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Structural Investigation on Newly Synthesized Schiff Base Complexes of Cu(II), Ni(II) and Zn(II) Metal Ions by Conventional Method

Gagi Tauhidur Rahman[1], Md. Kudrat-E-Zahan[3, *], ABM Nazmul Islam[2], M. M. Haque[3], Md. Akhter Farooque[3]

[1]Department of Material Science and Engineering, Faculty of Engineering, University of Rajshahi, Rajshahi, Bangladesh
[2]Department of Chemistry, Khulna University, Khulna, Bangladesh
[3]Department of Chemistry, Faculty of Science, University of Rajshahi, Rajshahi, Bangladesh

Abstracts

Transition metal complexes of Co(II), Cu(II), Ni(II) and Zn(II) Containing Bidentate Schiff base, derived from the condensation of ethylenediamine and 4-anisaldehyde were synthesized and characterized by IR, UV-Vis., and some physical measurements. IR spectral studies show the binding sites of the Schiff base ligand with the metal ion. Molar conductance data and magnetic susceptibility measurements give evidence for monomeric and electrolytic nature of the complexes. Structural studies show that all the complexes are tetrahedral.

Keywords

Transition Metal Complex, Bidentate Ligand, Schiff Base

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1. Introduction

Schiff bases are condensation products of primary amines with carbonyl compounds and they were first reported by Hugo Schiff in 1864. These compounds containing a general formula RHC=N-R' where R and R' are alkyl, aryl, cyclo alkyl or heterocyclic groups are also known as anils, imines or azomethines [1]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents, especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion [2, 3]. Schiff bases are well known for their biological applications as antibacterial, antifungal, anticancer and antiviral agents [4, 5]. Also, Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer herbicidal applications, [6] antitubercular activities [7] and chelating abilities which give it attracted remarkable attention. [8].

Recently, we studied few mixed ligand complexes containing heterocyclic amine as secondary ligands and few Schiff base containing complexes [9-13]. In the present work, transition metal complexes of Cu(II), Ni(II) and Zn(II) containing bidentate Schiff base, derived from the condensation of ethylenediamine and 4-anisaldehyde were synthesized and characterized by conventional method.

2. Experimental

2.1. Reagents and Chemicals

All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to standard procedures.

2.2. Physical Measurements

The melting or decomposition temperatures of all the prepared

* Corresponding author
E-mail address: kudrat.chem@ru.ac.bd (Md. Kudrat-E-Zahan)

metal complexes were observed in an electro thermal melting point apparatus model No.AZ6512. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance was used for the present investigation. Infrared spectra as KBr disc were recorded in a SIMADZU FTIR-8400 (Japan) infrared spectrophotometer, from 4000-400 cm^{-1}. The absorbances of the complexes were recorded on SHIMUDZU Spectrophotometer.

3. Synthesis

3.1. Synthesis of Schiff Base [N^1-(4-Methoxy-Benzylidene)-Ethane-1, 2-Diamine], ($C_{10}H_{14}N_2O$)

Ethylenediamine (0.30 g, 5 mmol) in absolute ethanol (20 mL) was added to an ethanolic (30 mL) solution of p-anisaldehyde (0.68 g, 5 mmol). The mixture was stirred for 4 hours at ambient temperature and allowed to stand for 5 days. Yellow crystal was observed and filtered off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.2. Synthesis of $[Zn(C_{10}H_{14}N_2O)_2](NO_3)_2$

0.594 g (2 mmol) of $Zn(NO_3)_2.6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.188g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing zinc salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A yellow precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.3. Synthesis of $[Ni(C_{10}H_{14}N_2O)_2](NO_3)_2$

0.582 g (2 mmol) of $Ni(NO_3)_2.6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.164 g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing nickel salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A blue precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.4. Synthesis of $[Cu(C_{10}H_{14}N_2O)_2]Cl_2$

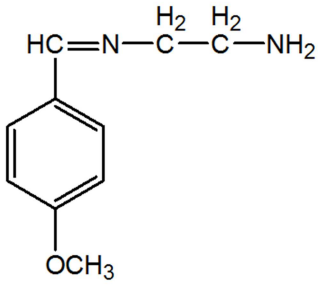
0.741 g (2 mmol) of $Cl_2CuO_8.6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.482 g of Schiff base was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing copper salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A purple precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

