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Coordination Polymers of Monoaryl Thioureas

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ABSTRACT

From analytical studies, infrared and reflectance spectra, and magnetic and thermogravimetric measurements of Co(II) and Ni(II) complexes with various monoaryl thioureas, it was concluded that the complexes are polymeric coordination complexes with an octahedral geometry. These were synthesized by refluxing the ethanolic solutions of metal salt and the ligand in the mole ratio 1:2 at pH ~7 on a water bath. All the complexes are dark colored, amorphous solids insoluble in common organic solvents. Elemental analysis indicated a metal:ligand ratio of 1:1 in all the complexes except in the Co(II) complex with o-anisyl thiourea, where it is 1:2 and there is coordination of two water molecules to the central metal ion. The thermal stability of the complexes is also discussed.

INTRODUCTION

A substantial amount of work has been done on the synthesis and characterization of coordination compounds with thiourea and its substituted derivatives as ligands [1-4], but very rarely has the

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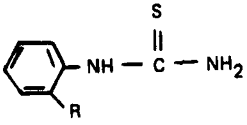
coordinating nature of these ligands been explored in order to synthesize polymeric complexes [5-7]. Thiourea derivatives generally coordinate with metal ions through sulfur and sometimes through nitrogen atom. Although coordination in thiourea complexes through both the sulfur and nitrogen atom is very rare [8], we have observed such a bidentate nature of these complexes in our coordination polymers. Besides the thermal stability of these coordination polymers, they have been of considerable interest due to the wide variety of stereochemical arrangements exhibited by them.

The present article describes the preparation, general properties, composition, infrared and reflectance spectra, magnetic measurements, and thermogravimetry of the solid complexes formed by monoaryl thiourea (I) with Co(II) and Ni(II):



(I)

where R stands for H–, $-CH_3$, $-OCH_3$, –Cl.

EXPERIMENTAL

Materials

Aryl amines (A.R.) used in the synthesis of ligands were purified by distilling once just before use. Ammonium thiocyanate was from E. Merck (G.R.) and was used as received. Cobalt(II) chloride, cobalt(II) bromide, and nickel(II) chloride were from B.D.H. (AnalaR) and were used without further purification. Dehydrated alcohol was also distilled before use.

Preparation of Monoaryl Thioureas (I)

Ligands (I) were synthesized from the corresponding arylamine hydrochloride and ammonium thiocyanate by Kurzer's method [9].

Preparation of the Complexes

Ethanolic solutions of the metal salt and the ligand were mixed in a 1:2 mole ratio, and the pH of the mixture was adjusted to ~7 with alcoholic NaOH. The original blue color of the solution turned dark with the appearance of particles. The mixture was refluxed on a water bath for half an hour. The hot reaction mixture was filtered and the precipitate was washed repeatedly with ethanol, chloroform, and petroleum ether.

Properties

All the complexes are dark colored, amorphous solids, insoluble in common organic solvents (viz., ethanol, chloroform, carbon tetrachloride, nitromethane, ether). The cobalt(II) chloride complexes are sparingly soluble, the cobalt(II) bromide complex decomposes, and the nickel(II) chloride complex remains insoluble in N,N-dimethylformamide. Due to their insoluble nature, molecular weight determinations are not possible by the usual methods. All the complexes are stable toward heat and do not decompose even at high temperatures.

Composition

The metal contents were determined by decomposing the complexes with concentrated nitric acid and titrating against EDTA. Sulfur and chlorine were estimated by Messenger's and Stepnov's methods, respectively. Anion was found to be absent in the complex prepared from cobalt(II) bromide. The results of elemental analyses are given in Table 1.

Spectral Studies

The IR absorption spectra were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer Model-577 in CsI pellets in the range 4000-200 cm^{-1}. UV visible reflectance spectra were taken in the 200-1500 nm range. Visible spectra in DMF solutions were recorded on a Unicam SP 8-100 spectrophotometer in the 400-800 nm range. Magnetic susceptibilities were determined by Gouy's method at room temperature. For thermogravimetric studies in air, samples were heated at a rate of 10°C/min up to 500°C.

