Synthesis and physicochemical studies on Ni(II) complex of 2-hydroxy-acetophenonethiosemicarbazone and its square-planar adducts with nitrogen donors

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Abstract. NiL$_2$X$_2$ complex and its adducts of the type NiL (base), where L is a 2-hydroxy-acetophenonethiosemicarbazone, X=Cl and base (ammonia, pyridine, aniline, o-, m-, p-toluidine and water) have been synthesised and characterised by analysis, magnetic moments, electronic and infrared spectra.

Keywords. Ni(II) adducts; Ni(II) complexes; 2-hydroxy-acetophenonethiosemicarbazone.

1. Introduction

There is an extensive and interesting study on coordination behaviour of salicylaldehyde thiosemicarbazone with different metal ions (Ablov and Gerbeleu 1965; Patel et al 1979). We report here the preparation and characterisation of nickel (II) complex of 2-hydroxy-acetophenone thiosemicarbazone (HAT) and its adducts with ammonia, pyridine, aniline, o-, m-, p-toluidine and water.

2. Experimental

All the solvents and reagents used were guaranteed reagents. HAT was prepared by the method reported in the literature (Patel et al 1973). The parent complex Ni(HAT)$_2$Cl$_2$ was isolated as follows. The concentrated ethanolic solution of HAT in slight excess over the Ni(II) : HAT ratio 1 : 2 was added dropwise and with constant stirring to a slightly acidic ethanolic solution of nickel(II) chloride. The reaction mixture was refluxed for 1 hr, concentrated to about 20% of the original volume and allowed to cool slowly to get the green product.

In the preparation of adduct complexes of ammonia/pyridine, the required amount of HAT was dissolved in it, while for that of other bases (o-, m-, p-toluidine); the required amount of HAT and 2 grams of base were dissolved in a
minimum quantity of ethanol. The solution thus obtained was added to the aqueous solution of Ni(II) chloride in such a way that Ni(II) : HAT ratio remained 1 : 1. The reaction mixture was then kept on a steam bath for 30 min and cooled to get a red brown product. Brown Ni(HAT)H₂O was prepared by adding an aqueous solution of sodium acetate to the ethanolic 1 : 1 [Ni(II) : HAT) mixture. The products obtained by the above procedures were filtered and washed with small amounts of ethanol and then with ether.

Nickel(II) was estimated in each compound by titrating against standard EDTA after decomposing the complexes and also by gravimetric oxide method. Carbon, hydrogen and nitrogen in the complexes were determined by microanalytical methods. Sulphur was estimated as BaSO₄ by Carius method (Vogel 1958). The chloride (13.33%) was determined by Mohr’s method. Magnetic susceptibilities were measured on a standard Gouy balance using Hg[Co(NCS)₄] as the calibrant. The visible spectra of the solutions and diffuse reflectance spectra of the complexes were measured on a Beckman-DU spectrophotometer. The infrared spectra were recorded in KBr on Spectromom-2000 spectrophotometer. The conductivities of the complexes in absolute ethanol were measured using “Konduktskop Metrohm Herisau” conductometer.

3. Results and discussion

3.1. Nature of the HAT

HAT can take any of the following two forms:

\[ \text{It shows strong and sharp band at } 830 \text{ cm}^{-1} \text{ which may be assigned mainly due to } \nu_{\text{C=S}} \text{ with some contribution from either } \delta_{\text{NH}_{2}} \text{ or } \nu_{\text{C=S}} \text{ (Campbell and Grazesko-wiak 1967). There is no infrared band at 2560–70 cm}^{-1} \text{ and this excludes the presence of thiol (mercapto) form of the ligand at least in the solid state (Poddar and Saha 1975). The strong band at 1570 cm}^{-1} \text{ can be tentatively assigned to } \nu_{\text{C=N}} \text{ (Wiles and Suprunchuck 1969). It shows four bands at 3200, 3250, 3300 and 3400 cm}^{-1} \text{ and may be assigned to } \nu_{\text{NH}} \text{. The band at 3000 cm}^{-1} \text{ may be tentatively assigned to } \nu_{\text{C=O}} \text{ and the strong band at 1310 cm}^{-1} \text{ may be mainly due to } \nu_{\text{C=O}} + \delta_{\text{NH}_{2}} \text{ (Beecroft et al 1974).} \]

3.2. Nature, bonding and structure of the complexes

Elemental analyses (table 1) indicate the metal-to-ligand ratio to be 1:2 for the parent complex and metal : ligand : base ratio to be 1 : 1 : 1 for the adducts. Thus the composition of the parent may be given as Ni(HAT)₂Cl₂ and that for the adducts as Ni(HAT) (base).