



Reaction of N-ethoxycarbonylpyrrole-2-thiocarboxamide and N-phenylcarbamoypyrrole-2 thiocarboxamide with $[M(PEt_3)_4]$ (M=Ni, Pd, and Pt)

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ABSTRACT

In this paper, the reactions of $[M(PEt_3)_4]$ (M=Ni, Pd, and Pt) were Carried out with N-PhenylCarbonylPyrrole-2-thiocarboxamide (ETH) and N-Phenylcarbamoypyrrole-2-thiocarboxamide (PTH). The product of the these reactions were characterized on the basis of analytical, spectral (IR, UV and Visible) and magnetic studies. A tentative structure has been proposed to these complexes.

Key words:

INTRODUCTION

A large number of papers have appeared on the study of complexes with the ligands having Sulphur and Nitrogen donor atoms.^{1,2} Although the purpose of these investigations were mainly to get a clear understanding of the nature of bond formed between Sulphur atom of the ligand and the central metal ion, but a coherent picture of the donor acceptor relationship between Sulphur and metal ions is still not clear. Further, the metal Complexes of β -diketones and their derivatives exhibit interesting Properties,³ there exist however, a Possibility to modify these Properties if one replaces -CH group between to Corbonyl or thiocarbonyl groups by a more electronegative N atom in β -diketones. It will, therefore, be interesting to study metal Complexes of β -diketones type ligands having sulphur as donor atom's, so that a

Correlation could be sought between different Physico-chemical Properties of the Various metal Complexes. This paper reports the synthesis and characterization of several complexes of N-Ethoxycarbonylphyrrole-2 thiocarboxamide(A) and N- Phenylcarbamoypyrrole-2 thiocarboxamide(B) with various metal ions.

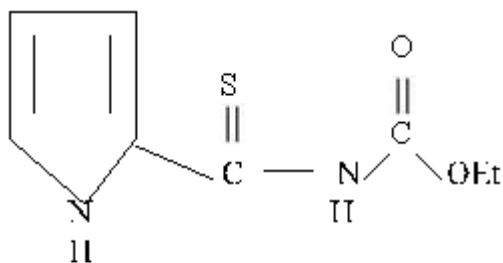
EXPERIMENTAL

N - Ethoxycarbonylpyrrole - 2 - thiocarboxamide and N-Phenyl Carbamoypyrrole-2-thicarboxamide according to the Procedure described in $[M(PEt_3)_4]$ (M=Ni, Pd and Pt) were prepared according to the literature methods⁴.

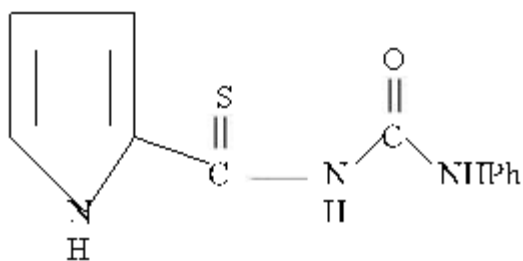
Preparation of metal complexes

$[Ni(PEt_3)_2(LH)]$ (LH=ETH on PTH)

To a solution of $[Ni(PEt_3)_4]$ (0.42g~



(A)



(B)

0.8mmol) in 20ml CH_2Cl_2 was added one equivalent of ligand LH (0.16g or 0.20g respectively, 0.8mmol). The resultant solution was stirred for 3h and filtered. The filtrate is removed to smaller volume 20ml Et_2 -Hexane (1:1V | V) was added to this solution where by a coloured Precipitate of the complex was formed. It was filtered and washed with Et_2O -Hexane (2x2ml) and dried in vacuo.

