ISSN:0976-4933
Journal of Progressive Science
Vol. 02, No.02, pp 134-137 (2011)

Synthesis and Characterization of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes of [5'-amino-3'-methylmercapto-4'-alkylpyrazole-5, 6-(5"-chloro)-benzo (4-a)]-3-alkyl-4-hydropyrimidone

A. K. Pandey* and Shweta Srivastava
Department of Chemistry, S.C. Collage, Ballia- 277001, India
Email - sgapandey@yahoo.com

Abstract

A few complexes of [5'-amino-3'-methylmercapto-4'-alkylpyrazole-5,6-(5"-chloro)-benzo(4-a)]-3-alkyl-4-hydropyrimidone with Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized by elemental analyses, IR, UV-vis spectroscopies ESR and magnetic susceptibility measurements.

Keywords - Heterocyclic ligand, heterometallic, IR, ESR, molar conductance.

Introduction

Imidazole, a five-membered nitrogen heterocycle is an ubiquitous ligand in chemical and biological systems. Histidine plays an important role in stabilizing the active sites of a number of metalloproteins. In particular, copper protein such as azurin (Norris, *et al*., 1968), plastocyanin (Guss, *et al*., 1983), hemocyanin (Solomon, *et al*., 1983 and Bannister, 1977) and tyrosinase (Karlin, *et al.,* 1985 and Wilcox, *et al.,* 1985) are known to contain several imidazole molecules as ligands per copper centre. These systems share the common feature of chelating through nitrogen. In the absence of interfering substituents, the geometry of the resulting chelate ring is essentially invariant.

Many reports have appeared in literature on transition metal complexes with the heterocyclic ligands containing nitrogen (Crane, *et al.,* 1995, Holz, *et al.,* 1996, Rzepka, *et al.,* 1996, Storrier, *et al.,* 1996, Saravanan, *et al.,* 1996 and Sigel, *et al.,* 1990). Here we report the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with [5'-amino-3'-methylmercapto-4'-alkylpyrazole-5,6-(5"-chloro)-benzo(4-a)]-3-alkyl-4-hydropyrimidone (L), Fig 1.

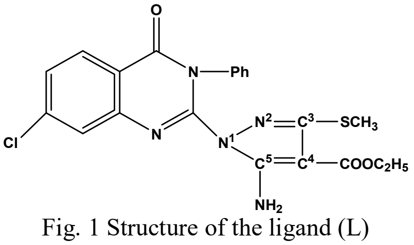


Fig. 1 Structure of the ligand (L)

Experimental

To a hot stirring solution of ligand (L) (0.910 gm, 2 mmol) was added a solution of $CuCl_2.2H_2O$ (0.171 gm, 1 mmol) in 10 ml ethanol. A light green colored precipitate was obtained. The whole content was digested on a water bath for one hr, then cooled to room temperature and filtered, washed with water followed by ethanol and dried under vacuum.

Nickel(II), Cobalt(II) and Zinc(II) complexes were prepared similarly by the reaction of their respective metal chlorides and ligand in same molar ratio as reported above for copper complex, but the excess solvent was reduced to minimum volume (~5 ml) in all cases which yielded solid crystalline complexes. The metals were estimated gravimetrically by standard procedure (Vogel, 1978) after decomposing with HNO_3 whereas chlorine and sulphur were estimated as silver chloride and barium sulphate respectively, after decomposing the complexes with fusion mixture and Na_2O_2 together in a nickel crucible. Carbon, hydrogen and nitrogen were determined microanalytically at Department of Chemistry, Banaras Hindu University, India and Central Drug Research Institute, Lucknow, India. The infrared spectra of ligand and complexes were recorded on Perkin-Elmer 783 spectrophotometer using KBr and nujol mull pelleted samples (4000-200 cm^{-1} range). ESR spectra were recorded on Varian X-band E_4 spectrometer in the solid state as well as in solution (DMSO) of the complexes. Molar conductance was measured on Dist 1 HANNA digital conductivity meter. The diamagnetic corrections were made using Pascal's constant (Levis, *et al.,* 1960). The empirical compositions of the complexes along with their physical and analytical data are represented in Table No 1.

