



Studies on the Cu (II) and Co (II) Complexes with N,N'-bis (2-benzothiazolyl) -2,6 Pyridine Dithiocarboxamides

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ABSTRACT

The ligand N,N'-bis (2-benzothiazolyl)-2,6-pyridine dithiocarboxamides and its Cu (II) and Co (II) complexes were synthesized. Their structures were elucidated on the basis of elemental analysis, analytical data, magnetic moments, electronic spectral and IR Spectral studies. The complexes were found to be monomeric and nonelectrolytic in nature. On the basis of electronic spectral studies the complexes were concluded to be distorted octahedral. The IR Spectrum suggested that the ligand behaved as uninegative bidentate ligand coordinating through nitrogen and sulphur atoms.

Key words: N,N'-bis(2-benzothiazolyl)-2,6-pyridine dithiocarboxamide, 2,6-pyridine dithiocarboxylic acid, 2-aminobenzothiazole, spectral study,).

INTRODUCTION

The coordination chemistry of amide ligand is an important part of a number of chemical investigations. Sigel and Martin¹ reviewed the structure and stability of metal ion complexes of amide, oligopeptides and related ligands. In recent years, pyridine carboxamides, a burgeoning class of multidentate ligands have received much importance because these ligands have found use in asymmetric catalysis,^{2,3} molecular receptors,^{4,5} dendrimer synthesis⁶. Many derivatives of pyridine dithiocarboxamides show anti inflammatory, antipyretic and analgesic activities⁷⁻⁸.

In this paper the synthesis of N,N'-bis (2-benzothiazolyl) -2,6-pyridine dithiocarboxamide(I) and isolation of their Cu(II) and Co(II) complexes are reported. The complexes were characterized using elemental analysis, magnetic moments, UV – Visible spectra and IR Spectral Studies.

MATERIAL AND METHODS

The solubility of all complexes were tested in cold and hot water, in common organic solvents and all the complexes were found to be insoluble.

UV – Vis spectrum was recorded in solid state by diffuse reflectance method due to insoluble nature of complexes using Barium sulphate as inert material. IR spectra were obtained on Perkin Elmer 157 or 577 model in nujol mull or Potassium bromide/ Cesium iodide disc. The estimation of Cu and Co were carried out in our laboratory by using Vogel's method⁹.

Synthesis of ligand BPD

2,6 – Pyridine dithiocarboxylic acid (1.99 g, 10mmol) and thionyl chloride (20-25 ml) were refluxed under anhydrous conditions for 4-6 h. The excess thionyl chloride was removed under reduced pressure and the remaining mixture was cooled at 0°C and dry pyridine (30-35 ml) was added followed by 2-aminobenzothiazole (3.0 g, 20mmol) with occasional stirring, until the evolution of HCl had ceased. The solid obtained was poured into ice cold water (200 ml), filtered off and washed with 5% NaHCO₃ solution, then with hot water and ethanol. The resulted black crude product was recrystallized from dioxane. The purity of compound was checked by TLC.

Synthesis of the complexes

A solution of 5mmol of MCl₂ [where M = Cu (II) and Co (II)] in ethanol (10ml) was added to the ligand (2.31g, 5mmol) suspended in nitrobenzene (10ml) and the mixture was refluxed for 12h. The obtained precipitate was filtered off, washed with water and ethanol and dried in air. All the isolated complexes were insoluble in most organic solvents, but soluble in DMF and DMSO.

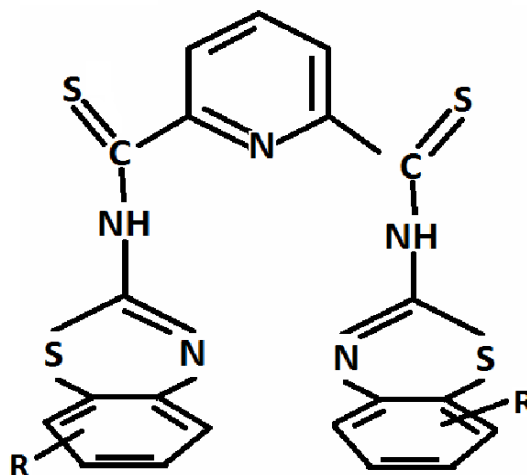
The complexes decompose without melting when heated above 310°C.

RESULTS AND DISCUSSION

Elemental analysis showed that formula of ligands was C₂₁H₁₃N₅S₄(H₂L₁), C₂₃H₁₇N₅S₄(H₂L₂) and the formula of complexes were ML₂ where M = Cu (II) and Co (II) ions. The complexes were insoluble in water, benzene and other common solvents but were soluble in DMSO and DMF. The complexes were characterized by IR and UV absorption data.

IR Spectra

The infrared spectrum of the ligand showed a band around 3254 cm⁻¹ which was assigned to ν_{NH} vibration. The N-H stretching appeared in all complexes as a very weak band. While > C = S group of ligand absorbed around 1180 cm⁻¹ and exhibited medium strong bands and > C = S group of complexes registered a lower shift of around 25 to 27 cm⁻¹ and appeared at 1155cm⁻¹ as medium band. This indicated thio enolisation of > C = S group during the complex formation.



