

## Synthesis and structural studies on divalent transition metal complexes of 5-acetyl 2,4-dihydroxy acetophenone semicarbazone

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**Abstract :** The synthesis of divalent transition metal complexes of a new dibasic, bis-chelating ligand 5-acetyl 2,4-dihydroxy acetophenone semicarbazone (H<sub>2</sub>-ADAS) with Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup> and their characterization on the basis of their elemental analyses, conductivity, magnetic moments, infrared and electronic spectral data has been studied.

Metal to ligand ratio in all the chelates has been found to be 1 : 1. The Schiff base behaves in a dibasic pentadentate manner with OO and ONN donor atoms. All the complexes have been assigned octahedral stereochemistry. The ligand H<sub>2</sub>-ADAS forms polymeric metal complexes with first row divalent transition metal ions.

**Keywords :** Transition metals, semicarbazone, synthesis.

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Transition metal complexes derived from multidentate ligands containing derivatized aromatic carbonyl cores have profusely enriched the field of coordination chemistry<sup>1</sup>. 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. The term bis-chelates was brought in to denote two chelating ligands producing metal complexes with metal-to-ligand ratio as 1 : 2. 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. The metal complexes synthesized from such ligands have been observed to possess interesting structural features like polymerism, antiferromagnetism and unusual geometries. Ni<sup>II</sup> complex of 2,5-dihydroxy *p*-benzoquinone (dhq)<sup>2</sup> wherein the ligand exhibits bis-bidentate nature has been reported.

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. In view of the importance of

multidentate bis-chelating ligands, the investigation on metal complexes of 5-acetyl 2,4-dihydroxy acetophenone (H<sub>2</sub>-ADA) and a number of its derivatives has been carried out in our laboratories<sup>3</sup>. Herein we report the synthesis of hitherto unknown, unsymmetric bis-chelating ligand 5-acetyl 2,4-dihydroxy acetophenone semicarbazone (H<sub>2</sub>-ADAS) and its metal complexes with Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup>.

### Results and discussion

The elemental analysis of metal complexes (Table 1) suggest metal to ligand ratio as 1 : 1. The analysis of metal, carbon, hydrogen and nitrogen support the following composition which derive further support from spectral and magnetic data, [ML.H<sub>2</sub>O], where M = Mn<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Cu<sup>II</sup> and Zn<sup>II</sup>; L = (ADAS)<sup>2-</sup> or (C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>)<sup>2-</sup>. Due to high insolubility of this complexes, molecular weight determinations were not feasible.

#### IR spectra :

Infrared spectra of the metal complexes exhibit characteristic changes with the free ligand spectrum (Table 2). There is a general broadening and merging of νNH

**Table 1.** Analytical and conductivity data of metal complexes of H<sub>2</sub>-ADAS

Complex	Analysis (%) : Found (Calcd.)				$\Omega_M$ (mho cm <sup>2</sup> mol <sup>-1</sup> )
	N	C	H	M	
Mn <sup>II</sup> -ADAS	12.99 (13.04)	40.95 (40.99)	3.39 (3.41)	16.78 (16.82)	12
Co <sup>II</sup> -ADAS	12.84 (12.88)	40.45 (40.49)	3.33 (3.37)	18.01 (18.09)	24
Ni <sup>II</sup> -ADAS	12.87 (12.86)	40.37 (40.42)	3.35 (3.36)	18.07 (18.10)	30
Cu <sup>II</sup> -ADAS	12.68 (12.72)	40.03 (40.00)	3.28 (3.33)	19.05 (19.09)	25
Zn <sup>II</sup> -ADAS	12.56 (12.61)	39.60 (39.63)	3.24 (3.30)	19.77 (19.81)	22

**Table 2.** Characteristic infrared frequencies of the complexes of H<sub>2</sub>-ADAS

Compd.	$\nu_{\text{NH}_2}$	$\nu_{\text{OH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	New bands
H <sub>2</sub> -ADAT	3450 3349	3063-2600	1650	1610	1238 1265	-
Mn <sup>II</sup> -ADAT	3385	-	1622	1585	1253 1283	861, 523, 440
Co <sup>II</sup> -ADAT	3372	-	1615	1589	1250 1282	845, 562, 480
Ni <sup>II</sup> -ADAT	3375	-	1620	1579	1248 1280	849, 570, 460
Cu <sup>II</sup> -ADAT	3380	-	1610	1593	1252 1285	949, 828, 569, 475
Zn <sup>II</sup> -ADAT	3383	-	1620	1595	1250 1283	950, 837, 532, 462

and  $\nu_{\text{OH}}$  frequencies in the spectra of metal complexes. The IR spectral studies show that all the phenolic groups get deprotonated during complex formation. The nature and intensity of the bands in the above mentioned region will support the presence of H<sub>2</sub>O. The rocking and wagging modes of water provide support for their coordination. A negative shift in  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  and positive shift in  $\nu_{\text{C-O}}$ , support the involvement of carbonyl oxygen, azomethine nitrogen and phenolic oxygens<sup>5</sup> in coordination.

Based on IR spectra, it is proposed that the ligand behaves as a bis-chelating system utilizing a bidentate OO sequence (phenolic and carbonyl oxygens) and a tridentate ONN sequence (phenolic oxygen, azomethine nitrogen and hydrazino nitrogen). Such a mode of metal binding, through five binding centres per ligand spread over two chelating sequences invariably leads to polynuclear complexes or metal complex polymers. Magnetic susceptibility and electronic spectral data (Table 3) provide further evidence in this regard.

