

## Synthesis and electronic spectral studies on some mixed Ligand diaminedithiolate complexes of nickel(II).

Mahesh Kumar, Dept. of Chem.  
M.M College Bhargalpur  
Biswajit Kumar Biswas  
At-Goalgaon, Po- Shikarpur,  
Dist-Uttar Dinajpur, (W.B) 733201

**Abstract** : Three mixed ligand complexes of the Ni(L)(mcda) where L : en, O-phen or bipy and mcda 1- methoxycarbonyl-1-cyanoethylene-2,2-dithiolate have been synthesized and characterised by elemental analysis and visible electronic spectroscopy. Electronic Spectra show that geometry around nickel ion is square planar

(**Key Words** : Diimine, dithiolate, complex nickel)

### Introduction

Mixed ligand complexes of the type pt(diamine)(dithiolate) have been studied for their luminescence behaviour. Mixed ligand complexes of other metals with nitrogen sulphur donors have also been reported. These complexes have been studied for their various applications such as, sensitizer non linear optical material, preparation of metal sulfide film, electrical conductivity and biological.

Synthesis characterization and properties of some mixed ligand complexes of nickel with various heterocyclic bases and dithiolate ligand, [S<sub>2</sub>C=C(CN)COOC<sub>2</sub>H<sub>5</sub>]<sub>2</sub> have appeared in literature recently. In the present work synthesis, and characterization of complexes of nickel with various diamine ligands and dithiolate ligands, 1-methoxy carbonyl-1, 1- cyanoethylene-2,2-dithiolate have been reported.

### Experimental

All the chemicals used were of analytical reagent grade. Sulfur was estimated as BaSO<sub>4</sub> and nickel by standard gravimetric procedure visible spectra was recorded in ethanol. The dithiolate ligand, Na<sub>2</sub>S<sub>2</sub>C(CN)COOCH<sub>3</sub> was synthesized by reported method. Finally crushed NaOH (8 g 0.2 mole) was taken in 40 ml methanol, and a solution of ester methylcyanoacetate (0.1 mol) and CS<sub>2</sub> (10ml., 0.1 mol) in 20ml methanol was added to it dropwise with constant stirring and maintaining temperature in the range 15-20°C. Yellow product formed was filtered off, washed with alcohol, ether and dried in vacuum over CaCl<sub>2</sub>.

#### Synthesis of complexes Ni(L) ( S<sub>2</sub>C=C(CN)COOMe); L=en, O-phen or bipy

To 15 ml aqueous ethanolic solution nickel acetate (2mmol) 20 ml of an aq. ethanolic solution/suspension of ethylenediamine (2mmole) was added with stirring. The product, thus formed, was filtered off, washed with ethanol and ether dried in vacuum over CaCl<sub>2</sub>.

Two other complexes of nickel with diamine ligands, o-phen and bipy and dithiolate ligand were prepared similarly by taking metal and diamine ligand in 1:1 molar ratio followed by addition of solution dithiolate ligand.

## Results and discussion

Formation of these complexes is believed to take place via following reactions coordination compounds were established using physicochemical methods.



### (i) Materials:

All the chemicals needed were of BDH(A.R.) grade and were used as received without further purification.

### (ii) Synthesis of coordination compounds:

0.01 mole of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in hot water and filtered. 0.02 mole of the ligand(LH) was dissolved in hot ethanol and the solution was filtered hot. The two solutions were mixed in round-bottom flask and pH of the solution was adjusted using  $\text{NH}_4\text{OH}$  and  $\text{HCl}$ . The mixture was refluxed for about 5 hours over a water bath using water condenser. The precipitated solids were filtered under suction and dried at  $110^\circ\text{C}$  in an electronic oven for about 4 hours. Their m.p.'s were

then recorded. All the coordination compounds were found to be insoluble in common solvents like water, ethanol, CS, methanol but were soluble in DMF and DMSO.

### (ii) Measurements:

Elemental analyses were carried out using a Perkin Elmer 2400 elemental analyser. Molar conductance was measured using 10<sup>-3</sup> M solution in DMF at  $30^\circ\text{C}$  on Toshniwal TSM-15 bridge. Magnetic susceptibility measurements were done at room temperature by Gouy's balance using  $\text{Co}[\text{Hg}(\text{CNS})_4]$  as the standard. The UV-Visible spectra of coordination compounds were recorded on Shimadzu 2100 spectrophotometer. The IR spectra were recorded using KBr pellet on a Perkin Elmer 283 IR spectrophotometer. The <sup>1</sup>H NMR spectra were recorded with 90 MHz NMR spectrophotometer using TMS as internal indicator. Molecular mass of the coordination compounds was determined cryoscopically.

## Results and Discussion:

The analytical data (Table-1) were in good agreement with the proposed stoichiometry of the coordination compounds. The observed molecular masses of coordination compounds showed their monomeric nature. The molar conductance data (Table-2) for  $[\text{Cu}(\text{LH})_2\text{Cl}_2]$ , prepared, at pH=10.0 (alkaline medium) showed their non-electrolytic nature. The molar conductance value of 182  $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  for  $[\text{Cu}(\text{LH})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ , prepared at pH=7.0 (neutral medium) indicated its 1:2 electrolytic nature. The electrolytic nature of this coordination compound is due to the presence of two chloride ions outside the coordination sphere. It was further confirmed by the addition of  $\text{AgNO}_3$  reagent to the coordination compound solution leading to the formation of two moles of white precipitate of  $\text{AgCl}$  per mole of coordination compound.

