



Synthesis and Spectral Studies of Some Transition metal Complexes

DAYA VEER and MUKESH BABOO

Department of Chemistry, Hindu College, Moradabad - 244 001, India.

*Corresponding author E-mail: dayaveer9411089708@yahoo.com

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ABSTRACT

Complexes of M(III) & M(II) transition metals with N, N'-ethylene-bis-(2-amino-benzamide) have been prepared and characterized by elemental analyses, molar conductivity, magnetic susceptibility measurements, thermal studies, IR and electronic spectra. Based on these studies octahedral geometry has been proposed for these complexes.

Key words: Schiff base, Octahedral & Transition Metal.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and their complexing ability containing different donor atoms is widely reported^{1,2}. The chemistry of Transition metal complexes containing schiff bases continues to be of interest on account of their interesting structural features and also because of their biological importance^{3,4}.

The coordination complexes of the schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological process⁵⁻⁷.

The polydentate schiff bases are well known to coordinate with various metal ions to form

metallic complexes with theoretical and practical applications of different type⁸. These ligand systems have gained considerable importance because of their utility as model compounds in bioinorganic studies as well as their potential as catalysts in many reactions⁹. They find application in the determination of transition metal ions¹⁰⁻¹³ in the study of acid base equilibrium acidity constants value¹³ & for analytical purposes¹⁵.

EXPERIMENTAL

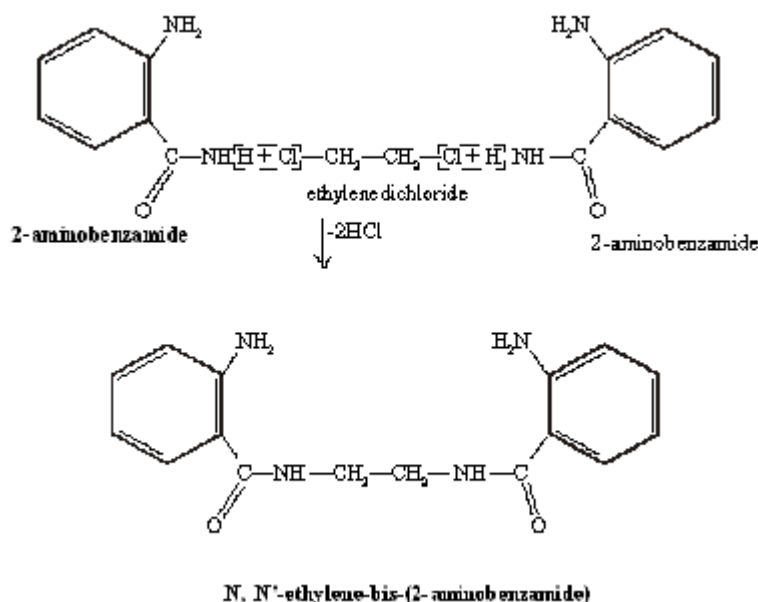
All the chemicals and reagents used for this research work were of highest purity or A.R. Grade. The chemicals used were 2-aminobenzamide and ethylene dichloride. The solvents used were methanol, ethanol and DMF. Ethanol was double distilled in the lab before use whereas other solvents were used as procured. The

metals used were Fe (III), Ti(III), Mn(III), V(III), Co(III), Ru(III), MoO(V), MoO₂(VI) UO₂(VI) and Ru(II). Ti(III) chloride was prepared in the lab by standard method while all other metal salts were used as procured.

Preparation of ligand

Preparation of N,N'-ethylene-bis-(2-aminobenzamide)

1 mole of ethylene dichloride and 2 mole of 2-aminobenzamide were dissolved in methanol & refluxed for 3 hr. The solid product so obtained was filtered, washed with methanol and dried in vacuum dessicator.



Preparation of Complexes

N, N'-ethylene-bis-(2-aminobenzamide) was dissolved in methanol, the pH of the solution was adjusted to 6.0 by adding methanolic solution of NaOH. The metal salt was dissolved in methanol and gradually added to the solution of the ligand with constant stirring. The microcrystalline complexes formed were suction filtered and washed with hot methanol several times. The products were dried in vacuo over anhydrous calcium chloride.

