

Studies on Schiff Base Complexes of Cobalt(II) and Cadmium(II) Derived from Histidine with Acetylacetone

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Schiff base complexes of cobalt(II) and cadmium(II) prepared by the condensation of acetylacetone with histidine has been synthesized and characterized by elemental analysis, molar conductance, magnetic moment, thermogravimetric analysis and infrared spectra. These Schiff base complexes are non-electrolytes. Magnetic and spectral data indicate the Co(II) and Cd(II) complexes to be tetrahedral.

Key Words: Cobalt(II), Cadmium(II), Complexes, Histidine.

INTRODUCTION

The transition metal complexes of Schiff base derived from acetylacetone with various amino acids have been the subject of intensive research, however, comparatively less attention has been paid to systems where Schiff base is derived acetylacetone with some amino acids. Most of the relevant work has dealt with complexes of the amino acids and Schiff bases, which are believed to be intermediates in biologically important animation processes¹. Although the Schiff bases derived from a variety of aldehydes and ketones and amines have been studied extensively as nitrogen donors. The complexes of the acetylacetone with amino acids have been comparatively little investigated so far. The present paper records the synthesis and characterization of Co(II) and Cd(II) complexes derived from acetylacetone and histidine.

EXPERIMENTAL

Histidine and acetylacetone (BDH) have been used without purification. Metal(II) acetates were of A.R. grade. The Schiff base was prepared by the condensation of acetylacetone with histidine.

The Schiff base metal complexes were prepared by the adding ethanolic solution of the Schiff base ligand drop-wise to the aqueous solution (0.1 M) of metal salt in a round bottom flask drop wise with constant stirring. After the addition, the mixture was allowed to stand on water bath for an hour. The metal complex so obtained as amorphous mass/crystals filtered out and washed with ethanol and dried in vacuum dessicator².

RESULTS AND DISCUSSION

(Acetylacetonone-histidine) cobalt(II) complex: The gravimetric estimation of the metal ion and elemental analysis of the complex formed by the interaction of the Schiff base ligand acetylacetonone-histidine with cobalt(II) acetate suggest that empirical formula of the complex is $[\text{Co}(\text{C}_{11}\text{H}_{15}\text{N}_3\text{O}_4)]$ (Table-1). The increase in melting point of the complex from that of the ligand also indicates the formation of the complex.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF
SCHIFF BASE AND ITS METAL(II) COMPLEXES

Complexes m.f./m.w.	Colour (m.p., °C)	Elemental analysis (%): Found (calcd.)				Magnetic moment (BM)
		C	H	N	M	
Acetylacetonone-histidine $\text{C}_{11}\text{H}_{15}\text{O}_3\text{N}_3$	Yellowish brown (179)	56.95 (55.90)	7.85 (6.33)	19.01 (17.72)	–	–
(Acetylacetonone: histidine)cobalt(II) $[\text{Co}(\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_3)\cdot\text{H}_2\text{O}]$ (311.94)	Brownish green (260)	43.51 (42.32)	5.98 (4.81)	14.58 (13.46)	19.96 (18.89)	4.46
(Acetylacetonone: histidine)cadmium(II) $[\text{Cd}(\text{C}_{11}\text{H}_{13}\text{N}_3\text{O}_6)\cdot 3\text{H}_2\text{O}]$ (401.40)	Light yellow (255)	34.05 (32.88)	5.91 (4.73)	11.58 (10.46)	29.35 (28.00)	Diamagnetic

The molar conductivity measurements carried out in methyl alcohol, DMF and DMSO at 10^{-3} M dilution indicate the non-electrolytic nature of the complex.

The IR spectra of the complex (Table-2) shows a broad band at 3405 cm^{-1} which may be assigned to $\nu(\text{O-H})$ vibrations. This is indicative of the involvement of water molecule in coordination with the metal ion. This is further supported by thermal analysis³. The absence of a stretch band at 3436 cm^{-1} in the IR spectra of the complex suggests the deprotonation of intramolecularly H-bonded (OH) and involvement of enolic O-atom in chelation with the metal ion. The downward shift of $\nu(\text{C-O})$ band in the IR spectra of the complex also supports the chelation through enolic O-atom⁴. The shift of $\nu(\text{C=N})$ stretch band and $\nu(\text{COO}^-)$ symmetrical stretch band to lower frequency in the IR spectra of the complex, is indicative of the involvement of azomethine nitrogen and carboxylate oxygen in coordination with the metal ion. Therefore, the ligand acetylacetonone-histidine acts in dibasic tridentate manner⁵.

