Synthesis and Structural Studies of First Row Transition Metal Complexes with Tetradentate ONNO Donor Schiff Base Derived from 5-Acetyl 2,4-dihydroxyacetophenone and Ethylenediamine

PULIMAMIDI SARITHA REDDY^{§*},
P.V.ANANTHALAKSHMI[§] and V. JAYATYAGARAJU

[§]Department of Chemistry, University College for Women
Osmania University, Hyderabad-500001, Andhra Pradesh, India

Department of Chemistry, Addis Ababa University
P.O .Box 1176, Addis Ababa, Ethiopia

abbareddysaritha@hotmail.com

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Abstract: Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared by template reaction of 5-acetyl 2,4-dihydroxyacetophenone (H₂-ADA) and ethylenediamine in the presence of metal ions. The complexes have been characterized on the basis of elemental analyses, conductivity, magnetic moments, infrared and electronic spectral data. The Schiff base binds to metal ions in bis-multidentate ONNO mode leading to two dimensional Schiff base polymers. All the complexes have been assigned octahedral stereochemistry.

Keywords: Template reaction, 5-Acetyl 2,4-dihydroxyacetophenone, Ethylenediamine, Bis-multidentate mode, Schiff base polymers.

Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions^{1,2}. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species. Schiff base metal complexes were investigated for fungicidal, fungistatic, bactericidal and bacteristatic activities³⁻¹⁰.

Polynuclear complexes derived from multidentate ligands have documented interesting structural features¹¹⁻¹⁸. Literature survey on multidentate ligands having oxygen, nitrogen donor systems reveals an extensive investigation on a number of ONN and ONO donor

sequences which have resulted in the formation of polynuclear metal chelates¹⁹⁻²¹. A class of ligands with more than one independent chelating sequence substituted on a single phenyl function exemplify bis - chelating ligands which can bind two metal ions simultaneously and form polynuclear complexes²²⁻²⁴.

The concept of bis-denticity becomes interesting to study if a variety of symmetric and asymmetric bis-chelating systems are developed and employed in the formation of metal complexes. In view of the importance of multidentate bis-chelating ligands, the investigation on metal complexes of 5- acetyl 2,4-dihydroxyacetophenone (H_2 -ADA) and a number of its derivatives has been carried out in our laboratories. The present paper deals with the synthesis and characterization of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of H_2 -ADAEN, Schiff base formed by condensation of 5-acetyl 2,4-dihydroxyacetophenone and ethylenediamine.

Experimental

All the chemicals used were of analar grade. Solvents were dried and distilled before use. Melting points of the complexes were determined on Toshniwal hot stage melting point apparatus and are uncorrected. Carbon, hydrogen and nitrogen analysis was carried out using HERAEUS CHN – Rapid analyser. Chloride analysis was carried out by Mohr's method and metal contents were estimated on a Perkin- Elmer - 2380 atomic absorption spectrometer. The conductivity of metal complexes was measured using a Digisun Digital conductivity meter model D 1909 having dip type cell calibrated with KCl solution. Mass spectra was recorded in a Perkin-Elmer Hitachi RMU 6L spectrometer. UV Vis – NIR spectra were recorded in solid state on a UV Cary 2390 spectrometer. Magnetic susceptibilities of the complexes were recorded on a Faraday balance (CAHN- 7550-03) at room temperature using $Hg[Co(NCS)_4]$ as standard. Diamagnetic correction using Pascal's constants and temperature independent paramagnetic corrections were computed. EPR was recorded on a Jeol SE - 3X Spectrometer at room temperature.

Synthesis of the ligand and metal complexes

H_2 -ADAEN, Schiff base formed by the condensation of 5-acetyl 2,4-dihydroxyacetophenone (H_2 - ADA) and ethylenediamine could be isolated only in the presence of metal ions.

Synthesis of H_2 -ADA

5-Acetyl 2,4-dihydroxyacetophenone was synthesized by reported procedure^{25,26}.

Preparation of the complexes

A general method was adopted for the preparation of all the complexes. To 0.005 mol (0.99 g) of 5-acetyl 2,4-dihydroxyacetophenone dissolved in 15 mL of ethanol, 0.005 mol of ethylenediamine was added and refluxed for about two hours. The pH of the solution was adjusted to 8 with the help of dil. NaOH solution. A yellow solution indicated the formation of the Schiff base. Methanolic solution of the metal chloride was added to the Schiff base solution while stirring. The reaction mixture was refluxed again for four hours. The metal chelates thus separated out were filtered, washed repeatedly with methanol, petroleum ether and diethyl ether and dried *in vacuo*. The purity of the complexes was tested by TLC using different solvent mixtures. The analytical data and proposed formulae for the complexes are given in Table 1.

