

## Synthesis & Characterization of Coordination Polymers of Cobalt(II) & Nickel(II) with Some Monoarylthioureas

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The coordination polymers of cobalt(II) and nickel(II) with *N*-phenyl-, *o*-chlorophenyl- and *p*-chlorophenyl-thioureas have been synthesised. The elemental analyses show the composition of the complexes as  $[\text{CoLCl}_2 \cdot 2\text{H}_2\text{O}]_n$ ,  $[\text{CoL}_2 \cdot 2\text{H}_2\text{O}]_n$ , and  $[\text{NiLCl}_2 \cdot 2\text{H}_2\text{O}]_n$ . The IR spectral studies show that coordination occurs through sulphur and nitrogen atoms of the ligands. The electronic spectral and magnetic measurement studies reveal octahedral geometry around the metal ions. On the basis of insolubility of complexes, and their high thermal stabilities, polymeric structures are proposed for these complexes.

Thioureas can act as monodentate as well as bidentate ligands. Coordination through sulphur of thiocarbonyl group and nitrogen of thioamide group simultaneously can lead to the formation of polymeric complexes. But very rarely such type of complexes have been synthesised. Recently, the synthesis of thermally resistant inorganic polymers has attracted much attention due to aerospace requirements of heat resistant materials. In continuation of our earlier papers<sup>1-4</sup>, we report herein the synthesis and characterization of a few coordination polymers of Co(II) and Ni(II) with arylthioureas.

Aniline, *o*-chloroaniline and *p*-chloroaniline used were of AR grade. The other chemicals used were ammonium thiocyanate (E Merck, GR); cobalt(II) chloride, cobalt(II) bromide and nickel(II) chloride (BDH, Ar). The monoarylthiourea ligands, namely *N*-phenylthiourea (PTU), *o*-chlorophenylthiourea (OCPTU) and *p*-chlorophenylthiourea (PCPTU) were synthesised by the interaction of respective arylamine hydrochlorides with ammonium thiocyanate. The coordination polymers of cobalt(II) and nickel(II) were prepared by the method reported earlier<sup>1</sup>. Metal contents and chlorine were estimated volumetrically and sulphur was estimated gravimetrically. Bromine was found to be absent in complexes prepared from cobalt(II) bromide.

The IR spectra were recorded on a Perkin-Elmer Grating infrared Spectrophotometer Model-577 in CsI pellets in the range 4000-200  $\text{cm}^{-1}$ . UV visible reflectance spectra were recorded in the range 50000-

6000  $\text{cm}^{-1}$ . Visible spectra in DMF solution were recorded on a Pye Unicam SP 8-100 spectrophotometer in the range 25,000-12,500  $\text{cm}^{-1}$ . Magnetic susceptibilities were determined by Gouy's method at room temperature.

All the complexes prepared are air stable, dark coloured powders, insoluble in water and common organic solvents. Nickel(II) complexes are insoluble, cobalt(II) chloride complexes are sparingly soluble and cobalt(II) bromide complexes decompose in DMF. The insoluble nature of the complexes indicate their polymeric nature.

The analytical data (Table 1) of the complexes are in accordance with the proposed formulae. The analytical data suggest the presence of two water molecules in the coordination polymers. The association of two aqua ligands also satisfies the maximum coordination number of the metal ions in view of 1:1 (metal:ligand) stoichiometry of the complexes. The appearance of broad bands at 3400, 1660 and 650-665  $\text{cm}^{-1}$  in the IR spectra of the complexes further supports the presence of water in coordination sphere<sup>5</sup>.

On comparing the IR spectra of ligands with those of polymeric complexes it is observed that the  $\nu(\text{NH})$  bands ( $\sim 3120\text{-}3400 \text{ cm}^{-1}$ ) are considerably shifted towards higher frequency on complexation. This large shift is attributed to the nitrogen coordination<sup>1-4</sup>. The  $\delta(\text{NH}_2)$  mode (1605-1620  $\text{cm}^{-1}$ ) is reduced in intensity and shifted towards higher frequency side. These observations alongwith the upward shift of the thioamide I and II bands are compatible with the nitrogen coordination. The thioamide III (1050-1085