RESULTS AND DISCUSSION

From analytical data (Table 1) a metal to ligand mole ratio of 1:1, as expected for a chain polymer, is inferred for all the complexes except for Complex E which was prepared from cobalt bromide and which has a mole ratio of 1:2. Coordination of two molecules of water

TABLE 1. Analytical Data of N-Monoaryl Thiourea-Metal Complexes

Complexes[a]			Elemental analysis		
			Sulfur	Chlorine	Metal
1. $[Co(PTU)Cl_2.2H_2O]_n$	(A)	Calc	10.06	22.33	18.54
		Found	10.01	22.25	18.48
2. $[Co(OTTU)Cl_2.2H_2O]_n$	(B)	Calc	9.64	21.39	17.76
		Found	9.52	21.28	17.68
3. $[Co(OCPTU)Cl_2.2H_2O]_n$	(C)	Calc	9.08	20.14	16.72
		Found	8.99	20.06	16.62
4. $[Co(OATU)Cl_2.2H_2O]_n$	(D)	Calc	9.20	20.40	16.94
		Found	9.12	20.31	16.88
5. $[Co(OATU)_2.2H_2O]_n$	(E)	Calc	13.94	-	12.84
		Found	13.87	-	12.78
6. $[Ni(OATU)Cl.2H_2O]_n$	(F)	Calc	10.25	11.37	18.80
		Found	10.09	11.34	18.69

[a] PTU = N-phenyl thiourea, OTTU = o-tolyl thiourea, OCPTU = o-chlorophenyl thiourea, OATU = o-anisyl thiourea.

per metal ion is indicated for all complexes. Such an association of water in a coordination polymer has been reported by other workers [10-12].

Infrared Spectra

The comparative data of the IR spectra of the ligands and complexes are given in Tables 2A and 2B. Only the bands perturbed on complexation have been listed. The IR spectra of the ligands show three bands due to NH stretching vibrations in the 3 μm region, but the Co(II) chloride complexes show a strong and sharp band only at 3560 cm^{-1}. The sharpness of the band may be due to less hydrogen bonding in the complexes as compared to the ligands, but this large shift (more than 100 cm^{-1}) cannot be solely attributed to decreased hydrogen bonding. Similarly, in Complexes E and F, considerable shifting of ν(NH) frequencies toward higher wave numbers is observed, but these bands are very broad. While the NH frequencies should remain substantially unaffected on bonding through sulfur, coordination through nitrogen results in a marked increase in absorption in the

TABLE 2A. Selected IR Spectral Bands of Ligands and Their Complexes (frequencies in cm^{-1})[a]

Ligand/complex	ν(NH)	ν(OH)	δ(OH)	$\delta(NH_2)$	Thioamide I
PTU	3420s 3270s 3180s	-	-	1610s	1520s
$[Co(PTU)Cl_2.2H_2O]_n$	3560vs	3390br	1660m, s, br	1630w	1550ms
OTTU	3380s 3270s 3180s	-	-	1620s	1525sh
$[Co(OTTU)Cl_2.2H_2O]_n$	3560s	3440br	1655s	1620s	1550s
OCPTU	3340s, br 3240s, br 3170s, br	-	1660m	1620w	1555m 1535w
$[Co(OCPTU)Cl_2.2H_2O]_n$	3570vs	3400br	1660m	1620w	1555m 1535w
OATU	3475s 3340s 3180s	-	-	1610vs	1535vs
$[Co(OATU)Cl_2.2H_2O]_n$	3560s	3420br	1650w, br	1600s	1550w, br
$[Co(OATU)_2.2H_2O]_n$	3540sh 3460br 3340br	3400br	1650s	1615ms	1550s
$[Ni(OATU)Cl.2H_2O]_n$	3480br	3400br	1650w, br	1590ms, br	1530w, br

[a] s = strong, vs = very strong, m = medium, w = weak, br = broad, sh = shoulder.

