

Reactions of Nickel (II) & Copper (II) Ions with 2-Thiopyrrole-1,2-dicarboximide & N-Carbamoylpyrrole- 2-thiocarboxamide in Presence of Various Nitrogen Containing Heterocyclic Bases

R SAHEB, S K DIKSHIT* & U C AGARWALA

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016

Received 25 May 1983; revised and accepted 5 August 1983

Reactions of 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH) with Cu(II) and Ni(II) ions in the presence of several N-bases lead to the formation of $[\text{Cu}(\text{TP})(\text{TPH})\text{Py}]\text{H}_2\text{O}$, $[\text{Cu}(\text{TP})(\text{TPH})\text{Imid}]\text{H}_2\text{O}$, $[\text{Ni}(\text{TP})_2\text{B}]\cdot x\text{H}_2\text{O}$ (where B is the organic base), $[\text{Cu}(\text{CPT})(\text{CPTH})]\text{H}_2\text{O}$ and $[\text{Ni}(\text{CPT})_2]$ complexes. The complexes, thus obtained have been characterised by means of chemical analyses, infrared and electronic spectral studies and magnetic measurements.

The coordination chemistry of 2-thiopyrrole-1,2-dicarboximide (TPH) and N-carbamoylpyrrole-2-thiocarboxamide (CPTH) with a variety of soft metal ions has been previously reported¹. These ligands interact with Co(II) and Co(III) compounds in the presence of N-bases to give interesting and less known diamagnetic Co(II) complexes²⁻⁵. As an extension of our earlier work¹⁻³ and in order to fully define the coordination chemistry of this important class of ligands, we now report the results of reactions of Ni(II) and Cu(II) ions with these ligands in presence of various nitrogen containing heterocyclic bases.

Materials and Methods

All the chemicals used were either chemically pure or of AR grade.

The infrared spectra were recorded in KBr on a Perkin-Elmer model-580 spectrophotometer in the range $4000-250\text{ cm}^{-1}$ and electronic spectra were recorded on a Cary model 17D UV visible spectrophotometer. Magnetic measurements were carried out on a standard Gouy balance.

(i) Reaction of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ with TPH in presence of pyridine, imidazole and $\beta(\gamma)$ -picoline

An ethanolic solution (25 ml) of TPH (0.5 g, 3 mmol) was slowly added with stirring to an aqueous solution (30 ml) of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ (0.4 g, 1.5 mmol) containing about 1 ml of pyridine, whereby an intense reddish violet solution was obtained. It was refluxed for 30 min on a water-bath. This resulted in the formation of reddish coloured crystalline product which was separated by centrifugation, washed successively with water, small amounts of ethanol, ether and dried *in vacuo*. To the centrifugate, excess water was further

added and refluxed on a water-bath to precipitate more of the complex. The complex did not melt upto 200°C . It was observed that the complex did not precipitate in the absence of base.

(ii) Reaction of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ with TPH in presence of organic bases

An aqueous solution (25 ml) of copper sulphate pentahydrate (0.25 g, 1 mmol) containing pyridine (2 ml) was treated with an ethanolic solution (25 ml) of TPH (0.35 g, 2.3 mmol). The colour of the solution was changed immediately to red followed by slow precipitation of the complex. The mixture was stirred for 5 min, allowed to stand for 30 min at room temperature, the precipitate filtered off, washed several times with water, small amounts of ethanol and finally with ether.

In the above reaction in the absence of pyridine, the solid obtained analysed for $[\text{Cu}_2(\text{TP})_2(\text{TPH})\text{H}_2\text{O}]$ and did not melt upto 280°C .

(iii) Bis(N-carbamoylpyrrole-2-thiocarboxamidato)nickel(II), $[\text{Ni}(\text{CPT})_2]$

An ethanolic solution (25 ml) of CPTH (0.5 g, 3 mmol) was treated with an aqueous solution (25 ml) of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ (1.6 g, 6 mmol). The resulting solution was refluxed for 30 min, whereby a red crystalline precipitate settled down which was suction filtered, washed successively with water, ethanol, ether and dried *in vacuo*.

