Asian Journal of Chemistry Vol. 12, No. 4 (2000), 1216–1220

Gravimetric Estimation of Ni(II) and Cu(II) with Tetradentate Ligands Derived from Substituted *o*-Hydroxy Ketones

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Gravimetric estimation of Ni(II) and Cu(II) with bis(2- hydroxy-4,6-dimethoxyacetophenone)-ethylenediamine and bis (2-hydroxy-5-methoxyacetophenone)-ethylenediamine was performed in aqueous ammonical medium. All the complexes are square-planar in geometry. The complexes have been characterised on the basis of elemental analysis, magnetic, conductance and spectral data.

INTRODUCTION

Schiff bases derived from ethylenediamine and salicylaldehyde[1] are reported for the formation of metal complexes. In the present study Schiff bases derived from ethylenediamine and 2-hydroxy-4,6-dimethoxyacetophenone and 2-hydroxy-5-methoxy acetophenone were synthesised in the ratio of 2 : 1. Schiff bases are bis(2-hydroxy-4,6-dimethoxyacetophenone)-ethylenediamine ($BHDAENH_2$) and bis(2-hydroxy-5-methoxyacetophenone)-ethylenediamine ($BHMAENH_2$).

EXPERIMENTAL

The chemicals used were of BDH, AR or E. Merck extra pure grade.

Preparation of ligands: Methanolic solutions of hydroxy ketones (0.02 M) were mixed with ethylenediamine (0.01 M) and heated for about 4 h.

Preparation of complexes: Aqueous metal salts were treated with strong ammonia solution (6 N) till intense blue colouration was obtained. They were treated with methanolic solution of the ligand in 1 : 1 ratio, digested on steam bath for about 1 h and left overnight in the cold. The solid coloured compounds were filtered, washed with water and methanol and dried over fused calcium chloride.

The metal complexes were decomposed with 1 M perchloric acid and metal content was estimated[2, 3]. C, H and N were determined at CDRI Lucknow.

The magnetic moment measurements were carried out at room temperature by Gouy method. The conductivities of the complexes were determined with the help of systronics conductivity meter bridge in 10^{-3} M DMF solution. Electronic and infrared spectral data were made available to us by the courtesy of CDRI, Lucknow.

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RESULTS AND DISCUSSION

Elemental analysis, metal-ligand ratio and conductivity measurements data (Table 1) indicate these complexes to be non-electrolyte in nature. Magnetic moments of Ni(II) complexes are diamagnetic (Table-2). These observations indicate square-planar geometry of Ni(II) complexes.

TABLE-1
ANALYTICAL DATA AND CONDUCTIVITY MEASUREMENTS OF THE COMPLEXES

Name of the ligand and complex (colour)	m.f.	% Analysis, Found (Calcd.) C	H	N	M	Conductivity ohm^{-1} cm^{-2} mole
BHDAENH$_2$ (Yellow)	$C_{22}H_{28}O_6N_2$	62.41 (63.46)	6.78 (6.73)	6.68 (6.73)	–	–
BHMAENH$_2$ (Yellow)	$C_{20}H_{24}O_4N_2$	67.36 (67.42)	6.80 (6.74)	7.81 (7.86)	–	–
[Ni (BHDAEN)] (Orange yellow)	$[Ni(C_{22}H_{26}O_6N_2)]$	55.79 (55.84)	5.56 (5.50)	5.86 (5.92)	12.37 (12.42)	14
[Ni (BHMAEN)] (Yellow)	$[Ni(C_{20}H_{22}O_4N_2)]$	58.10 (58.15)	5.40 (5.33)	6.73 (6.78)	14.17 (14.22)	13
[Cu (BHDAEN)] (Grey green)	$[Cu(C_{22}H_{26}O_6N_2)]$	55.23 (55.28)	5.52 (5.44)	5.81 (5.86)	13.25 (13.30)	16
[Cu (BHMAEN)] (Green)	$[Cu(C_{20}H_{22}O_4N_2)]$	57.43 (57.48)	5.35 (5.27)	6.64 (6.70)	15.13 (15.20)	17

TABLE-2
ELECTRONIC SPECTRA (IN SOLID STATE) AND MAGNETIC SUSCEPTIBILITY OF COMPLEXES, BAND ASSIGNMENTS (cm^{-1})

