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Preparation and Structural Characterization of some Thocarboxamide complexes of Zn(II)

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Abstract

The complexes [$ZnX(PPh_3)_2L$] [X=Cl, Br, I; L=N-Ethoxycarbonylpyrrole-2-thiocarboxamide(ETH) and N-Phenylcarbamoylpyrrole-2-thiocarboxamide(PTH)] have been synthesized. These have been characterized by elemental analysis, magnetic susceptibility measurement, IR, and UV-visible spectral techniques. The structures have proposed on the basis of analytical, magnetic and spectroscopic studies.

Keywords-Thocarboxamide complexes, heterocyclic bases and spectroscopic methods.

Introduction

The important biological processes Sumczyński *et al.* (2020), Chylewska *et al.* (2016), Nassar et al. (2012), Lamon *et al.* (1968) involve metal ions which coordinate with a wide range of ligands having sulphur, nitrogen and oxygen atoms as donating sites. These ligands are multi-functional in nature and capable of encasing metal ions in an organic sphere. To study the biological processes, there has been in recent years Vogel (1968), Nassar *et al.* (2013) an increasing interest in the syntheses and prototype 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 importance Dede *et al.* (2009). These complexes have been found to show biological activities antiviral, antibacterial and anti-tumor which lead to have great interest in the chemistry of these compounds, particularly with the transition metal ions.

A large number of experiments have been carried out to understand the nature of metal sulphur bond, the donor properties of sulphur, the position of ligands containing thiocarbonyl sulphur as donor sites in the spectrochemical and nephelauxetic series etc. have not yet been well understood.

Experimental

Material and Methods

The experiments were performed in open aerobic condition at room temperature. The solvents were dried and distilled before use following standard procedures. All reagent grade chemicals were obtained from commercial source and were used as received. 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 Kanpur, IR was recorded as KBr pellets 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.

Preparation of thiocarboxamide ligands (ETH and PTH)

Ligand N-Ethoxycarbonylpyrrole-2-thiocarboxamide (ETH) was prepared by literature method Nakamoto (1963). The initial step in the synthesis of these ligands is to prepare ethoxycarbonyl isothiocyanate (SCNOOEt) Lamon (1968).

(i) Ethoxycarbonyl isothiocyanate (SCNOOEt)

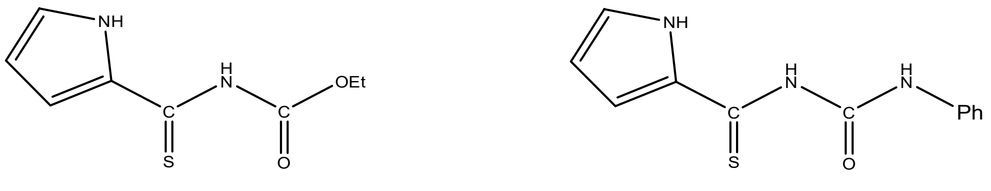
A reaction mixture of 700 ml of acetonitrile and 194 g (2.0 mol) of KSCN was warmed on a steam bath and the warm mixture was treated, part wise with 217 g (2.0 mol) of ethylchloroformate. Heating was continued until the reaction mixture became hot and inorganic precipitate thickened rapidly. At this point the mixture became yellow and the heat source removed and reaction was allowed to continue till completion. The reaction mixture was allowed to cool slowly till reach to room temperature, chilled and filtered. The resultant was concentrated under reduced pressure and the residual oil is distilled. Yield 161 g (BP. 51-55/13 mm). Re-distillation at 10 mm showed that the bulk of material distilled at 44-46 ^{o}C.

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

Both ice cooled mixture of 16.8 g (0.25 mol) of pyrrole and 32.8 g (0.25 mol) of ethoxycarbonyl isothiocyanate, was taken together, stirred occasionally and cooled as needed to prevent its temperature form rising above 40^{o}C. Within one hr the mixture had solidified and 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 mixture gave pure compound in the form of yellow crystals. m.p. 98-99 ^{o}C. 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.

