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Synthesis and Characterization of Complexes of Co(II), Ni(II), Cd(II), Hg(II) and Pd(II) With Some N-phenyl-N¹-2-[4-Phenyl-(Substituted) Thiazolyl]-Thioureas

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The Synthesis and characterization of the complexes of Co(II), Ni(II), Pd(II), Cd(II) and Hg(II) with N-phenyl-N¹-2-(4-phenylthiazolyl)thiourea (PPT) and N-phenyl-N¹-2-(4-methylphenylthiazolyl)thiourea (PMPT) and Co(II), Cd(II), and Hg(II) complexes of N-phenyl-N¹-2-(4-p-chlorophenylthiazolyl) thiourea (PCPT) are included in this paper. Based on analytical results, electronic and infrared spectral data and magnetic susceptibility measurements, plausible structures have been proposed.

Introduction

Thiourea and its derivatives form a variety of complexes of different symmetries with various metal ions. Ni(II) complexes, for example, assume tetrahedral, octahedral or tetragonal geometry, with various degrees of distortion in some cases¹⁻³. Pd(II) and Pt(II) complexes display basically fourfold coordination, with a strong tendency to form penta-coordinated adducts⁴⁻⁵. Some investigations on Co(II) complexes of substituted thioureas⁶ show that Co(II) has a pronounced tendency to form tetrahedral complexes of the general formula CoL_2X_2 . If X be nitrate or acetate, its stereochemistry changes from tetrahedral to octahedral geometry with X acting as a bidentate ligand⁷. Polymeric complexes of Co(II) thiocyanate with thiourea and N-methyl thiourea are found to be octahedral⁸. There are reports about the existence of penta-coordinated thiourea complexes also⁸ of the type $[CoL_3X_2]$.

Extensive work is reported on the complexing behaviour of disubstituted thiourea. In these complexes it is shown that one of the coordination sites is thiocarbonyl sulphur⁹⁻²⁵. In this paper we report the synthesis and characterization of complexes of Co(II), Ni(II), Cd(II), Hg(II) and Pd(II) with some N-phenyl-N¹-2-[4-phenyl(substituted) thiazolyl]thioureas.

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Experimental

The chemicals used were all of Analar or chemically pure grade and the ligands used were prepared according to the reported procedure²⁶.

Ligand solution in n-butanol with a few drops of DMF was used for complex preparation.

Preparation of Metal Complexes of N-Phenyl-N¹-2-(4-Phenylthiazolyl) Thiourea (PPT)

To a hot solution of PPT (4 mmol) in 40 ml of n-butanol containing a few drops of DMF, a warm solution of $NiCl_2 \cdot 6H_2O$ (4 mmol) in 40 ml n-butanol were added. The mixture was digested over a water bath for one hour. A pale yellowish green complex separated. It was cooled, filtered and washed with hot butanol and finally with ether. The complex was dried at 100°C.

Dichloro[N-phenyl-N¹-2-(4-phenylthiazolyl) thiourea]cobalt(II)

The complex was prepared by the procedure given above by using $CoCl_2 \cdot 6H_2O$ in place of $NiCl_2 \cdot 6H_2O$. The dried complex was yellowish brown in colour.

Dichloro[N-phenyl-N¹-2-(4-phenylthiazolyl) thiourea]cadmium(II)

The complex was prepared by the procedure given above using $CdCl_2 \cdot 2H_2O$ in place of $NiCl_2 \cdot 6H_2O$. A white crystalline complex was obtained.

Dichloro[N-phenyl-N¹-2-(4-phenylthiazolyl) thiourea]palladium(II)

To a boiling solution of PPT (4 mmol) in n-butanol containing a few drops of DMF, a solution of $PdCl_2 \cdot 2H_2O$ (4 mmol) in water containing KCl crystals were added dropwise. A red orange coloured complex separated on cooling. It was washed and dried as stated above.

Preparation of Metal Complexes of N-Phenyl-N¹-2-(4-p-methylthiazolyl) Thiourea (PMPT) and N-Phenyl-N¹-2-(4-chlorophenylthiazolyl)-Thiourea (PCPT)

Co(II), Ni(II), Pd(II), Cd(II) and Hg(II) complexes of PMPT and Co(II), Ni(II), Cd(II), and Hg(II) complexes of PCPT were prepared by the same method as described for the complexes of PPT by using appropriate metal ion solutions.