#### Magnetic susceptibility :

In general the magnetic moments are in good agreement with the expected high spin configurations. Mag-

**Table 3.** Magnetic and electronic spectral data of the complexes of H<sub>2</sub>-ADAS

Complex	$\mu_{\text{eff}}$ (B.M.) Expt.	Electronic spectral bands ( $\nu_{\text{max}}$ cm <sup>-1</sup> )
Mn <sup>II</sup>	5.95	22720, 27000, 32000, 35700
Co <sup>II</sup>	4.82	8390, 17700, 25570
Ni <sup>II</sup>	2.89	8420, 9020, 25000
Cu <sup>II</sup>	1.94	8400, 10000, 13500

netic data shows that Mn<sup>II</sup> complex has spin free octahedral geometry<sup>6</sup>, Ni<sup>II</sup> and Cu<sup>II</sup> complexes possess octahedral geometry. High magnetic moment value for Co<sup>II</sup> complex may be due to high orbital contribution<sup>7</sup>. The values of magnetic moments show that despite polymeric nature, 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 spectral data provide supporting evidence for octahedral geometry.

#### Electronic spectra :

The electronic spectra of Mn<sup>II</sup> complex exhibit a num-

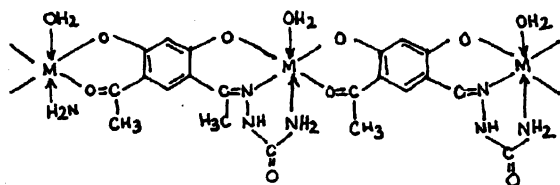
ber of bands which may be attributed to the spin forbidden transitions involving  ${}^6A$  ground state and several higher energy quartet states in accordance with octahedral geometry.

The electronic spectra of cobalt(II) complexes show bands, assigned to  ${}^4T_1 \rightarrow {}^4T_2$  (F) ( $\nu_1$ ),  ${}^4T_1 \rightarrow {}^4A_2$  ( $\nu_2$ ) and  ${}^4T_1$  (F)  $\rightarrow$   ${}^4T_1$  (P) ( $\nu_3$ ) transitions respectively. The ratio of  $\nu_2/\nu_1$  is 2 : 1 which falls in the range 1.9–2.2 which is expected for  $\text{Co}^{\text{II}}$  complex in octahedral geometry<sup>8</sup>.

The electronic spectrum of  $\text{Ni}^{\text{II}}$  complex is assigned to  ${}^3A_2 \rightarrow {}^3T_2$  ( $\nu_1$ ),  ${}^3A_2 \rightarrow {}^3T_1$  (F) ( $\nu_2$ ) and  ${}^3A_2 \rightarrow {}^3T_1$  (P) ( $\nu_3$ ) transitions for an octahedral splitting.

The electronic spectrum of  $\text{Cu}^{\text{II}}$  complex can be assigned to  ${}^2B_1 \rightarrow {}^2A_1$ ,  ${}^2B_1 \rightarrow {}^2B_2$  and  ${}^2B_1 \rightarrow {}^2E$  transitions which are due to distorted octahedral geometry.

On the basis of IR, magnetic and electronic spectral data, it may be concluded that the ligand  $\text{H}_2\text{-ADAS}$  forms polymeric metal complexes with  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ . Octahedral geometries of the complexes as supported by spectral and magnetic data are consistent with the composition of the complexes arrived on the basis of elemental analysis. The binding mode in the complexes is probably rigid from charge and configurational points to result in stable octahedral geometries. This is probably the reason for the inability of the ligand to accommodate higher valent  $\text{Cr}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  in complex formation. Despite multidensity of the ligands and polymeric nature of complexes, normal high spin equivalent magnetic moments have been exhibited by the complexes. Lack of metal-metal interactions is another notable feature. This is justified because the spin density on each metal ions in octahedral geometry is well separated from another metal ion by bulky phenyl groups as shown in Fig. 1 (Tentative structure).



M =  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$

Fig. 1. Complexes of  $\text{H}_2\text{-ADAS}$ .

## Experimental

**Synthesis of the ligand :** 5-Acetyl 2,4-dihydroxy acetophenone [ $\text{H}_2\text{-ADA}$ ] was synthesized by reported proce-

dures<sup>9,10</sup>. The Schiff base used was prepared by the usual method of condensation of  $\text{H}_2\text{-ADA}$  with semicarbazide hydrochloride. The product thus obtained was analytically pure. The ligand was characterized by elemental analysis, IR, (Table 1)  ${}^1\text{H}$  NMR studies.

**Synthesis of metal complexes :** To the methanolic solution of divalent metal chloride (0.0025 mol), 0.005 mol methanolic solution (30 ml) of  $\text{H}_2\text{-ADAS}$  was added in small amounts to get a clear solution. The pH of the reaction mixture was adjusted to 7 by adding sodium hydroxide (0.2 g) in methanol and then the mixture was refluxed for 4 h. The colored product obtained was filtered in hot condition and was washed thoroughly with small amounts of methanol, petroleum ether, diethyl ether and dried in vacuum. The purity of the complexes was tested by TLC using different solvent mixtures.

All the chemicals used were of AnalaR grade. Solvents were dried and distilled before use. 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 Atomic Absorption spectrometer Perkin-Elmer 2380. The conductivity of metal complexes was measured using Digisun Digital conductivity meter model D1909 having dip type cell calibrated with KCl solution. Mass spectra were recorded in Perkin-Elmer Hitachi RMU 6L spectrometer.  ${}^1\text{H}$  NMR data was obtained on Varian 1-200 MHz, using  $\text{DMSO}-d_6$  and  $\text{CDCl}_3$  solutions. UV-VIS-NIR spectra were recorded in solid state on UV Cary 2390 spectrometer. Magnetic susceptibilities of the complexes were recorded on a Faraday balance (CAHN-7550-03) at room temperature using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as standard.

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