(iii) N-Phenylcarbamoylpyrrole-2-thicarboxamide(PTH)

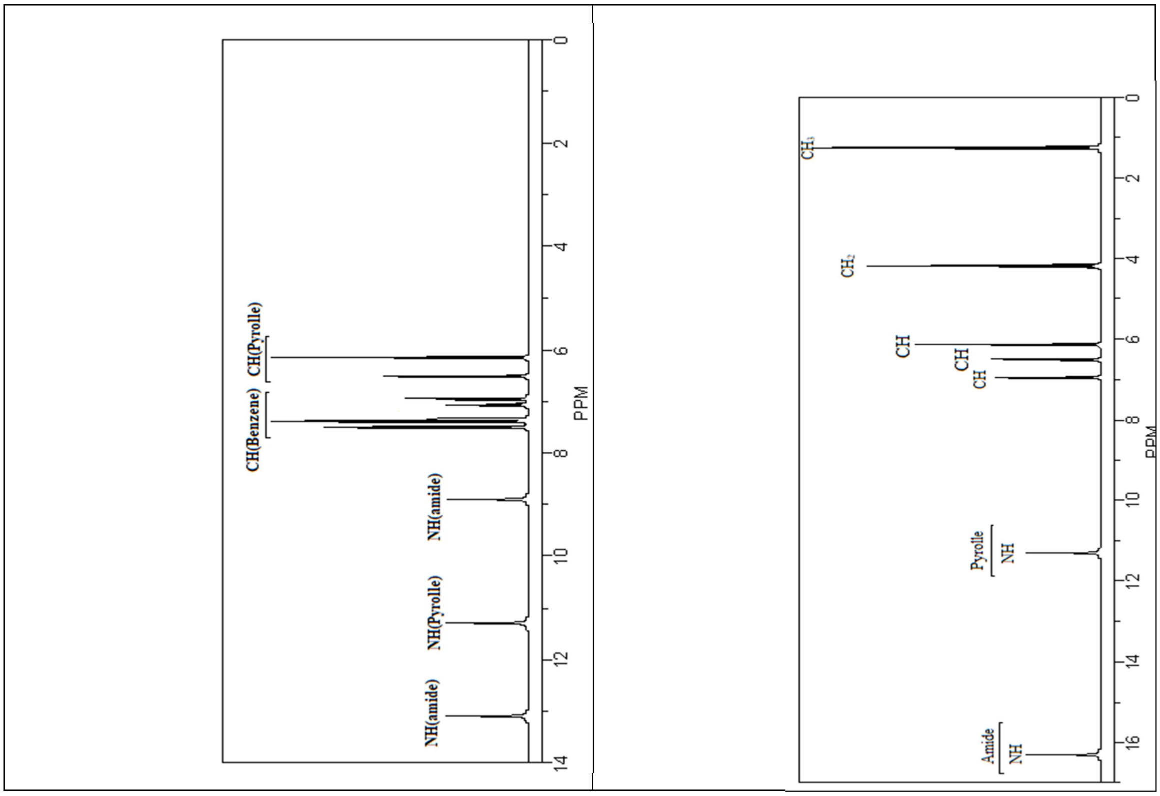
Mixture containing 1.0 g of N-ethoxycarbonylpyrrole-2-thicarboxamide and 5 ml of aniline was boiled for about one minute and the resulting solution was cooled, filtered and wash the precipitate with carbon tetrachloride. Thus the complex 1.1 g (92 %) of N-phenylcarbamoylpyrrole-2-thicarboxamide ($C_{12}H_{11}ON_3S$) was obtained. Re-crystallized from ethanol yielded the pure compound in the form of yellow crystals.m.p. 231-214 ^{0}C. Anal.calcd: C 58.8; H 4.5; N 17.1; S 13.1. Found: C 58.9; H 4.4; N 16.8; S 12.8.



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

N-Phenylcarbamoylpyrrole-2-thiocarboxamide (PTH) (b)

Fig. 1 Structure of the ligands.



Preparation of metal complexes

(i) Preparation of Zn(ETH) complexes

First step involves preparation of benzene solution (25 ml) containing ligand (ETH) and ZnX_2 (1:1) was slowly mixed with 0.5 g of triphenylphosphine at room temperature. The light yellow solution formed was refluxed for 1hr and evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 ml), petroleum ether (15 ml) was added and solution was stand for 3-4 hr. The resulting yellow microcrystalline compound was filtered, washed several times with petroleum ether and dried in vacuo and analyzed (Table 1).

(ii) Preparation of Zn(PTH) complexes

A solution of one equivalent of ZnX_2 and 0.5 g triphenylphosphine in 25 ml benzene was taken in 100 ml flask fitted with a condenser and water circulatory system. One equivalent of ligand (PTH, 0.17 g) was added in it and stirred for 2 hrs whereby light to dark yellow compounds with X(Cl, Br, I) were formed. These are filtered, washed several times with petroleum ether and dried in vacuo and analyzed (Table 1).

Analysis and estimation

The complexes were digested in aqua- regia for some time until residue give transparent colour mineral acids and the solution is used for detection of metal ion and sulfur (Nakamoto, 1963, Lamon, 1968). Zinc was estimated as Zn(8-hydroxyquinaldinate), sulfur as $BaSO_4$, halogens as AgX (X = Cl, Br and I) and phosphorous as phosphomolybdate (Burton and Riley,1955).

