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# Synthesis and characterization of some mixed ligand complexes of Co (II) and Co(III) with N-Ethoxycarbonylpyrrole-2-Thiocarboxamide (ETH) and various nitrogen containing heterocyclic bases

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## Abstract

The complexes of type $[M(ETH)_2(X)H_2O]$ [M = Co(II) or Co(III); X = pyridine, β-picoline and imidazole] have been synthesized. They have been characterized by analytical analysis, magnetic susceptibility measurement, IR, and UV-visible spectroscopic methods. In all the complexes metals are six coordinate with octahedral geometry about Co (II) and Co (III).

**Keywords–**Heterocyclic bases**,** N-ethoxycarbonylpyrrole-2-thicarboxamide, spectroscopic methods

## Introduction

A number of important biological processes (Shulman *et al.* 1964, McAuliffe and Murray, 1972) involve metal ions which coordinate with a wide range of ligands having sulphur, nitrogen and oxygen atoms as donor sites. These ligands are generally poly functional in nature capable of encasing metal ions in an organic sphere. To understand these biological processes, there has been in recent years[3,4] an increasing interest in the syntheses and design of new model ligands which could lead to metal complexes with properties similar ones found in biological process. In course of study it is found that ligands containing sulphur or –HNC(S)- groups not only play a significant role but have very important pharmacological properties[5]. They have been found to show antiviral and anti-tumor activity which lead to a very great interest in the chemistry of these compounds, particularly in relation to the transition metal ions. A large number of work have been carried out to understand the nature of metal sulphur bond, the donor properties of sulphur

in general, the position of ligands containing thiocarbonyl sulphur as donor sites in the spectrochemical and nephelauxetic series etc. have not yet been well understood.

## Experimental Section

### General Procedures

All experiments were carried out in open aerobic condition. The solvents were purified and necessarily dried before use following standard procedures. All reagent grade chemicals were obtained from commercial source and used without further purification. The melting point of the ligands and complexes were determined in open capillaries using Gallenkamps apparatus and are uncorrected. The experimental details pertaining to elemental analysis were performed at IIT Kanpur, IR is recored in KBr in the range (250-4000 $cm^{-1}$), UV-visible on Carry Model-17 DUV spectrophotometer and magnetic susceptibility of the complexes were recorded with the help of Gouy balance at room temperature using $Co[Hg(SCN)_4]$ as calibrant and corrections were made for diamagnetism using Pascal's constant.

### 1. Synthesis of thiocarboxamide ligands

The ligand N-Ethoxycarbonylpyrrole-2-thiocarboxamide (ETH) was prepared by literature method[6]. The first step in the synthesis of these ligands is to prepare ethoxycarbonyl isothiocyanate (SCNOOEt)[7].

### (a) Ethoxycarbonyl isothiocyanate (SCNOOEt)

A mixture of 700 ml of dry acetonitrile and 194 g (2.0 mol.) of potassium thiocyanate was warmed on a steam bath. The warm mixture was treated, portion wise with 217 g (2.0 mol) of ethylchloroformate. Heating was continued until the reaction mixture became hot and inorganic precipitate thickened rapidly. At this point the mixture became yellow. The heat source removed and reaction was allowed to run its course. The reaction mixture was allowed to cool to room temperature slowly, chilled and suction filtered. The filtrate was concentrated under reduced pressure and residual oil distilled. Yield 161 g (b.p. 51-55/13 mm). Re-distillation at 10 mm showed that the bulk of material distilled at 44-46 $^oC$.

### (b) N-Ethoxycarbonylpyrrole-2-thiocarboxamide (ETH)

A mixture of 16.8 g (0.25 mol) of pyrrole and 32.8 g (0.25 mol) of ethoxycarbonyl isothiocyanate, both ice cooled was swirled occasionally and cooled as needed to prevent its temperature form rising above 40$^oC$. Within about one hr the mixture had solidified, whereupon it was allowed to stand overnight. Following repeated washing of the product

with petroleum ether, there was obtained 46.2 g (93 %) of N-ethoxycarbonylpyrrole-2-thicarboxamide ($C_8H_{10}O_2N_2S$). Recrystallization from aqueous ethanol gave pure compound in the form of yellow crystals. m.p. 98-99 $^oC$. Anal. calcd: C 48.5; H 5.1; N 14.1; S 16.2. Found: C 48.3; H 4.9; N 13.8; S 15.8.

**Preparation of metal complexes**

**(a) Co(II) ETH complexes**

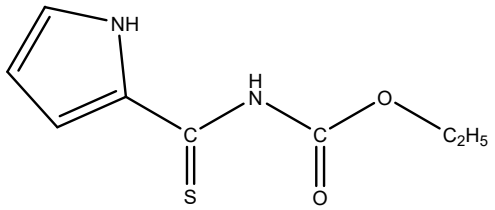
0.25 g (~1 mmol) of $CoSO_4.7H_2O$ was dissolved in 30 ml of water followed by addition of 5 ml of pyridine, β-picoline and 10 ml of aqueous solution of imidazole (0.272 g, 4 mmol). An ethanolic solution of the ligand 10 ml (0.38 g, 2 mmol) was slowly added at lower temperature (10 $^oC$) to each of the metal ion solution containing N-heterocyclic bases separately. The resultant solution was stirred for about 1hr and refluxed at 60 $^oC$. A colored precipitate of each of the complex was formed (Table 1). These complexes were filtered, washed several time with cold water and dried in vacuo. These complexes were analyzed and the results of chemical analysis are given in Table 1.