Table 1—Analytical Data of the Complexes

Complexes	Found (Calc.), %		
	S	Cl	M
$[\text{Co}(\text{PCPTU})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$	9.01 (9.08)	30.11 (30.22)	16.62 (16.72)
$[\text{Co}(\text{PTU})_2 \cdot 2\text{H}_2\text{O}]_n$	15.93 (16.04)	—	14.70 (14.77)
$[\text{Co}(\text{PCPTU})_2 \cdot 2\text{H}_2\text{O}]_n$	13.59 (13.68)	—	12.49 (12.59)
$[\text{Co}(\text{OCPTU})_2 \cdot 2\text{H}_2\text{O}]_n$	13.54 (13.68)	—	12.48 (12.59)
$[\text{Ni}(\text{PTU})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$	11.21 (11.34)	12.52 (12.58)	20.75 (20.80)
$[\text{Ni}(\text{PCPTU})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$	9.98 (10.10)	22.35 (22.42)	18.49 (18.54)
$[\text{Ni}(\text{OCPTU})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$	9.95 (10.10)	22.36 (22.42)	18.42 (18.54)

Table 2—Electronic Spectral and Magnetic Data

Complexes	$\mu_{\text{eff}}$ (in BM)	Wavelength ( $\text{cm}^{-1}$ )	Assignment	Geometry
[Co(PCPTU)Cl <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub> (i) in solid state	5.349	18691	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
		17241		
		13888	${}^4A_{2g}$	
(ii) in DMF solution	5.387	16447	${}^4A_{2g} \rightarrow {}^4T_1(P)$	Tetrahedral
		14970		
[Co(PTU) <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub>	5.387	18518	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
		17891		
		14084	$\rightarrow {}^4A_{2g}$	
[Co(PCPTU) <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub>	5.432	18691, 16806	-do-	-Do-
		14084, 8333		
		8333		
[Co(OCPTU) <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub>	5.426	18691, 16806,	-do-	-Do-
		14084, 8333		
		8333		
[Ni(PTU)Cl <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub> <sup>*</sup>	3.227	24390	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	-Do-
		12500		
		8333	$\rightarrow {}^3T_{1g}(F)$	
[Ni(PCPTU)Cl <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub> <sup>‡</sup>	3.249	24390	$\rightarrow {}^3T_{2g}$	-Do-
		12500		
		8403		
[Ni(OCPTU)Cl <sub>2</sub> ·2H <sub>2</sub> O] <sub>n</sub> <sup>†</sup>	3.281	25000	-do-	-Do-
		12345		
		8333		

\*  $10 Dq = 8333 \text{ cm}^{-1}$ ,  $B = 792 \text{ cm}^{-1}$ ,  $\beta = 0.750$

‡  $10 Dq = 8403 \text{ cm}^{-1}$ ,  $B = 778 \text{ cm}^{-1}$ ,  $\beta = 0.737$

†  $10 Dq = 8333 \text{ cm}^{-1}$ ,  $B = 823 \text{ cm}^{-1}$ ,  $\beta = 0.779$

$\text{cm}^{-1}$ ) and C=S stretching ( $750\text{--}810 \text{ cm}^{-1}$ ) modes of the free ligands either get split or appear at lower frequencies or get reduced in intensity on complexation. This observation indicates the coordination of sulphur to the metal ion. The presence of  $\nu(\text{M}-\text{S})$  and  $\nu(\text{M}-\text{N})$  bands in the far infrared spectra of the complexes further confirms coordination through sulphur and nitrogen. This conclusion supports the polymeric structures assigned to the complexes.

The values of magnetic moments (Table 2) obtained for the cobalt(II) and nickel(II) complexes are in good agreement with the expected values for high spin octahedral complexes of respective metals<sup>6,7</sup>.

The reflectance spectra (Table 2) for these complexes are similar to those normally observed for octahedral Co(II) and Ni(II) complexes<sup>8</sup>. The electronic parameters for Ni(II) complexes give more evidence in support of octahedral stereochemistry. However, the  $\nu_2$  band ( $\sim 14000 \text{ cm}^{-1}$ ) observed for Co(II) complexes is quite strong. This is somewhat unusual for octahedral Co(II) complex, since the  $\nu_2$  band, being a two electron transition ( $t_{2g}^5 e_g^2 \rightarrow t_{2g}^3 e_g^4$ ) should possess a weaker intensity than the other bands. Strong bands

occurring in this region are generally associated with the presence of tetrahedral cobalt complex. The absorption band found in the tetrahedral region ( $\sim 14000 \text{ cm}^{-1}$ ) can be attributed to the terminal tetrahedral units of octahedral polymer chains. It is assumed that the length of chains is relatively short<sup>1,4</sup>.

The cobalt(II) chloride with PCPTU dissolves partially and gives deep blue coloured solution in DMF which is characteristic of tetrahedral species. Two bands are observed near  $14,800$  and  $16,400 \text{ cm}^{-1}$  associated with the  $\nu_3$  transition of the tetrahedral symmetry. Since no absorption is observed in  $20,000\text{--}18,000 \text{ cm}^{-1}$ , it can be concluded that octahedral species are not present in the solution. Therefore, it is suggested that in DMF solution octahedral polymer chains are broken into tetrahedral monomer units.

