



Complexes of [5'-amino-3'-methylmercapto-4'-alkylpyrazole-5,6-(5''-chloro)-benzo (4-a)] -3-alkyl-4-hydropyrimidone

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Abstract: A few complexes of [5'-amino-3'-methylmercapto-4'-alkylpyrazole-5,6-(5''-chloro)-benzo(4-a)]-3-alkyl-4hydropyrimidone 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.

Key Words: Heterocyclic ligand, heterometallic, IR, ESR, molar conductance.

1. INTRODUCTION:

Imidazole, a five-membered nitrogen heterocycle is a 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 (14), plastocyanin (4), hemocyanin (2,18) and tyrosinase (7,22) 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 (3,5,15,16,17,19). 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-S.6-(5''chloro)-benzo(4-a)]-3-alkyl-4-hydropyrimidone (L), Fig 1.

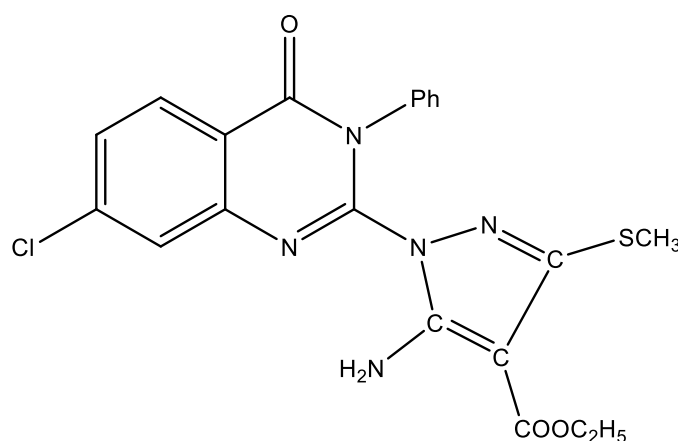


Figure 1. Structure of the ligand (L)



2. MATERIALS AND METHODS:

EXPERIMENTAL:

To a hot stirring solution of ligand (L) (0.910 gm, 2 mmol) was added a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.171 gm, 1 mmol) in 10 ml ethanol, A light green coloured 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 but the excess solvent was reduced to minimum volume (10ml) in all cases which yielded solid crystalline complexes. The metals were estimated gravimetrically by standard procedure (21) after decomposing with HNO_3 , whereas chlorine was 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 ($4000\text{-}200\text{ cm}^{-1}$ range). ESR spectra were recorded on Varian X-band E4 spectrometer in the solid state as well as in solution (DMSO) of the complexes (23). Molar conductance was measured on Dist I HANNA digital conductivity meter. The diamagnetic corrections were made using Pascal's constant (11). 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

Complex	Colour	M.P. (°C)	C	H	N	M	S	Cl	μ_{eff} (B.M.)	Molar Conductance ($\text{Ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$)
Ligand	Colourless	197	55.62 (55.32)	4.20 (3.95)	15.90 (15.36)	-	7.5 (7.02)	7.21 (7.79)	-	-
$\text{Co(L)}_2\text{Cl}_2$	Deep Green	240	24.37 (24.21)	1.70 (1.67)	6.43 (6.72)	5.39 (5.66)	2.92 (3.07)	6.50 (6.81)	4.75	20.00
$\text{Ni(L)}_2\text{Cl}_2$	Light Blue	205 (d)	24.27 (24.21)	1.69 (1.72)	6.65 (6.72)	5.62 (5.64)	3.01 (3.07)	6.75 (6.81)	3.05	10.0
$\text{Cu(L)}_2\text{Cl}_2$	Light Green	305-7	24.04 (24.01)	1.64 (1.72)	6.57 (6.69)	6.10 (6.07)	3.10 (3.06)	6.72 (6.78)	1.68	12.0
$\text{Zn(L)}_2\text{Cl}_2$	Colourless	260	24.11 (24.06)	1.65 (1.61)	6.57 (6.51)	6.16 (6.12)	3.01 (2.95)	6.61 (6.32)	Dia	5.02

Where 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 $6.01\text{ to }25.0\text{ Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ 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 $\nu_{\text{asym}}(\text{NH}_2)$, $\nu_{\text{sym}}(\text{NH}_2)$ and ν_{NH} , respectively (20,8,1). The shift of these peaks toward lower wave number by $\approx 140 \text{ cm}^{-1}$, 80 cm^{-1} and 60 cm^{-1} in cobalt (II), nickel (II), copper (II) and Zn (II) complexes respectively (24) 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 $-\text{NH}_2$ group (12).

