

New Tetrahedral Co(II) Complexes of Substituted Thioureas

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Some new Co (II) complexes of N, N'-di (*o*-tolyl)thiourea (DoTTU), N, N'-di(*m*-tolyl)thiourea (DmTTU) and N, N'-di(*o*-anisyl)thiourea (DoATU) have been prepared and characterised. Magnetic and spectral evidences show that they are pseudo-tetrahedral. The D_q and β values are reported and their significance discussed.

THIOUREA ligands form a variety of complexes of different stereochemistries with various metal ions. Ni(II) complexes, for example, assume tetrahedral, octahedral or tetragonal geometry, the latter with various degree of axial perturbation^{1,2}. Pd(II) and Pt(II) display basically four-fold coordination, but with strong tendency to form penta-coordinated adducts^{3,4}. Previous investigations on Co(II) complexes⁵ of substituted thioureas show that Co(II) has a pronounced tendency to form tetrahedral complexes of the general formula CoL_2X_2 . When X is nitrate or acetate, the stereochemistry changes from tetrahedral to octahedral with X acting as a bidentate group⁶. Polymeric complexes of Co(II) thiocyanate with thiourea and N-methylthiourea have been found to be octahedral⁷. There has been also a report about the existence of penta-coordinated thiourea complex⁷ of the type CoL_3X_2 .

The authors have recently investigated some Ni(II) complexes⁸ with substituted thiourea ligands which were found to be tetragonal with the composition NiL_4X_2 . The interesting feature of these complexes was that they retained their tetragonal geometry even in solution. This was contrary to the earlier reports on the Ni(II) complexes of substituted thioureas which dissociated in solution to give tetrahedral NiL_2X_2 species irrespective of their initial composition⁹. The extra stability of these Ni(II) complexes was attributed to the steric factors of the substituted thiourea ligands. These observations on the Ni(II) complexes lead us to extend the investigation to the Co(II) complexes to find out whether the structural characteristics of these ligands could influence the geometry and other properties of the cobalt complexes.

Materials and Methods

The ligands (L) used in the present work; N, N'-di(*o*-tolyl) thiourea (DoTTU); N, N'-di(*m*-tolyl) thiourea DmTTU and N, N'-di(*o*-anisyl) thiourea (DoATU) were prepared by refluxing appropriate primary amine and carbon disulphide (2:1 ratio) in ethanol¹⁰. The Co(II) complexes were prepared by mixing the appropriate cobaltous halide and the ligand (L) in stoichiometric amounts (1:2) in *n*-

butanol and heating for about 5 min. On cooling, the complex separated out which was recrystallised from *n*-butanol. Characterisation of these complexes was done on the basis of C, H, N analyses.

Infrared spectra were recorded in KBr on a Perkin Elmer 137 spectrophotometer. Magnetic susceptibility measurements were done by Gouy method in solid and in chloroform solution. Hg [Co(NC S)₄] was used as the calibrant. The electronic spectra were measured on Cary 14 and Cφ10 Russian spectrometers¹¹ in nujol or in chloroform solution.

Results and Discussion

The analytical data (Table 1) show that these compounds have the general composition CoL_2X_2 . The infrared spectra of the ligands and the corresponding Co(II) complexes were compared with the IR spectra

TABLE 1 — CHARACTERISATION AND MAGNETIC MOMENT DATA FOR Co(II) COMPLEXES

Compound	Found (Calc.), %			μ_{eff} (B.M.)*
	C	H	N	
(DoTTU) ₂ Cl ₂ Co	56.32 (56.10)	5.10 (4.98)	8.51 (8.72)	4.75† (—)
(DoTTU) ₂ Br ₂ Co	48.62 (49.24)	4.30 (4.37)	7.35 (7.66)	4.78 (4.56)
(DoTTU) ₂ I ₂ Co	43.95 (43.69)	4.90 (4.88)	7.00 (6.78)	4.80 (4.59)
(DmTTU) ₂ Cl ₂ Co	56.41 (56.10)	5.02 (4.98)	8.81 (8.72)	4.60† (—)
(DmTTU) ₂ Br ₂ Co	49.50 (49.24)	4.54 (4.37)	8.10 (7.66)	4.71 (4.42)
(DmTTU) ₂ I ₂ Co	44.00 (43.69)	4.00 (3.88)	7.12 (6.78)	4.80 (4.56)
(DoATU) ₂ Cl ₂ Co	51.00 (51.06)	4.51 (4.54)	8.20 (7.99)	4.61† (—)
(DoATU) ₂ Br ₂ Co	44.90 (45.28)	3.80 (4.02)	7.32 (7.04)	4.64 (4.37)
(DoATU) ₂ I ₂ Co	40.10 (40.54)	3.35 (3.60)	6.45 (6.30)	4.70 (4.50)

*Measurements carried out at room temperature (300–303K); values in parentheses indicate values in chloroform solution.