TABLE-2
INFRARED SPECTRAL DATA (IN cm^{-1})

Name of ligand/complex	$\nu(\text{C=N})$	$\nu(\text{COO}^-)$	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
Acetylacetonone-histidine	1653	1445	3463	1547	–	–
(Acetylacetonone-histidine)cobalt(II)	1618	1416	3405	1509	–	–
(Acetylacetonone-histidine)cadmium(II)	1614	1410	3398	1510	512	421

The magnetic susceptibility measurements carried out at room temperature gives a value of 4.46 BM which indicates the presence of three unpaired electrons in the complex. Therefore, the high spin tetrahedral stereochemistry may be suggested for this 1:1 cobalt(II) complex⁶ (Fig. 1a).

(Acetylacetonone-histidine) cadmium(II) complex: The gravimetric estimation of metal ion in and elemental analysis of the complex indicates the 1:1 metal: ligand stoichiometry. The vast difference between the melting points of the ligand and the complex is also suggestive of the formation of the complex. On the basis of elemental analysis the empirical formula of this light yellow colored complex could be given as: $[\text{Cd}(\text{C}_{11}\text{H}_{19}\text{N}_3\text{O}_6)]$.

The molar conductivity measurements carried out in methanol, DMF and DMSO at 10^{-3} M dilution shows non-electrolytic behavior of the complex.

The infrared spectra of the complex when compared with that of ligand reveals that $\nu(\text{C}=\text{N})$ stretch band at 1653 cm^{-1} and $\nu(\text{COO}^-)$ symmetrical stretch band at 1445 cm^{-1} are shifted to lower frequency in the complex⁷. This downward shift is suggestive of the involvement of azomethine N-atom and carboxylate O-atom in coordination with the metal. The two stretch bands in the lower region at 512 cm^{-1} (Cd-N) and at 421 cm^{-1} (Cd-O) also support the presence of coordinated azomethine nitrogen and carboxylate oxygen.

The IR spectra of the complex shows a band at 3398 cm^{-1} assignable to $\nu(\text{O-H})$ vibrations is suggestive of the involvement of water molecules in coordination⁸. A medium broad band appears at 3436 cm^{-1} assignable to $\nu(\text{O-H})$ vibrations in the IR spectra of the ligand is absent in the complex which suggests the involvement of enolic oxygen in chelation with the metal ion. It is further supported by the downward shift in $\nu(\text{C-O})$ vibrations in the spectra of the complex⁹. The magnetic susceptibility measurements carried out at room temperature suggest the diamagnetic nature of the complex which indicates spin paired octahedral stereochemistry for this 1:1 cadmium(II) complex¹⁰. The above analytical data suggest the following octahedral geometry for this light-yellow coloured 1:1 (acetylacetonone-histidine)cadmium(II) complex¹¹ (Fig. 1b):

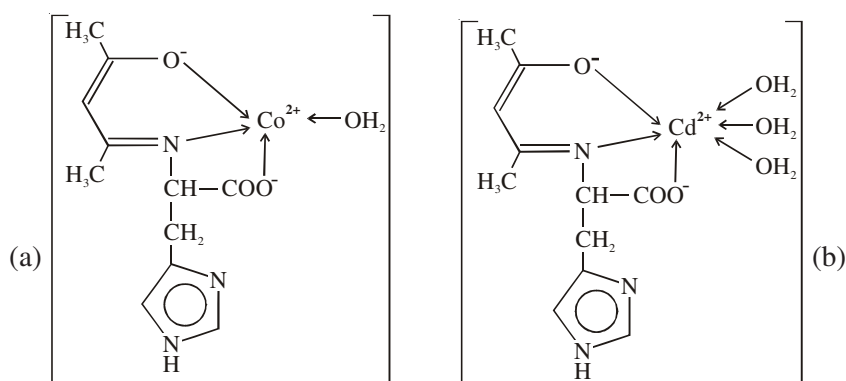


Fig. 1. Suggested structure of meta(II) complexes

ACKNOWLEDGEMENTS

The author is grateful to Dr. N.K. Agarwal, Head, Department of Chemistry, Principal, Bareilly College, Bareilly for extending all possible facilities.

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(Received: 22 April 2009;

Accepted: 22 December 2009)

AJC-8209