TABLE 2B. Selected IR Spectral Bands of Ligands and Their Complexes (frequencies in cm^{-1})

Ligand/complex	ν(NCN)B_1	ν(NCN)A_1	Thioamide II	Thioamide III	ν(C=S)
PTU	1480s	1440s	1310s	1050s	750s
$[Co(PTU)Cl_2.2H_2O]_n$	1500ms	1450ms 1430sh	1350m	1055s 1025s	755m
OTTU	1490s	1450s	1290s	1040s	760s
$[Co(OTTU)Cl_2.2H_2O]_n$	1495ms	-	1360s	1055ms 1050ms 1035ms 1025ms	755ms 740w,br
OCPTU	1480s	1410vs	1320s	1055ms	760vs
$[Co(OCPTU)Cl_2.2H_2O]_n$	1480m	1415m 1405sh	1360w,br	1025ms	740s,br
OATU	1495s	1440s	1310s	1065s 1050s	770vs
$[Co(OATU)Cl_2.2H_2O]_n$	1505vs	1445sh 1415ms	1330m	1050ms	750s
$[Co(OATU)_2.2H_2O]_n$	1490w	1425sh 1410w	1355s	1050w	750s
$[Ni(OATU)Cl.2H_2O]_n$	1495s	1410w	1340w,br	1040m	740ms

3-μm region and a decrease in frequency of NH stretching vibration [13]. Thus the N–H modes should be either lowered or split or both, with sometimes a decreased intensity if coordination takes place through nitrogen. This criterion is, however, complicated by the varying degrees of hydrogen bonding likely to occur in the substituted thioureas and their metal halide complexes [4]. Although ligand stretching frequencies are usually shifted to lower frequencies on complexation in some metal nitrile [14] and metal-biuret [15] complexes, ν(C≡N) and ν(NH), respectively, are found at higher frequencies than those of the free ligands. Pyridylthioureas on complexation with Co(II) and Ni(II) chlorides also show considerable positive shifting of ν(NH) [8]. Therefore, we conclude that the magnitude of shift in our studies also indicates that metal-ligand bonding is through nitrogen.

The intensity of the NH_2 deformation vibration which appears near 1600 cm^{-1} in ligands is reduced in the complexes. The wavenumber of this band is either unchanged or shifted to a lower value. This observation is a further support for nitrogen coordination in the complexes.

The wavenumber of the thioamide I band is shifted toward the higher side on complexation. The NCN vibration of the B_1 type appears with reduced intensity in the complexes with almost no change in frequency. The A_1 type of NCN vibration which occurs around 1420 cm^{-1} in the ligands shows a decreased intensity in all the complexes and splitting in most of them, while the wavenumber is almost unchanged. The band near 1310 cm^{-1} in the spectra of the ligands is assigned to thioamide II. The frequency of this band is considerably increased with a reduction in intensity on complexation. The thioamide III band near 1050 cm^{-1} and a band near 760 cm^{-1} involve mainly stretching vibrations due to C=S. The wavenumbers of both bands are lowered and their intensities are diminished on complexation. This is an indication of sulfur coordination.

Thus a large increase in ν(NH), reduction in intensity of $\delta(NH_2)$ and NCN stretching vibration, and lowering of ν(C=S) wavenumbers on complexation indicate that the ligands are coordinated through both nitrogen and sulfur. The presence of coordinated water is evident by the appearance of bands at 3400, 1660, and 650-665 cm^{-1} [16].

A band of medium intensity observed in the 460-520 cm^{-1} range in the spectra of complexes can be assigned to δ(C=S). ν(M–N) bands are observed in the 360-380 cm^{-1} range. One band due to metal-chloride stretching vibration appears at about 290 cm^{-1} in nickel(II) complexes whereas two such bands are observed in the 290-310 cm^{-1} range for cobalt(II) complexes. Metal-sulfur stretching vibrations appear as a band of medium intensity at about 230 cm^{-1} in nickel(II) complexes, while two such bands are observed for cobalt(II) complexes near 280 and 260 cm^{-1}. These observations in the far infrared spectra further support coordination through both sulfur and nitrogen. The probable structures for the complexes are shown in Fig. 1.

