International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.2, No.3, pp 1494-1500, July-Sept 2010

Synthesis and Structural Studies of First Row Transition Metal Complexes with Pentadentate ONNNO Donor Schiff Base derived from 5- Acetyl 2,4 – Dihydroxy Acetophenone and Diethylene Triamine

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Abstract : Cr (III), Mn (II), Fe(III), Co(II), Ni (II) and Cu (II) Complexes were prepared by template reaction of 5-acetyl 2,4 – dihydroxy acetophenone (H_2-ADA) and diethylene triamine 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 ONNNO mode leading to two dimensional Schiff base polymers . All the complexes have been assigned octahedral stereochemistry.

Keywords : template reaction, 5-acetyl 2,4– dihydroxy acetophenone, ethylene diamine, 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 in the periodic table(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(3-11).

In recent years there has been considerable interest in the synthesis and use of functionalized polymers having chelating abilities due to their practical convenience, operational flexibility and formation of coordination with high metal to polymer bond energies(12-15). Polynuclear complexes derived from multidentate ligands have documented interesting structural features(16-23). 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 chelates(24-26). 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 complexes(27-29).

The concept of bis- denticity becomes interesting to study if a variety of symmetric and unsymmetric bis-chelating systems are developed and employed in the formation of metal complexes(30-32). 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-ADADTA, Schiff base formed by condensation of 5-acetyl 2,4 –dihydroxy acetophenone and dithylene triamine.

Experimental

Methods and materials

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-ADADTA, Schiff base formed by the condensation of 5- acetyl 2,4 – dihydroxy acetophenone (H_2- ADA) and diethylene triamine could be isolated only in the presence of metal ions.

Synthesis of H_2-ADA

5-acetyl 2,4 – dihydroxy acetophenone was synthesized by reported procedure(33-34).

Preparation of the complexes

A general method was adopted for the preparation of all the complexes. To 0.005 mol(0.99g) of 5-acetyl 2,4 – dihydroxy acetophenone dissolved in 15 ml of ethanol, 0.005 mol of diethylene triamine 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 Data of Metal Complexes of H_2 – ADADTA

Complexes with molecular formula	Calcd. (Found) %				Λ_M (mho cm^2 $mole^{-1}$)
	Metal	Carbon	Hydrogen	Nitrogen	
Cr(III)	15.85	51.20	5.48	12.80	12
$CrC_{14}H_{18}N_3O_3$	(15.79)	(51.15)	(5.46)	(12.77)	
Mn(II)	16.56	50.60	5.72	12.65	6
$MnC_{14}H_{19}N_3O_3$	(16.49)	(50.54)	(5.68)	(12.59)	
Fe(III)	16.86	50.60	5.42	12.65	15
$FeC_{14}H_{18}N_3O_3$	(16.80)	(50.56)	(5.40)	(12.60)	
Co(II)	17.55	50.00	5.65	12.50	12
$CoC_{14}H_{19}N_3O_3$	(17.47)	(49.98)	(5.63)	(12.46)	
Ni(II)	17.68	49.92	5.64	12.48	14
$Ni\ C_{14}H_{19}N_3O_3$	(17.59)	(49.89)	(5.61)	(12.44)	
Cu(II)	18.52	49.40	5.58	12.35	4
$Cu\ C_{14}H_{19}N_3O_3$	(18.45)	(49.34)	(5.56)	(12.28)	
Zn(II)	19.00	49.12	5.55	12.28	6
$Zn\ C_{14}H_{19}N_3O_3$	(18.94)	(49.06)	(5.50)	(12.23)	

Results and Discussion

All the metal complexes except that of zinc are colored 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 ^{o}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. The presence of coordinated water in divalent metal complexes 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.

Thermogravimetric analysis

The thermo grams reveal the presence of one mole of coordinate water per mole of the complex in Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes. The absence of coordinated water in Cr(III) and Fe(III) complexes is established by TG analysis. The deaquation is one step process in all the divalent metal chelates and it occurs at 138^{0} C for Mn(II) complex, 145 ^{0} C for Co(II) and Ni(II) complexes and 152 ^{0}C for Cu(II) complex.