3.5. Synthesis of $[Co(C_{10}H_{14}N_2O)_2](NO_3)_2$

0.582 g (2 mmol) of $Co(NO_3)_2.6H_2O$ was dissolved in 5 mL ethanol in a conical flask. 1.164 g of Schiff base- was taken in another small beaker and was dissolved in 10 ml ethanol. Then the solution was poured in the conical flask containing cobalt salt solution and stirred for 4 hours at ambient temperature and allowed to stand for half an hour. A brown precipitate was observed. The precipitate was filtrated off on a Buchner funnel and dried in a vacuum desiccator over anhydrous $CaCl_2$.

4. Results and Discussion

Infrared spectral components of the Schiff Base are shown in Table-1. The spectral data of the ligands showed a strong absorption band at (1580-1640) cm^{-1} due to ν(C=N) stretching indicating the condensation have taken place between the CHO moiety of 4-anisaldehyde and $-NH_2$ moiety of ethylenediamine. The other Band obtained are at (3045-3165) cm^{-1} due to aromatic ν(C-H) stretching. Band at (3400-3595) cm^{-1} due to ν(O-H) stretching. A band at (3300-3500) cm^{-1} due to ν(N-H) stretching of $ν(NH_2)$ modes. The structure of the synthesized Schiff base is shown in figure-1.



N^1-(4-Methoxy-benzylidene)-ethane-1,2-diamine

Fig. 1. Structure of Schiff base ($C_{10}H_{14}N_2O$).

Table 1. Selected infrared spectral components and melting points of the Schiff base.

Ligands	Melting point °C	ν(C=N) cm^{-1}	ν(C-H) of aromatic cm^{-1}	$ν(NH_2)$ cm^{-1}
SB ($C_{10}H_{14}NO$) Yellow crystal	110	1606	3061	3467

All the complexes were characterized by the elemental analysis, conductance measurements, magnetic moment and spectroscopic studies. The elemental analysis of C, H and N (Table-3) of the compounds are consistent with the proposed formula. The conductance (Table-2) values of the complexes are in the region at 44 to 58 ohm^{-2} cm^2 mol^{-1} reveal that the complexes are electrolytic in nature [14].

Infrared spectral data of the complexes (Table-4) showed a strong absorption band at (1580-1640) cm^{-1} for ν(C=N) stretching. Band at (3020-3165) cm^{-1} due to aromatic ν(C-H) stretching. The Band at (500-600) cm^{-1} due to ν(M-N)

stretching, which indicated the co-ordination through N atom to the metal. A band at (3300-3500) cm^{-1} due to ν(N-H) stretching of ν(NH_2) modes.

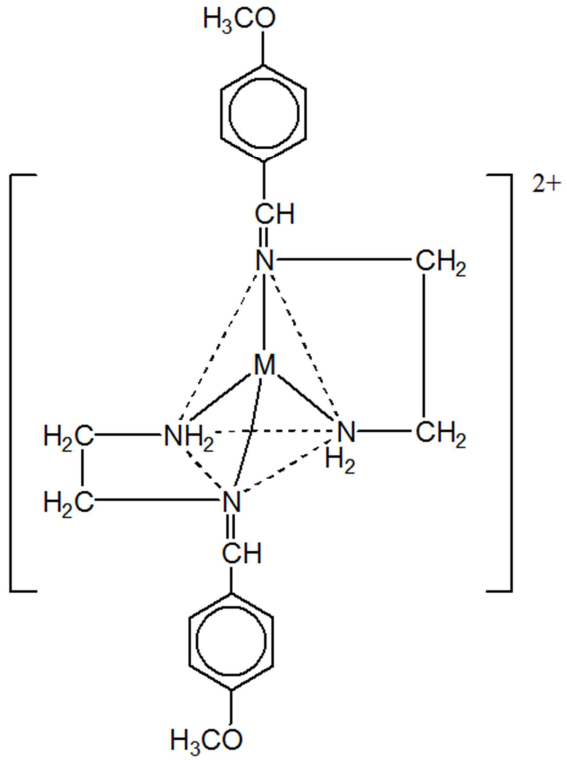


Fig. 2. Tetrahedral structure of the complexes.

