RESEARCH ARTICLE

Synthesis and Characterization of Mixed Ligand Complexes with Ethyl -α- Isonitrosoacetoacetate and Dienes

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Abstract: Mixed ligand Co(II), Ni(II) and Cu(II) complexes Co(EINA)$_2$(PPD), Ni(EINA)$_2$(PPD) and Cu(EINA)$_2$(PPD), formed with ethyl-α-isonitrosoacetoacetate and dienes have been synthesized and characterized by their elemental analysis, infra red spectra and magnetic measurements. Ethyl-α-isonitrosoacetoacetate shows a tridentate behavior with coordination occurring through two oximino nitrogen atoms and further two coordination sides of metal ion are satisfied by oxygen atom. Diene acts as a bidentate ligand coordinating through the two nitrogen of the amino group.

Keywords: Synthesis, characterization, Co(II), Cu(II) and Ni(II), Ethyl-α-isonitrosoacetoacetate, Dienes

Introduction

The role of mixed ligand complexes in biological systems is well known[1]. Synthesis and charecterization of some bivalent simple metal complexes of isonitrosoacetophenon have been reported[2-5]. Ethyl-α-isonitrosoacetoacetate (EINA) is bidentate ligand containing two corboxylate groups and NH group. It can coordinate with the metal ion through the only two oximino nitrogen atom acting as a bidentate ligand. It also coordinate through the corboxylate oxygen atom and the nitrogen of the amino group and thus acts as a bidentate ligand. Complexes of Co(II), Ni(II) and Cu(II) of diamidediimine macrocyles[6] and mixed ligand complexes of Co(II) and Cu(II) has been reported[7]. The present paper outlines the synthesis and characterization of mixed ligand complexes formed with ethyl-α-isonitrosoacetoacetate and *p*-phenylenediamine (PPD).

Experimental

All the chemicals used were of analytical grade.

Preparation of mixed ligand complexes

A warm ethanolic solution of metal salts (0.01 M) was added to ethanalic solution of ligand (0.02 M) and *p*-phenylenediamine (0.01 M). The resulting solution was refluxed for about six

hours. The complex thus formed was filtered and washed with alcohol and dried in vacuum over fused $CaCl_2$ The metal estimation was carried out by standard method and nitrogen by Kjeldahl method. The conductance was measured in DMF and DMSO solvent on and Elico CM-82 Conductivity Bridge. The magnetic susceptibility measurement at room temperature was made on Gouy's balance. The IR spectra were recorded on Perkin-Elmer-137 instrument in Nujol mull/KBr pellets ^{1}H NMR spectra were recorded on a Bruker WP 80 SY spectrometer.

Results and Discussion

The elemental analysis shown in Table 1 indicates that all the metal complexes have 1:2 stoichiometry and are dark colour substances, soluble in DMF and DMSO. The molar conductance values obtained for these complexes at the concentration of 10^{-3} are in the range of 2.9 to1.07 ohm^{-1} mo1 cm^2. These values are too low to account for any dissociation of the complexes can be regarded as non-electrolytes. The magnetic moment values for Cu(II) complexes are in the range of 1.58 BM, Ni(II) complexes 2.46 BM and Co(II) 4.28 BM having octahedral structure.

Table 1. Elemental analysis and magnetic moment of the complexes

S. No	Empirical formula	% of Carbon	% of Hydrogen	% of Nitrogen	% of Metal	Molar conductance concentration 10^{-3}	
		Found Calc.	Found Calc.	Found Calc.	Found Calc.	Magnetic moment µBM	
1	Cu(EINA)$_2$ (PPD)	44.35 (44.30)	5.40 (5.33)	11.50 (11.48)	13.30 (13.33)	1.07	1.58
2	Ni(EINA)$_2$ (PPD)	44.80 (44.72)	5.45 (5.38)	11.62 (11.59)	12.25 (12.20)	1.87	2.46
3	Co(EINA)$_2$ (PPD)	44.70 (44.74)	5.42 (5.38)	11.62 (11.60)	12.18 (12.15)	2.9	4.28

The infrared spectra of HEINA, PPD and its metal complexes with Co(II), Ni(II) and Cu(II) have been recorded. And the significant infra red bands are summarized in Table 2. Coordination sites of the HEINA, PPD have been determined by careful comparison of infra red spectra of the complexes. The infra red spectra of HEINA and PPD gave a strong band at 3410 cm^{-1} which may be assigned to OH and N-OH group. Which was absent in metal complexes.

Table 2. Significant infra red bands

Assignments	HEINA	Ni(EINA)$_2$PPD	CO(EINA)$_2$PPD	Cu(EINA)$_2$PPD
Ar-H	3250	3218	3220	3224
OH &N-OH	3410	-----	-----	---
-O-H	-----	3216	3326	3220
C=O	1620	----	----	-----
C=N	-----	1590	1604	1610
CH$_3$	1190	1168	1200	1170

The infra red spectra of HEINA gave a strong band at 1620 cm^{-1} which may be attributed to the ester C=O. The infra red spectra of metal complexes gave two new band at 3216 cm^{-1} and 1590 cm^{-1} which is due to O-H and –C=N group take part in coordination of ligand.

The strong band due to $\upsilon C = O$ seen at 1620 cm^{-1} in (HEINA) (PPD) is absent in all the complexes indicating a successful attachment of carboxyl oxygen to metal ion. The $\upsilon C = N$ band appear in the 1590-1628/cm reason for metal complexes of (HEINA) (PPD) while ligand frequency for $\upsilon C = N$ band appear at 1610/cm shift of the band towards the low frequency region indicates wider delocalization of the electric charge in the newly form chelate ring. This also suggest the strong bonding of $\upsilon C = N$ group with the metal in coordination.

References

1.   Sigel H, Metal, Ions in Biological Systems, Mixed ligand complexes, Dekker M, New York Chapter I, Vol. 2, 1973.
2.   Natrajan C and Hussain A N, *Indian J Chem.,* 1983, **22A**, 527.
3.   Talwar U B and Halder B C, *J Inorg Nucl Chem.,* 1970, **32,** 213-220.
4.   Prakash D, Singh B P and Gupta O P, *Vijnana Parishad Anusandhan Patrika,* 1992, **35(4)**, 305.
5.   Banerjee A K, Layten A J, Nyholm R S and Truter M R, *J Chem Soc.,* 1970, **292A**, 18-84
6.   Ahmed A A, BenGuzzi S A and Hadi A A, *J Sci Appl.,* 2007, 79.
7.   Singh Mahesh K, Das Arijit and Paul Bijaya, *J Coord Chem.,* 2009, **62(16),** 2745-2754.