Results and discussion

The analysis of data suggest that the ligands in all the complexes of Zn(II) attached as mono dentate if one assumes that the metal ions take the normally preferred geometries.

Table 1. Analytical data of the thiocarboxamide Zn(II) complexes.

Complex	Colour	Elemental Analysis, Found(Calculated)							
		MP (^oC)	C	H	N	P	S	Halide	M
$[Zn(PPh_3)_2$ (ETH)Cl]	Light Yellow	120	64.25 (64.32)	5.20 (5.6)	3.38 (3.41)	7.44 (7.55)	3.22 (3.19)	4.38 (4.30)	7.85 (7.83)
$[Zn(PPh_3)_2$ (ETH)Br]	Light Yellow	170	67.29 (67.24)	4.51 (4.62)	3.31 (3.23)	2.81 (2.16)	3.56 (3.69)	9.15 (9.24)	7.35 (7.43)
$[Zn(PPh_3)_2$ (ETH)I]	Light Yellow	190	57.72 (57.81)	3.31 (3.38)	3.15 (3.06)	2.35 (2.29)	3.48 (3.50)	13.82 (13.91)	6.92 (7.00)
$[Zn(PPh_3)_2$ (PTH)Cl]	Light Yellow	140	66.32 (66.35)	4.61 (4.72)	4.72 (4.83)	7.81 (7.14)	3.62 (3.68)	4.15 (4.08)	7.32 (7.42)
$[Zn(PPh_3)_2$ (PTH)Br]	Light Yellow	170	63.21 (63.12)	4.71 (4.60)	4.71 (4.60)	6.85 (6.79)	3.55 (3.50)	8.72 (8.76)	8.05 (8.15)
$[Zn(PPh_3)_2$ (PTH)I]	Light Yellow	210	60.15 (60.03)	4.32 (4.37)	4.32 (4.37)	6.35 (6.46)	3.38 (3.33)	13.18 (13.23)	6.65 (6.80)

The IR bands in pyrrole moiety 1550, 1470, 1400, 1140, 1040, 995 and 750 cm^{-1} were present in the spectrum which is the characteristic of the ligand (Dede et al. 2009). The positions of these bands did not shift in the spectra of complexes which indicate that –NH group of pyrrole is not participating in the bond formation. As expected the oxygen atom of $–OC_2H_5$ group in ETH (a) participate in the complex formation. The characteristic bands of phenyl group in PTH were stationary, further the nitrogen being hard base and delocalization of the lone in phenyl ring has less probability of bond formation with metal (Hogarth et al. 2009). It is therefore assumed that bonding in complexes occurs through –C(S)-NH-C(O)- moiety of the ligands.

The Infrared spectra of $[ZnX(PPh_3)_2ETH]$ show band at 3345 due to ν(N-H) and weak bands at 640 and 675 cm^{-1} due to τ(NH). Band at 1780 cm^{-1} due to ν(CO) remains stationary and at 1125 cm^{-1}, 875 cm^{-1} due to ν(C=S) and thioamide band-IV ν(C=S). The thioamide band-I [δ(NH) + ν(CN]) at 1500 cm^{-1} increases in all complexes by 30 cm^{-1} and new band of weak intensity in 270-300 cm^{-1} may be assigned due to ν(Cu-S)[11] vibration.

Table 2. Assignments of major IR bands of ligand and complexes

Ligand (ETH)	Complexes	Assignments
3345(s)	3345(m,s)	ν(N-H)

3145(m)	3145(m, s)	
1775(s)	1780(m, s)	ν(C=O)
1500(w)	1530(w)	Thioamide band I and amide band II
1125(s)	1105(m, s)	Thioamide band I
875(m, s)	860(w)	Thioamide band IV major contribution of ν(NH-CO) group
845(m, s)	850(w)	τ(N-H) in the cis form of (NH-CO) group
640(m), 600(w)	675(w)	τ(N-H)
	270 – 300 (w)	ν(Zn-S)
Ligand (PTH)		
3400(s)	3400 (± 5 cm^{-1})	ν(N-H)
3250(m)	3250 (± 5 cm^{-1})	ν(N-H)
3160(s)	3160 (± 5 cm^{-1})	ν(C=O)
1730(s)	1725(m, s)	Amide band I major contribution from ν(C=O)
1655(m, s)	1660(w)	Mixed vibration arising due to ν(C=N), δ(N-H)
1250(m, s)	1260(ws)	Thioamide band I, II and amide band II, III
805(m, s)	790(ws)	Thioamide band IV having major contribution from ν(C=S)
	270-290 (w)	ν(Zn-S)

This suggest that Zn (II) is bonded to ligand through sulfur. [ZnX$(PPh_3)_2$PTH] complexes show bands ν(N-H) at 3400 and 3250 cm^{-1}, amide band-I at 1730 cm^{-1}, ν(C=S) at 1145 cm^{-1}, thioamide band-IV mainly due to ν(C=S) at 805 cm^{-1}, a weak band at 270-290 assigned to ν(Cu-S) and thioamide band-I at [δ(NH) + ν(C=N]) at 1655 cm^{-1} clearly suggest that Zn(II) is bonded to the ligand through sulfur.

