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Coordination Polymers of Tolylthioureas

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ABSTRACT

The coordination complexes of o- and p-tolylthioureas with Co(II) and Ni(II) have been synthesized and characterized with the help of elemental analysis, infrared and reflectance spectra, and magnetic and thermogravimetric measurements. The complexes are found to be polymeric in nature with an octahedral geometry. A metal-to-ligand ratio of 1:1 was found in all the complexes except for cobalt(II) bromide where it was 1:2. Coordination of two water molecules per metal atom has been found in all the polymers. Relative thermal stability is also discussed.

INTRODUCTION

Certain limitations of organic polymers, mainly their stability only up to a certain limiting temperature range, usually from 100 to 200°C, has given impetus to the search for inorganic polymeric complexes of higher resistance to heat and oxidation or with new combinations of properties which are not encountered in the organic field. Recently, interest in the synthesis of a wide variety of coordination polymers

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has also increased in response to aerospace requirements for heat-resistant materials. Coordination polymeric complexes are also gaining importance in this respect.

Very rarely have polymeric complexes of substituted thioureas been studied. Further, monoaryl thioureas are among the least studied derivatives of thiourea used for complex formation. In our laboratory we are working on a project to synthesize and characterize the polymeric complexes of substituted thioureas with some transition metal ions. Few have been reported elsewhere [1, 2].

In the present communication the polymeric complexes of o- and p-tolylthioureas with Co(II) and Ni(II) are described. Complexes have been characterized by elemental analysis, IR and electronic spectra, and magnetic and thermogravimetric measurements.

EXPERIMENTAL

Materials

Arylamines (o- and p-toluidines) were used to synthesize ligands. Ortho-toluidine was distilled just before use while p-toluidine (A.R.) was used without further purification. Ammonium thiocyanate (E. Merck, G.R.), cobalt(II) chloride, cobalt(II) bromide, and nickel(II) chloride were BDH (AnalaR) grade and were used as such. Freshly distilled dehydrated alcohol was used as the solvent in the preparation of complexes.

Preparation and Characterization of the Polymers

Ortho- and para-tolylthioureas, used as ligands, were prepared by the interaction of the respective toluidine hydrochlorides with ammonium thiocyanate by using Kurzer's method [3]. The method employed for the preparation of polymeric complexes was the same as that described in an earlier communication [1]. These complexes are dark colored solids, insoluble in such common organic solvents as ethanol, chloroform, carbon tetrachloride, ether, nitromethane, and dioxane. In N,N-dimethylformamide (DMF) the nickel(II) chloride polymers are insoluble and the cobalt(II) bromide polymeric complexes decompose. Polymeric complexes of cobalt(II) chloride suspended in DMF give a colloidal solution which, after 24 h, turns blue with some insoluble material settled at the bottom. This solution was then filtered before obtaining its visible spectrum.

The insoluble nature of the complexes prevented molecular weight determination by the usual methods.

The metal content was determined by decomposing the complexes with concentrated nitric acid and titrating against EDTA. Sulfur was estimated gravimetrically by Messenger's method [4] as barium

TABLE 1. Analytical Data

Complexes[a]		Elemental analysis		
		Sulfur	Chlorine	Metal
1. $[Co(PTTU)Cl_2.2H_2O]_n$	Calculated	9.64	21.39	17.76
	Found	9.50	21.32	17.70
2. $[Co(OTTU)_2.2H_2O]_n$	Calculated	14.99	-	13.80
	Found	14.92	-	13.65
3. $[Co(PTTU)_2.2H_2O]_n$	Calculated	14.99	-	13.80
	Found	14.88	-	13.74
4. $[Ni(OTTU)Cl.2H_2O]_n$	Calculated	10.84	12.03	19.88
	Found	10.77	12.00	19.78
5. $[Ni(PTTU)Cl.2H_2O]_n$	Calculated	10.84	12.03	19.88
	Found	10.98	11.92	19.81

[a] PTTU = p-tolylthiourea, OTTU = o-tolylthiourea.

sulfate by first oxidizing a definite amount of polymeric complex with alkaline potassium permanganate with subsequent addition of barium chloride. Chlorine was estimated by Stepnov's method [5]. Bromine was found to be absent in the complexes prepared from cobalt(II) bromide. The results of the elemental analyses are depicted in Table 1.

Spectral Studies

The infrared spectra were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer Model 557 in CsI pellets in the range 4 000-200 cm^{-1}. The visible spectrum of the cobalt(II) chloride complex in DMF was recorded on a Pye-Unicam SP 8-100 spectrophotometer in the range 400-800 nm. UV-visible reflectance spectra were taken in the 200-1 500 nm range.

Magnetic susceptibilities were determined by Guoy's method [6] at room temperature.