The UV-visible spectrum (Table-5) for the complexes are 332 nm (3.90), 282 nm (1.67), 351 nm (4.00) and 289 nm (3.17). The electronic spectra showed bands in the region 200-420 nm due to charge transfer only [15]. The observed magnetic moment values of the complexes at ambient temperature are given in Table-4. The observed magnetic moment value of Zn(II) complex is diamagnetic indicating the absence of unpaired electron. It appears from the magnetic moment data of Zn(II) complex display diamagnetic behavior and hence, is of low spin tetrahedral complex [15]. The magnetic moment value of Ni(II) complex is 3.25 B.M. corresponding to two unpaired electrons. It appears from the magnetic moment data of Ni(II) complex display paramagnetic behavior and hence, is of high spin tetrahedral complex [15]. The observed magnetic moment value of Cu(II) complex is 2.43 B.M. corresponding to one unpaired electrons. It appears from the magnetic moment data of Cu(II) complex display paramagnetic behavior and hence, is of high spin tetrahedral complex [15]. The observed magnetic moment value of Co(II) complex is 4.09 B.M. corresponding to three unpaired electrons. It appears from the magnetic moment data of Co(II) complex display paramagnetic behavior and hence, is of high spin tetrahedral complex [15].

5. Conclusion

On the basis of the elemental analysis, magnetic moment, conductance measurements, IR spectra, UV-visible spectra and other physical properties, the suggested structures of the complexes are tetrahedral in nature as shown in Figure-2.

Table 2. Analytical data and physical properties of the complexes.

Complexes	Colour	Melting point/ decomp. temp. (± 5°C)	% Yield	Molar conductance (ohm^{-2} cm^2 mol^{-1})
$[Zn(C_{10}H_{14}N_2O)_2](NO_3)_2$	Yellow	300 (above)	66	55
$[Ni(C_{10}H_{14}N_2O)_2](NO_3)_2$	Blue	250(d)	65	50
$[Cu(C_{10}H_{14}N_2O)_2](NO_3)_2$	Purple	260(d)	63	44
$[Co(C_{10}H_{14}N_2O)_2](NO_3)_2$	Brown	180(d)	60	58

Where, d = decomposition.

Table 3. Elemental analysis data of the complexes.

Complexes	% Carbon		% Hydrogen		% Nitrogen	
	Calculated	Found	Calculated	Found	Calculated	Found
$[Zn(C_{10}H_{14}N_2O)_2](NO_3)_2$	44.03	43.92	5.17	5.08	15.39	15.20
$[Ni(C_{10}H_{14}N_2O)_2](NO_3)_2$	44.54	44.49	5.23	5.11	15.59	15.44
$[Cu(C_{10}H_{14}N_2O)_2](NO_3)_2$	48.93	48.80	5.75	5.62	11.42	11.33
$[Co(C_{10}H_{14}N_2O)_2](NO_3)_2$	44.53	44.45	5.23	5.05	15.58	15.40

Table 4. Selected infrared spectral bands of the complexes (as KBr disc).

Complexes	ν(NH_2). cm^{-1}	ν(C = N). cm^{-1}	ν(C-H) of aromatic cm^{-1}	ν(M-N) cm^{-1}	μ_{eff} in B.M.
$[Zn(C_{10}H_{14}N_2O)_2](NO_3)_2$	3413	1604	3057	509	Dia
$[Ni(C_{10}H_{14}N_2O)_2](NO_3)_2$	3330	1582	3125	520	3.25
$[Cu(C_{10}H_{14}N_2O)_2](NO_3)_2$	3366	1582	3137	525	2.43
$[Co(C_{10}H_{14}N_2O)_2](NO_3)_2$	3434	1583	3060	573	4.09

Table 5. UV-visible spectral bands of the complexes in dimethyl sulfoxide (DMSO).

complexes	λ_{max} (nm)	Absorbance
$[Zn(C_{10}H_{14}N_2O)_2](NO_3)_2$	332	3.90
$[Ni(C_{10}H_{14}N_2O)_2](NO_3)_2$	282	1.67
$[Cu(C_{10}H_{14}N_2O)_2](NO_3)_2$	351	4.00
$[Co(C_{10}H_{14}N_2O)_2](NO_3)_2$	289	3.17

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