Analytical, Magnetic and Spectral Data

Sulphur and metal ions in the complexes were estimated by standard methods²⁷. Carbon, hydrogen and nitrogen were analysed on microscale at CDRI Lucknow. The results are given in Table 1.

Magnetic susceptibilities of all the complexes were determined at room temperature with a Gouy balance. With the exception of Co(II) complexes, all complexes diamagnetic in nature.

The absorption spectra of the ligand and the complexes were recorded on a Beckman DU-6 spectrophotometer in the range 200-900 nm. The absorption bands and their assignments are given in Table 2. The infrared spectra of the ligands and the metal complexes in KBr/CsI phase were taken on a Perkin-Elmer 1330 infrared spectrophotometer in the range 4000-200 cm^{-1} . The major infrared bands and their assignments are given Table 3.

Results and Discussion

The analytical results show that Co(II), Ni(II), Cd(II), Pd(II), form $MLCl_2$ type complexes, while Hg(II) forms ML_2Cl_2 type.

Table 1. Analytical Data of PPT, PCPT and PMPT Complexes

Compound	Calc. (Found) %					
	C	H	N	S	M	Cl
<i>Co(C₁₆H₁₃N₃S₂)Cl₂</i>	43.55 (43.23)	2.95 (3.04)	9.53 (9.88)	14.52 (14.91)	13.37 (13.07)	16.08 (18.42)
<i>Ni(C₁₆H₁₃N₃S₂)Cl₂</i>	43.58 (43.40)	2.95 (2.86)	9.53 (9.71)	14.53 (19.34)	13.32 (13.58)	16.09 (16.39)
<i>Pd(C₁₆H₁₃N₃S₂)Cl₂</i>	39.32 (40.02)	2.66 (2.78)	8.60 (8.44)	13.11 (31.25)	21.79 (21.52)	14.52 (15.00)
<i>Cd(C₁₆H₁₃N₃S₂)Cl₂</i>	38.84 (38.74)	2.63 (2.94)	8.50 (8.62)	12.95 (13.11)	2.74 (22.92)	14.34 (14.76)
<i>Hg(C₁₆H₁₃N₃S₂)₂Cl₂</i>	42.98 (43.09)	2.91 (2.75)	9.40 (9.31)	14.33 (14.50)	22.45 (22.28)	7.44 (7.82)
<i>Co(C₁₆H₁₂N₃S₂Cl)Cl₂</i>	40.40 (40.82)	2.52 (2.32)	8.84 (8.65)	13.47 (13.81)	12.40 (12.58)	22.38 (22.71)
<i>Ni(C₁₆H₁₂N₃S₂Cl)Cl₂</i>	40.42 (40.62)	2.53 (2.40)	8.84 (8.63)	13.47 (13.28)	12.36 (12.82)	22.39 (22.50)
<i>Cd(C₁₆H₁₂N₃S₂Cl)Cl₂</i>	36.31 (36.71)	2.27 (2.39)	7.94 (8.04)	12.10 (12.43)	21.26 (21.52)	20.11 (20.15)
<i>Hg(C₁₆H₁₂N₃S₂Cl)₂Cl₂</i>	39.90 (39.64)	2.49 (2.61)	8.73 (8.98)	13.30 (13.71)	20.84 (21.12)	11.05 (11.35)
<i>Co(C₁₇H₁₅N₃S₂)Cl₂</i>	44.85 (44.43)	3.30 (3.42)	9.23 (9.51)	14.07 (14.25)	12.96 (13.14)	15.59 (16.02)
<i>Ni(C₁₇H₁₅N₃S₂)Cl₂</i>	44.87 (45.08)	3.30 (3.51)	9.24 (9.35)	14.08 (14.01)	12.91 (12.76)	15.60 (15.82)
<i>Pd(C₁₇H₁₅N₃S₂)Cl₂</i>	40.61 (40.85)	2.99 (3.08)	8.36 (8.58)	12.74 (13.08)	21.18 (21.34)	14.12 (14.41)
<i>Cd(C₁₇H₁₅N₃S₂)Cl₂</i>	40.53 (40.94)	2.98 (2.69)	8.34 (8.60)	12.72 (12.78)	22.33 (22.54)	14.09 (14.38)
<i>Hg(C₁₇H₁₅N₃S₂)Cl₂</i>	44.28 (44.60)	3.26 (3.18)	9.12 (9.18)	13.89 (14.02)	21.77 (21.36)	7.69 (7.81)

Magnetic Susceptibility

The magnetic moments of Co(II) complexes were found to be in the range of 2.1 to 2.13 B.M²². This suggests a low spin square planar geometry. This may be due to the mixing of the higher ligand field term $2_{A_{2g}}$ with $2_{A_{1g}}$ ground term on account of spin-orbit coupling whereby the magnetic moment of the cobalt complex goes above the spin value of 1.73 B.M²⁹.