Table 1. Analytical and conductivity data of metal complexes of H₂ – ADAEN

Complex	Analysis	Found	(Calcd) %		ΩM mho cm ² mol ⁻¹
	C	H	M	N	
CrC ₁₂ H ₁₅ O ₄ N ₂	47.47(47.52)	4.92(4.95)	17.09(17.16)	9.18(9.24)	22
MnC ₁₂ H ₁₆ O ₄ N ₂	46.92(46.90)	5.17(5.21)	17.87(17.91)	9.07(9.12)	16
FeC ₁₂ H ₁₅ O ₄ N ₂	46.84(46.90)	4.85(4.88)	18.19(18.24)	9.05(9.12)	27
CoC ₁₂ H ₁₆ O ₄ N ₂	46.26(46.30)	5.10(5.14)	18.92(18.97)	9.02(9.00)	12
NiC ₁₂ H ₁₆ O ₄ N ₂	46.18(46.22)	5.10(5.13)	18.99(19.10)	8.92(8.98)	10
CuC ₁₂ H ₁₆ O ₄ N ₂	45.64(45.71)	5.01(5.07)	19.94(20.00)	8.85(8.88)	14
ZnC ₁₂ H ₁₆ O ₄ N ₂	45.32(45.42)	4.98(5.04)	20.43(20.50)	8.76(8.83)	16

Results and Discussion

All the metal complexes except that of zinc are coloured and are stable to air and moisture. They are insoluble in common organic solvents but soluble in DMSO and DMF. They do not melt or decompose until 300 °C. Analytical data shows metal to ligand ratio as 1:1 in all the complexes. The analysis suggests the presence of hydroxide ions in Cr(III) and Fe(III) complexes. All the complexes possess coordinated water which derives further support from thermal analysis. Low conductance values of these complexes measured in DMSO solutions show that all these complexes are non electrolytes indicating that hydroxide ions in Cr(III) and Fe(III) complexes are within the coordination sphere.

Infrared spectra

IR spectral data of the complexes are given in Table 2. The spectra of metal complexes do not show the characteristic features due to νNH_2 (sharp doublet 3300-3200 cm⁻¹), δNH_2 (1600 cm⁻¹; broad) and ΩNH_2 (800-900 cm⁻¹) which are the features of ethylenediamine. The spectra of the complexes also miss the band patterns observed with respect to H₂-ADA, specifically broad strong band due to νOH (3000-2500 cm⁻¹)²⁷ and $\nu C=O$ (1659 cm⁻¹)²⁸. Instead the complexes prominently show broad strong bands in the region 3400 - 3000 cm⁻¹, sharp strong bands in the region 1540-1580 cm⁻¹ and other medium to low intensity bands in the low frequency region. Based on these features it is suggested that the metal complexes are formed by the condensed product between H₂-ADA and ethylenediamine, which is a two dimensional polymer. The broad bands in the region 3400-3000 cm⁻¹ are attributed to water molecules along with / without hydroxide ions. The variability of band position in the region 1540-1580 cm⁻¹ characteristic of $\nu C=N$ will undoubtedly show its involvement in coordination²⁹. The absence of strong band in 1659 cm⁻¹ region is a strong evidence, for the condensation involving both the carbonyl groups with the primary amine function of ethylene diamine.

Table 2. Characteristic infrared frequencies of the complexes of H₂ – ADAEN cm⁻¹

Compound	νNH_2	νOH	$\nu C=O$	$\nu C=N$	$\nu C-O$	New bands
Ligand	3300 – 3200	3000 – 2500	1659	–	1256	–
Cr(III) complex	-	-	-	1553	1287	714,550,479
Mn(II) complex	-	-	-	1551	1265	786,625,492
Fe(III) complex	-	-	-	1558	1264	744,602,480
Co(II) complex	-	-	-	1559	1278	783,671,579
Ni(II) complex	-	-	-	1544	1261	798,688,621
Cu(II) complex	-	-	-	1555	1261	788,696,616
Zn(II) complex	-	-	-	1560	1265	784,685,490

This data will more than prove the existence of condensed product in the complexes. The modification of band structure with positive shift in ν C–O region corresponding to H₂ - ADA is a proof of phenoxide bonding. Non ligand bands observed in the region 590 - 440 cm⁻¹ will establish M – N and M – O bonding³⁰. Thus IR data proves the existence of two dimensional Schiff base polymer, binding with ONNO sequence around the metal ions.