Yield. $[\text{Ni}(\text{PEt}_3)_2(\text{ETH})]$, 0.31g, 80%,
 $[\text{Ni}(\text{PEt}_3)_2(\text{PTH})]$, 0.28g, 65%

$[\text{Pd}(\text{PEt}_3)_2(\text{LH})]$ (LH=ETH or PTH)

A suspension of $[\text{Pd}(\text{PEt}_3)_4]$ (0.29g~0.5mmol) in benzene (15ml) was added one equivalent (0.5mmol) of LH (ETH, 0.1g, PTH, 0.12g) with constant stirring. The resultant solution was refluxed for 3h then filtered and reduced to smaller volume. It was kept in refrigerator for 30 minutes where by crystalline precipitate of the complex formed. It was filtered and washed with Et_2O (2x2ml), Pet ether (60-80) (2x2ml) and dried in vacuo.

Yield: $[\text{Pd}(\text{PEt}_3)_2(\text{ETH})]$, 0.19g, 70%
 $[\text{Pd}(\text{PEt}_3)_2(\text{PTH})]$, 0.20g, 70%

$[\text{Pt}(\text{PEt}_3)_2(\text{LH})]$ (LH= ETH or PTH)

A Suspension Of $[\text{Pt}(\text{PEt}_3)_4]$ (0.20g,

0.3mmol) and one Equivalent of LH (0.3mmol) (ETH, 0.05g; PTH, 0.07g) in acetone- TMF (20ml, 1:1 V çV) was heated under reflux for 10 min, during which the colour of the solution changes. It was filtered and concentrated to 5ml. On adding 20ml petroleum ether (60-80°) Precipitate of the complex formed. It was filtered, washed with petroleum ether (60-80°) (2x2ml) and dried in vacuo.

Analyses

A weighed amount of complex was taken in a Pyrex beaker. It was decomposed by digesting it with aquaregia for some time until the residue gave transparent solution with dil. mineral acids. This solution was used to estimate metal ions and sulphur.

Estimation of Nickel, Palladium and Platinum

Ni and Pd were estimated as their dimethyl glyoximate and weighing as $\text{M}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$ (M=Ni or Pd) and Pt as K_2PtCl_6 .

Estimation of Sulphur

Sulphur was estimated as BaSO_4 . Carbon, Hydrogen and Nitrogen analyses were Performed by the microanalytical section of the Indian Institute of Technology, Kanpur (U.P.) India. The analytical results are given in Table II-1.

Infrared Spectra

Infrared spectra of the ligand and metal complexes were recorded with a Perkin- Elmer 580 Diffraction grating Infrared Spectrophotometer in the range $4000\text{-}250\text{cm}^{-1}$ range. Samples were Prepared as Potassium bromide Pellets. The major bands of the infrared spectra of the ligand and complexes are given in Table II-2.

Magnetic Susceptibility Measurements

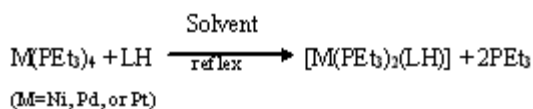
Magnetic Properties of the Complexes were checked with the help of Goway balance at room temperature.

Visible Spectra

The absorption Spectra of the ligand and Complexes were measured in CH_2Cl_2 on Cystromic 108 spectrometer from 200-900nm. The results are given in Table II-3.

RESULTS AND DISCUSSION

Treatment of $[M(PEt_3)_4]$ ($M = Ni, Pd, \text{ or } Pt$) with one equivalent of LH (ETH or PTH) in a solvent (CH_2Cl_2 or Benzene or Acetone- DMF) undergo replacement of two molecules of PEt_3 by one molecule of LH.



