

Complexes of Co(II) & Ni(II) with N-*p*-Tolyl- & N-*p*-Chlorophenyl-dithiocarbamates

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Complexes of Co(II) and Ni(II) with N-*p*-tolylidithiocarbamate and N-*p*-chlorophenylidithiocarbamate have been prepared. Structures and modes of coordination have been suggested on the basis of magnetic, electronic and infrared spectral data which clearly indicate that Co(II) forms diamagnetic square planar complexes. The dithiocarbamates behave as a bidentate ligand coordinating through both the sulphur atoms. Far infrared data indicate the presence of ν_{M-S} bands in the region of 350-395 cm^{-1} in these complexes.

THE ability of dithiocarbamate group to form complexes of the type $R_2N-C \begin{array}{l} \diagup S \\ \diagdown S \end{array} M/n$,

(where R=alkyl or aryl group) with a large number of metal ions in various oxidation states is well established¹⁻⁸. A survey of the literature¹⁻¹⁹ indicates that although a lot of work has been done on the metal complexes of N, N-disubstituted dithiocarbamates, not much work has been done on complexes of N-monosubstituted dithiocarbamates. This prompted us to undertake the preparation of stable complexes of Co(II) and Ni(II) with N-*p*-chlorophenylidithiocarbamate (*p*-Cl.Dtc) and N-*p*-tolylidithiocarbamate (*p*-t. Dtc). The structures of these complexes have been established on the basis of analytical, magnetic, infrared and electronic spectroscopic data¹.

Materials and Methods

All the chemicals used were either of Analar or chemically pure grade. The ligands were prepared by a slightly modified method described in literature^{20,21}.

Preparation of metal complexes: (i) *Bis*(N-*p*-chlorophenylidithiocarbamate) *bis*aquo cobalt(II) — Aqueous solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.4 g) and freshly prepared ammonium salt of N-*p*-chlorophenylidithiocarbamate (2.2 g) were mixed together (metal:ligand ratio=1:2). Dark green precipitates of the complex which separated out immediately were filtered, washed with water and dried at 100-110° for 2-3 hr [Found: C, 33.8; H, 2.8; N, 5.2; S, 25.3; Co, 11.5. $\text{Co}(p\text{-Cl.C}_6\text{H}_4\text{.NHCS}_2)_2(\text{H}_2\text{O})_2$ requires C, 33.6; H, 2.6; N, 5.6; S, 25.6; Co, 11.8%].

(ii) *Bis*(N-*p*-tolylidithiocarbamate)-*bis*aquo cobalt(II) *monohydrate* — This dark green complex was prepared by the method described above in (i). The complex obtained was dried at 80-90° for 2 hr [Found: C, 40.3; H, 4.5; N, 5.7; S, 26.7; Co, 12.1. $\text{Co}(p\text{-CH}_3\text{C}_6\text{H}_4\text{.NHCS}_2)_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ requires C, 40.2; H, 4.6; N, 5.9; S, 26.8; Co, 12.3%].

(iii) *Bis*(N-*p*-achlorophenylidithiocarbamate)Ni(II) — This yellowish green complex was prepared

by the method described in (i) using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. [Found: C, 36.4; H, 2.3; N, 5.8; S, 27.9; Ni, 12.5. $\text{Ni}(p\text{-Cl.C}_6\text{H}_4\text{.NHCS}_2)_2$ requires C, 36.2; H, 2.2; N, 6.0; S, 27.6; Ni, 12.6%].

(iv) *Bis*(N-*p*-aratolylidithiocarbamate)Ni(II) *tetrahydrate* — This yellowish green complex was also prepared and isolated by the method described in (i) using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. The complex was dried at 80-90°C for 2 hr. [Found: C, 38.6; H, 4.6; N, 5.4; S, 26.0; Ni, 11.9. $\text{Ni}(p\text{-CH}_3\text{C}_6\text{H}_4\text{.NHCS}_2)_2 \cdot 4\text{H}_2\text{O}$ requires C, 38.8; H, 4.8; N, 5.7; S, 25.9; Ni, 11.8%].

Physical measurements — Magnetic susceptibilities of the complexes were measured at room temperature using a Gouy balance and mercury(II) tetrathiocyanato cobalt(II) as the calibrant. Electronic spectra of the complexes were recorded in acetone on a Hilger and Watts UV spectrophotometer 700. Infrared spectra of the ligands and complexes were measured on Perkin-Elmer 237 and Perkin-Elmer 521 spectrophotometers.

