

Synthesis and Characterization of Co (II), Ni (II) and Cu (II) Complexes With Ethyl - α - Isonitrosoacetoacetate(HEINA)

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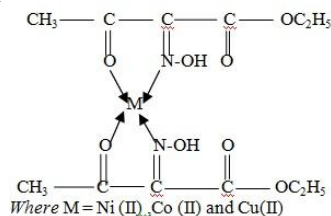
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Abstract: Ethyl- α -Isonitrosoacetoacetate has been prepared by reacting Ethyl acetoacetate and sodium nitrite. Co (II), Ni (II) and Cu (II) Complexes have been prepared by reacting metal acetate with this ligand Ethyl- α -Isonitrosoacetoacetate. All these complexes are dark in colour. They have been characterized by elemental analysis, magnetic measurements and spectral studies. The complexes were found to have composition ML_2 , where L = Ethyl- α -Isonitrosoacetoacetate and M = Cu (II), Ni (II) and Co (II). On the basis of elemental and spectral studies six coordinated octahedral geometry assign for Co (II), Ni (II) and square plane for Cu (II) complexes.

Key-words: Magnetic susceptibility, cobalt, nickel, copper, ethyl- α -isonitrosoacetoacetate

I. Introduction

There is great interest in synthesis and characterization of coordination compounds. This is because the coordinated ligand are biologically more active than the uncoordinated one.¹ The Co (II) complex of 2- acetyloxybenzoic acid (aspirin), a ligand used as an analgesic is reported to be more significantly active as an anti- inflammatory agent than the uncoordinated one.² Coordinating ability of isonitrosoacetophenon and its derivatives with transition element³⁻⁶, alkali metal⁷⁻⁹ and alkaline earth metal¹⁰. On coordination the biological activity of mixed ligand metal complexes of ethyl- α -isonitrosoacetoacetate changes markedly. In view of these interesting properties of ligand metal complexes, synthesis and characterization of Co (II), Ni (II) and Cu (II) of ethyl- α - isonitrosoacetoacetate are reported.



II. Experimental

All the chemicals used were of analytical grade.

2.1 Preparation of Ligand

Ethyl acetoacetate 1.4 moles and 3.5 mole of glacial acetic acid were taken in three naked round bottom flask fitted with thermometer, reflux condenser and mechanical stirrer and cooled in ice bath at 0⁰ C and a solution of 95 % sodium nitrite was added over a period of one hour and temperature being kept between 5⁰ C to 10⁰ C. This mixture mixed with double distilled water and stirring for two hour and extracted with ether. After drying ether solution with sodium sulphate the solvent was distilled off on a steam bath the crude product was dissolved in toluene and cooled to -13⁰ C to -15⁰ C. The separated white crystals were filtered, washed and analyzed.

2.2 Preparation of complexes

A warm ethanolic solution of metal acetate (0.01 m) was added to ethanolic solution of ligand (0.02 m). The resulting solution was refluxed for about six hours. The complex thus formed was filtered, washed with alcohol and dried at 110⁰ C for 4 to 6 hours. Re-crystallized from chloroform and analyzed for Carbon, Hydrogen, and Nitrogen.

III. Result and Discussion

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

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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. The elemental analysis shown in table-1 indicates that all the metal complexes have 1:2 stoichiometry and are dark in colour, soluble in DMF and DMSO. The molar conductance values obtained for these complexes at the concentration of 10^{-4} is in the range of $0.30-0.535\text{ohm}^{-1} \text{ mol cm}^2$. These values are too low to account for any dissociation of the complexes can be regarded as non-electrolyte. The magnetic moment values for Cu (II) complexes are in the range of 5.05 – 5.14 BM indicating that the Cu (II) complexes are typically high spin complexes and having square planer structure. The Ni (II) complexes were found to diamagnetic indicating octahedral coordination of ligands around Ni (II) ion. The CO (II) complexes exhibit magnetic moment in the range of 2.34-2.95 BM suggestive of octahedral nature for these complexes. HEINA shows a broad band around 3400 cm^{-1} is assigned to the hydrogen bonded –OH stretching this assignment is further confirming by the presence of new bond at 2460 cm^{-1} . HEINA reveals two peaks at 1760 cm^{-1} and 1745cm^{-1} which may be attributed to the ester C=O and Ketone C=O respectively. The band near 1640 cm^{-1} may be assign to the C=N stretching frequency which is usually appeared in the spectra of oxime in the range $1685 -1650 \text{ cm}^{-1}$. The peak 1470 cm^{-1} may possible be due to CH_2 . The asymmetric and symmetric bending modes of CH_3 overlap with bands at 1458 cm^{-1} and 1378 cm^{-1} respectively. Stretching band and COOC_2H_5 group at 1268 cm^{-1} and 1078 cm^{-1} .

The N-O frequency in simple oxime appears between $930-960 \text{ cm}^{-1}$ in the peak near 1168 cm^{-1} and 950 cm^{-1} in HEINA may therefore attributed to N-O stretching mode¹¹.

Table-1: Elemental Analysis and Magnetic Moment of the Complexes

Compounds	% C	%H	%N	%Metal	μ	Molar Conductance	Concentration
HEINA	45.30 45.28	5.60 5.70	5.80 8.80	----	----	----	----
Cu(EINA) ₂	37.74 (37.64)	4.77 (4.81)	7.33 (7.40)	16.65 (16.1)	0.95	0.520	$1.25 \times 10^{-4} \text{M}$
CO(EINA) ₂	38.20 (38.10)	4.77 (4.88)	7.42 (7.50)	15.64 (15.17)	2.91	0.030	$1.1 \times 10^{-3} \text{M}$
Ni(EINA) ₂	38.22 (38.30)	4.77 (4.85)	7.43 (7.50)	15.58 (15.61)	2.34	0.535	$6.1 \times 10^{-4} \text{M}$

Table-2:

Assignments	HEINA	Ni(EINA) ₂	CO(EINA) ₂	Cu(EINA) ₂
OH	3400	3400	3200	3200
Ester C=O	1760	2142	2420	2390
Ketone C=O	1745	----	----	1740
C=N	1640	1605	1600	1610
CH_3	1458	1410	1410	1440
	1378	1390	1380	1388
COOC_2H_5	1268	1300	1310	----
	1078	1135	1090	
N--O	970	965	960	965

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