(iv) N-Carbamoylpyrrole-2-thiocarboxamidato (N-carbamoylpyrrole-2-thiocarboxamide)copper(I)monohydrate, $[\text{Cu}(\text{CPT})(\text{CPTH})]\text{H}_2\text{O}$

This compound was prepared by the method similar to the one described in (ii) except that CPTH and 0.1 ml of pyridine were used in place of TPH and 2 ml of pyridine.

Results and Discussion

The characterisation data of the complexes are recorded in Table 1. TPH complexes of nickel were slightly soluble in ethyl alcohol and acetone and soluble in chloroform, dichloromethane, nitrobenzene, DMF, DMSO and other similar organic solvents. Copper complexes of TPH and CPTH and the nickel complex of CPTH were slightly soluble in these solvents. All the complexes are high melting, diamagnetic solids.

Since the ligands are polyfunctional and possess four potential donor atoms, infrared spectra of the ligands⁶ and those of the complexes were compared in order to decide the bonding sites. Owing to the extensive mixing of $\delta(\text{NH})$, $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{S})$, $\tau(\text{NH})$ modes, the infrared spectra were characterised by the presence of a number of IR bands. The complications also arose by the presence of bases linked to the metal ion. Also, the characteristic frequencies of the pyrrole ring were mixed with those of the other heterocyclic bases⁶. Since pyrrole ring nitrogen is poorly basic, it was assumed that the bonding may be taking place through C(S)-NH-C(O)-moiety of the ligands. This made unambiguous assignment of the bands and location of donor sites in the ligands rather difficult. However, on comparing the spectra of the complexes with those of the ligands a few characteristic features emerged which were common in all of them. For the sake of clarity of the discussion, the complexes of similar type are grouped together.

Ni(II) complexes of TPH

The spectra of the complexes, $[\text{Ni}(\text{TP})_2\cdot\text{B}]\cdot x\text{H}_2\text{O}$,

Table 1—Analytical Data of the Complexes

Complexes	Found (Calc) %				
	C	H	N	S*	M*
$[\text{Ni}(\text{TP})_2\text{Py}]\cdot 2\text{H}_2\text{O}$	42.5 (42.9)	2.8 (3.2)	15.1 (14.7)	13.7 (13.4)	12.5 (12.2)
$[\text{Ni}(\text{TP})_2\beta\text{-(or } \gamma)\text{pic}]\cdot \text{H}_2\text{O}$	45.4 (45.9)	3.1 (3.2)	15.2 (14.8)	13.5 (13.6)	12.2 (12.3)
$[\text{Ni}(\text{TP})_2\text{Imid}]\cdot 2\text{H}_2\text{O}$	39.3 (38.9)	2.4 (2.2)	17.8 (18.1)	13.6 (13.8)	12.3 (12.5)
$[\text{Cu}(\text{TP}) (\text{TPH})\text{Py}]\cdot \text{H}_2\text{O}$	43.6 (44.0)	3.1 (3.0)	14.8 (15.0)	13.6 (13.7)	13.5 (13.7)
$[\text{Cu}(\text{TP}) (\text{TPH})\text{Imid}]\cdot \text{H}_2\text{O}$	39.5 (40.0)	2.9 (2.7)	18.5 (18.6)	14.0 (14.2)	13.8 (14.0)
$[\text{Ni}(\text{CPT})_2]$	36.7 (36.5)	2.8 (3.0)	21.0 (21.3)	16.0 (16.2)	14.5 (14.6)
$[\text{Cu}(\text{CPT}) (\text{CPTH})]\cdot \text{H}_2\text{O}$	34.8 (34.5)	3.3 (3.6)	19.8 (20.1)	15.3 (15.3)	15.1 (15.2)

*Estimated gravimetrically.

were almost similar. The systematic shifts were more or less in the same direction but the wavenumbers by which the positions of the bands shifted were slightly different. The major changes in the band positions in spectra of the complexes to those of the ligand are as follows:

(i) The position of the band due to $\nu(\text{NH})$ around 3200 cm^{-1} disappeared in the complexes and new bands appeared around 3300 cm^{-1} which may be characteristic bands of the respective bases present in the complexes. This suggested the deprotonation of the imide ring of the ligand which was also indicated by the charge balance in the complexes.