Thermogravimetric experiments were carried out using a thermobalance assembled from a Cahn RG Electrobalance, a Nichrome-wound furnace temperature controller (Model 400), a temperature programmer (Model 500), and a multipen recorder (Rikadenki). Weight vs time, temperature vs time, and dw/dt vs time plots were recorded on a three-pen recorder. The sample holder was a platinum boat and the thermocouple junction was placed within 1-2 mm, directly under the sample holder. The heating rate was 8°C/min and the polymers were heated up to 900°C in air.

RESULTS AND DISCUSSIONS

Stoichiometry

The analytical data (Table 1) reveal a metal-to-ligand mole ratio of 1:1 for cobalt(II) chloride and nickel(II) chloride complexes while this ratio is 1:2 for complexes prepared from cobalt(II) bromide. Coordination of two molecules of water per metal ion is indicated for all the complexes.

Infrared Spectra

The structurally important IR spectral bands of the ligands and the corresponding bands in the complexes are listed in Table 2. The assignments are based on IR studies of substituted thioureas and their complexes [7, 8]. Three bands are observed in the ligand spectrum due to NH stretching vibrations in the 3-μm region. On complexation with cobalt(II) bromide and nickel(II) chloride, these bands become broader and are appreciably shifted upward (> 100 cm^{-1}). For the cobalt(II) chloride complex, only one strong and sharp band is observed at 3 560 cm^{-1}. This large shift toward higher wavenumber is attributed to nitrogen coordination [8]. The NH_2 deformation vibration of ligands at 1 620 cm^{-1} appears with reduced intensity on complexation. This further affirms involvement of nitrogen in complex formation. This contention finds support by the slight increment in frequency and reduction in intensity of the band near 1 520 cm^{-1} assigned to the thioamide I vibration in the ligand.

The frequency of the thioamide II band of the ligands is considerably increased in complexes with reduction in intensity. Thioamide III and C=S stretching vibrations appear with lowered wavenumber and reduced intensity in complexes. These observations are compatible with the sulfur coordination in the complexes. Thus, the IR spectral study shows coordination of ligands to metal ions through both nitrogen and sulfur, resulting in the formation of polymeric chains.

The appearance of bands at 3 400, 1 660, and 650-665 cm^{-1} in complexes gives evidence for the presence of coordinated water [9].

Sulfur and nitrogen coordination is further supported by observations in the far-IR spectra of the complexes. ν(M–N) bands appear in the 360-380 cm^{-1} range. In nickel(II) complexes a band due to ν(M–Cl) vibration occurs at about 290 cm^{-1} whereas two such bands are ob-

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

Ligand/complex	ν(NH)	$\delta(NH_2)$	Thioamide I	Thioamide II	Thioamide III	ν(CS)
OTTU	3 380s	1 620s	1 525sh	1 290s	1 040s	760s
	3 270s					
	3 180s					
$[Co(OTTU)_2.2H_2O]_n$	3 440s,br		1 550ms	1 345m,br	1 040s	770s,br
	3 340s,br	1 595s			1 016sh	
$[Ni(OTTU)Cl.2H_2O]_n$	3 400m,br	1 620m,br	1 520m	1 295sh	1 050ms,br	745m,br
	3 230m,br				1 020ms	
PTTU	3 450s	1 620vs	1 535s	1 320vs	1 075vs	765s
	3 280s					
	3 180s					
$[Co(PTTU)Cl_2.2H_2O]_n$	3 560s	1 620vw	1 540w	1 380w,br	1 060vw	740ms,br
$[Co(PTTU)_2.2H_2O]_n$	3 400vs,br	1 605w	1 540w	1 370w,br	1 070vw	760w,br
$[Ni(PTTU)Cl.2H_2O]_n$	3 440m,br	1 620w,br	1 550m,br	1 360m,br	1 050ms	

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

served in the 290-310 cm^{-1} range for the cobalt(II) complexes. ν(M–S) vibrations appear as a band of medium intensity at 230 cm^{-1} in Ni(II) complexes and at 280 and 260 cm^{-1} for Co(II) complexes.

Electronic Spectra and Magnetic Measurements

The reflectance spectra and magnetic moments (Table 3) for the complexes are consistent with the octahedral stereochemistry of Co(II) and Ni(II) ions. For Co(II) complexes, near 18 000 cm^{-1}, a ν_3 band due to the transition ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ is observed. Spin-orbit splitting of the ${}^4T_{1g}(P)$ state is responsible for the double peak observed for this transition [10]. The ν_1 transition gives rise to the band in the near-infrared region. The strong band near 14 000 cm^{-1} is observed in the range of the ν_2 (${}^4T_{1g} \rightarrow {}^4T_{2g}$) transition, but the ν_2 band should possess a much lower intensity than the other two bands since it is a two-electron transition. Generally, bands in this region are observed for tetrahedral Co(II). Therefore, it is suggested that complexes are in the form of octahedral polymeric chains with terminal tetrahedral units [11]. The length of the chains must be relatively short, so appreciable absorption due to tetrahedral units is observed.