Magnetic susceptibilities

Magnetic susceptibilities of the complexes calculated from room temperature instrumental data and metal ligand stoichiometries are presented in Table 3. The magnetic moments are in good agreement with the expected high spin configurations. These values show that there are no metal - metal interactions in these complexes. The absence of antiferromagnetic interactions is justified because the metal ions are separated by bulky diamagnetic benzene rings, which efficiently check the spin neutralisation.

Table 3. Magnetic and electronic spectral data of the complexes of H₂ – ADAEN

Complex	μ_{eff} experimental	Electronic spectral bands
Cr(III) complex	3.94	17200, 22700, 26000
Mn(II) complex	5.95	12800, 25000
Fe(III) complex	5.92	12000, 24700
Co(II) complex	4.10	8890, 17860, 21550
Ni(II) complex	2.42	8400, 10200, 19600
Cu(II) complex	1.62	12000, 12987, 14084, 17391, 21147

Electronic spectra

The electronic spectrum of Cr(III) shows three intense bands, characterised in the descending order of frequency to represent the transitions ${}^4A_2 \rightarrow {}^4T_1$ (P); ${}^4A_2 \rightarrow {}^4T_1$ (F) and ${}^4A_2 \rightarrow {}^4T_2$ (F).

Mn(II) and Fe(III) complexes show a number of electronic spectral bands, attributed to a number of spin forbidden transitions involving 6A_1 ground state and several higher energy quartet states in accordance with octahedral geometry.

Electronic spectrum of Co(II) complex shows bands, assigned to 4T_1 (F) $\rightarrow$ 4T_2 (F), 4T_1 (F) $\rightarrow$ 4A_2 (F) and 4T_1 (F) $\rightarrow$ 4T_1 (P) transitions respectively which are in support of octahedral arrangement of binding centres around the metal ion. The electronic spectrum of Ni(II) complex is assigned to ${}^3A_2 \rightarrow {}^3T_2$, ${}^3A_2 \rightarrow {}^3T_1$ (F) and ${}^3A_2 \rightarrow {}^3T_1$ (P) transitions for octahedral geometry.

The spectrum of Cu(II) complex shows medium intensity multiple bands, assigned to various transitions involving 2B_1 ground term and 2B_2 , 2A_2 and 2E higher energy terms due to distorted octahedral geometry.

EPR spectrum of copper(II) complex

The EPR spectrum of copper(II) complex at liquid nitrogen temperature has been evaluated to give $g_{\parallel}$ and $g_{\perp}$ values as 2.199 and 2.083. The g values indicate a distorted octahedral geometry. Since $g_{\parallel} > g_{\perp} > 2.0023$, the ground state³¹ of Cu(II) is $d_{x^2-y^2}$ and the symmetry is tetragonally distorted octahedral.

Antimicrobial activity

Preliminary studies on the bactericidal properties of the metal complexes indicate promising activity against *Staphylococcus aureus*. Detailed studies are in progress.

Conclusion

Based on the positions of νNH_2 , $\nu\text{C}=\text{N}$ and $\nu\text{C}-\text{O}(\text{phenolic})$ in the spectra of the complexes of H_2 -ADAEN, it is concluded that H_2 -ADA and ethylenediamine undergo 1:1 condensation and bind to metal ions in bis-multidentate ONNO mode leading to two dimensional Schiff base polymers. On the basis of analytical, thermal, conductivity, magnetic and spectral data, octahedral geometries have been proposed for all the complexes. (Figure 1)

$\text{M} = \text{Ce(III)}, \text{Fe(III)}, \text{ML(OH) H}_2\text{O}; \text{X} = \text{OH}, \text{M} = \text{Mn(III)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}, \text{ML}_2\text{H}_2\text{O}; \text{X} = \text{H}_2\text{O}$

Figure 1. Complexes of H_2 - ADAEN

Despite multidenticity of the ligands and polymeric nature of the complexes, normal high spin equivalent magnetic moments have been exhibited by the complexes. Lack of metal metal interactions is another notable feature. The absence of antiferromagnetic interactions is justified because the consecutive metal ions in the two dimensional polymeric network are separated by bulky diamagnetic benzene rings which efficiently check spin neutralisation.

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