(ii) The position of the amide-I band, having contribution from $\nu(\text{CO})$, which appeared at around 1765 cm^{-1} in the spectrum of the ligand shifted (sometime with splitting) towards lower wavenumbers in the spectra of the complexes, indicating involvement of the carbonyl oxygen in the bond formation⁷ with the central metal atom.

(iii) The ligand bands at 1560 and 1440 cm^{-1} shifted to lower wavenumbers whereas that at 1350 cm^{-1} disappeared in the spectra of the complexes. The positions of the ligand bands due to the amide-III and thioamide II and III in the region $1350\text{--}1190\text{ cm}^{-1}$ remained almost unaltered in the spectra of the complexes. These bands have been assigned to the mixed vibrations having contributions from $\nu(\text{C}=\text{N})$, $\delta(\text{NH})$, $\delta(\text{C}=\text{C})$, $\delta(\text{CH})$ modes. The shifts in 1560 and 1440 cm^{-1} bands suggest the bonding through nitrogen after deprotonation; this was also corroborated by the absence of the band at 3200 cm^{-1} due to $\nu(\text{NH})$.

(iv) The ligand band at 966 cm^{-1} was absent in the spectrum of picoline complex but was present in the spectra of the other two complexes with a small negative shift.

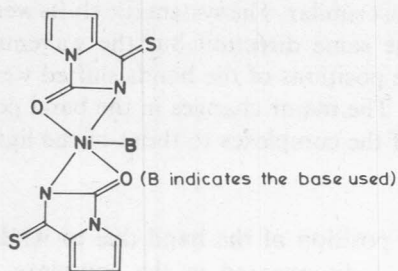
(v) The thioamide band IV⁸ (around 840 cm^{-1}) which has major contribution from $\nu(\text{C}=\text{S})$, was either split into two or remained unaltered in the spectra of the complexes, suggesting thereby that the thiocarbonyl sulphur was not the bonding site.

(vi) New bands of medium intensity in the region $500\text{--}300\text{ cm}^{-1}$ appearing in the spectra of the complexes could be assigned to $\nu(\text{M-O})$ or $\nu(\text{M-N})$ modes of vibration.

In view of the above and if the preferred geometries around the metal ions are assumed, the following bonding sites (See structure I) in the metal complexes may be proposed:

Copper complexes of TPH and CPTH

Copper complexes of TPH and CPTH analysed for $[\text{Cu}(\text{TP}) (\text{TPH})\text{B}]\cdot \text{H}_2\text{O}$ (B = pyridine, imidazole) and



STRUCTURE I

Cu(CPT)(CPTH), respectively. The systematic shifts in the band positions along with the assignments of the major bands are as follows:

(i) The ligand band at 3200 cm^{-1} due to $\nu(\text{NH})$ disappeared in the spectrum of the complexes; instead bands around 3440 and 3360 cm^{-1} appeared. The band at 3100 cm^{-1} of the NH group of pyrrole remained stable. In the spectrum of the CPTH complexes all the ligand bands in the region $3500\text{--}2900\text{ cm}^{-1}$ disappeared except the ones at 3380 and 3270 cm^{-1} assigned to NH_2 group.

(ii) The position of the amide band I (νCO) shifted towards higher wavenumbers in the spectra of the TPH complexes. The position of the same band in the spectra of CPTH complexes practically remained unchanged. This ruled out the possibility of bonding of metal ions through carbonyl oxygen and suggested that the nitrogen atom of the $-\text{C}(\text{O})\text{NHC}(\text{S})-$ moiety might be involved in the bond formation.

