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Gravimetric Estimation of Ni(II) and Cu(II) Ions with Bis-Salicylidene-Ethylene Diamine

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Gravimetric estimation of Ni(II) and Cu(II) ions with bis-salicylidene-ethylene diamine was performed in ammonical medium. The complexes are square-planar in geometry. The complexes have been characterized on the basis of elemental analysis, magnetic susceptibility, molar conductance and spectral data.

Key Words: Gravimetric, Ni(II), Cu(II), Bis-salicylidene-ethylene diamine.

INTRODUCTION

Schiff base derived from ethylene diamine and salicylaldehyde is reported for the formation of metal complexes. In the present study Schiff bases derived from bis-salicylidene-ethylene diamine were synthesized. Complexes of Ni(II) and Cu(II) with the present Schiff base were synthesized and used for gravimetric estimation.

EXPERIMENTAL

The chemicals used were of BDH, AR or E-Merck extra pure grade. The ligand bis-salicylidene-ethylenediamine was prepared as follows:

Salicylaldehyde (7.1 mL) was mixed with ethylene diamine (2.2 mL). The reaction mixture was stirred well, refluxed for about 1 h and cooled, when yellow coloured product was obtained. The crude product was crystallized from methanol. The crystalline product was dried and its melting point was recorded (m.p. 127°C). The compound is soluble in alcohol and acetone. However, it is highly soluble in dioxane, pyridine and dimethyl formamide, but insoluble in water.

Preparation of complexes

Bis-salicylidene-ethylenediamine Ni(II): An aqueous solution of nickel(II) chloride was treated with strong ammonia solution (6 N) till blue colouration was obtained. It was treated with an alcoholic solution of the ligand in the molar

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proportion 1 : 1, digested on steam bath for *ca.* 1 h and left overnight in the cold. The orange yellow coloured precipitate was filtered, washed with cold water and dried in air. The compound is insoluble in water and methanol, slightly soluble in acetone and highly soluble in pyridine. On thermal analysis, it was found to decompose above 330°C, the final product being nickel oxide. Before this temperature there is no loss in weight.

Bis-salicylidine-ethylenediamine Cu(II) complex: A deep blue ammonical solution of an copper(II) sulphate was treated with an alcoholic solution of the ligand in 1 : 1 molar ratio. A grey green precipitate separated. This was digested on the steam bath for 1 h and then left to stand for 1/2 h, filtered, washed with water and dried in an air oven. The compound is insoluble in water and methanol, slightly soluble in acetone and highly soluble in pyridine. It decomposes readily in mineral acids and also when heated above 300°C.

The analytical data are given in Table-I.

TABLE-1
ANALYTICAL DATA AND CONDUCTIVITY MEASUREMENT
OF THE LIGAND AND COMPLEXES

Compound	% Analysis: Found (Calculated)				Conductivity (ohm^{-1} cm^{-2} mol)
	C	H	N	M	
$C_6H_{16}N_2O_2$	71.59	6.02	10.38	—	—
(Ligand)	(71.64)	(5.97)	(10.44)		
$Ni(C_6H_{16}N_2O_2)$	59.06	4.37	8.56	18.03	14
	(59.13)	(4.31)	(8.62)	(18.07)	
$Cu(C_6H_{16}N_2O_2)$	58.22	4.29	8.42	19.21	16
	(58.27)	(4.24)	(8.49)	(19.27)	