The Compound are air stable, soluble in CH_2Cl_2 or benzene, Partially soluble in DMF or Benzene and insoluble in $CHCl_3$, DMF or DMSO. On Comparing the Stoichiometry of these. Compound with known Preferences, the analytical data suggest that ligands in all the complexes is functioning as bidentate. As a bidentate, it can link, through any two of the five donor sites viz., Nitrogen, Oxygen and Sulphur. The IR Spectral studies of ligand and complexes are taken to know the possible modes of linkages in the complexes. The Positions of meior I.R bands present in the spectra of the ligand and complexes are give in Table II-1'. Since attempt to deuterate the ligand, failed, our tentative assignments are based on the comparative IR spectral studies of a number of related compounds.⁴

Characteristic IR bands of pyrrole moiety (1550, 1470, 1400, 1140, 1040, 995, and 750 cm^{-1}) were present in the spectrum of lignad⁵. The position of these bands did not shift in the spectra of complexes (maximum shift $\pm 5 cm^{-1}$). This indicates that NH group of pyrrole moiety is not participating in the bond formation. It is highly unlikely that Oxygen of - OEt group will participate in bond formation with the metal. NH group of - NHPH group in PTH is less basic owing to the delocalization of lone pair of electron in phenyl ring. It is, therefore, assumed that - CSNH C(O) moiety of the ligand is participating the bond formation with the metal and the meior shift in the positions of the bands are expected to be in thioamide and amide bands. The meior changes in the band positions in the spectra of the complexes compared to those of ligand along with the discussions are as follows.

$M(PEt_3)_2(ETH)$ ($M = Ni, Pd \text{ or } Pt$)

(1) The ligand bond at 3360 cm^{-1} due to $\nu(NH)$

shifted towards lower wave numbers and appeared around 3310 cm^{-1} suggesting increased electro negativity of nitrogen atom of the-CSNHC(O)- moiety and absence of deprotonation in the complexes.

(2) The thioamide⁶⁻⁸ band I and II arising due to coupled vibration of $\delta(NH)$ and $\nu(CN)$ at 1540 and 1340 cm^{-1} shifted towards higher ware number.

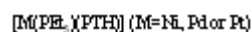
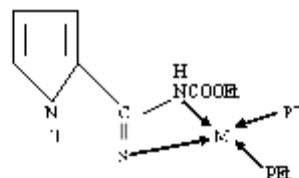
(3) The broad band at 1050 and 870 cm^{-1} of the free ligand shifted towards lower wave numbers ($\sim 20 cm^{-1}$) in the spectra of the complexes. The band at 1070 cm^{-1} have been assigned to thioamide band III having meior contribution from $\nu(C-N)$ and $\nu(C-S)$ in the normal coordinate. The band at 870 cm^{-1} in assigned to C-S (thioamide band IV). The shift in the positions of these bands towards lower wave numbers in the complexes further confirmed the bonding of the metal through thiocarbonyl sulphur.

(4) The position of ligand band at 495 cm^{-1} assigned to $\delta(C=S)$, shifted towards lower ware numbers ($\sim 20 cm^{-1}$).

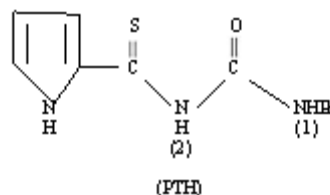
(5) The characteristic bands of triethyl phasphine at 2962, 2872, 2853, 1467, 700 and 500 cm^{-1} were present in all the complexes¹.

(6) The new bands around 470-350, and 450-300 in the spectra of all the complexes are assigned to mixed $\nu(M-N)$ and $\nu(M-S)$ vibrations.¹⁰

From the forgoing discussions of IR spectra, the following bonding scheme is assumed.



The are two NH group in the side chain of the ligand.



The NH group(1) will not Participate in bonding due to following two reason.

- NH(1) is less basic than NH(2) to the delocalization of nitrogen lone pair electron density in the ring.
- There is a steric hindrance of phenyl group when nitrogen lone pair undergoes bond formation with a lewis acid (metal atom).

Thus the bonding pattern of PTH with metal atom is almost same as ETH. The shift of characteristic PTH bands are as follows.

- All the characteristic bands of pyrrole moiety are Present in complexes.
- The ligand band 3410 and 3260 cm^{-1} becomes broad and that at 3160 cm^{-1} due to $\nu(\text{NH})$ of $-\text{CSNHCO}-$ moiety remains stationary ($\pm 5\text{cm}^{-1}$) in all the complexes.