†Measurements not made in chloroform solution because of poor solubility.

of some well-characterised dialkyl and phenyl substituted thioureas to ascertain the mode of bonding from the ligand to the metal ion. It is observed^{11,12} that on sulphur coordination the frequency of the bands around 1515 and 1280 cm^{-1} increases by 25 to 30 cm^{-1} and 10 cm^{-1} respectively and the frequency of the 770 cm^{-1} band decreases while on nitrogen coordination the shifts are in the reverse order. In the case of present compounds the 1515 and 1280 cm^{-1} bands are shifted upwards by 20 and 10 cm^{-1} while the 770 cm^{-1} band is shifted downwards by 5 cm^{-1} . Thus our results are in conformity with coordination through sulphur in the present thiourea ligands.

The μ_{eff} values in solid state and in chloroform solution lie in the range 4.60–4.80 B.M. (Table 1). This is the range observed for pseudo-tetrahedral Co(II) complexes though pseudo-octahedral complexes can also have μ_{eff} values in this range. However, the other experimental data (vide infra) agree more closely with the pseudo-tetrahedral arrangement. The solution μ_{eff} values are very close to the values in solid phase indicating that no structural changes take place on dissolution. Thus the magnetic susceptibility data are suggestive of tetrahedral geometry for these complexes.

Further support to this geometry comes from the electronic spectral data (Table 2). All the complexes show split bands in the regions 5,000–8,000 and 13,000–16,500 cm^{-1} , both in nujol and chloroform.

For tetrahedral environment there are three possible transitions, ${}^4T_2(F) \leftarrow {}^4A_2(\nu_1)$; ${}^4T_1(F) \leftarrow {}^4A_2(\nu_2)$; and ${}^4T_1(P) \leftarrow {}^4A_2(\nu_3)$. Of these, the ν_1 band occurs at very low energies (3000–5000 cm^{-1}) and is not observed in most cases. In the present complexes both the bands are split and we assign the split bands around 7000 cm^{-1} to ν_2 transition and those around 15,000 cm^{-1} to ν_3 transition in a tetrahedral symmetry. The splitting is due to the lowering of symmetry and in principle there can be a maximum of three components^{13,14}. Thus the position and intensity of the spectral bands, the magnetic moment values and the analytical data all favour tetrahedral geometry for the Co(II) complexes.

The Dq , B' and β values for these compounds lie in the ranges 350–400 cm^{-1} , 640–750 cm^{-1} and 0.56–0.75 respectively. Particularly interesting are the values of B' and β which indicate strong nephelauxetic effect in the ligands giving additional support to sulphur coordination from the ligand^{15,16}. The values decrease as $\text{CoL}_2\text{Cl}_2 > \text{CoL}_2\text{Br}_2 > \text{CoL}_2\text{I}_2$. The Dq and β values are in good agreement with the values for some other tetrahedral sulphur compounds of the CoS_2X_2 chromophores^{16,17}.

In conclusion we can say that the ligands which generated tetragonal nickel (II) complexes form only pseudo-tetrahedral Co(II) complexes. This is not surprising since Co(II) has a very strong tendency to form tetrahedral complexes compared to Ni(II) complexes.

TABLE 2 — BAND POSITIONS (ν , cm^{-1}) AND EXTINCTION COEFFICIENTS (ϵ , litre mole $^{-1}$ cm^{-1}) OF ELECTRONIC BANDS OF COBALT (II) COMPLEXES AT ROOM TEMPERATURE (300–303 K)

Compound	Medium	$\nu(\epsilon)$
(DoTTU) ₂ Cl ₂ Co	nujol	5, 410, 6,060, 8,000, 14,490, 15,870
(DoTTU) ₂ Br ₂ Co	nujol	5,715, 7,850, 13,420, 14,390, 15,020
	chloroform	5,475(120), 6,900(66), 13,550(63), 14,530sh(62), 14,888(58), 15,620(56)
(DoTTU) ₂ I ₂ Co	nujol	5,555, 7,325, 13,330, 14,750
	chloroform	5,265(110), 6,670(108), 13,970(50), 14,810(60)
(DmTTU) ₂ Cl ₂ Co	nujol	5,555, 7,405, 13,380, 16,390
	chloroform*	13,440, 14,710, 15,620
(DmTTU) ₂ Br ₂ Co	nujol*	13,390, 14,250, 15,460
	chloroform	5,225(106), 6,060(116), 7,065(100), 13,440(43), 14,710(69), 15,620(58)
(DmTTU) ₂ I ₂ Co	nujol*	13,700, 14,490
	chloroform	5,365(112), 7,145(107), 13,930(55), 14,970(62)
(DoATU) ₂ Cl ₂ Co	nujol	5,000, 7,405, 14,080, 15,620, 17,200
(DoATU) ₂ Br ₂ Co	nujol	4,650, 6,450, 14,810, 15,750
	chloroform	5,350(12), 6,665(77), 13,510(71), 14,710(68), 15,650(65)
(DoATU) ₂ I ₂ Co	nujol*	13,700, 14,600
	chloroform	5,555(96), 7,145(90), 13,890(70), 14,750(76)

*The near IR electronic spectra were not recorded.

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