Electronic Spectra

A) Palladium(II) and Nickel(II) Complexes

The geometry of these complexes is square planar, Ni(II) being in low spin state only. However, not all bands were actually observed. This may be due to some of their being effectively masked by charge transfer. The bands that were actually observed and their assignments are given in Table 2.

B) Cobalt(II) Complexes The electronic spectra of Co(II) complexes exhibit two prominent bands, one of medium intensity at 14000-16500 cm⁻¹ and the second of high intensity at 18000-20000 cm⁻¹ in chloroform solution. This is attributable to $2_{A_{1g}} \rightarrow 2_{B_{1g}}$ and $2_{A_{1g}} \rightarrow 2_{E_g}$ transitions, respectively, in square planar geometry³⁰. The relatively high intensity of the second band may be due to charge transfer expected in the

range of 28500-30000 cm^{-1} .

Table 2. Magnetic Susceptibility Electronic Spectral Bands and Their Probable Assignments

Complex	μ_{eff} . B.M	Band Positions		Assignments	
		nm	cm^{-1}		
(1)	(2)	(3)	(4)	(5)	
$Co(C_{16}H_{13}N_3S_2)Cl_2$	2.11	W_1	643	15552	$2A_{1g} \rightarrow 2B_{1g}$
		W_2	557	17953	$2A_{1g} \rightarrow 2E_g$
$Co(C_{16}H_{12}N_3S_2Cl)Cl_2$	2.09	W_1	656	15244	$2A_{1g} \rightarrow 2B_{1g}$
		W_2	556	17985	$2A_{1g} \rightarrow 2E_g$
$Co(C_{17}H_{15}N_3S_2)Cl_2$	2.13	W_1	-	-	-
		W_2	557	17953	$2A_{1g} \rightarrow 2E_g$
$Ni(C_{16}H_{12}N_3S_2)Cl_2$	O	W_1	580	17241	$1A_{1g} \rightarrow 1A_{2g}$
		W_2	523	19120	$1A_{1g} \rightarrow 1B_{1g}$
		W_3	-	-	-
$Ni(C_{16}H_{12}N_3S_2Cl)Cl_2$	O	W_1	580	17241	$1A_{1g} \rightarrow 1A_{2g}$
		W_2	523	19120	$1A_{1g} \rightarrow 1B_{1g}$
		W_3	-	-	-
$Ni(C_{17}H_{15}N_3S_2)Cl_2$	O	W_1	560	17857	$1A_{1g} \rightarrow 1A_{2g}$
		W_2	480	20833	$1A_{1g} \rightarrow 1B_{1g}$
		W_3	380	26315	$1A_{1g} \rightarrow 1E_g$
$Pd(C_{16}H_{13}N_3S_2)Cl_2$	O	W_1	-	-	-
		W_2	500	20000	$1A_{1g} \rightarrow 1B_{1g}$
		W_3	380	26315	$1A_{1g} \rightarrow 1E_g$
$Pd(C_{17}H_{15}N_3S_2)Cl_2$	O	W_1	556	17985	$1A_{1g} \rightarrow 1A_{2g}$
		W_2	486	20576	$1A_{1g} \rightarrow 1B_{1g}$
		W_3	382	26178	$1A_{1g} \rightarrow 1E_g$

Table 3. Major Infrared Band Positions (cm^{-1}) and Their Probable Assignments of PPT, PCPT and PMPT and the Complexes

Ligand	Complexes	Assignments
3200 B	3200 ± 10 MB	$\nu_{(N-H)}$
2950 M	2950 ± 20 M	$\nu_{(C-H)}$
1595 S	1600 ± 20 S	$\nu_{(C=N)}$
1500 MS	1495 ± 10 M	$\nu_{as}(N-C-N)$
1390 S	1320 ± 20 M	$\nu_{sy}(N-C-N)^+ \quad \nu(C=S)$
815 MS	815 M	$\nu_{(C-S)}(ring)$
780 S	-	$\nu_{(C=S)}$ phenyl group with 5 adj. H atoms
-	770 ± 5 M	Phenyl group with 5 adj. H atoms
-	730 ± 5 M	$\nu_{(C=S)}$
-	440 ± 10 W	$\nu_{(M-N)}$
-	360 ± 10 W	$\nu_{(M-S)}$
-	325 ± 5 W	$\nu_{(M-Cl)}$