The blue color of the solution of cobalt(II) chloride complex in DMF is characteristic of tetrahedral Co(II) [12]. The two bands observed in the solution spectrum are associated with ${}^4A_2 \rightarrow {}^4T_1(P)$ transition of tetrahedral symmetry [11]. The nonexistence of octahedral species in equilibrium in solution is evident by the absence of absorption in the 20 000-18 000 cm^{-1} region. Therefore, it is inferred that the octahedral chains are broken into tetrahedral monomeric units in solution.

The ligand field parameters for Ni(II) complexes were calculated by assuming $\nu_1 = \Delta_0$ or 10 Dq and solving the approximate equation $(\nu_2 + \nu_3 - 3\Delta_0)/10$ [13]. Values of the ligand field splitting energy (10 Dq), the Racah parameter (B), and the nephelauxetic factor for the nickel(II) chloride complexes of ortho- and para-tolylthiourea were 8 403 cm^{-1}, 729 cm^{-1}, and 0.690; and 8 333 cm^{-1}, 818 cm^{-1}, and 0.774, respectively. The low values of 10 Dq indicate that the ligands produce very weak fields. The position of the d-d bands (Table 3), the ligand field parameters, and the value of the magnetic moment all indicate octahedral geometry around the nickel(II) in these complexes.

The octahedral geometry of the central metal atom in all these complexes accounts for the occupation of two coordinating sites by water molecules.

Thermal Decomposition

The thermal decomposition of these coordination polymers was studied by using the thermogravimetric method. All the compounds are quite stable toward heat and do not decompose completely even at high temperatures.

Perusal of Table 4 and Fig. 1 indicates that the initial weight loss which corresponds to the loss of water molecules occurs at 150 and 200°C, while the nickel complexes seem to be more stable and initially only one water molecule is lost and the second molecule is lost at even higher temperatures, 400 to 450°C. The loss of water at high temperatures indicates its presence in the coordination sphere. Weight loss up to 900°C in chlorine-containing complexes corresponds to the loss of chlorine. On comparing the thermogravimetric data (Table 4), the order of stability of various complexes is

$$[\mathrm{Ni(OTTU)Cl.2H_2O}]_n > [\mathrm{Ni(PTTU)Cl.2H_2O}]_n > [\mathrm{Co(OTTU)Cl_2.2H_2O}]_n$$

$$> [\mathrm{Co(OTTU)_2.2H_2O}]_n > [\mathrm{Co(PTTU)Cl_2.2H_2O}]_n > [\mathrm{Co(PTTU)_2.2H_2O}]_n$$

It is apparent from the order of stability that the complexes with o-substituted ligands are more stable than their p-analogs. For polymers containing phenylene groups, the following correlation between orientation and stability appears to prevail: $p > m > o$ [14]. It is a general assumption that coordination polymers with p-substituted ligands are more stable than their o-analogs, but our observations are just the opposite.

This disagreement may be explained as follows. The greater stability of ortho complexes than that of para complexes can be attributed to the fact that electrical factors may predominate over steric factors for the methyl substituent. The electron-donating property of the methyl group is a result of an inductive effect which is not effective over longer distances (i.e., a larger number of intervening carbon atoms). Therefore, there may be a greater electron density distribution over the thioamide group when the methyl group is on the ortho position, which in turn results in greater stability of the complex despite the larger steric hindrance imposed by the o-substituent as compared to the p-analog.

The greater stability of nickel complexes compared to cobalt complexes is in agreement with the spectrochemical series, according to which nickel complexes are always more stable than cobalt complexes, irrespective of the ligand.

TABLE 3. Electronic Spectra and Magnetic Moments of Complexes

Complex	μ_{eff} in BM	Wavelength nm	Wavelength cm^{-1}	Assignment	Geometry
$[Co(OTTU)_2.2H_2O]_n$	5.327	540	18 518	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
		580	17 241		
		700	14 285	$^4T_{1g} \rightarrow {}^4A_{2g}$	
		1 200	8 333	$^4T_{1g} \rightarrow {}^4T_{2g}$	
$[Ni(OTTU)Cl.2H_2O]_n$	3.33	420	24 390	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Octahedral
		810	12 345	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
		1 190	8 403	$^3A_{2g} \rightarrow {}^3T_{2g}$	