Table No.1 Physical and Analytical data of the Metal Complexes

			Calcd. (Analyses Found) %						μ_{eff}	Molar
Complexes	**Colour**	**M.P.**							(B.M.)	**Conductance** (ohm^{-1} cm^2 mol^{-1})
		(^{O}C)	C	H	N	M	S	Cl		
L	Colorless	197	55.62	4.20	15.90	-	7.5	7.21	-	-
			(55.32)	(3.95)	(15.36)	-	(7.02)	(7.79)		
$[Co(L)_2Cl_2]$	Deep green	240	24.37	1.70	6.43	5.39	2.92	6.50		
			(24.21)	(1.67)	(6.72)	(5.66)	(3.07)	(6.81)	4.75	20.00
$[Ni(L)_2Cl_2]$	Light blue	205^d	24.27	1.69	6.65	5.62	3.01	6.75		
			(24.21)	(1.72)	(6.72)	(5.64)	(3.07)	(6.81)	3.05	10.0
$[Cu(L)_2Cl_2]$	Light green	305-7	24.04	1.64	6.57	6.10	3.10	6.72		
			(24.01)	(1.72)	(6.69)	(6.07)	(3.06)	(6.78)	1.68	12.0
$[Zn(L)_2Cl_2]$	Colorless	260	24.11	1.65	6.57	6.16	3.01	6.61		
			(24.06)	(1.61)	(6.51)	(6.12)	(2.95)	(6.32)	dia	5.02

d = decomposed

The metal complexes were found quite stable at room temperature. Complexes were soluble in acetone and few were soluble in DMF and DMSO only. The copper complexes were found partially soluble in DMF and DMSO. Molar conductance values of the complexes came in the range of 6.01 to 25.0 ohm^{1}cm^{2}mol^{-1} which indicated that all complexes behave as non-electrolytes.

The ligand showed IR peaks at 3440, 3220 and 3180 cm^{-1} which were assigned as $\nu_{asym}(NH_2)$, $\nu_{sym}(NH_2)$ and νNH, respectively (Umapathy, *et al.,* 1986, Lane*, et al.,* 1962 and Ainscough, *et al.,* 1984). The shift of these peaks toward lower wave number by ~140 cm^{-1}, 80 cm^{-1} and 60 cm^{-1} in cobalt(II), nickel(II), copper(II) and Zn(II) complexes respectively indicated the involvement of the NH_2 group of the pyrazole moiety in the coordination. The broad peak appeared in the region of 3500-3300 cm^{-1} was assigned to a mixed vibration due to coordinated $-NH_2$ group (Mishra, 2003).

The ligand peak observed at ~1570 cm^{-1} is assigned to δNH_2 shifted to lower wave numbers by ~ 70-100 cm^{-1} in all complexes indication the participation of $-NH_2$ group of pyrazolyl moiety supported by the bands observed in the region of ~1500-1550 cm^{-1} which is attributed to N-C-N(pyrimidone moiety) coupled with N-N=C(of the pyrazolyl moiety) groups. The peaks observed at ~410, ~420, and ~450 cm^{-1} are assigned ν(M-N=C) in the spectra of the zinc(II), cobalt(II), nickel(II) and copper(II) complexes respectively. Additionally, the IR spectra of all complexes showed a very similar band at ~300 and ~360 cm^{-1} in the spectra of nickel(II) and copper(II) complexes assigned as ν(M-Cl) in which both chlorines are expected to be trans to each other.