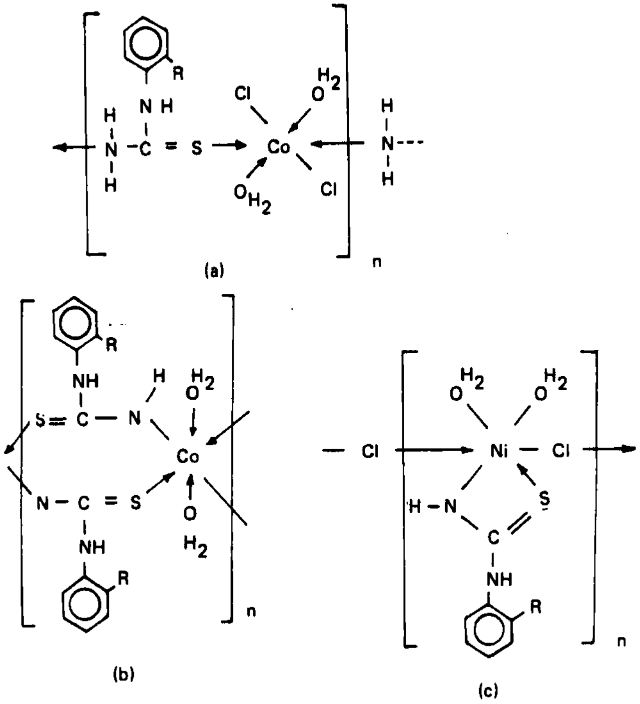


FIG. 1. Structures for the coordination polymers. (a) R = $-H$, $-CH_3$, $-OCH_3$, $-Cl$. (b) R = $-OCH_3$. (C) R = $-OCH_3$.

The influence of complexation on the ligand spectra in the 3-μm region for the cobalt(II) chloride complex is somewhat different than that for Complexes E and F. This may be attributed to a difference in the nature of bonding in the two cases. In complexes with nickel(II) chloride and cobalt(II) bromide, a salt linkage is probably formed with ligands by replacement of a proton from the thioamide group, whereas there may be a coordinate linkage in cobalt(II) chloride complexes. This is in agreement with the stoichiometry of these complexes (Table 1).

Electronic Spectra and Magnetic Measurements

Since the electronic spectra of solutions are highly dependent upon the nature of the solvent and the concentration of the solute, we take the spectra of the solids as the true electronic spectra of the complexes. These spectra do not, of course, yield any information on

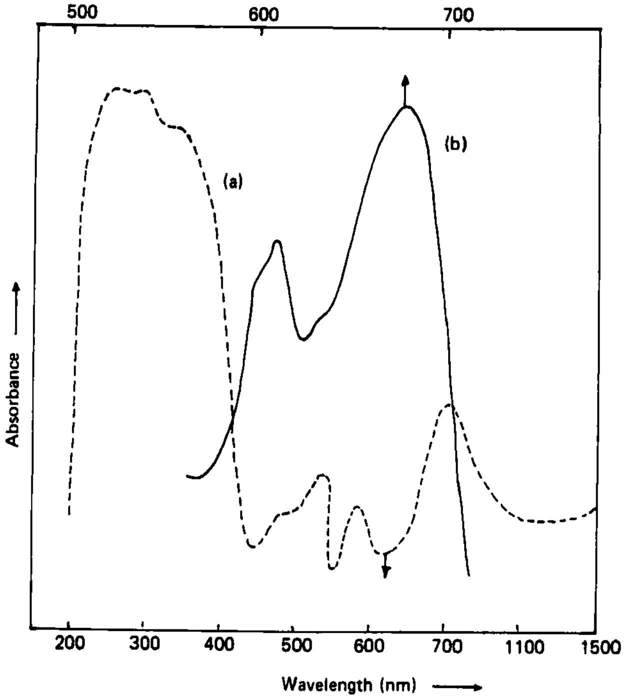


FIG. 2. Electronic spectra of the coordination polymer $[Co(OATU)Cl_2.2H_2O]_n$. (a) Reflectance spectrum. (b) Spectrum in DMF solution.

