

BKR 2010137/22201

Coordination Compounds of Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} with Tridentate ONS Donor Azo dye Ligands.

Bipin B. Mahapatra* and Saroj Ku. Panda **

**P.G. Department of Chemistry, G.M. (Autonomous) College, Sambalpur – 768004 (Orissa). India

Telephone No : - 06632401177

E-mail: mahapatra.bipin@yahoo.com*, sarjobadmal@gmail.com**

(Received September 7, 2010; Accepted December 10, 2010)

ABSTRACT : Twelve monomeric co-ordination compounds of Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Hg^{II} with two ONS tridentate azodye ligands have been synthesized. The characterizations of these compounds have been made basing upon analytical conductance, magnetic susceptibility, I.R, electronic spectra, E.S.R. and N.M.R. spectral data. The Co^{II} and Ni^{II} complexes are found to be octahedral, Cu^{II} complexes are distorted octahedral and Zn^{II} , Cd^{II} and Hg^{II} complexes are found to be four co-ordinated possibly with tetrahedral geometry.

Key words: Azodye complexes, Co-ordination compounds, Metal complexes.

Introduction

The synthesis of co-ordination compounds using polydentate azodyes as ligands is of recent interest. Besides laboratory and industrial applications, the chemotherapeutic use¹ (Gaind *et al*, 1964) of azodyes has inspired the modern chemists to prepare new metal chelates by reacting with new polydentate azodyes with different transitional and non-transitional metal ions, in order to study their pharmacological properties. In continuation of our earlier work² (Mahapatra *et al* 2009), the present paper describes the preparation of two new oxygen, nitrogen and sulphur donor tridentate azodye ligands (Figs. 1 & 2) and their twelve monomeric co-ordination compounds.

Materials and Methods

All the chemicals were of B.D.H. or E. Merck grade. Metal, carbon, hydrogen, nitrogen and chlorine were estimated by standard methods³ (Vogel, 1969). Conductivity measurement in DMF was made using Toshniwal CL 01-06 Conductivity bridge. Magnetic moment was measured at RT by Gouy method. I.R. Spectra (KBr) were recorded on an IFS 66U Spectrophotometer, electronic spectra (10^{-2}M in acetone) using Hilger-Watt uvispeck spectrophotometer, N.M.R. spectra on a Jeol GSX 400 with acetone-d₆ as solvent and TMS as internal standard and ESR spectra on an E₄- spectrometer.

**To whom correspondence should be addressed.

Preparation of the ligand:

Preparation of ammonium phenyldithiocarbamate

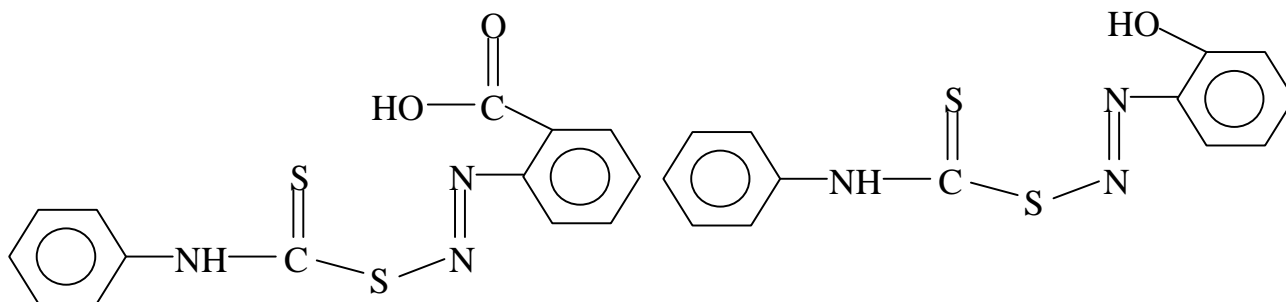
Conc. ammonium hydroxide (8.5 ml) was added slowly to distilled aniline (9.13 ml) at 0 – 5°C in an ice salt freezing mixture. Then distilled carbon disulphide (6.0 ml) was added drop wise with constant stirring for 1 hour with the help of a mechanical stirrer. The resulting white crystalline solid was obtained with decomposition temperature 33 - 35°C. It was dried on exposure to air.