Characterization of Ligand and Metal Complexes

The colour of the ligand and its metal complexes were noted. The m.p. of the ligand and its complexes were determined by open capillary method and are uncorrected. The ligand and its complexes were subjected to elemental analyses for C, H and N whereas metal was estimated

gravimetrically in the Lab. The electronic spectra of the complexes were recorded with the help of Beckman DU. The I.R. spectra were recorded at CDRI, Lucknow in KBr phase.

RESULTS AND DISCUSSION

The complexes are stable in air except those of Ti(III) & V (III) and are non hygroscopic. These are insoluble in water and common organic solvents, but soluble in DMF, DMSO and acetonitrile. The analytical data suggested 1:1 metal : ligand stoichiometry for the complexes. The molar conductance values of the complexes suggested 1:3 electrolytic nature for trivalent metal ion & 1: 2 for divalent metal ion complexes.

Magnetic moment & electronic spectra

The magnetic moment of Fe(III) complex

Table 1: Analytical and physical data of complexes found (Calcd), %

S. No.	Complex	found (Calcd), %					ΔM mho cm ² B.M. mol ⁻¹	$-\mu_{\text{eff}}$ B.M.
		C	H	N	Cl	M		
1.	[Ti(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₃	40.09 (40.13)	4.58 (4.59)	11.69 (11.70)	22.25 (22.26)	9.99 (10.01)	125	1.69
2.	[V(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₃	39.87 (39.88)	4.55 (4.56)	11.62 (11.63)	22.11 (22.12)	10.57 (10.58)	130	2.88
3.	[Fe(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₃	39.46 (39.47)	4.51 (4.52)	11.50 (11.51)	21.88 (21.89)	11.47 (11.48)	128	5.97
4.	[Mn(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₃	39.54 (39.55)	4.52 (4.53)	11.52 (11.53)	21.86 (21.87)	11.30 (11.31)	135	4.90
5.	[Co(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₃	12.12 (12.13)	39.20 (39.22)	4.48 (4.49)	11.43 (11.44)	21.75 (21.76)	135	Diamagnetic
6.	[Ru(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₃	36.10 (36.11)	4.11 (4.13)	10.52 (10.53)	20.01 (20.03)	18.99 (19.01)	125	1.88
7.	[Ru(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O) ₂]Cl ₂	38.69 (38.70)	4.41 (4.43)	11.27 (11.28)	14.30 (14.31)	20.36 (20.37)	85	Diamagnetic
8.	[UO ₂ (C ₁₆ H ₁₈ N ₄ O ₂) ₂]NO ₃	28.14 (28.15)	2.62 (2.63)	12.30 (12.31)	-	34.88 (34.89)	80	Diamagnetic
9.	[MoO ₂ (C ₁₆ H ₁₈ N ₄ O ₂) ₂]Cl ₂	39.41 (39.42)	3.68 (3.69)	11.49 (11.50)	14.57 (14.58)	19.69 (19.70)	85	Diamagnetic
10.	[MoO(C ₁₆ H ₁₈ N ₄ O ₂)(H ₂ O)]Cl ₃	36.60 (36.61)	3.79 (3.81)	10.65 (10.67)	20.29 (20.30)	18.27 (18.29)	130	1.84

is 5.97 B.M. corresponding to five unpaired electrons and a high spin state of Fe(III) ion. Three bands have been observed in electronic spectrum at 11235, 21740 and 27780 cm⁻¹ corresponding to ⁶A_{1g} → ⁴T_{1g}, ⁶A_{1g} → ⁴T_{2g} and ⁶A_{1g} → ⁴E_g transitions respectively suggesting an octahedral geometry¹⁶. The Ti(III) complex shows magnetic moment of 1.69 B.M. for one unpaired electron. The higher value may be due to orbital contribution. A single broad band has been observed at 19230 cm⁻¹ for Ti(III) complex derived from the transition. ²T_{2g} → ²E_g for an octahedral symmetry¹⁷. This band is unsymmetrical in shape and is indeed made up of two closely shaped bands. The second band appears as a hump and may be due to the presence of Jahn-Teller distortion in the complex. The UO₂(VI) complex as expected for f₀ configuration is diamagnetic in nature. Magnetic moment for Mn(III) complex is 4.90 mB revealing the high spin nature of the complex corresponding to four unpaired electrons. Electronic spectrum shows a strong band at 20000 cm⁻¹ which can be assigned to ligand to