The electronic spectra (Lever, 1968 and Nandi, *et al.,* 1988) of the ligand and complexes Table 2, showed bands at 26700 and 25000 cm^{-1} which may be assigned to an intraligand charge transfer $M \rightarrow L(\pi^*)$ transitions respectively. The ligand field bands for the cobalt(II) complex were observed at 5700, 6700 and 16400 cm^{-1} and are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition respectively. The nickel(II) complex showed three bands at 12000, 16700 and 24300 cm^{-1} which were attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively. These bands are lying in the same energy regions as expected from other octahedral complexes of nickel(II) (Lever, 1984). The copper(II) complex showed a weak band in the region 13000 cm-1, characteristic of distorted octahedral stereochemistry. The values of 10Dq, B' and β for these complexes were calculated (Lever, 1984 and Jena, et al., 1999).

Table 2 .Electronic spectral data of the ligand and metal complexes

Compounds	Bands	Assignment	Crystal field parameters		
	(cm^{-1})		Dq	B (cm^{-1})	β (cm^{-1})
L	34000	Intraligand transition	--	--	--
$[Co(L)_2Cl_2]$	8600	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	425.05	535.0	0.6
		$\rightarrow {}^4A_{2g}(F)$			
		$\rightarrow {}^4T_{1g}(P)$			
$[Ni(L)_2Cl_2]$	9600	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	950.2	775.3	0.8
	15400	$\rightarrow {}^3T_{1g}(F)$			
	26600	$\rightarrow {}^3T_1g(P)$			
$[Cu(L)_2Cl_2]$	14700	$^2B_{2g} \rightarrow {}^2E_g$		—	—
	15400	$^2B_{1g} \rightarrow {}^2A_{1g}$		—	—

The ESR spectrum Fig. 2 of the copper(II) complex showed a broad peak giving values of $g_{II} = 2.3138$, $g_{\perp} = 2.0969$, $g_{av} = 2.1692$, $A_{II} = 146.6$ Gauss and $A_{\perp} = 45.0$ Gauss. g_{II} and $g_{\perp}$values are typical for orthorhombic geometry and likewise assignment may also be made in the present case. The ESR spectrum of nickel (II) complex showed a broad peak giving a value of $g_{iso} = 2.0165$, but it also showed hyperfine splitting when the gain was increased ten times ($G = 2x10^4$). The number of ESR peak in this spectrum indicated four nitrogen environments around nickel(II) complex.

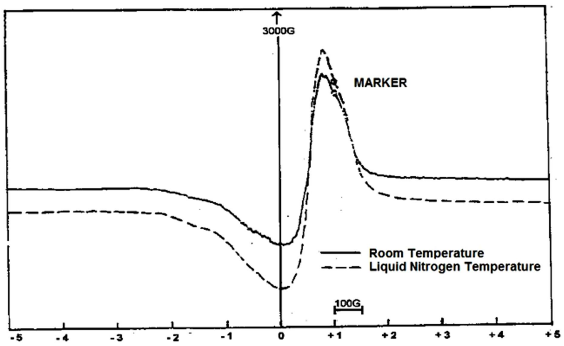
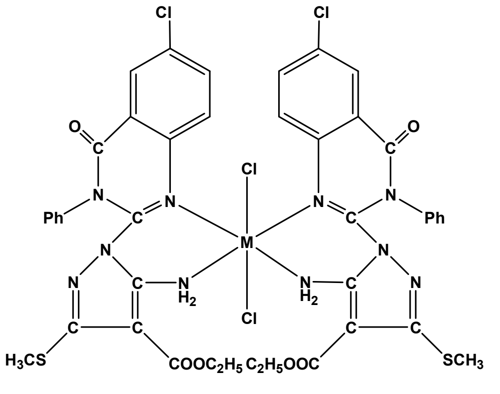


Fig 2. ESR Spectrum of $[Cu(L_2)Cl_2]$



M = Co(II), Ni(II) and Cu(II)

Fig 3. Suggested structure for the complexes (ML_2Cl_2)

The magnetic moment values calculated for the metal complexes, suggested the octahedral co-ordination about nickel(II), copper(II), cobalt(II) complexes respectively. Zinc(II) complex was found to be tetrahedral. The magnitude of these parameters and spectral pattern suggest octahedral geometry for the cobalt(II), nickel(II), copper(II) complexes Fig 3, agrees with few others reported earlier (Lever, 1968) and tetrahedral geometry for zinc(II) complexes.