The diamagnetism of the complexes indicated copper ion to be in $+1$ oxidation state which shows that the ligand acted as reducing agent towards metal ion. Since two ligands are participating in the bond formation, one of the ligand molecules should act as neutral while the other as monobasic. There existed, however, another possibility where diamagnetism of the copper(II) complexes might arise because of the strong antiferromagnetic interactions between two cupric ions via the bridging S atom⁹⁻¹¹. It is undoubtedly very difficult to decide between the two alternatives. Since the ligands can act as reducing agent, the first alternative is preferred. In case it is presumed that copper is present in $+1$ oxidation state, a linear geometry of the complex is preferred with bonding of the metal ion through nitrogen atom. The possibility of the copper complex having copper in $+2$ oxidation state may also be ruled out on the basis of electronic spectra (vide infra) which did not show the characteristic band due to metal-metal interaction around 375 nm as observed by Yamada *et al.*^{9,10} in the spectra of the complexes where partial or complete quenching of magnetic moment occurred. Since these

complexes have been found to be almost insoluble in the organic solvents, a polymeric structure is assumed.

Nickel complexes of CPTH

(i) The ligand band at 3200 cm^{-1} due to $\nu(\text{NH})$ of $-\text{C}(\text{O})-\text{NH}-\text{C}(\text{S})-$ moiety disappeared in the spectra of the complexes while the position of the other bands in this region remained practically the same.

(ii) The position of the amide band-I, having major contribution from $\nu(\text{CO})$ shifted slightly to lower wavenumber (-5 cm^{-1}). The shift is so small that one may not feel confident of assigning carbonyl oxygen as bonding site. However, the magnitude of this shift can be explained as follows. The bonding of the metal ion with the nitrogen of $-\text{C}(\text{O})-\text{NH}-\text{C}(\text{S})-$ moiety is expected to render $\nu(\text{CO})$ to shift towards higher wavenumber. This will result in two opposing interactions, one trying to lower the $\nu(\text{CO})$ (via bonding through CO) while the other to shift the position of $\nu(\text{CO})$ towards higher wavenumber and thus causing a very small shift in the position of $\nu(\text{CO})$.

(iii) The shifts in the positions of thioamide bands and amide bands in the region $1500\text{--}1200\text{ cm}^{-1}$, on complexation were found to be varying. The positions of some of the bands shifted to higher wavenumbers while those of the remaining ones to lower wavenumbers. It was, therefore, not possible to infer any thing from these shifts.

(iv) The position of thioamide band (IV) having major contribution from $\nu(\text{C}=\text{S})$ shifted to higher wavenumbers ($+10\text{ cm}^{-1}$) corroborating the bonding of the metal ion through nitrogen of the $-\text{C}(\text{O})\text{NH}-\text{C}(\text{S})-$ moiety.

(v) The new bands in the region $300\text{--}400\text{ cm}^{-1}$ could be assigned to mixed vibrations of $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$.

Magnetic properties of nickel and copper complexes

Since the complexes of nickel(II) with TPH analysed for the coordination number five around the metal ion, both square pyramidal or trigonal bipyramidal geometries can be assigned to the complexes. Although the complexes having coordination number five are extensively studied and have been subject matter of several review articles¹²⁻²⁰ dealing with almost all aspects of chemistry, yet a clear picture of the nature of their electronic spectra and stereochemistries is not explicitly explored. However, square pyramidal geometry is tentatively assigned to the nickel complexes of TPH although trigonal bipyramidal geometry is not ruled out.

The nickel complex of CPT, $\text{Ni}(\text{CPT})_2$, has been found to be diamagnetic and hence a square planar geometry is assigned to it.