**Analysis**

The analysis of cobalt and sulfur were carried out by the methods given else where[8]. Carbon, hydrogen and nitrogen analyses were performed by the micro analytical section of the IIT, Kanpur. The results are given in Table 1.

**Results and Discussion**

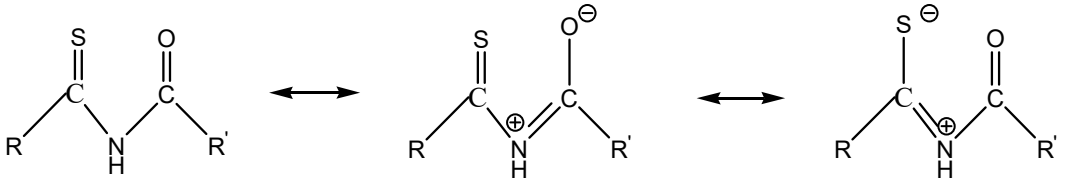
The analytical data (Table 1) suggest that the ligands in all the complexes behave as bi-dentate of one assume that metal ions take their normally preferred geometries. As a bi-dentate, ligands can link with metal ions through any two or one of the five donor sites. These sites are nitrogen, oxygen and sulfur.




**N-Ethoxycarbonylpyrrole-2-thiocarboxamide (ETH)**

Figure 1 Structure of the ligand

The IR spectral studies of the ligands and their complexes were compared to know the possible mode of linkages. The positions of major IR bands present in the spectra of the ligand and complexes are given in Table 2. Our tentative assignments are based on the comparative IR studies of a number of related compounds given in literture[6], ordinarily only I is considered II and III may be predominant under certain conditions,




**(I)** **(II)** **(III)**

R = Pyrrolyl
R' = -OEt
**ETH**

Thus, donor abilities of the ligands can be best understood by considering the above resonance structure on functioning as (I) the ligands may behave as neutral bi-dentate, coordinating through oxygen and sulfur. In the resonance forms (II) and (III) the ligands may behave as uni-negative through oxygen and sulfur. The IR spectra of the ligands in solid form display the bands due to $\nu_{NH}$ at 3360 and 3145 $cm^{-1}$ but show no absorption band at 2500 $cm^{-1}$ indicating that in solid state the ligand exists as the thione form (I) and not as thiol form (III). The relative frequency of NH vibration is probably due to hydrogen bonding between NH and C=S group[9]. The characteristic IR bands of pyrrole moiety 1550, 1470, 1400, 1140, 995 and 750 $cm^{-1}$ were present in the spectrum of the ligand[10]. The positions of these bands do not shift in the spectra of the complexes (maximum shift ± 5 $cm^{-1}$). This indicates non-involvement of the nitrogen atom of the pyrrole moiety in the bond formation. Also nitrogen of the pyrrole ring is poorly basic and deprotonation of pyrrole's NH group can place in highly basic media in which the ligand is unstable. It is therefore assumed that bonding in complexes takes place with -C(S)NHC(O)- moiety of the ligand and major shifts in the position of the IR should be due to ν(N-H), ν(C=O), ν(C=S) and amide band IV.

**Co (II) ETH Complexes**

In these complexes two bands at 3360(s) and 3145(m) $cm^{-1}$ in the spectrum of the ligand disappeared in the spectra of the complexes and a medium new band appeared around 3340 $cm^{-1}$. This could be probably due to deprotonation of one of the two –NH groups during the formation of the complexes. Since the position of this band (3340 $cm^{-1}$) corresponds to the one found in the spectrum of the pyrrole. It is assumed that –NH group of the pyrrole in not deprotonated. The amide band at 1775 $cm^{-1}$ which arises owing to the

normal coordinate having major contribution form $\nu_{CO}$, shifted towards lower wave number indicating coordination through CO group. Bonding of the metal ion with oxygen atom of the carbonyl group will shift the position of the thioamide and band due to $\nu_{CO}$ of the– OEt toward the higher wave numbers. The broad band at 1500, 1310, 1260 $cm^{-1}$ due to thioamid and amide and at 1190 $cm^{-1}$ due to –OEt shifted to higher frequencies confirms the bonding of metal with carbonyl and sulfur of the thicarbonyl group. Thioamide band which appears at 800 $cm^{-1}$ for $\nu_{(C=S)}$ in ligands appeared at 875 $cm^{-1}$ which further suggest bonding of metal with thiocarbonyl sulfur. Two bands at 630(m) and 600(w) $cm^{-1}$ disappeared and a new band around 625 $cm^{-1}$ appeared in spectra of the complexes which is assigned to $\tau_{NH}$. This is probably due to deprotonation of one >NH group. Two new bands around 470 and 350 $cm^{-1}$ appeared in the complexes due to coupled vibration from $\nu_{MO}$[11] and $\nu_{MS}$[12]. A weak band at 845 $cm^{-1}$ absent in the complexes spectra, which could be due to $\tau_{NH}$ of cis form of –NHCO[13] group. The characteristic bands of pyridine, β-picoline and imidazole where found in spectra of complexes[14]. It is therefore concluded that ligand ETH is bonded to metal through thiocarbonyl sulfur and carbonyl oxygen.