Preparation of o-hydroxy/o-carboxyphenylazophenyldithiocarbamate :-

To a cold solution of freshly prepared ammoniumphenyldithiocarbamate (9.3 gm in 100 ml), a cold aqueous solution of equimolecular amount of the diazonium chlorides obtained from O-aminophenol/O-aminobenzoic acid was added drop wise with stirring. The resulting solid compounds of reddish brown azodyes were obtained. These were then washed with distilled water, dried and crystallized from absolute ethanol.

Preparation of the complexes :-

The metal chlorides in ethanol were mixed separately with the ligands in dioxane in 1:1 molar ratio. The resulting solutions were heated to ~60 – 70°C for about 1 hour in a heating mantle. On cooling the P^H of the solutions were raised to ~7. The solid complexes thus separated were then washed with ethanol followed by ether and then dried in vacuum.



[Fig-1]

[Fig-2]

Results and Discussion

The co-ordination compounds synthesized have the compositions $[M(L/L^1)Cl(H_2O)_2]$, $[M^1(L/L^1)Cl]$ where $M=Co^{II}$, Ni^{II} , Cu^{II} ; $M^1=Zn^{II},Cd^{II}$, Hg^{II} ; $LH = o$ -carboxyphenylazophenyldithiocarbamate ($C_{14}H_{11}N_2OS_2$) (Fig 1) $L^1H = o$ -hydroxyphenylazophenyldithiocarbamate. ($C_{13}H_{11}N_2OS_2$) (Fig 2). All the complexes are either crystalline or amorphous in nature, and soluble in common organic solvents. The non-electrolyte nature of the complexes in DMF is shown from the low conductance values ($4.2 - 5.6 \Omega^{-1} cm^2 mol^{-2}$). Both the ligands can be represented by two possible structure 3(a) and 3(b). In structure 3(a) the secondary nitrogen atom is bonded to the metal ions and in structure 3(b) the bonding of thione sulphur to the metal ions is observed.

The 'g_{av}' values of the complexes [CuLCl(H₂O)₂] and [CuL¹Cl(H₂O)₂] were found to be 2.0979 and 2.0441 respectively by Kneubuhl's method¹⁴(Kneubuhl, 1966). This type of spectra may be due to dynamic or pseudo rotational behaviour of Jahn-Teller distortion. The covalent nature of the Cu-L band is indicated from low 'g_{av}' value (< 2.3). This value is consistent with Cu-O and Cu-N bonded copper complexes.

The Zn^{II}, Cd^{II} and Hg^{II} complexes are suggested to be four-coordinated probably with tetrahedral geometry basing upon analytical, conductance and i.r spectral data.

Hence both the azodyes behave as tridentate ligands being bonded through azo nitrogen, phenolic or carboxylic oxygen and thione sulphur atoms.

Table-1 Analytical and Physical data of the complexes:

Compound	Colour	%Metal Found (Calculated)	%Nitrogen Found (Calculated)	%Sulphur Found (Calculated)	μ _{eff} B.M.
LH (C ₁₄ H ₁₁ N ₂ S ₂ O ₂)	Reddish brown	-	9.1 (9.24)	20.9 (21.12)	-
L ¹ H (C ₁₃ H ₁₁ N ₂ S ₂ O)	Reddish brown	-	9.9 (10.18)	23.1 (23.27)	-
[CoLCl (H ₂ O) ₂]	Violet	13.5 (13.63)	6.3 (6.47)	14.7 (14.80)	5.0
[CoL ¹ Cl (H ₂ O) ₂]	Brown	14.4 (14.57)	6.8 (6.92)	15.7 (15.82)	5.1
[NiLCl (H ₂ O) ₂]	Brown	13.4 (13.57)	6.3 (6.48)	14.7 (14.81)	3.1
[NiL ¹ Cl (H ₂ O) ₂]	Reddish brown	14.3 (14.51)	6.8 (6.93)	15.7 (15.83)	3.0
[CuLCl (H ₂ O) ₂]	Coffee colour	14.4 (14.53)	6.2 (6.40)	14.5 (14.64)	1.8
[CuL ¹ Cl (H ₂ O) ₂]	Brown	15.4 (15.53)	6.7 (6.84)	15.5 (15.64)	1.8
[ZnLCl]	White	16.0 (16.23)	6.8 (6.95)	15.7 (15.89)	-
[ZnL ¹ Cl]	Brownish white	17.3 (17.44)	7.3 (7.47)	16.9 (17.07)	-
[CdLCl]	white	24.8 (24.99)	6.0 (6.22)	14.1 (14.23)	-
[CdL ¹ Cl]	White	26.5 (26.64)	6.5 (6.63)	14.9 (15.17)	-
[HgLCl]	Grey	37.1 (37.28)	5.0 (5.20)	11.7 (11.89)	-
[HgL ¹ Cl]	Brown	39.1 (39.32)	5.3 (5.49)	12.4 (12.54)	-