The diamagnetic behaviour of the copper complexes is interesting. The charge balance of the complex

showed copper to be present in +1 oxidation state. Thus, the charge balance along with the magnetic data suggested that ligands have reduced copper(II) to copper(I). It seems all the more possible because sulphur ligands have a tendency to reduce copper from +2 to +1 oxidation state. However, another possibility exists for quenching the magnetic moment by metal-metal interaction²¹ through the formation of a σ , π or δ -bond but the first alternative (reduction of Cu^{2+} to Cu^+) is preferred over the second.

Near IR, visible and ultraviolet spectra

The complexes of nickel, viz. $[\text{Ni}(\text{TP})_2\text{Py}]$, $[\text{Ni}(\text{TP})_2\text{pic}]$, $[\text{Ni}(\text{TP})_2\text{Imid}]$ showed almost identical spectra recorded in chloroform as solvent in the region 1800-220 nm. The band positions and their assignments are listed in Table 2. These assignments are based on the assumption of square pyramidal geometry of the complexes. The lowest energy band was assigned to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. It is known²² for a series of octahedral nickel complexes of the type $[\text{Ni}(\text{DMF})_6](\text{ClO}_4)_2$ and $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ (ref. 23) that the lowest energy transition occurs at 8380 cm^{-1} (${}^3A_{2g} \rightarrow {}^3T_{2g}$) and 10526 cm^{-1} (${}^3A_{2g} \rightarrow {}^3T_{2g}$), respectively. Since there is a lowering of symmetry from O_h to C_{4v} point group one expects a drop in the value of ν_1 ($\sim 7092\text{ cm}^{-1}$) as well as increase in the number of bands in the electronic spectra which are well in agreement with the observed facts. The lower energy bands are probably the ligand field bands which might be safely assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ (1111 cm^{-1}). The other band occurred at 18180 cm^{-1} . The band around 8333 cm^{-1} did not appear in picoline and imidazole complexes. The high energy transitions may be assigned to the charge transfer occurring due to highest occupied molecular orbital of the ligand to the lowest unoccupied metal orbitals, or intraligand charge transfer bands.

Owing to the very low solubility of $\text{Ni}(\text{CPT})_2$ in CHCl_3 , the spectrum was recorded in nujol. The intensity of the two bands at 17857 (broad) and 21277 cm^{-1} suggested them to occur due to $d-d$ transition. The other two bands ($26320, 35714\text{ cm}^{-1}$) were assigned to the charge transfer, $L(\pi) \rightarrow xy$ and intraligand, $L(\pi) \rightarrow L(\pi^*)$ transition bands, respectively which involved thiocarbonyl group of the ligand²⁴.

The spectrum of copper complex of TPH, recorded in nujol, exhibited only two high energy broad bands with the maxima at 35714 and 41667 cm^{-1} . These bands have been assigned to the intraligand charge transfer $L(\pi) \rightarrow L(\pi^*)$ transitions. Other copper complexes showed similar behaviour. On the basis of the above arguments the following tentative geometries have been assigned to the complexes:

Table 2—Electronic Spectral Bands of Complexes* and Their Assignments

Compound (Solvent)	$R_{\text{max.}}$ (cm^{-1})	Assignment
$[\text{Ni}(\text{TP})_2\text{Py}] \cdot 2\text{H}_2\text{O}$ (Chloroform)	7092	$\nu_1, d_{z^2} \rightarrow d_{x^2-y^2}$
	8333(m,br)	—
	11111(br)	$d_{xy} \rightarrow d_{x^2-y^2}$
	18180(br)	—
	22222	Charge transfer
	27400	Charge transfer
$[\text{Ni}(\text{TP})_2\beta\text{-(or } \gamma\text{)-pic}] \cdot \text{H}_2\text{O}$ (Chloroform)	35561	Intraligand
	7067	$\nu_1, d_{z^2} \rightarrow d_{x^2-y^2}$
	11111(br)	$d_{xy} \rightarrow d_{x^2-y^2}$
	21980	Charge transfer
	27027	Charge transfer
	34722	Intraligand
$[\text{Ni}(\text{CPT})_2]$ (Nujol)	17857	$d_{x^2-y^2} \rightarrow d_{xy}$
	21277	$d_{xz} \rightarrow d_{xy}$
	26320	Charge transfer,
		$L(\pi) \rightarrow d$
	35714	Intraligand, $L(\pi) \rightarrow L(\pi^*)$
$[\text{Cu}(\text{TP})(\text{TPH})\text{Py}] \cdot \text{H}_2\text{O}$ (Nujol)	35714	Intraligand
	41667	Intraligand