**Co (III) ETH complexes**

The position of the bands of ligand and N-heterocyclic bases were same except that ν(M-OH) and δ(M-OH) in all the complexes were found at around 3400 $cm^{-1}$ and 1650 $cm^{-1}$.

**Magnetic properties**

Co (II) complexes were found to be paramagnetic. The magnetic moments of complexes were in the range of 4.1 to 4.2 BM. These values suggest the octahedral geometry around Co (II) in these complexes[15]. Further, the diamagnetic nature of Co (III) complexes shows octahedral coordination in low spin states.

**Electronic Spectra**

The near ultraviolet spectrum of the ligand(ETH) in chloroform showed two absorption bands at 27300 $cm^{-1}$ and 22200 $cm^{-1}$ assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition respectively. The $n\rightarrow\pi^*$ transition is due to charge transfer from sulfur or nitrogen atom at lower energy and less intense than to $\pi\rightarrow\pi^*$[16]. In the spectrum of all the Co (II) and Co (III) complexes, two intense bands at 23500 and 27000 $cm^{-1}$ were found. The high intensity of peak indicates that this is due to electric dipole allowed transition not to d-d. The position of the band at 23500 $cm^{-1}$ is depending upon the metal ion and solvent. These observations suggest that this band should arise due to charge transfer band involving metal to ligand. This is probably due to transition of the lone pair of electrons from O or S to higher unfilled levels of the metal ion of due to transition from metal ion to empty anti bonding orbitals of the ligand. The electronic spectra of most of Co (II) complexes have high spin

electronic configuration. The ground state is $^4T_{1g}$ (F). Three transitions predicted are $^4T_{1g}$(F)→$^4T_{2g}$ (F), $^4T_{1g}$(F)→$^4A_{2g}$ (F) and $^4T_{1g}$ (F)→$^4T_{1g}$ (P). The $^4T_{1g}$ (F)→$^4A_{2g}$ (F) transition is two electron transition and is not observed. A weak band at 19,500 $cm^{-1}$ assigned to $^4T_{1g}$ (F)→ $^4T_{1g}$ (P) transition. Other band at 90,000 $cm^{-1}$ is assigned to $^4T_{1g}$ (F)→$^4T_{2g}$ (F). Besides these charge transfer band at 22400 $cm^{-1}$ and intra-ligand band at 28000 $cm^{-1}$ is also observed.

## Electronic spectra of Co (III) complexes

Co (III) complexes are generally spin paired and show two transition band in visible region. The bands are $^1A_{1g}$→$^1T_{1g}$ and $^1A_{1g}$→$^1T_{1g}$[17]. Most of the complexes show bands at 17600, 18200, 22400 and 28000 $cm^{-1}$. The bands at 17000 and 18200 $cm^{-1}$ are assigned to $^1A_{1g}$→$^1T_{1g}$ and $^1A_{1g}$→$^1T_{2g}$ respectively. The other bands are assigned as charge transfer and intra-ligand band.

## Conclusion

On the basis of analytical analysis and spectral studies octahedral geometry about Co(II) and Co(III) has been assigned

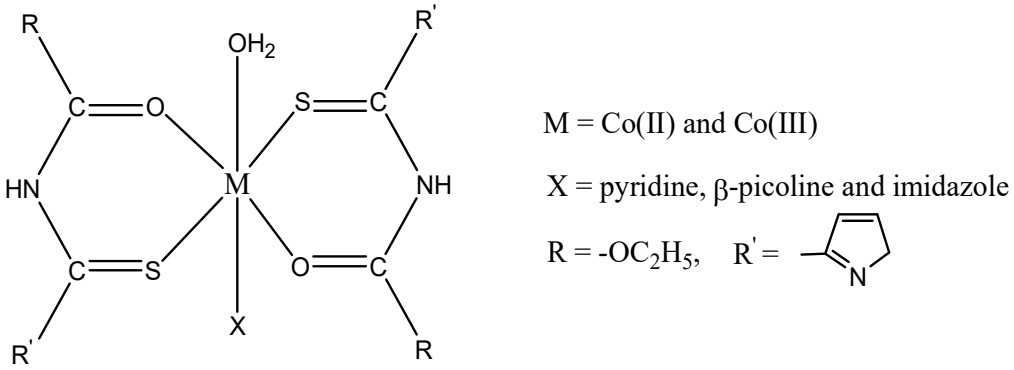



**Figure 2 Structure of the complex**

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