**Table – 1**  
**Micrianalytical data of coordination compounds**

Sl. No.	Coordination compounds	% Found (% Calculated)						Molecular mass found( Calculated)	M.P.
		C	H	N	S	Cl	Cu		
1	[Cu(LH) <sub>2</sub> Cl <sub>2</sub> ] Light Blue	53.71 (53.85)	3.92 (3.89)	12.44 (12.56)	9.68 (9.57)	10.75 (10.62)	9.62 (9.49)	670.4 (668.5)	193 <sup>o</sup> C
2	[Cu(LH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> Deep Blue	51.38 (51.10)	4.16 (4.25)	11.87 (11.92)	9.25 (9.08)	10.32 (10.07)	9.22 (9.01)	701.2 (704.5)	196 <sup>o</sup> C
3	[Cu(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] Greenish Yellow	56.88 (57.00)	4.39 (4.43)	13.46 (13.30)	10.24 (10.13)	-	10.31 (10.05)	628.4 (631.4)	206 <sup>o</sup> C

NiL ] (CH<sub>3</sub>COO)<sub>2</sub> + Na<sub>2</sub>S<sub>2</sub>C<sub>2</sub>(CN)COOCH<sub>3</sub> Ni(L)(S<sub>2</sub>C<sub>2</sub>(CN)COOCH<sub>3</sub>) + 2CH<sub>3</sub>COONa + L Where L is diimine ligand.

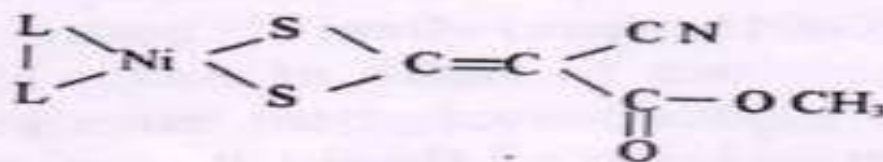
### Electronic Spectra

Visible spectrum of the complex, [Ni(en)(mcda)] show absorption band at 425 nm and somewhat broad band at 600 nm. In the complex Ni(o-phen)(mcda)] an absorption band at 475 nm with shoulder at 440 nm position have appeared. Visible spectrum of [Ni(bipy)mcda] has band at 615 nm position. Band around 800 nm has not been found in these complexes ruling out octahedral geometry. The electronic spectra of complexes suggest square planar geometry around nickel ion." Spectra of these complexes are comparable.

On the basis of foregoing discussion and earlier literature of mixed ligand M(diimine) (dithiolate) complexes, following geometry has been proposed tentatively.

L=en, o-phen or bipy

Fig.1 Proposed structure of the complexes .



L = en, o-phen or bipy

**Fig. 1 Proposed structure of the complexes.**

## References

1. J. A. Zuleta, M.S.Burberly, R.Eisen berg, Coordination Chemistry Reviews, 97, 47 (1990)
2. S.D. Cumines and R.Eisenberg, J.Am.Chem. Soc., 118(8), 1949 (1996).
3. MK.Singh, A. Das, B.Paul, Journal of coordination Chemistry, 62, 2745 (2009).
4. P.J.Rani, S. Thirumaran, European Journal of Medicinal Chemistry, 62, 139 (2013).
5. M.K.Singh, S.Sutradhar, B. Paul, D. Barman &A.Das,J. Indian Chem. Soc., 90, 163 (2013).
6. S.D. Cummings, Lap-TakCheng., and R.Eisenberg, Chem, Mater, 9, 440 (1997).
- 7 E.A.M. Geary, L.J. Yellowlees, L.A. Jack, I.D.H. Oswald, S. Parsons, N.H.irata, J. R. Durrant&N.Robertson, Inorg.Chem, 44(2), 242 (2005).
8. S.D. Cumines Lap-Tak Cheng and R.Eisenberg, Chem. Mater. 9(2).440 (1997).
9. N. Srinivasan, S.Thirumaran, &S.Ciattini, SpectrochimicaActa Part A: Molecular and Biomolecular spectroscopy, 102, 263 (2013).
10. Z.Hao, Z. Tang. Q.Shi, InorganicaChimicaActa, 284(1) 112, (1999).
11. C.A.Bolos, A.T. Chaviara, D.Mourelatos, Z.Lakovidou, E.Mioglou, E.Chrysogelou, A. Papageorgiou, Bioorganic & Medicinal Chemistry, 17(8) 2142 (2009).
12. M.K.Singh, S. Sutradhar, B. Paul, D. Barman and A.Das., J. Indian Chem Soc.,90, 1 (2013)
13. K.A. Jensen and L. Henriksen, Acta Chem. Scand 22, 1108 (1968).
14. A.I. Vogel "A Text Book ofQuantitative Inorganic Analysis" Longmans, London (1961).
- 15 A.B.P. Lever Inorganic Electronic Spectroscopy 2nd Edition, Elsevier Publication (1984).