Gravimetric Estimation

Ni(II) with Bis-salicylidine ethylenediamine: 4.784 g of nickel sulphate ($NiSO_4{\cdot}7H_2O$; BDH AnalaR) was taken in a 1 L measuring flask and dissolved in distilled water. 1–2 mL of conc. H_2SO_4 was added. From this solution 10 mL, 15 mL, 25 mL, . . . , 100 mL were taken out by means of a pipette and added in a beaker. After that each set was diluted by distilled water to make the volume to 100 mL. Now 1% solution of ligand was prepared in alcohol. To 100 mL of the above prepared solution, concentrated ammonia (6 N) was added till a clear blue solution was obtained. After that 1% alcoholic solution of the ligand was added slowly with constant stirring. Orange yellow precipitation occurred immediately. The solution was digested on steam bath for *ca.* 1 h and left to stand for overnight. Finally the complex was filtered through a previously washed, dried and weighed sintered glass crucible (G-3). The precipitate was dried to constant weight in a hot air oven at 115°C and weighed as $Ni(C_{16}H_{14}N_2O_2)$. Similar experiment was performed for each solution and for higher accuracy triplicate experiments for each set were done. The amount of precipitate is recorded in Table-2.

Cu(II) with Bis-salicylidine ethylenediamine: 3.29 g of $CuSO_4 \cdot 5H_2O$, (BDH, AnalaR) was taken in a 1 L measuring flask and dissolved in distilled water. 1 to 2 mL of conc. H_2SO_4 was added. From this solution 10 mL, 15 mL, 20 mL, 25 mL, . . . 100 mL were taken out by means of a pipette and added to a beaker. After this each set was diluted by distilled water to make the volume 100 mL and conc. NH_3 was added till the solution was clear. Now 1% solution of the ligand was prepared in alcohol. To 100 mL of metal solution prepared as above, alcoholic solution of the ligand was added slowly with constant stirring. Grey green precipitation started immediately. After the addition of the ligand solution, the whole mass was digested on steam both for *ca.* 1 h and then left for *ca.* 1 h to settle. The complete precipitation was tested with the supernatant liquid. Finally the complex was filtered through a previously washed, dried and weighed sintered glass crucible. The precipitate was washed serveral times with cold water and dried in a hot air oven at 110°C and weighed as $[Cu(C_{16}H_{14}O_2N_2)]$. The amount of precipitate obtained in each set is recorded in Table-2.

TABLE-2

Amount of metal (mg)	Wt. of Ni-complex (mg)	Expected wt. of complex (mg.)	Error (mg)	Wt. of Cu complex (mg)	Expected wt. of complex (mg)	Error (mg)
10	55.2	55.3	0.1	51.6	51.9	0.1
15	82.7	82.9	0.2	77.7	77.8	0.1
20	110.4	110.6	0.2	103.7	103.8	0.1
25	138.2	138.3	0.1	129.6	129.7	0.1
30	165.8	165.9	0.1	155.5	155.7	0.2
35	193.4	193.6	0.2	181.5	181.6	0.1
40	221.0	221.2	0.2	207.5	207.6	0.1
45	248.8	248.9	0.1	233.4	233.5	0.1
50	276.4	276.6	0.2	259.3	259.5	0.2
55	304.1	304.2	0.1	285.3	285.4	0.1
60	331.6	331.9	0.3	311.2	311.3	0.1
65	359.3	359.9	0.2	337.2	337.3	0.1
70	387.1	387.2	0.1	363.0	363.2	0.2
75	414.7	414.8	0.1	389.1	389.2	0.1
80	442.3	442.5	0.2	415.0	415.1	0.1
85	470.1	470.2	0.1	440.9	441.1	0.2
90	497.6	497.8	0.2	466.9	467.0	0.1
95	525.3	525.5	0.2	492.8	493.0	0.2
100	553.1	553.2	0.1	515.8	515.9	0.1