The ligand peak observed at $\approx 1570 \text{ cm}^{-1}$ is assigned to δNH_2 shifted to lower wave numbers by $\approx 70\text{-}100 \text{ cm}^{-1}$ in all complex's indication the participation of $-\text{NH}_2$ group of pyrazolyl moiety supported by the bands observed in the region of 1500-1550 cm^{-1} (25) which is attributed to N-C-N (primidone moiety) coupled with N-N=C (of the pyrazolyl moiety) groups. The peaks observed at ≈ 410 , ≈ 420 , and $\approx 450 \text{ cm}^{-1}$ are assigned $\nu(\text{M-N}=\text{C})$ in the spectra of zinc (II), cobalt (II), nickel (II) and copper (II) complexes respectively. Additionally, the IR spectra of all complexes showed very similar band at ≈ 300 and $\approx 360 \text{ cm}^{-1}$ and in the spectra of nickel (II) and copper (II) complexes assigned as $\nu(\text{M-Cl})$ in which both chlorines are expected to be trans to each other.

The electronic spectra (9,8, 13) of the ligand and complexes in Table 2, showed bands at 26700 and 25000 cm^{-1} which may be assigned to an intra ligand charge transfer $\text{M} \rightarrow \text{L}(\pi^*)$ transitions respectively. The ligand field bands for the cobalt (II) complex were observed at 5700, 6700 and 16400 cm^{-1} are assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ respectively. The nickel (II) complex showed three bands at 12000, 16700 and 24300 cm^{-1} which were attributed to ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions respectively (26). These bands are lying in the same energy regions as expected from other octahedral complexes of nickel (II) (10). 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 (10, 6).

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

Compounds	Bands (cm^{-1})	Assignment	Crystal Field Parameters		
			Dq	B	β
L	34400	Intra ligand transition	-	-	-
Co(L) ₂ Cl ₂	5700	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	425	535.0	0.6
	6700	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$			
	16400	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$			
Ni(L) ₂ Cl ₂	9600	${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$	950.2	775.3	0.8
	12000	${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}(\text{F})$			
	16700	${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$			
Cu(L) ₂ Cl ₂	13000	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	-	-	-

3. RESULT AND DISCUSSION:

The ESR spectrum Fig. 3 of the copper (II) complex showed a broad peak giving values of $g_{\parallel} = 2.3138$, $= 2.0969$, $g_{\text{av}} = 2.1692$, $A_{\parallel} = 146.6$ Gauss and $G_{\parallel} = 45.0$ Gauss 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 $g_{\text{iso}} = 2.0165$, but it also showed hyperfine splitting when the gain was increased ten times ($G = 2 \times 10^4$). The number of ESR peak in this spectrum indicated four nitrogen environments around nickel (II) complex.

The magnetic moment values calculated for the metal complexes, suggested the octahedral co-ordination for nickel (II), copper (II) and cobalt (II) respectively. zinc (II) complex was found to be tetrahedral. The magnitude of these parameters and spectral pattern suggests octahedral geometry for nickel (II), copper (II) and cobalt (II) complexes fig. 2, agrees with few other reported earlier (9) and tetrahedral geometry for zinc (II) complexes.