Results and Discussion

The electronic spectrum of *bis*aquo-*bis*(*p*-chlorophenylidithiocarbamate) Co(II) complex exhibits a band at 15600 cm^{-1} and another split band with maximum absorptions at 17000 and 18200 cm^{-1} . These bands have low intensities corresponding to *d-d* transitions. From the positions and intensities of these bands it may be suggested that the environment around Co(II) ion is octahedral. *Bis*aquo-*bis*(*p*-tolylidithiocarbamate) Co(II) *monohydrate* also gives rise to a similar electronic band at 15400 cm^{-1} and a split band having maximum absorption at 16600 cm^{-1} and 18500 cm^{-1} indicating the octahedral environment of Co(II) ion in this complex also. However, the magnetic moments of 2.1 and 4.0 B.M. respectively are abnormally low and this may be due to a large tetragonal distortion along the Z-axis as suggested by Stoufer *et al.*²² This is also apparent from the fact that two water molecules present at the Z-axis are completely different from the two bidentate thiocarbamate ligands which form the square plane of the octahedral structure. The large difference in the

magnetic moments of these two Co(II) complexes may be partly due to the large difference in electro-negativity of the *p*-chlorophenyl dithiocarbamate and *p*-tolylidithiocarbamate ligands as suggested by several workers²³⁻²⁵ and partly due to difference in the degree of distortion of the two complexes. The distortion in octahedral symmetry of these complexes is also apparent from the splitting of the high energy electronic band of these complexes. Thus, on the basis of their octahedral symmetry assignments of these bands have been made as follows: 15600 and 15400 bands in these complexes are due to ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition and the split band with maximum absorptions at 17000, 18200 cm^{-1} and 16600, 18500 cm^{-1} are due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition.

The values of Dq, B' and β for $[\text{Co}(p\text{-Cl.Dtc})_2(\text{H}_2\text{O})_2]$ have been calculated to be 928 cm^{-1} , 773 cm^{-1} and 0.69 respectively. These values for $(\text{Co}(p\text{-t.Dtc})_2(\text{H}_2\text{O})_2) \cdot \text{H}_2\text{O}$ have been found to be 840, 700 cm^{-1} and 0.625 respectively. The low values of β for these complexes suggest bonding to the metal ion through sulphur²⁶⁻²⁸ of thiocarbamate group.

The infrared spectra of the ligands show absorption bands at 3420-3440 and 1400-1420 cm^{-1} corresponding to the presence of ammonium ion²⁹ in the ligands. However, the infrared spectra of these Co(II) complexes do not contain these bands indicating a change from $-\text{S}-\text{NH}_4$ to $-\text{S}-\text{Co(II)}$ linkage. The N-H stretching mode is observed in the spectra of the ligands as well as those of the complexes indicating absence of deprotonation of the N-H group of the ligand. The $\nu\text{C}=\text{S}$ band is observed at 730 cm^{-1} in the *p*-chloro ligand and at 720 cm^{-1} in the *p*-tolyl ligand which shift to 700 and 705 cm^{-1} in the spectra of the corresponding complexes indicating coordination through thiocarbonyl group of the ligand. It is, therefore, clear that coordination in these complexes occurs through the thiol sulphur as well as through thiocarbonyl sulphur and the complexes have distorted octahedral structures.

The diamagnetism of the two Ni(II) complexes indicates that they are square planar in structure. The electronic spectra of bis(*p*-chlorodithiocarbamate)Ni(II) show absorption bands at 15380 ($\epsilon=225$) and 18500 cm^{-1} ($\epsilon=225$). The corresponding bands of bis(*p*-tolylidithiocarbamate)Ni(II) tetrahydrate are observed at 15625 ($\epsilon=280$) and 17240 cm^{-1} ($\epsilon=240$). These bands are in the range of square planar Ni(II) complexes³⁰ and are due to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_{1g}$ transitions. In addition to these two bands, other two high energy bands at 21280 and 23260 cm^{-1} may be charge transfer bands. The infrared spectrum of $[\text{Ni}(p\text{-t.Dtc})_2] \cdot 4\text{H}_2\text{O}$ shows broad absorption in the range 3600-3400 cm^{-1} corresponding to $\nu\text{H}_2\text{O}$. This absorption is absent in the infrared spectrum of $\text{Ni}(p\text{-Cl.Dtc})_2$. Bands due to NH_4^+ ion are present in the spectra of the ligands and are absent in the spectra of corresponding Ni(II) complexes. $\nu\text{C}=\text{S}$ band which is

observed in the range of 720-730 cm^{-1} undergoes a red shift of about 20-30 cm^{-1} on coordination to Ni(II) ion in these complexes. These spectral changes are similar to those found in Co(II) complexes and indicate bonding through thiol sulphur and thiocarbonyl sulphur of the thiocarbamate ligands. This observation is also in agreement with previous works on N,N-disubstituted thiocarbamate ligands.

The far infrared spectra of the Co(II) complexes show new bands in the range of 350-390 cm^{-1} which may be due to $\nu\text{Co}-\text{S}$ mode. The corresponding range for $\nu\text{Ni}-\text{S}$ is 370-395 cm^{-1} .

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