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Characterisation of Some Copper(II), Nickel(II) and Cobalt(II) Coordination Compounds with N-2-Carbomethoxyphenyl-N^1-phenylthiourea

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A number of coordination compounds of the types, $M(HL)_2$, $M(H_2L)_2X_2$ and $M(HL)_2Y_2$ where M = Co(II), Ni(II) or Cu(II), H_2L = N-2-carbomethoxyphenyl-N^1-phenylthiourea, X = Cl^- or Br^- and Y = ammonia or pyridine have been synthesised and characterised on the basis of elemental analyses, magnetic susceptibility, infrared and electronic spectral data.

INTRODUCTION

Extensive studies[1–5] have been made on coordination compounds of transition metal ions with thiourea and substituted thiourea as ligands where ligands behave as monodentate or bidentate chelating agents but limited work has been reported on coordination compounds with ligands showing higher denticity. We are studying the coordination compounds of cobalt(II), nickel(II) and copper(II) with thiourea as ligands with such substitutents which provides a coordination site in addition to the two coordination sites already existing in thiourea. In the present communication we report a series of coordination compounds of the types, $M(HL)_2$, $M(H_2L)_2X_2$ and $M(HL)_2Y_2$; [M = Co(II), Ni(II), Cu(II); H_2L = N-2-carbomethoxy phenyl-N^1-phenylthiourea; X = Cl^- or Br^- and Y = ammonia or pyridine].

EXPERIMENTAL

The ligand, N-(2-carbomethoxyphenyl)-N^1-phenylthiourea, (H_2L) was prepared according to the literature method[6] by reacting methyl anthranilate with phenylisothiocyanate in methanol (m. p. 284°C; lit. 285°C). All the chemicals were of Aldrich reagents. The ligand was recrystallised with dioxane before use. Bromide salts of cobalt(II), nickel(II) and copper(II) were prepared by dissolving the respective metal carbonates in minimum volume of hydrobromic acid followed by crystallization. A similar procedure was used for the preparation of all the complexes. The preparation of one typical complex is described below for each of the series of complexes.

Bis-(N-2-carbomethoxyphenyl-N^1-phenylthiourea) Copper(II), $Cu[HL]_2$

Copper(II) acetatemonohydrate of BDH make (1.0 g; 0.005 mol) in ethanol

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was treated with an ethanolic solution of the ligand (2.86 g; 0.01 mol) and the resulting solution was refluxed over a hot water bath for 1 h when a greenish yellow crystals were obtained. It was filtered and washed thoroughly with ethanol. It was recrystallised with DMF and analysed as $Cu(C_{15}H_{13}N_2O_2S)_2$ within ± 1% deviation in the analytical data.

Dichlorobis-(N-2-carbomethoxyphenyl-N^1-phenylthiourea) Nickel(II), [Ni(H_2L)$_2Cl_2$]

A solution of nickel(II) chloride hexahydrate in ethanol (1.1 g; 0.005 mol) was treated with an ethanolic solution of the ligand (2.86 g; 0.01 mol). The mixture was refluxed over a hot water bath for 3 h. It was then cooled and green compound was filtered, washed, dried and analysed as $Ni(C_{15}H_{12}N_2O_2S)_2Cl_2$.

Bis-(N-2-carbomethoxyphenyl-N^1-phenylthiourea) dipyridine Cobalt (II) [Co(HL)$_2$Py$_2$]

An ethanolic solution of cobalt(II) chloride hexahydrate (1.18 g; 0.005 mol) was treated with an ethanolic solution of the ligand (2.86 g; 0.01 mol) and refluxed over a hot water bath for an hour. The freshly distilled pyridine (5 ml) was added dropwise with constant stirring to the cold solutions and refluxed again for 2 h over a hot water bath. Light brown crystals appeared which were filtered, washed, dried and analysed as $Co(C_{20}H_{18}N_3O_2S)_2$.

Elemental analysis were done using standard procedures[7]. Magnetic moments were determined by Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. The infrared spectra of the coordination compounds were recorded on a Beckman IR-20 spectrophotometer. Analytical, spectral and magnetic moment data are recorded in Table 1.

RESULTS AND DISCUSSION

The infrared spectrum of the ligand, H_2L shows a strong band at 3200 cm^{-1} which can be assigned[6] to ν_{N-H}. The intensity of this band has decreased significantly in the spectra of the coordination compounds of the types $M(HL)_2$ and $M(HL)_2Cl_2$ with a slight lowering in the position as well indicating partial deprotonation and involvement in coordination. In the spectrum of the complexes of the types $[M(H_2L)_2X_2]$, the position and intensity of this band have remained practically unaffected indicating its non-involvement in coordination and absence of deprotonation.

The second band of spectral significance is a medium intensity band at 1730 cm^{-1} in the spectrum of ligand which can be attributed to ν(C=O)[8]. The position of this band in all the three series of compounds have been lowered and appears in the region, 1690–1700 cm^{-1}. The shift is undoubtedly due to coordination of the oxygen atom of $>C=O$ group to the metal atom. The remaining bands in the region 1200–1800 cm^{-1} have remained practically unchanged and can be assigned to the phenyl ring vibrations.

The spectrum of the ligand shows a very sharp and strong band at 1080 cm^{-1} and has been assigned to $\nu(C=S)$. This band has also undergone a downward shift indicating the coordination of the sulphur atom to the metal atom.