M=Medium; B=Broad; S=Strong; W=Weak; V=Very

Infrared Spectra

The IR spectra of the ligands are highly complex and show a large number of bands. A relatively sharp band of medium intensity appears in the spectra of the ligands near 780 cm^{-1} . This is assigned to $\nu_{(C=S)}$ vibrations. In the spectra of metal complexes, a band of similar intensity appears at around 730 cm^{-1} . This is indicative of coordination through the S atom of the C=S group⁹⁻²⁵, whose force constant decreases after coordination.

The next region of the spectra of the ligands and the complexes is between $1700\text{-}1400\text{ cm}^{-1}$. The band around 1595 cm^{-1} in the spectra of the ligands can be assigned to C=N stretching vibrations of the thiazole ring. The shift of the $\nu(C=N)$ band towards a higher frequency region indicates metal to ligand π -electron interactions¹⁶⁻¹⁸.

If bonding of metal ions takes place through sulphur and nitrogen to form chelates as explained above, one would expect new bands in the region of $350\text{-}450\text{ cm}^{-1}$ due to $\nu(M-S)$ and $\nu(M-N)$, respectively, coupled with other modes of vibrations in the ligand molecules. These are actually observed.

These important features of the spectra of the ligand and the metal complexes provide a consistent picture that leads us to propose structures as shown in Figure 1.

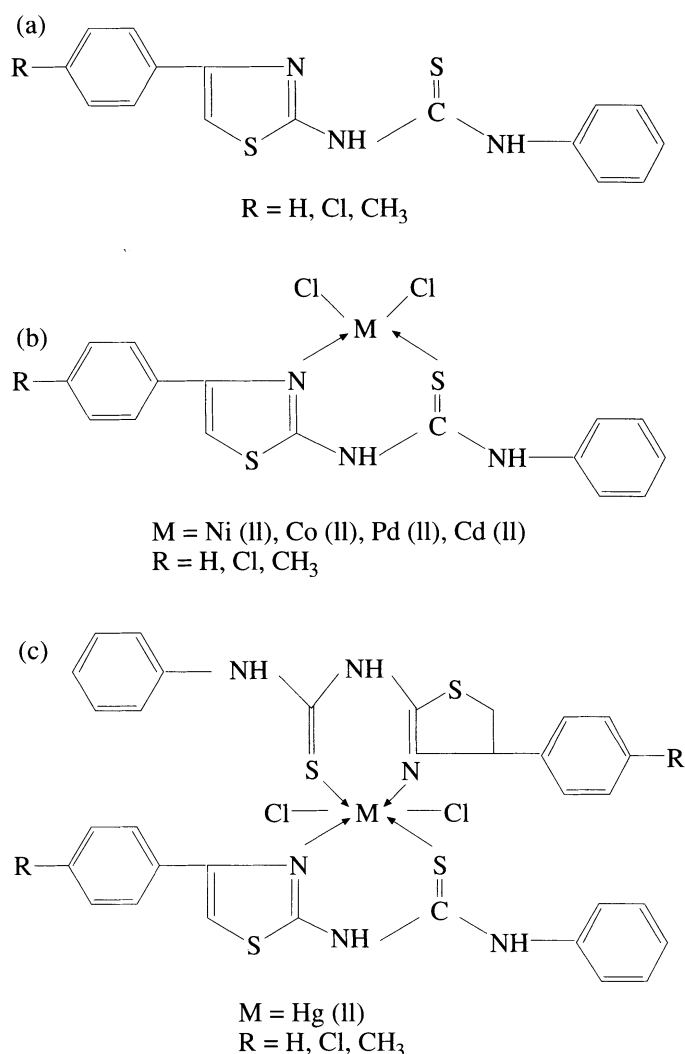


Figure 1.

On the basis of spectral and magnetic, susceptibility and micro-analysis data, and keeping in view the preferences of the metal ions, square planar structures are proposed for Co(II), Ni(II) and Pd(II) complexes (Figure 1 (b)), tetrahedral structure for Cd(II) complexes and octahedral structure for Hg(II) complexes (Figure 1(c)).

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