$[Co(PTTU)Cl_2.2H_2O]_n$:					
Solid	5.369	542	18 450	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
		575	17 391		
		710	14 084	$^4T_{1g} \rightarrow {}^4A_{2g}$	
DMF solution		608	16 447	$^4A_{2g} \rightarrow {}^4T_1(P)$	Tetrahedral
		676	14 792		
$[Co(PTTU)_2.2H_2O]_n$	5.391	535	18 691	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
		585	17 094		
		720	13 883	$^4T_{1g} \rightarrow {}^4A_{2g}$	
		1 220	8 195	$^4T_{1g} \rightarrow {}^4T_{2g}$	
$[Ni(PTTU)Cl.2H_2O]_n$	3.316	400	25 000	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Octahedral
		815	12 269	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
		1 200	8 333	$^3A_{2g} \rightarrow {}^3T_{2g}$	

TABLE 4. Thermogravimetric Data in Air of the Polymeric Metal Complexes with Tolylthioureas

	Percentage weight loss in complexes[a]		
Temperature, °C	$[Co(OTTU)_2.2H_2O]_n$	$[Co(PTTU)_2.2H_2O]_n$	$[Ni(OTTU)Cl.2H_2O]_n$
20	0.0	0.0	0.0
50	0.0	0.0	0.0
100	1.33	6.65	1.33
150	2.67	10.64[b]	3.38
200	8.67[b]	17.29	7.32[c]
250	9.33	20.67	7.98
300	11.33	22.66	8.65
350	14.00	25.99	9.31
400	16.67	29.31	11.31
450	20.67	33.97	12.64[b]
500	23.33	37.34	13.30
800	23.33	38.00	16.63
850	24.67	42.66	18.67
900	30.00	47.98	23.99

TABLE 4 (continued)

Temperature, °C	Percentage weight loss in complexes[a] $[Ni(PTTU)Cl.2H_2O]_n$	$[Co(PTTU)Cl_2.2H_2O]_n$	$[Co(OTTU)Cl_2.2H_2O]_n$
20	0.0	0.0	0.0
50	0.0	0.0	0.0
100	1.99	3.99	
150	3.33	11.31[b]	2.38
200	6.65[c]	13.97	
250	7.32	14.63	16.64
300	7.98	15.30	
350	8.65	15.96	14.29
400	11.97[b]	19.67	
450	15.30	20.00	17.66
500	15.96	20.66	
800	18.62	24.32	
850	20.00	25.99	
900	25.32	31.97	

[a] Reference 1.

[b] Loss of two water molecules.

[c] Loss of one water molecule.

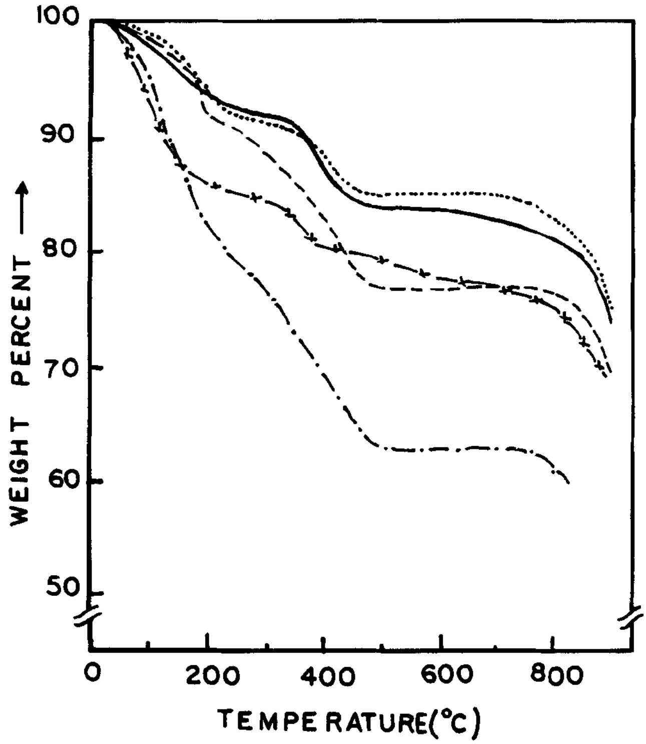

FIG. 1. Thermogravimetric curves for the coordination polymers: (- -) $[Co(OTTU)_2.2H_2O]_n$, (- ·) $[Co(PTTU)_2.2H_2O]_n$, (×-) $[Co(PTTU)Cl_2.2H_2O]_n$, (· ·) $[Ni(OTTU)Cl.2H_2O]_n$, (—) $[Ni(PTTU)Cl.2H_2O]_n$.

From the above discussion it is inferred that the complexes are polymeric in nature with an octahedral geometry; i.e., structures similar to the coordination polymers of some other monoaryl thioureas [1].

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