*Only representative complexes are included as nujol mull.

$[\text{Ni}(\text{TP})_2\text{B}]$	—Square pyramidal
$[\text{Ni}(\text{CPT})_2]$	—Square planar
$[\text{Cu}(\text{TP})(\text{TPH})\text{B}] \cdot \text{H}_2\text{O}$	—Tetrahedral or linear, polymeric
$[\text{Cu}(\text{CPT})_2]$	—Linear, polymeric.

References

- 1 Saheb R, Agarwala U & Dikshit S K, *Indian J Chem*, **20A** (1981) 1196.
- 2 Singh T & Agarwala U, *Indian J Chem*, **19A** (1980) 750, 755, 991; aheb R, Agarwala U & Dikshit S K, *Indian J Chem*, **22A** (1983) 24.
- 3 Cotton F A, Dunn T G & Wood J S, *Inorg Chem*, **3** (1964) 1495.
- 4 Boshnic B, Jackson W G & Lo S T D, *Inorg Chem*, **13** (1974) 2598.
- 5 Sitran S & Cellon E, *Inorg chim Acta*, (1982) L80.
- 6 Rao C N R, *Chemical applications of infrared spectroscopy*, (Academic Press, New York), 1963, 318, 324-331.
- 7 Nakamoto K, *Infrared and Raman spectra of inorganic and coordination compounds*, (John Wiley, New York), 1978, 231.
- 8 Suzuki I, *Bull chem Soc Japan*, **35** (1962) 1286, 1456.
- 9 Yamada Y, Nakamura H & Tsuchiada T, *Bull chem Soc Japan*, **31** (1958) 303.
- 10 Yamada Y, Nakamura H & Tsuchiada T, *Bull chem Soc Japan*, **33** (1960) 1278.
- 11 Khuller I P & Agarwala U C, *Can J Chem*, **53** (1975) 1165.
- 12 Ibers J A, *Annual Rev phys Chem*, **16** (1965) 380.
- 13 Muettterties E L & Schunn R A, *Q Rev*, **20** (1966) 245.

- 14 Blake A B, Chipperfield J R, Nelson P G & Stoneman C F, *Annual Rep The chem Soc, London*, **64A** (1967) 310.
- 15 Sacconi L, *Pure appl Chem*, **17** (1968) 95.
- 16 Chadwick B M, Chipperfield J R, Nelson P G & Stoneman C F, *Annual Rep chem Soc, London*, **65A** (1968) 336.
- 17 Orioli P L, *Coord Chem Rev*, **6** (1971) 285.
- 18 Sacconi L, *Coord Chem Rev*, **8** (1972) 351.
- 19 Furlani C, *Coord Chem Rev*, **3** (1968) 141.
- 20 Hoskins B F & Williams F D, *Coord Chem Rev*, **9** (1972-73) 365.
- 21 Harris C M, Hoskins B F & Martin R L, *J chem Soc*, (1959), 3728.
- 22 Drago R S, Meek D W, Joesten M D & LaRoche L, *Inorg Chem*, **2** (1963) 124.
- 23 Drago R S, Meek D W & Joesten M D, *Inorg Chem*, **2** (1963) 1056.
- 24 Hosyana H, Tanka J & Nagakura S, *Bull chem Soc Japan*, **33** (1960) 850.