All the complexes show diamagnetic properties suggest their tetrahedral coordination in d^{10} state (Kumar et al. 2009). Electronic spectrum of the complexes [ZnX$(PPh_3)_2$ETH] showed two absorption band at 27400 cm^{-1}(s) and 22250 cm^{-1}(w) assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively for ligand in chloroform. The reason for assigning 22250 cm^{-1} band to $n \rightarrow \pi^*$ since sulfur or nitrogen atom occurs at lower energy and are less than occurs intense than $\pi \rightarrow \pi^*$ transition (Hogarth et al., 2009) and secondly the nature and position of band is in solvent dependent. All the Zn (II) complexes showed one intense band at 24000 cm^{-1} assigned to M→L charge transfer (Singh *et al.* 2015). The electronic bands of the complexes (24200, 28200 cm^{-1}) taken just after dissolution, shifted towards lower wave number (23530, 27200 cm^{-1}) when taken after about 4 hr.

The electronic spectrum of $[ZnX(PPh_3)_2PTH]$ show bands at 27780 and 24150 cm^{-1} which is due to charge transition of ligand. The complexes with d^{10} system did not show d-d transition except the intra-ligand band around 27100 cm^{-1} and that due to M→L transiton around 22200 cm^{-1}. However there is as hypsochromic shift of 100 cm^{-1} in 24200 cm^{-1}. The band at 28000 cm^{-1} disappear, this may due to bonding of metal ion through thiocarbonyl sulfur which lowers the energy of non-bonding as well as π levels thus increasing the $\pi\rightarrow\pi^*$ transition (Sabin *et al.*, 1992, Lippard and Uero, 1968, Fackler *et al.,* 1998, Singh etal., 2011, Czerwienic and Yersin, 2011). The behavior of these complexes couldn't be established in chloroform because they are insoluble in this solvent.

Conclusion

On the basis of elemental analysis, IR, electronic spectral and magnetic moment studies, tetrahedral geometry is proposed to these complexes (Fig. 2 & 3).

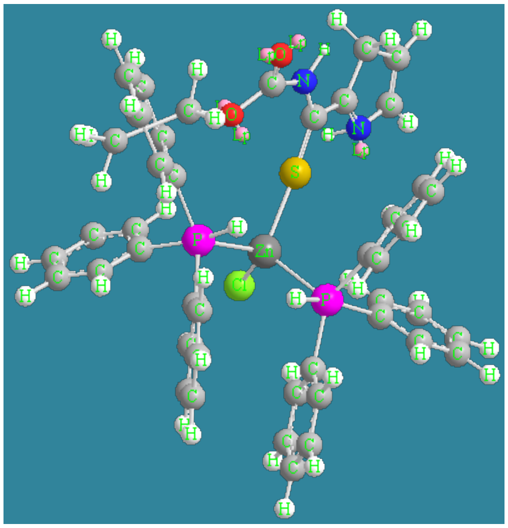


Fig. 2. Minimize 3D Ultra structure of the $[ZnCl(PPh_3)_2ETH]$

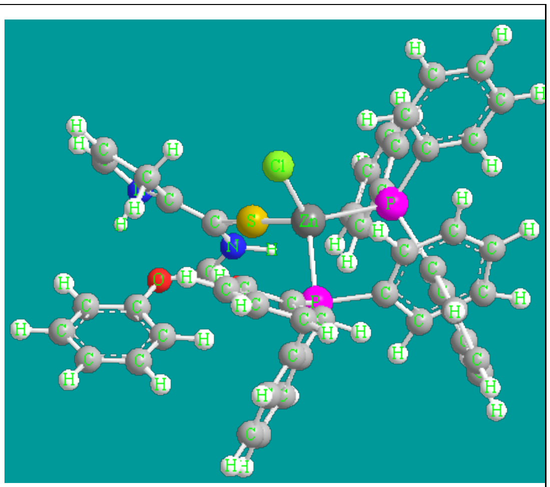


Fig. 3. Minimize 3D Ultra structure of the $[ZnCl(PPh_3)_2PTH]$

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