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 υ NH_2 (sharp doublet 3300-3200 cm^{-1}) , δ NH_2 (1600 cm^{-1}; broad) and Ω NH_2 (800 – 900 cm -1) which are the features of diethylene triamine. The spectra of the complexes also miss the band patterns observed with respect to H_2-ADA, specifically broad strong band due to υOH (3000-2500 cm $^{-1}$)(35) and υ C=O (1650 cm $^{-1}$) (36). Instead the complexes prominently show broad strong bands in the region 3400 –3000 cm^{-1}, sharp strong bands in the region 1558 – 1590 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 H_2 – ADA and diethylene triamine , 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 1558 – 1590 cm^{-1} characteristic of υ C=N will undoubtedly show its involvement in coordination(37). 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 diethylene triamine. This data will more than prove the existence of condensed product in the complexes. The modification of band structure with positive shift in υ C–O region corresponding to H_2 – ADA is a proof of phenoxide bonding and a negative shift of υ NH band(3200 cm $^{-1}$) by 20 cm $^{-1}$ in all the complexes suggests the participation of NH group of diethylene triamine in complexation. Non ligand bands observed in the region 590 – 440 cm^{-1} will establish M – N and M – O bonding (38). Thus IR data proves the existence of two dimensional Schiff base polymer, binding with ONNNO 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.

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); $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^4T_2$.

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 $^3A_2 \rightarrow {}^3T_2$, $^3A_{2g} \rightarrow {}^3T_1(F)$ 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_{av} value as 2.092. The tendency of g tensor is exhibiting isotropic nature. The ESR spectrum which lacks the hyperfine structure suggests the predominant effect due to exchange interactions among the Cu (II) ions. The ligand environment around Cu(II) may be octahedral.

Antimicrobial activity

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

Table 2. Characteristic Infra Red Frequencies of Complexes of H_2 - ADADTA(Cm^{-1})

COMPOUND	υNH_2	υOH	υC=O	υC=N	υC-O	New bands
Ligand	3300-3200	3000-2500	1659	-	1256	-
Cr(III) complex	-	-	-	1579	1279	744,514,479
Mn(II) complex	-	-	-	1567	1276	740,588,440
Fe(III) complex	-	-	-	1558	1265	781,576,474
Co(II) complex	-	-	-	1590	1265	668,590,523, 442
Ni(II) complex	-	-	-	1567	1276	776,598,519
Cu(II) complex	-	-	-	1583	1279	776,520,440
Zn(II) complex		-	-	1579	1275	740,519,442

Table 3. Magnetic and electronic spectral data of the complexes of H_2 – ADADTA

Complex	μeff experimental	Electronic spectral bands
Cr(III) complex	3.85	17390,22727,25000
Mn(II) complex	5.98	25320 - 33400
Fe(III) complex	6.02	27000 – 37000; 27000,28388,29152,32667,36727
Co(II) complex	4.75	8160, 16940, 18870, 19608,22189
Ni(II) complex	2.85	8400,14730, 21050
Cu(II) complex	1.74	12100 - 21140 12100, 15873, 20000