TABLE-3
INFRARED SPECTRA (cm^{-1}) OF BIS-SALICYLIDINE ETHYLENEDIAMINE AND ITS METAL COMPLEXES

Bis-salicylidine ethylenediamine		Ni(II) complex		Cu(II) complex	
Bands	Assignments	Bands	Assignments	Bands	Assignments
3200	O—H stretching (H-bonded)	3200	O—H str. (H-bond)	3200	O—H str. (H-bond)
3060	C—H stretching	3060	C—H str.	3060	C—H str.
3000	Aromatic C—H stretching	3000	Aromatic C—H str.	3000	Aromatic C—H str.
2275		2275		2275	
2240	Skeletal vibration	2240		2240	
2160		2160	Skeletal vibrations	2160	Skeletal vibrations
2110		2110		2110	
2045		2045		2045	
1920		1920	Characteristic vibration of *o*-substituted benzene	1920	Characteristic vibration of *o*-substituted benzene
1900	Characteristic vibration of *o*-substituted benzene	1900		1865	
1865		1865		1600	C=N str.
1615	v(C=N)	1600	C=N str.		
1560		1565		1565	
1320	C—N bending	1305	C—N bending	1305	C—N bending
1295	C—H bending				O—H bending
1250	v(C—O) (Phenolic)	1265	C—O phenolic	1265	C—O str. (phenolic)
1020	C—H bending		O—H bending		O—H bending
945	C—H bending	930	C—N bending	930	C—N bending
750	Characteristic vibration of *o*-substituted benzene with 4- adjacent H-atoms	750	Characteristic vibration of 0-substitute benzene with 4-adjacent H-atom	750	Characteristic vibration of 0-substituted benzene with 4-adjacent H-atom
	—	520	v(Ni—N)	520	v(Cu—N)
	—	450	v(Ni—O)	450	v(Cu—O)

RESULTS AND DISCUSSION

Ni(II) complex

The complex was found to be diamagnetic. The molar conductance (ohm^{-1} cm^{2} mole^{-1}) in 10^{-3} M solution was found to be 14 indicating the non-electrolytic nature of the compound (Table-1).

Intrepretation of infrared spectra is somewhat complicated due to duplication of similar groups and hence many combination bands appeared (Table-3). The broad band observed in the ligand around 3200 cm^{-1} assignable to phenolic —OH (hydrogen bonded) stretching frequency disappears in the chelate showing deprotonation of phenolic proton through complexation. A strong band near 1250

cm^{-1} observed in the ligand attributed to phenolic C—O vibration increases appreciably by 15–20 cm^{-1} on complexatation. This also supports the fact that chelation of the ligand to metal ion occurs through phenolic oxygen.

Bands at 3000, 2275, 2240, 2160, 2110, 2045, 1920, 1900, 1865 and 750 cm^{-1}, present in the ligand, remain unaffected on complex formation. This indicates that these bands are due to skeletal modes of vibration of the molecule as such. The ligand shows bands around 1615, 1320 and 940 cm^{-1}, assignable to stretching and bending modes of vibration of C=N, lowers appreciably by about 10–20 cm^{-1} on complexation. This suggests coordination through nitrogen atom of azomethine (C=N) group. A new band around 520 cm^{-1} exhibited by the complex is assigned to metal nitrogen stretching vibrationd[1,2] as well as N—M—N bending type. A new band at 450 cm^{-1} exhibited by the complex is attributed to the ν(Ni—O) bond. It is concluded that the ligand behaves as tetradentate ligand co-ordinating through two nitrogen atoms and by deprotonation of two phenolic hydrogen.

Magnetic susceptibility measurements suggest this complex to be diamagnetic which indicates that the complex is a square-planar one[3].

Cu(II) complex

The compound is paramagnetic (μ_{eff} = 1.78 B.M.) in nature[3]. Molar conductance (ohm^{-1} cm^2 mol^{-1}) in 10^{-3} M solution was found to be 16 indicating the non-electrolytic nature of the compound. An assignment of the important IR absorption band is based on the study of infrared spectrum of the free ligand and its copper chelate. By comparison of these bands it is quite clear that the ligand bis-salicylidine ethylene diamine behaves as a tetradentate one coordinating through two nitrogen atoms and by deprotonation of two phenolic hydrogen.

A square-planar structure has been assigned for copper(II) complex[3].

It is concluded that the ligand bis-salicylidine ethylenediamine functions as an excellent reagent for the gravimetric estimation of Ni(II) and Cu(II).

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