ACKNOWLEDGEMENT: The authors are thankful to the Head, SAIF, I.I.T. Madras for providing I.R., N.M.R. and E.S.R. spectral data.

References

1. Gaiind K.N and Khanna J.M: *Indian J. Pharm* **26**, pp.34-38, 1964. Goodman L.S. and Gilman A: "*The Pharmacological basis of Therapeutics*". 4th Edⁿ, Mc. Millan, New York, P-III, 1970.
2. Mahapatra B.B. and Sarangi A. K: *J. Indian Chem. Soc* **86**: pp. 559-563. 2009. Mahapatra B.B. and Patel N: *J. Indian Chem. Soc* **86**: pp. 518-523 2009. Mahapatra B.B. and Patel N: *Bangladesh Journal of Scientific and Industrial Research* 44(4): pp. 445 – 452. 2009.
3. Vogel A.I: *Text Book of Quantitative Analysis*. 3rd Edⁿ. Longman London. 1969.
4. Deccan G.B. and Phillips R.J: *Coord. Chem. Rev* **33**, pp. 227-231, 1980. Bellamy L.J: "*The infrared spectra of complex molecules*", 3rd Edⁿ; Chapman and Hall, London. Nakamoto K: "*Infrared Spectra of Inorganic and Co-ordination Compounds*", 4th Edⁿ Wiley New York, pp. 230 – 233, 1986.
5. Mishra, L. K and Keshari, B. N: Thiohydrazides as complexing agent part 1 – complexes of Ni(II), Co(II & III), Cu(II), Zn(II), Cd(II), Pd(II) & Hg(II) with O – Hydroxyphenylthiohydrazide. *Indian J.Chem; Sect.A*, **28**: pp 883 - 887. 1981
6. King R.B and Bisnette M. B: Organonitrogen derivatives of Metal carbonyls. II. Aryl Azo derivatives of Molybdenum. *Inorg. Chem*, **5**, pp. 300-306, 1966.
7. Nakamoto K, Fujita T, Condrate R. A and Morimoto M: *J. Chem. Phys.*, **30**, pp.421-424, 1963.
8. Nakamoto. K: *Infrared Spectra of Inorganic and Co-ordination Compounds*. Wiley inter science New York: (1963)
9. Ferraro, J.R: *Low Frequency Vibration of Inorganic and Co-ordination Compound* Plenum press, New York USA: (1971).
10. Sacconi. L: *J. Inorg. Nucl. Chem.*, **18**, pp.73-77, 1968.
11. Lever A.B.P : "*inorganic electronic spectroscopy*". Elsevier, Asterdam, UK. Magree. R and Gordan. L: the infrastructure of chelate compounds – III : "*A study of some trivalent metal chelates compounds of 8-hydroxyquinoline in the region 5000-250cm⁻¹*". *Talanta* .10 : pp. 967-970,1963.
12. Yamada S: *Co-ord. Chem. Rev* 1 pp. 415-418, 1966. Proctor I. M, Halhway B. J and Nichol. P: *J.Chem.Soc(A)* pp.1678-1683, 1968..
13. Cotton F.A. and Wilkinson P.G: *Advanced Inorganic Chemistry*. 3rd Edⁿ, Wiley- Eastern New Delhi. 1985.
14. Kneubuhl F.K: Approximation in calculation of EPR parameters. *J.chem.Phys.* **33**, pp. 1074-1078, 1960.