band intensities. The reflectance spectra for cobalt(II) chloride complexes are similar to those normally observed in the case of octahedral cobalt(II) complexes [17]. The ν_3 band, which arises due to the transition $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$, is observed near 18,000 cm^{-1}. The double peak found for this absorption band is, as pointed out by Koide [18], due to spin-orbit splitting of the $^4T_{1g}(P)$ state. Following Ballhausen [17], the band in the near infrared (8000 cm^{-1}) corresponds to the ν_1 ($^4T_{1g}\rightarrow{}^4T_{2g}$) transition. Appreciable absorption is observed in the 14,000 cm^{-1} region. The transition $^4T_{1g}\rightarrow{}^4A_{2g}$ (ν_2 band) is assigned to octahedral Co(II) complexes absorption in this region. The ν_2 transition is a two-electron transition ($t_{2g}{}^5e_g{}^2\rightarrow t_{2g}{}^3e_g{}^4$), and thus it has a much lower oscillator strength than the other two bands [19]. Therefore, it has been frequently observed that the ν_3 band is stronger than the ν_2 band. Thus the intense band observed in the

TABLE 3. Thermogravimetric Data in Air of the Polymeric Metal Complexes with Substituted Thioureas

Temperature (°C)	Percentage weight loss in complexes[a]					
	A	B	C	D	E	F
50	0.0	0.0	0.0	0.0	0.0	0.0
110	1.19	1.59	2.50	1.03	0.05	1.68
150	2.38	2.38	5.00	2.06	4.75	2.79
170	4.76	4.76	7.00	3.09	7.00[b]	3.35
180	11.90[b]	6.50	8.50	3.61	7.50	4.44
190	13.69	7.14	10.00[b]	4.12	8.50	5.03
250	16.64	11.11[b]	15.00	5.15	11.00	8.38
310	25.00	11.90	17.00	7.73	12.50	10.06
330	28.57	12.70	19.00	12.89	12.50	10.61
350	29.76	14.29	20.00	15.98	13.00	11.73
410	33.33	15.87	21.50	24.74	15.50	16.20
450	34.52	17.56	29.00	28.87	21.50	18.44
500	-	17.46	29.00	-	28.00	20.67

[a] Formulas are given in Table 1.
[b] Loss of water.

650-700 nm region seems to be somewhat unusual for octahedral Co(II). Bands occurring in this region are generally associated with the presence of tetrahedral cobalt(II). Similar phenomena have been reported in the diffuse reflectance spectra of the octahedral polymeric complex of Co(II) thiocyanate with thiourea [6] and several octahedral polymeric cobalt(II)-pyrazine complexes [20]. It has been suggested [20] that the absorption band found in the "tetrahedral region" can be attributed to terminal tetrahedral units of the octahedral polymer chains, assuming that the length of chains is relatively short. Further, the magnitude of the magnetic moment (5.2-5.4 BM) is in good agreement with the expected value of octahedral cobalt(II) [21].

The cobalt(II) chloride complexes are sparingly soluble in DMF, yielding deep blue solutions, evidently containing tetrahedral cobalt(II) species [1]. The visible spectrum of the complex $[Co(OATU)Cl_2 \cdot H_2O]_n$ in DMF solution is shown in Fig. 2 along with the reflectance spectrum of the same complex. Two bands near 14,800 and 16,400 cm^{-1} were observed in the DMF solution of the complex. These are associated with the $^4A_2 \rightarrow ^4T_1(P)$ transition (ν_3 band) of tetrahedral symmetry [17]. There is no effect due to the addition of excess ligand on the absorption maxima of the solution spectra. The absence of any absorption band in the 500-550 nm region suggests that there is probably no octahedral species in equilibrium in solution. Thus it can be inferred that the polymeric chains are broken in solution and that tetrahedral monomeric units are obtained. King et al. [22] have shown a similar equilibrium for several cobalt(II) complexes where the octahedral structure changes to the less common tetrahedral structure in solution.

For the complex $[Co(OATU)_2.2H_2O]_n$ also, the relectance spectrum is typical of octahedral cobalt(II). This complex is insoluble in most organic solvents and is decomposed in DMF. Therefore, its solution spectra could not be determined. Its magnetic moment (5.3 BM) is further evidence for the octahedral geometry [21] of Co(II) in this complex.