Complexes	Band maximum (cm^{-1})			μ_{eff} (B.M.)
	(ν_1)	(ν_2)	(ν_3)	
	$^1A_{1g} \longrightarrow {}^1A_{2g}$,	$^1A_{1g} \longrightarrow {}^1B_{1g}$,	$^1A_{1g} \longrightarrow {}^1E_g$	
[Ni(BHDAEN)]	15350	20500	26100	Diamag
[Ni(BHMAEN)]	15100	20220	25580	Diamag
Combination band of	$^2B_{1g} \longrightarrow {}^2A_{1g}$	$^2B_{1g} \longrightarrow {}^2B_{2g}$	$^2B_{1g} \longrightarrow {}^2E_g$	
[Cu(BHDAEN)]		16380		1.81
[Cu(BHMAEN)]		16700		1.83

Magnetic moments of Cu(II) complexes lie in the range of 1.81–1.83 B.M. The mangetic moment value corresponds to one unpaired electron. Ray and Sen[4] have categorised magnetic moments between 1.73–1.84 B.M. to be associated with square-planar geometry. Sacconi *et al.*[5] and Kettle[6] have suggested that the values of magnetic moment for square planar complexes lie in the range 1.83–1.86 B.M, whereas for tetrahedral configuration the magnetic moment will be larger than 2.0 B.M. due to orbital contribution for the ground state configuration $^2T_2$. Thus the magnetic moment values of all the Cu(II) complexes indicate them to be Cu(II) square-planar geometry.

Electronic spectra of Ni(II) complexes show three bands in the range of 15,000 20,000 and 26,000 cm^{-1}. Manch and Fernilius[7] pointed out that square-planar nickel complexes have three spin allowed bands, namely:

$$^1A_{1g}(e_g{}^4a_{1g}{}^2b_{2g}) \longrightarrow {}^1A_{2g}(e_g{}^4a_{1g}{}^2b_{2g}{}^1b_{1g}{}^1)$$

$$^1A_{1g}(e_g{}^4a_{1g}{}^2b_{2g}) \longrightarrow {}^1B_{1g}(e_g{}^4a_{1g}{}^1b_{2g}{}^2b_{1g}{}^1)$$

$$^1A_{1g}(e_g{}^4a_{1g}{}^2b_{2g}) \longrightarrow {}^1E_g(e_g{}^3a_{1g}{}^2b_{2g}{}^2b_{1g}{}^1)$$

The three possible transitions can be represented as:

$$b_{2g} \longrightarrow b_{1g}({}^1A_{1g} \longrightarrow {}^1A_{2g})$$

$$a_{1g} \longrightarrow b_{1g}({}^1A_{1g} \longrightarrow {}^1B_{1g})$$

$$e_g \longrightarrow b_{1g}({}^1A_{1g} \longrightarrow {}^1E_g)$$

The $^1A_{1g} \longrightarrow {}^1A_{2g}$ transition occurs in the range of 14,000–18,000 cm^{-1} while the higher energy band $^1A_{1g} \longrightarrow {}^1B_{1g}$ occurs around 19,000–20,000 cm^{-1}. In planar complexes the $^1A_{1g} \longrightarrow {}^1E_g$ transition occurs in the range of 24,500–26,500 cm^{-1}. The electronic absorption band observed around 15,000 cm^{-1} is assigned to $^1A_{1g} \longrightarrow {}^1A_{2g}$ transition in planar field. The other transitions expected for planar Ni(II) complexes are listed in Table-2.

Electronic spectra of Cu(II) complexes show a band maximum around 16,000 cm^{-1}. Foster and Goodgame[8] as well as Holm *et al.*[9] have found that d-d band due to planar or octahedral field appears generally at higher energy (around 19,000 cm^{-1} in planar and around 15,000 cm^{-1} to 18,000 cm^{-1} in octahedral complexes), than those of pseudotetrahedral arrangements[10] (around 8,000 to 11,000 cm^{-1}). In case of octahderal or distorted tetragonal field a broad band is located in the range of 10,000 cm^{-1} to 14,000 cm^{-1}.