Table 1: Analytical Data Colour and melting Points of Complexes.

| Compound | Colour | m.p. °C | Found (Calcd) % | | | | | Metal |
|--|-------------------|------------|------------------|----------------|----------------|----------------|------------------|------------------|
| | | | C | H | N | S | P | |
| [Ni(PEt ₃) ₂ (ETH)] | Brown | 171 | 28.78 (29.22) | 4.12 (4.05) | 5.42 (5.68) | 6.34 (6.50) | 12.12 (12.58) | 11.6 (11.9) |
| [Ni(PEt ₃) ₂ (PTH)] | Brownish Black | 233 | 35.22 (35.57) | 4.05 (3.89) | 7.12 (7.28) | 5.62 (5.92) | 10.92 (11.48) | 10.68 (10.87) |
| [Pd(PEt ₃) ₂ (ETH)] | Yellow | 184 | 26.44 (26.6) | 3.88 (3.70) | 5.06 (5.18) | 5.64 (5.92) | 11.24 (11.47) | 19.14 (19.68) |
| [Pd(PEt ₃) ₂ (PTH)] | Yellow | 255 | 23.10 (23.6) | 3.88 (3.57) | 6.90 (7.15) | 5.18 (5.44) | 10.42 (10.55) | 18.00 (18.11) |
| [Pt(PEt ₃) ₂ (ETH)] | Orange | 198 | 22.68 (22.89) | 3.36 (3.17) | 4.28 (4.45) | 5.16 (5.08) | 9.48 (9.85) | 30.6 (31.0) |
| [Pt(PEt ₃) ₂ (PTH)] | Orange | 261 | 28.12 (28.40) | 3.26 (3.10) | 5.96 (6.21) | 4.62 (4.73) | 8.90 (9.17) | 28.2 (28.81) |

Table 2: Comparison of the major IR Bands of ligands and Complexes

| Compound | $\nu(\text{NH})$ | $\nu(\text{CO})$ | $\nu(\text{CS})$ | Thioamide Band | | | | Coordi- nation |
|--|---|-------------------|-------------------|-------------------|-------------------|-------------------|------------------|-------------------|
| | | | | I | II | III | IV | |
| ETH | 3360 _m 3140 _m | 1775 _s | 1120 _s | 1540 _s | 1340 _s | 1070 _s | 870 _m | |
| [Ni(PEt ₃) ₂ (ETH)] | 3310 _s | 1785 | 1100 | 1550 _s | 1350 _s | 1050 _s | 850 _m | |
| [Pd(PEt ₃) ₂ (ETH)] | 3310 _s | 1790 | 1100 | 1550 _s | 1350 _s | 1045 _s | 855 _m | |
| [Pt(PEt ₃) ₂ (ETH)] | 3310 _s | 1785 | 1100 | 1555 _s | 1350 _s | 1045 _s | 850 _m | |
| PTH | 3410 _m 3260 _m 3160 _m | 1720 _s | 1130 _s | 1525 _s | 1350 _s | 1010 _s | 860 _m | |
| [Ni(PEt ₃) ₂ (PTH) ₂] | 3405 _{br} 3240 | 1730 | 1110 | 1540 _s | 1375 _s | 1000 _s | 840 _m | |
| [Pd(PEt ₃) ₂ (PTH) ₂] | 3400 _{br} 3240 | 1735 | 1110 | 1540 _s | 1360 _s | 990 _s | 840 _m | |
| [Pt(PEt ₃) ₂ (PTH)] | 3400 _{br} 3240 | 1735 | 1110 | 1545 _s | 1370 _s | 995 _s | 840 _m | |