Thermogravimetric experiments were carried out in air up to  $900^\circ\text{C}$  with a heating rate of  $8^\circ\text{C}/\text{min}$  for the Co-PCPTU, Co-PTU and Co-OCPTU, and  $\text{CoCl}_2\text{-PCPTU}$  complexes. The complexes are stable and do not decompose completely even at higher temperatures. The decomposition starts at  $100^\circ\text{C}$  and the initial mass loss in the temperature range  $100\text{--}200^\circ\text{C}$

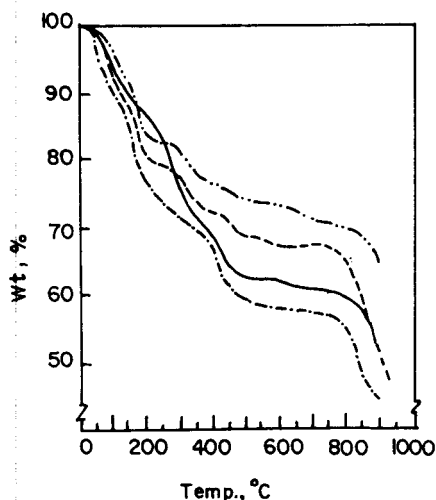
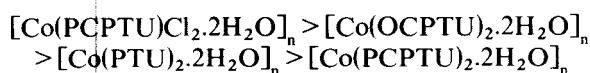


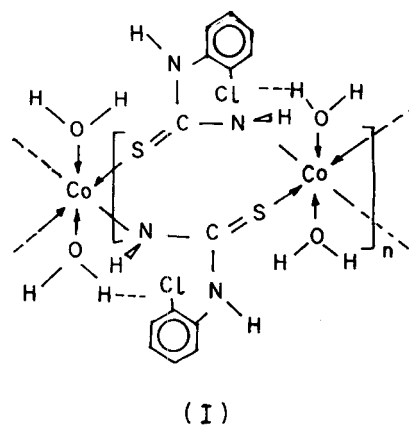
Fig. 1—Thermogravimetric Curves for the Coordination Polymers (.....);  $[\text{Co}(\text{PCPTU})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$  (—);  $[\text{Co}(\text{PTU})_2 \cdot 2\text{H}_2\text{O}]_n$  (- - - - -);  $[\text{Co}(\text{PCPTU})_2 \cdot 2\text{H}_2\text{O}]_n$  (— · — · —);  $[\text{Co}(\text{OCPTU})_2 \cdot 2\text{H}_2\text{O}]_n$

corresponds to the loss of two water molecules. Loss of water molecules at such a high temperature also indicates their coordinated nature. The maximum weight loss (%) up to  $900^\circ\text{C}$  is 34.63, 49.60, 54.63 and 49.90 for  $\text{CoCl}_2$ -PCPTU, Co-PTU, Co-PCPTU and Co-OCPTU respectively. The decomposition pattern of these complexes has been shown in Fig. 1.

On the basis of thermal decomposition data the order of thermal stabilities is



The high thermal stability of Co(II) chloride complex may be due to its 1:1 (metal:ligand) ratio as compared to 1:2 for Co(II) bromide complexes. The normally observed relation between orientation and thermal stability for aromatic polymers is  $p > m > o$ . However, the anomalous behaviour observed in this case i.e. greater stability of OCPTU complex of Co(II) bromide over its *p*-analog can be attributed to the different factors contributing to the stability of coordination polymers<sup>10,11</sup>. As is evident from the thermogravimetric curves (Fig. 1) the OCPTU-Co(II) coordination polymer is even more stable than PTU polymer, while it should be less stable due to the presence of electron-withdrawing chlorine atom. Furthermore, the PCPTU complex must be more stable because of less steric hindrance involved due to *p*-position of chlorine and also due to the fact that the inductive effect becomes less with the increasing number of intervening carbon atoms. However, observed facts are contrary to this expectation. Therefore, it is suggested that the chlorine in the *o*-position may be involved in intramolecular hydrogen bonding possibly with the hydrogen atom of



the coordinated water molecules. On the basis of these studies the structure (I) is tentatively proposed for this complex. The *trans*-isomer of the ligand, which is more predominating, is shown in the structure.

The analytical data, IR and electronic spectral studies indicate octahedral polymeric structures for these coordination complexes. Coordination through both the donors sulphur and nitrogen of the monoarylthioureas to the metal enables them to act as bidentate bridging ligands thereby resulting in the formation of polymeric complexes. The relative thermal stabilities of the coordination polymers are influenced by steric as well as electrical factors.

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