Sacconi[11] and Meek *et al.*[12] have observed that square-planar complexes have a complex broad band of relatively higher frequencies (16,000 cm^{-1}). The regular tetrahedral complexes of Cu(II) show no d-d absorption band in the region 10,000–20,000 cm^{-1}.

The observed band positions in the reflectance spectra of the above mentioned Cu(II) complexes are given in Table-2.

The above mentioned bands are assigned to combinations of $^2B_{1g} \longrightarrow {}^2A_{1g}$, $^2B_{1g} \longrightarrow {}^2B_{2g}$ and $^2B_{1g} \longrightarrow {}^2E_g$.

Thus all these results show that all the above metioned Cu(II) complexes studied in the present investigation possess square-planar geometry.

Comparison with main spectral bands of free ligand and its complexes throw important light as to the nature of ligand donor atoms. (Table-3)

TABLE-3

INFRARED SPECTRAL DATA (cm^{-1}) OF Ni (BHDAEN)

Complex	Band position (cm^{-1})	Assignment	Ligand	
			Band position (cm^{-1})	Assignment
[Ni (BHDAEN)]	–	–	3200 b	ν(H—O) str. (H-bond)*
	3060	ν(C—H) str.	3060	ν(C—H) str.
	1600		1615	
		ν(C═N) str.	1580	ν(C═N) str.
	1565			
	1305	(C—N) bending	1320	(C—N) bending
		–	1295	(O—H) bending
	1265	ν(C—O) phenolic	1250	ν(C—O) phenolic
	520	ν(M—N) str.		
	450	ν(M—O) str.		

The interpretation of IR spectra is complicated due to duplication of similar groups and hence many combination bands. An assignment of the important IR absorption bands based on the study of the IR bands of the ligand with those of its complex gives some important information regarding the nature of coordination sites.

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[13]. A strong band *ca.* 1250 cm^{-1} observed in the IR spectra of the ligand attributed to phenolic C—O vibration, increases appreciably by 15–20 cm^{-1} on complexation. This also supports the fact that chelation of the ligand to metal ion occurs through phenolic oxygen.

The ligand shows bands around 1615 cm^{-1} and 1320 cm^{-1} assignable to stretching and bending modes of vibrations of C═N, which lowers appreciably by about 10–20 cm^{-1} on complexation. This suggests coordination through azomethinic N-atom. A new band around 520 cm^{-1} exhibited by the complex is assigned to metal-nitrogen stretching vibration[14] as well as N—M—N bending type. A new band at 450 cm^{-1} exhibited by the complex is attributed to the ν(M—O) bond.[15]

Thus it is seen that the ligand behaves as tetradentate ligand coordinating through two nitrogen atoms and by deprotonation of two- phenolic hydrogen.

The results of gravimetric estimation of Ni(II) and Cu(II) ions with the help of $BHDAENH_2$ are recorded in Table-4.

TABLE-4

Ligand	Metal ion	Wt. of metal (mg)	Wt. of ppt. (mg)	Calculated wt. of ppt (mg)	Error (mg)
$BHDAENH_2$	Ni(II)	10	80.3	80.5	0.2
		30	241.4	241.5	0.1
		60	483.1	483.2	0.1
		90	724.6	724.7	0.1
		100	805.1	805.2	0.1
	Cu(II)	10	75.0	75.2	0.2
		30	225.5	225.6	0.1
		60	451.1	451.2	0.1
		90	676.6	676.8	0.2
		100	751.9	752.0	0.1
$BHMAENH_2$	Ni(II)	10	70.1	70.3	0.2
		30	210.8	210.9	0.1
		60	421.7	421.8	0.1
		90	632.6	632.7	0.1
		100	702.9	703.0	0.1
	Cu(II)	10	65.5	65.7	0.2
		30	197.0	197.1	0.1
		60	394.1	394.2	0.1
		90	591.2	591.3	0.1
		100	656.9	657.0	0.1

Thus the organic ligands bis(2-hydroxy-4,6-dimethoxyacetophenone)-ethylenediamine and bis(2-hydroxy-5-methoxyacetophenone)-ethylenediamine can be used as reagents for gravimetric estimation of Ni(II) and Cu(II) metal ions.

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(*Received:* 2 June 2000; *Accepted:* 17 July 2000) AJC-2078