Table 3: Electronic Spectra of ligand and Complexes

| Compounds | Band Position λ_{\max} (nm) | Assignments |
|--|--|-------------------------|
| ETH | 440 | $n \rightarrow \pi^*$ |
| | 365 | $\pi \rightarrow \pi^*$ |
| Ni(PEt ₃) ₂ (ETH) | 400 | CT |
| | 300 | CT |
| | 260 | IL |
| Pd(PEt ₃) ₂ (ETH) | 410 | CT |
| | 310 | CT |
| | 260 | IL |
| Pt(PEt ₃) ₂ (ETH) | 425 | CT |
| | 300 | CT |
| | 270 | IL |
| PTH | 415 | $n \rightarrow \pi^*$ |
| | 390 | $\pi \rightarrow \pi^*$ |
| [Ni(PEt ₃) ₂ (PTH)] | 360 | CT |
| | 410 | CT |
| | 300 | CT |
| [Pd(PEt ₃) ₂ (PTH)] | 260 | IL |
| | 425 | CT |
| | 310 | CT |
| [Pt(PEt ₃) ₂ (PTH)] | 270 | IL |
| | 430 | CT |
| | 310 | CT |
| | 275 | IL |

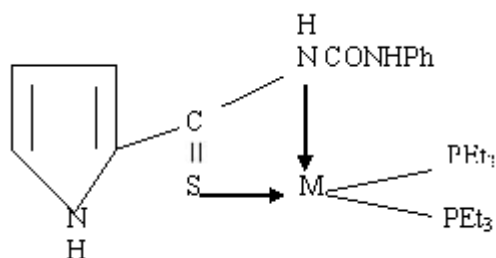
- (3) The thioamide band I and II (drising due to coupled vibrations of $\delta(\text{NH})$ and $\nu(\text{CN})$ at 1525 and 1350 cm^{-1}) shifted towards the higher wave number (10-15 cm^{-1})
- (4) The broad band at 1010 and 860 cm^{-1} (arising due to thioamide band III and IV respectively) shifted to lower wave number (10 cm^{-1}) in all the complexes.
- (5) Position of the ligand band 490 cm^{-1} assigned to $\delta(\text{C}=\text{S})$ shifted to lower wave number (20 cm^{-1})
- (6) The characteristic bands of triethylphosphire at 2962, 2872, 2853, 1467, 700 and 500 cm^{-1} were Present in all the complexes.
- (7) The new bands around 470-350 and 400-300 cm^{-1} in the spectra of all the complexes are assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ vibrations.

The similar bonding scheme of ETH and

PTH are proposed on the basis of forgoing I.R spectral studies of ligand and complexes.

Magnetic Properties

All the complexes were found to be diamagnetic, since the number of ligands two PEt₃ (monodentate) and One LH (bidentate). It is assumed that these metal atom are four coordinated tetrahedral.



Electronic Spectra

The electronic spectrum of ETH showed two bands at 440 and 365 nm which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions respectively. The electronic spectrum of PTH showed three bands at 415, 390 and 360 nm. Which are assigned to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and CT bands respectively. Usually $n \rightarrow \pi^*$ transitions involving N and Sulphur occur at lower energy and are less intense than $\pi \rightarrow \pi^*$ transition.¹¹⁻¹³ The spectra of almost all the complexes show the Presence of these bands with hypsochromic shift. The one intense band at 400-430 nm in all the complexes is assigned to $d\pi(\text{M}) \rightarrow d\pi(\text{P})$ of PEt₃. The high intensity of these bands suggest that they should be charge transfer an intraligand band. NO d-d transition bands are expected in these metal system (d^{10}). The hypsochromic shift of the bands at 440 and 415 nm of ligand ETH and PTH respectively, in their complexes may be due to stabilization of the energy of lone pair of electrons on complex formation. Similarly the hypstochromic shift of other bands of ligands in the spectra of complexes may be explained as that metal atom are bonded through thioccarbonyl sulphur and Nitrogen¹⁴. The bond formation lower the energy of non bonding Orbitals as well as π levels thus now more energy will be required to promote the electron from the n or π level to π^* orbital hence the observed hypsochromic shift. The assignments of all the bands are given in Table 1.

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