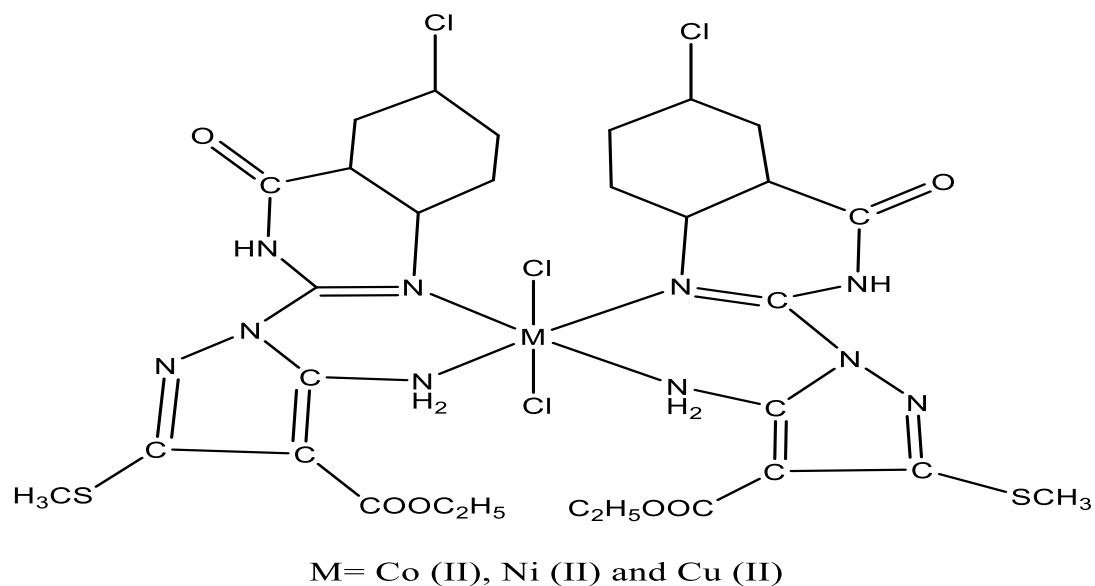


Figure 2. Suggested structure for the complexes $[ML_2Cl_2]$

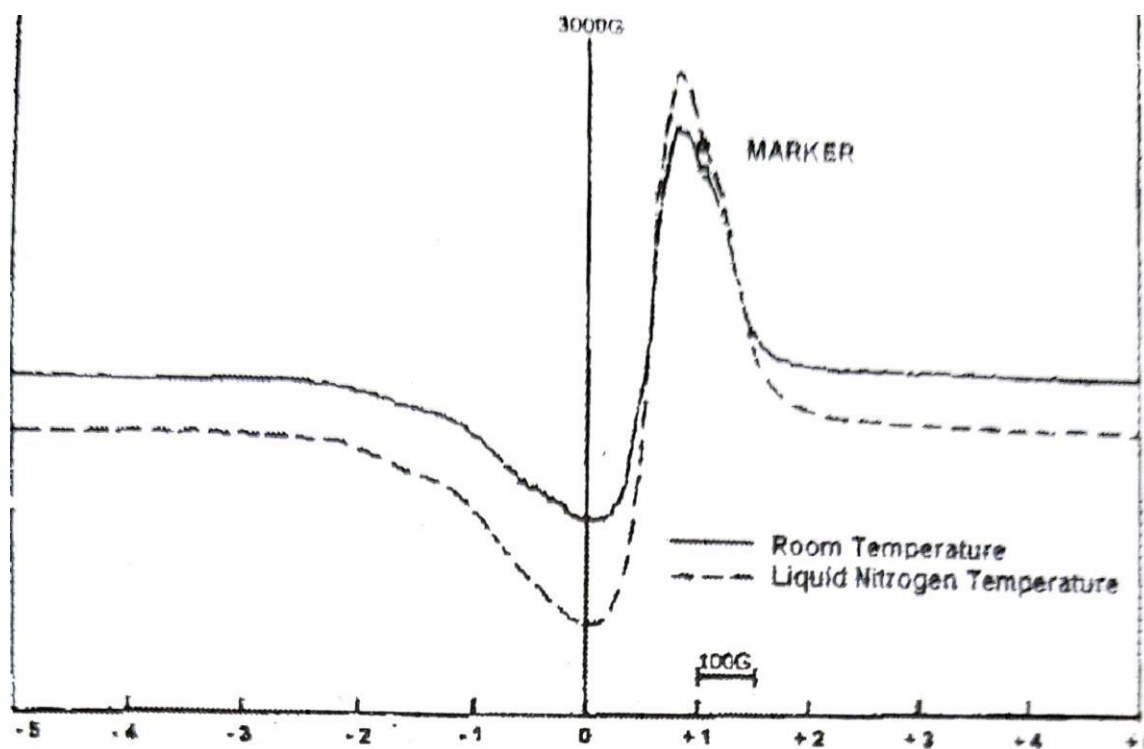


Fig. 3 ESR Spectrum of $[Cu(L_2)Cl_2]$

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