In the case of Ni(II)-complex d-d, transitions at 420 nm (ν_3), 820 nm (ν_2), and 1200 nm (ν_1) are observed which may be assigned to $^3A_{2g} \rightarrow ^3T_{1g}(P)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$, and $^3A_{2g} \rightarrow ^3T_{2g}$, respectively, a characteristic of octahedral geometry. The value of the ligand field splitting energy (10 Dq), Racah parameter (B), nephelauxetic factor (β), and magnetic moment (μ_{eff}) are 8333 cm^{-1}, 1056 cm^{-1}, 0.792, and 3.5 BM, respectively. The values of the spectral parameters and magnetic moment support the octahedral environment around nickel [23, 24].

The above discussion indicates an octahedral geometry around the central metal in all the complexes, thus accounting for the occupation of two coordinating sites by H_2O out of six in making the octahedral environment. Thus the electronic spectral study further supports the structures proposed for the polymeric complexes in Fig. 1.

Thermogravimetric Analysis

Thermogravimetric data in air (Table 3) indicate that these polymeric complexes decompose in a gradual manner. Representative curves of thermogravimetry (TG) and derivative thermogravimetry (DTG) for the complex $[Co(OATU)Cl_2.2H_2O]_n$ are shown in Fig. 3.

The experimental weight loss due to water approaches the theoretical amounts for dihydrates. The loss of water at higher temperatures indicates its presence in the coordination sphere. Considering the decomposition temperature as a measure of thermal stability for various complexes, the order of thermal stability for them may be

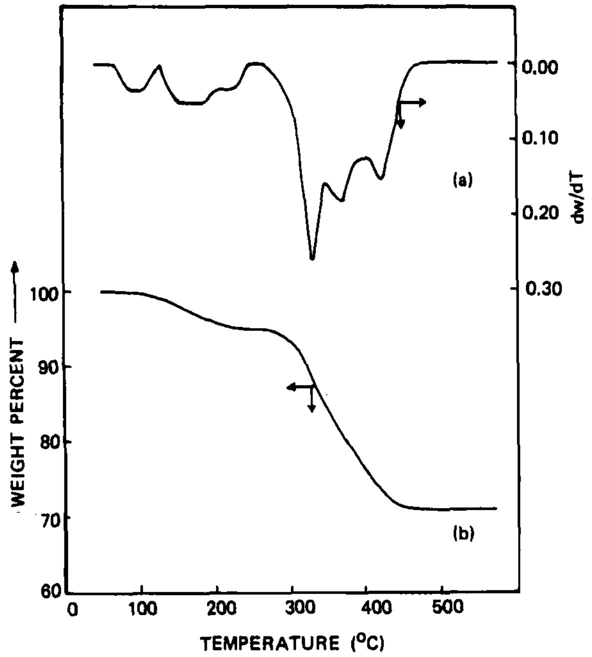


FIG. 3. Thermogravimetric (b) and derivative thermogravimetric (a) curves for the coordination polymer $[Co(OATU)Cl_2.2H_2O]_n$.

given as $[Ni(OATU)Cl.2H_2O]_n > [Co(OATU)Cl_2.2H_2O]_n > [Co(OTTU)Cl_2.2H_2O]_n > [Co(OCPTU)Cl_2.2H_2O]_n \simeq [Co(OATU)_2.2H_2O]_n > [Co(PTU)Cl_2.2H_2O]_n$.

Due to the presence of a methoxy group on the benzene ring in o-anisyl thiourea, which imparts a larger electron supply, the complexes with this particular ligand are more stable. However, the complex $[Co(OATU)_2.2H_2O]_n$ is less stable than the others, and this can be attributed to the molecule being more crowded because of the 1:2 metal-ligand ratio. Due to its electron-releasing methyl substituent, o-tolyl thiourea complex is next in stability. The cobalt(II) complex of o-chlorophenyl thiourea is more stable than that of phenyl thiourea in spite of the electron-withdrawing inductive effect of the chlorine. This can be ascribed to conjugative delocalization of the unshared pair of electrons on chlorine.

The insolubility of the complexes in common organic solvents and their thermal stability also supports their polymeric structures.

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