The infrared spectra thus indicates that the ligand behaves in a tridentate manner

utilising N, S and O atoms in coordination in the complexes $M(HL)_2$. In the complexes $[M(H_2L)_2X_2]$ and $[M(HL)_2Y_2]$ it behaves in a bidentate manner using both the donar atoms of group 16 of the periodic table. A strong band found in the spectrum of the ligand as well as in all the complexes at 760 cm^{-1} has been assigned to the *ortho* substituted benzene group.

TABLE 1
COLOUR, ANALYTICAL DATA, ELECTRONIC SPECTRA AND MAGNETIC MOMENT VALUES OF METAL COMPLEXES OF N-2-CARBOMETHOXYPHENYL-^{1}N-PHENYLTHIOUREA (H_2L):

Compounds	Colour	Found (Calc)%				λ_{max}	μ_{eff}
		M	N	S	Cl/Br	(cm^{-1})	B.M.
$Co(HL)_2$	Brown	9.47	8.95	10.31	—	13200	5.30
		(9.36)	(8.90)	(10.17)	—	19200	
$Ni(HL)_2$	Dark	9.42	8.96	10.11	—	10000	3.27
	brown	(9.33)	(8.90)	(10.18)	—	15600	
						24000	
$Cu(HL)_2$	Greenish	10.32	8.65	10.22	—	14500	1.71
	yellow	(10.02)	(8.83)	(10.10)	—	11200	
$Co(H_2L)_2Cl_2$	Green	8.46	7.65	9.10	10.23	13400	5.40
		(8.32)	(7.91)	(9.17)	(10.16)	19600	
$Co(H_2L)_2Br_2$	Yellowish	7.07	7.17	8.15	20.09	13500	5.50
	green	(7.37)	(7.01)	(8.13)	(20.31)	19800	
$Ni(H_2L)_2Cl_2$	Light	8.36	8.22	9.20	10.00	11000	3.38
	yellow	(8.41)	(8.02)	(9.17)	(10.16)	15400	
						23500	
$Ni(H_2L)_2Br_2$	Yellow	7.62	7.01	8.00	20.15	10500	3.42
		(7.46)	(7.12)	(8.13)	(20.31)	15800	
						23800	
$Cu(H_2L)_2Cl_2$	Light	9.14	7.89	9.20	10.15	15000	1.79
	green	(9.04)	(7.97)	(9.11)	(10.09)	11400	
$Cu(H_2L)_2Br_2$	Yellow	7.89	7.08	8.16	20.31	15200	1.83
		(7.93)	(6.99)	(8.08)	(20.19)	11600	
$Co(HL)_2(NH_3)_2$	Reddish	8.82	12.62	9.73	—	13700	5.35
	brown	(8.88)	(12.67)	(9.65)	—	20000	
$Co(HL)_2Py_2$	Light	7.61	10.72	8.05	—	12900	5.30
	brown	(7.48)	(10.67)	(8.13)	—	19100	
$Ni(HL)_2(NH_3)_2$	Brown	8.89	12.60	9.49	—	10700	3.51
		(8.85)	(12.67)	(9.65)	—	16000	
						24200	
$Ni(HL)_2Py_2$	Yellowish	7.39	10.77	8.23	—	10900	3.58
	green	(7.46)	(10.67)	(8.13)	—	16200	
						24500	
$Cu(HL)_2(NH_3)_2$	Greenish	9.55	12.89	9.60	—	15300	1.87
	yellow	(9.51)	(12.58)	(9.58)	—	11700	
$Cu(HL)_2Py_2$	Light	8.12	10.58	8.00	—	15500	1.90
	greenish	(8.02)	(10.64)	(8.08)	—	11900	
	yellow						

The spectra of the pyridine adducts shows an additional band near 650 cm^{-1} which has been assigned to pyridine breathing mode.

Far infrared end of the spectrum of complexes indicate three bands in the regions 600–500 cm^{-1}, 500–400 cm^{-1} and 400–300 cm^{-1} respectively which have been assigned to ν(M–O), ν(M–S) and ν(M–X) respectively.

During the course of the present investigation, it has been found (Table 1) that the copper(II) complexes have magnetic moments values in the range 1.8 to 1.9 B.M. which is usually observed for octahedral copper(II) complexes. Visible spectra of the complexes show two broad ligand field bands in the regions 11,000–12,000 cm^{-1} and 14000–15000 cm^{-1}. The bands may arise due to $^2A_{1g} \rightarrow {}^2B_{1g}$ and $^2A_{1g} \rightarrow {}^2B_{2g}$ transitions respectively in an distorted octahedral field with the chromophore, $CuN_2O_2S_2$ in the series $[Cu(HL)_2]$ and $[Cu(HL)_2Y_2]$ and $CuO_2S_2X_2$ in the series $[Cu(H_2L)_2X_2]$.

The nickel (II) complexes have magnetic moment values in the region 3.2–3.5 B.M. at room temperature. These values are typical of a nickel(II) ion in an octahedral environment. The three typical bands occuring in the regions, 10,000–11,000 cm^{-1}, 15,000–16,000 cm^{-1} and 25,000–26,000 cm^{-1} are due to transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively in an octahderal environment.

The cobalt (II) complexes show magnetic moment values in the range 5.0–5.2 B.M. at 25°C which are typical of cobalt(II) ion in an octahedral environment. The complexes exhibit two broad ligand field bands centred at 13,500 and 20,000 cm^{-1} respectively which can be assigned to the transitions, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively and suggest an octahedral environment around Co^{2+} ion. The third band corresponding to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ might have fallen in the near infrared range.

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