zn (II) < Cu (II)

Table 2: Important features of thermo gravimetric analysis (TGA)

Complexes	Total wt. for TG (mg)	Decomposition temperature (°C)	% of residue		Composition of the residue
			Found	Calc.	
3	19.5	275	17.96	18.01	CoO
4	18.4	270	17.87	17.91	NiO
5	21.1	265	18.84	18.88	CuO
6	16.3	285	19.14	19.17	ZnO
7	21.7	255	15.63	15.67	CoO
8	16.2	260	15.54	15.59	NiO
9	18.4	275	16.42	16.46	CuO
10	15.5	270	16.69	16.72	ZnO

Electronic spectra and magnetic properties

The magnetic moment values of the Co (II) complexes obtained from ligands HSAB and HSPB lie in the range 4.4 to 4.5 BM per Co (II) ion, normally observed for tetrahedral Co (II) complexes. The electronic spectra of these complexes exhibit bands in the region 8,850-9,400 cm^{-1} (1130-1064 nm), 16,000-17,000 cm^{-1} (625-588 nm) and 28,000 cm^{-1} (357 nm) assignable to $^4A_2 \rightarrow {}^4T_1$ (F) and $^4A_2 \rightarrow {}^4T_1$ (P) transitions respectively under tetrahedral environment while the high frequency band is assigned to charge transfer. It is interesting to note that though the complexes contain two Co (II) centers yet no split in band was observed indicating the metal centers to be in same chemical environment and nearly same tetrahedral field strength. The crystal field parameters 10 Dq, B and β as calculated following standard methods. By combining spectroscopic and magnetic data the spin orbit coupling coefficient λ has also been calculated. The data are also in good agreement with those of previously reported tetrahedral Co (II) complexes.

The observed μ_{eff} values for Ni (II) complexes lie in the range ~3.4 BM per Ni (II) ion which are higher than those of spin free hexa coordinated Ni (II) species. These values suggest the complexes to be in tetrahedral environment. The electronic spectra of these complexes in DMSO are very similar and found to possess two main bands at ~9,460 cm^{-1} (1057 nm) and ~15,800 cm^{-1} (633 nm) which may be attributed to $^3T_1 \rightarrow {}^3A_2$ (ν_2□) and $^3T_1 \rightarrow {}^3T_1$ (P) (ν_3) transition respectively under an approximately tetrahedral environment. The ν_1 band $^3T_1 \rightarrow {}^3T_2$ (F) was not observed in the wavelength range studied in the present complexes. Distinct bands due to two Ni (II) centers have not been observed in these complexes indicating that tetrahedral field strength is roughly of the same order. The values of ligand field splitting energy 10 Dq, nephelauxetic ratio of these complexes as calculated following the standard methods.

The μ_{eff} value of Cu (II) complexes lie in the range 1.9-2 B.M. per Cu (II) ion suggesting no major interaction between the unpaired electrons on different Cu (II) ions. Although the magnetic moment is poorly diagnostic, in such cases conclusion about probable stereochemistry may be drawn from the electronic spectral data of these complexes.

The electronic spectral data of these complexes in DMSO are very similar and characterized by showing two bands at ~8,500 cm^{-1} (1176 nm) and ~14,000 cm^{-1} (714 nm) which may be attributed to $^2B_2 \rightarrow {}^2A_1$ and $^2B_2 \rightarrow {}^2E$ transitions under D_{2d} symmetry. The band due to $^2B_1 \rightarrow {}^2B_2$ transition remains practically unobserved probably being spin forbidden.

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