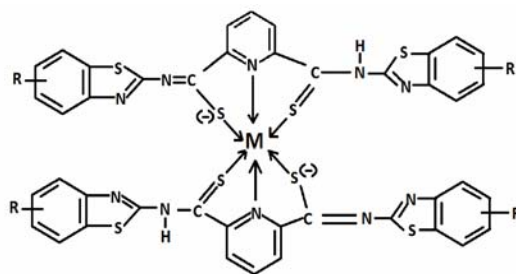
Where

R = H for H₂(L₁)

R = 5-methyl for H₂(L₂)

R = 7-methyl for H₂(L₃)

Fig. 1:



Where

R = H for H₂ (L₁)

R = 5 – CH₃ for H₂ (L₂)

R = 7 – CH₃ for H₂ (L₃)

Fig. 2:

Table 1 : Physical constant and elemental analysis of compound

Compound	Colour	m.p.	Yield	Elemental analysis							
				M		N		S		C	
				Found	Cal	Found	Calc.	Found	Calc.	Found	Calc.
H ₂ (L ₁)	Black	289°C	90%	-	-	15.11	15.10	27.64	27.84	54.42	54.52
H ₂ (L ₂)	Deep Brown	294°C	89%	-	-	14.25	14.28	26.06	26.09	56.21	56.28
H ₂ (L ₃)	Light Brown	298°C	88%	-	-	14.26	14.27	26.07	26.08	56.20	56.23
Cu (L _{1/2})	Deep Brown Black	Å300°C	78%	6.41	6.43	14.15	14.17	25.90	25.92	51.03	51.06
Cu (L _{2/2})	Dark Brown	Å295°C	76%	6.11	6.08	13.44	13.42	24.56	24.54	52.90	52.92
Cu (L _{3/2})	Dark Brown	310°C	75%	6.10	6.08	13.40	13.42	24.51	24.54	52.95	52.92
Co (L _{1/2})	Light Pink	305°C	80%	6.02	6.00	14.26	14.24	26.06	26.04	51.29	51.27
Co (L _{2/2})	Dark Pink	300°C	85%	5.68	5.67	13.48	13.47	24.66	24.63	53.15	53.12
Co (L _{3/2})	Dark Pink	295°C	85%	5.69	5.67	13.45	13.47	24.65	24.63	53.14	53.12

Table 2: Characteristics IR Band (in cm⁻¹) of ligand and complexes

Ligand	NH	>C=S	Thiocarboxamide	Benzothiazole	Pyridine ring stretching
H ₂ (L ₁)	3252(m)	1178(s)	1396(m),1049(m),786(w)	1610(s)	1540(m) 1457(m) 1444(m)
H ₂ (L ₂)	3256(m)	1180(s)	1398(m),1052(m),789(w)	1612(s)	1545(m) 1460(m) 1449(m)
H ₂ (L ₃)	3253(m)	1182(s)	1402(m),1054(m),793(w)	1614(s)	1549(m) 1464(m) 1453(m)
Cu (L _{1/2})	3250(w)	1153(m)	1340, 1005,760	1610(m)	1520(m) 1420(m) 1340(m)
Cu (L _{2/2})	3250(w)	1155(m)	1343,1008,764	1613(m)	1520(m) 1421(m) 1341(m)
Cu (L _{3/2})	3250(w)	1157(m)	1349,1012,768	1616(m)	1522(m) 1422(m) 1343(m)
Co (L _{1/2})	—	1154(m)	1343,1009,764	1613(m)	1537(m) 1442(m) 1358(m)
Co (L _{2/2})	—	1158(m)	1353,1015,772	1615(m)	1541(m) 1444(m) 1364(m)
Co (L _{3/2})	—	1160(m)	1345,1012,766	1610(m)	1539(m) 1440(m) 1360(m)

The benzothiazole absorption and pyridine ring absorption of ligand is also merged with the thio group and therefore a strong and medium absorption is displayed. The pyridine ring stretching of complexes registered a lower shift (except the first band) which indicated the involvement of N -atom in the ring coordination.

Electronic spectra

The electronic spectral bands in ligands were obtained at around 273 nm and 359 nm which might have arose due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

The electronic spectral bands in Cu (II) observed around 360 nm appeared due to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ mixed with internal ligand transition and the ${}^2B_{1g} \rightarrow {}^2E_g$ transition coupled with internal ligand transition and charge transfer transition occurred

at 275 nm. The only d-d transition of metal ion observed around 724 nm appeared to arise due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition.

In Co (II) complexes the electronic spectral bands (excluding the internal ligand transitions) were identified at around 512 nm and 460 nm and they were supposed to arise due to ${}^4T_{1g} (F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} (F) \rightarrow {}^4T_{1g} (P)$ transitions of approximately high spin octahedral Co (II) geometry. The Covalent character and 10Dq were calculated on the basis of data¹⁰ and found as

$$\alpha = 0.95, \quad \beta^0 = 5\%, \quad 10Dq = 13109\text{cm}^{-1}$$

CONCLUSION

The tentative structure of the complex, on the basis of above discussion were proposed as

REFERENCES

1. Sigel H., Martin R.B., *Chem. Rev.* **1982**, *82*, 385.
2. Conlon D.A., Yasuda N.A., *Catal Synth* **2001**, *1*, 343.
3. Trost B.M., Hachiya I., *J. Am. Chem. Soc.* **1998**, *120*, 1104.
4. Collinson S.R., Gelbrick T., Hurshtouse M.B., Tusher J.H.R., *Chem. Commun.* **2001**, 555.
5. Huc I., Krische M.J., Funeriu D.P., Lehan J.M., *Eur. J. Inorg. Chem.* **1999**, 1415.
6. Epperson J.D. Ming L.J., Baker G.R., Newkome G.R., *J. Am. Chem. Soc.* **2001**, *123*, 8583.
7. Matsujaki M., Okable H., Tanaka S., *Japan Kokai* **1982**, *77*, 33676.
8. Kumar, M., Saxena, P.N., *Orient J. Chem.*, **2012**, *28*(4), 1927-1931.
9. Vogel A.I., " *A text book of quantitative Inorganic Analysis* " Longmans, **1964**, P.P. 358 – 479.
10. Lever A.B.P, *J. Chem. Ed.*, **1968**, *45*(11), 711.