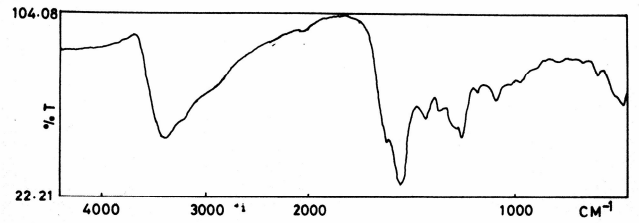


Figure 1: IR spectrum of Fe(III) H_2-ADADTA

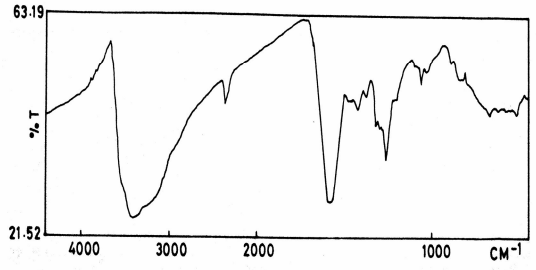


Figure 2: IR spectrum of Co(II) H_2-ADADTA

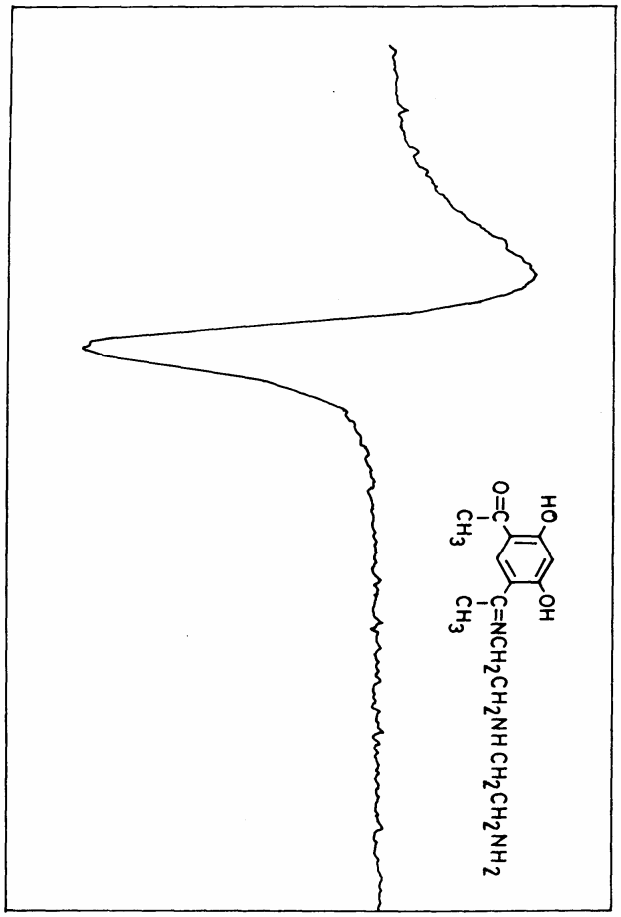
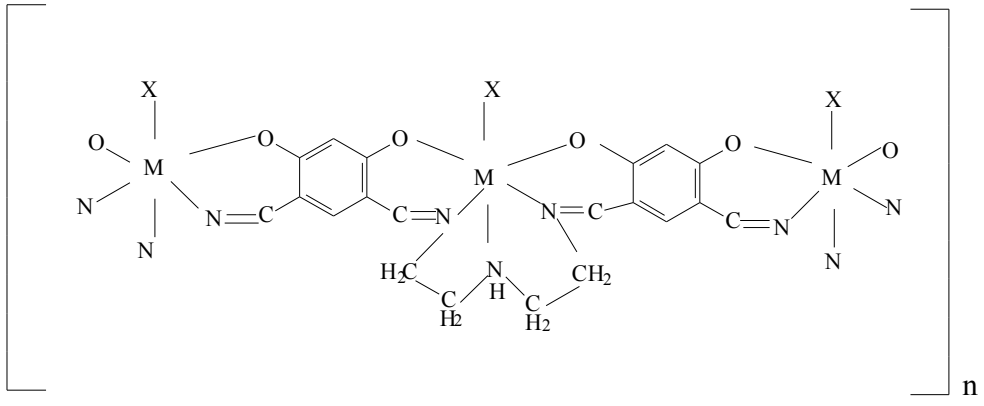


Figure 3: EPR spectrum of Cu(II) H_2-ADADTA



M = Cr(III) , Fe(III)
ML(OH) ; X = OH

M = Mn(II) , Co(II), NI(II), Cu(II), Zn(II)
ML.H_2O ; X = H_2O

Figure 4: Complexes of H_2-ADADTA

Conclusions

Based on the positions of υNH_2, $\upsilon C{=}N$ and $\upsilon C{-}O$(phenolic) in the spectra of the complexes of H_2-ADADTA, it is concluded that H_2-ADA and diethylene triamine undergo 1:1 condensation and bind to metal ions in bis-multidentate ONNNO 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 4)

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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