metal charge transfer and a shoulder at 18000cm⁻¹ may be assigned to the ⁵E_g → ⁵T_{2g} transition¹⁸⁻¹⁹ characteristic of octahedral geometry.

The Co(III) complex is diamagnetic (at 270) as expected for a low spin d₆ ion. The electronic spectrum of cobalt (III) complex displays bands at 15450, 21095 and 23370 cm⁻¹. These are similar to those reported for other six coordinated cobalt (III) complexes²⁰ and may be assigned to ¹A_{1g} → ³T_{2g}, ¹A_{2g} → ¹T_{2g} and ¹A_{1g} → ¹T_{2g} transitions respectively.

The electronic spectrum of V(III) complex was recorded in pyridine solution which showed bands at 16000 cm⁻¹ with a shoulder at 21000 cm⁻¹. The low energy band has been assigned to ³T_{1g} → ³T_{2g} whereas the high-energy band to ³T_{1g} → ³T_{1g} (P) transitions respectively, characteristic of octahedral geometry, which is further confirmed by the meff value of 2.88 B.M. for V (III) complex²¹.

The electronic spectrum of oxomolybdenum (V) complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from Mo=O bond. The electronic spectrum exhibited three distinct absorption bands in the ligand field region. The low intensity band at 13000 cm^{-1} in the long wavelength region is possibly due to first crystal field transition ${}^2B_{2g} \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{yz}, d_{xz}$), the second transition at 19000 cm^{-1} is assignable to ${}^2B_2 \rightarrow B_2$ ($d_{xy} \rightarrow d_{x^2-y^2}$), the third peak was observed at 30000 assignable to ${}^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_{z^2}$)²². The magnetic moment of MoO(V) complex is 1.84 B.M.

The electronic spectrum of MoO₂ (VI) complex has a single band due to charge transfer transition.

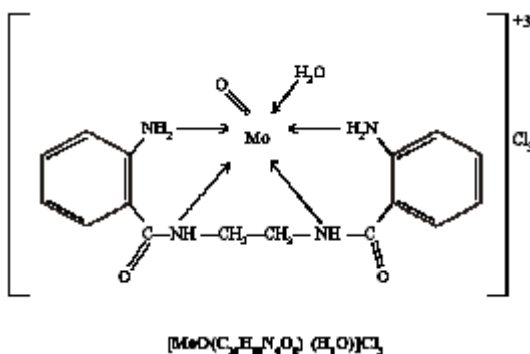
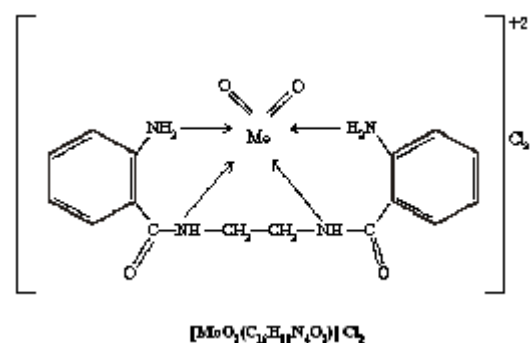
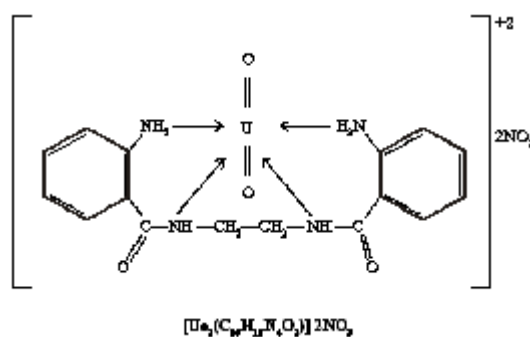
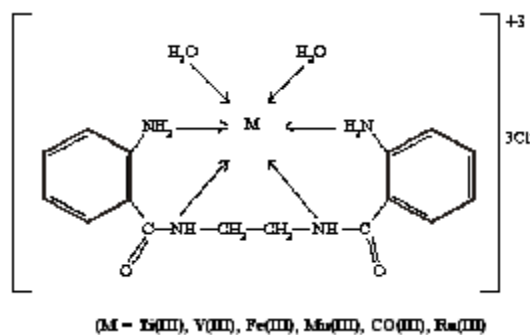
The μ_{eff} for Ru(III) complex was found to be 1.88 B.M. as expected for an octahedral complex with t_{2g}^5 configuration. Its electronic spectrum in chloroform displayed bands at 17860, 21500, 27780 and 33900 cm^{-1} which may be assigned to ${}^2T_{2g} \rightarrow {}^4T_{1g}$, ${}^2T_{2g} \rightarrow {}^4T_{2g}$, ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$ and charge transfer respectively. These are similar to those reported for octahedral Ru(III) complexes²³.