Acknowledgement

The authors thank the authorities of CDRI, Lucknow for providing elemental analysis, magnetic and IR Spectral, ESR spectral data respectively. We would also like to thank the referee who helped us in paper publishing. The authors are very much thankful to Dr. Akhilesh Prasad, Assistant Professor, Department of Chemistry, S.M.M. Town PG College, Ballia for the preparation of this manuscript.

References

1. Anscough, E.W., Brodil, A.M. and Larsen, N.G. (1984). *Inorg. Chim. Acta*. 60:25.
2. Bannister, J.V. (1977). *Structure and function of hemocyanin* (Verlag springer, Heidelberg, New York)
3. Crane, J.D., Hughes, R. and Sinn E. (1995). *Inorg. Chim. Aoto*. 23:181.
4. Guss, J.M. and Freeman, H.C. (1983). *Jounal of Molec. Biol*. 164:351.
5. Holz, R.D., Evdokimov, E.A. and Gobena, T.F. (1996), *Inorg. Chem*. 35:3808.
6. Jena, S., Rath, N. and Dash, K.C. (1999). *Indian J. of Chem*., 38A:350.
7. Karlin, K D. and Gultneh, Y. (1985). *J. Chem. Educ.,* 62:983.
8. Lane. T.J., Nakagawa, CSCI, Walter, J.L. and Kandathil, A.J. (1962). *Inorg. Chem.* 1:267.
9. Lever, A.B.P. (1968). *Inorganic Electronic Spectroscopy*, (Elsevier Amsterdam). 317.
10. Lever, A.B.P. (1984). *Inorganic Electronic Spectroscopy*, Elsevier. 446.
11. Levis, J. and Wilking, R.G. (1960). *Modern Co-ordination Chem*. D. Inter Science, New York. 403
12. Mishra, V. (2003). *J. Indian Chem. Soc*., 80:174-177.
13. Nandi, M.M., (Smt.) Ray, R. and Choudhary (Smt.) J. (1988). *Indian J. Chem*. 27A:687-690.
14. Norris, G.E., Anderson, B.F. and Baker, E.N. (1986). *J. Am chem. Soc*., 108:2784.
15. Rzepka, M., Surga, W., Korabik, M. and Mrozineki, J. (1996). *Pol. J. Chem*., 70:1.
16. Saravanan, N., Yusuff, K.K.M., Suresh, P.V. and Prabhy, G.N. (1996). *Synth. React. Inorg. Metal* Org. *Chem*., 26:901.
17. Sigel, H., Tribulet, R. and Yamauchi, Osamu. (1990). *Inorg. Chem*., 9:305.
18. Solomon, E.I., Penfield, K.W. and Wilcox, D.E.(Berlin). (1983). *Struct. Bonding*. 1:53.
19. Storrier, G.D. and Colbran, S.B. (1996). *J. Chem. Soc., Dalton Trans*., 10:2185.
20. Umapathy, P., Budhakar, A.P. and Dorai, C.S. (1986). *J. Indian Chem. Soc*. 63:714.
21. Vogel, A.I., *A text book of quantitative inorganic analysis*. (1978). 462, 489, 497.
22. Wilcox, D.E., Parras, A.G., Hwang, Y.T., Lerch. K., Winkier, M.B. and Solomon, E.I. (1985). *Journal of Am chem. Soc.* 107:4015.

Received on 26.12.2010, revised on 31.03.2011 and accepted on 15.08.2011