The study of magnetic properties has suggested diamagnetic nature of the Ru(II) complex. The electronic spectrum of the complex in CH_2Cl_2 shows a band at 22000 cm^{-1} . This band has been assigned to charge transfer transition arising from excitation of an electron from the metal t_{2g} level to unfilled molecular orbitals derived from π^* level of the ligand in accordance with the assignment made for similar octahedral Ru(II) complexes²⁴.

Infra Red Spectra

The three N-H stretching frequencies in their spectrum of ligand at 3460, 3360 and 3275 cm^{-1} were shifted to low frequencies side by 25-50 cm^{-1} . Further amide II absorption [$\nu(\text{C-H}) + \delta(\text{N-H})$] around 1500 cm^{-1} in the ligand spectrum is shifted by 55 cm^{-1} . These shifts are of considerable magnitude and confirm that this ligand coordinates through amine and amide nitrogen atom²⁴⁻²⁷.

The amide carbonyl absorption $\nu(\text{C=O})$ remain unaffected in the complex and indicates non coordination of carbonyl oxygen.



These coordination sites are further supported by the appearance of a new band in the far IR region of the complex at 460 cm^{-1} due to nM-N stretching vibration²⁸.

The analytical data and other evidences support the formation of only 1 : 1 complexes and thus the ligand is quadridentate coordinating through two amide nitrogen atoms and two amine nitrogen atoms.

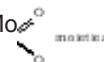
The coordinated nature of water molecules is suggested by ir and supported by TGA. The complexes showed a non-ligand band in the region of $3480\text{-}3510\text{ cm}^{-1}$ assignable to νOH vibrations, suggesting coordinated nature of water molecules. This is further supported by rocking and wagging modes appearing in the regions of $840\text{-}855\text{ cm}^{-1}$ and $735\text{-}750\text{ cm}^{-1}$ respectively. The thermograms showed inflection point corresponding to the loss of water molecules in the temperature range of $168\text{-}205^\circ\text{C}$.

In UO_2 complex bands at $910\text{-}930\text{ cm}^{-1}$ are assigned to ν_3 vibrations indicating linear character of UO_2 group²⁹.

A very strong band found at 940 cm^{-1} in the spectra of Mo(V) complex corresponds to $\text{nMo}=\text{O}$. Also strong bands exhibited by the dioxomolybdenum (VI) complexes at 930 and 900 cm^{-1} are attributed to $\text{n}_{\text{sym}}\text{O}=\text{Mo}=\text{O}$ and $\text{n}_{\text{asym}}\text{O}=\text{Mo}=\text{O}$ respectively of Cis - MoO_2 configuration due to the maximum utilization of the available dp orbitals for bonding with the OXO group³⁰.

CONCLUSION

On the basis of studies performed octahedral geometry has been proposed for all the synthesised complexes, with possible distortion in the case of oxo and dioxo molybdenum complexes due to $\text{Mo}=\text{O}$ and MoO_2



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