

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_2X_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 synthesized 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 (Ablon and Gerbelet 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 $Ni(HAT)_2Cl_2$ 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

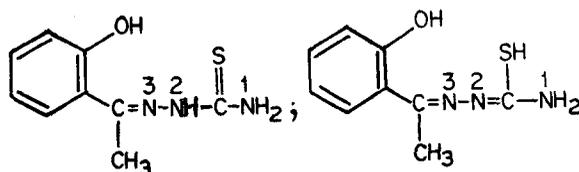
minimum quantity of ethanol. The solution thus obtained was added to the aqueous solution of Ni(II) chloride in such a way that Ni(II) : HAT ratio remained 1 : 1. The reaction mixture was then kept on a steam bath for 30 min and cooled to get a red brown product. Brown Ni(HAT)H₂O was prepared by adding 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 "Konduktoskop Metrohm Herisau" conductometer.

3. Results and discussion

3.1. Nature of the HAT

HAT can take any of the following two forms:



It shows strong and sharp band at 830 cm⁻¹ which may be assigned mainly due to $\nu_{C=S}$ with some contribution from either δ_{NH_2} or ν_{NCN} (Campbell and Grazesko-wiak 1967). There is no infrared band at 2560-70 cm⁻¹ 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 can be tentatively assigned to $\nu_{C=N}$ (Wiles and Suprunchuck 1969). It shows four bands at 3200, 3250, 3300 and 3400 cm⁻¹ and may be assigned to ν_{NH} . The band at 3000 cm⁻¹ may be tentatively assigned to ν_{OH} and the strong band at 1310 cm⁻¹ may be mainly due to $\nu_{C-N} + \delta_{NH_2}$ (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. The parent compound behaves as a 1 : 2 electrolyte in ethanol while the others are nonelectrolytes (Geary 1971) (table 2). Thus the composition of the parent may be given as Ni(HAT)₂Cl₂ and that for the adducts as Ni(HAT) (base).

Table 1. Analytical data of the Ni(II) complexes.

| Compound | Calculated % | | | | | Found % | | | | |
|-------------------------------------|--------------|------|-------|-------|-------|---------|------|-------|-------|-------|
| | C | H | N | S | Metal | C | H | N | S | Metal |
| L = HAT | | | | | | | | | | |
| [NiL ₂] Cl ₂ | 39.94 | 4.05 | 15.45 | 12.03 | 10.8 | 39.74 | 5.1 | 15.06 | 11.77 | 10.87 |
| [NiL NH ₃] | 38.3 | 3.90 | 19.86 | 11.70 | 20.67 | 39.3 | 4.00 | 19.58 | 11.34 | 20.48 |
| [NiL PY] | 48.74 | 4.35 | 16.25 | 9.283 | 17.02 | 49.74 | 3.79 | 16.23 | 9.51 | 16.78 |
| [NiL H ₂ O] | 36.9 | 4.4 | 14.38 | 10.93 | 20.05 | 37.5 | 5.1 | 13.71 | 11.28 | 20.31 |
| [NiL <i>o</i> -tolu] | 51.33 | 5.1 | 14.96 | 8.59 | 15.75 | 50.51 | 5.18 | 14.56 | 8.75 | 15.63 |
| [NiL <i>m</i> -tolu] | 51.33 | 5.1 | 14.96 | 8.59 | 15.75 | 52.76 | 5.3 | 14.25 | 8.83 | 15.51 |
| [NiL <i>p</i> -tolu] | 51.33 | 5.1 | 14.96 | 8.59 | 15.75 | 50.65 | 4.8 | 15.5 | 9.05 | 15.45 |
| [NiL Aniline] | 50.2 | 4.8 | 15.6 | 8.92 | 16.37 | 49.95 | 4.65 | 15.73 | 8.79 | 17.07 |

Table 2. Molar conductance and spectral data of Ni(II) complexes.

| Compound L = HAT | Molar conductance ohm ⁻¹ cm ² mol ⁻¹ | Reflectance spectra cm ⁻¹ | Absorption spectra in methanol cm ⁻¹ |
|-----------------------------------|--|--|--|
| Ni L ₂ Cl ₂ | 58.88 | 25000 17090 11110 | 24510 |
| [NiL NH ₃] | 0.9421 | 24390 17870 | 24390 |
| [NiL PY] | 2.278 | 24100 17700 | 24510 |
| [NiL H ₂ O] | .. | 24390 17700 | 24690 |
| [NiL <i>o</i> -tolu] | .. | 25000 18180 | 24390 |
| [NiL <i>m</i> -tolu] | .. | 24100 18180 | 24390 |
| [NiL <i>p</i> -tolu] | .. | 24100 18180 | 24390 |
| [NiL Aniline] | .. | 24390 18180 | 24390 |

The infrared spectra of the complexes show the shifting of bands at 830 cm^{-1} and 1570 cm^{-1} indicating the participation of sulphur and nitrogen³ in coordination to Ni(II). All the complexes studied show bands in the ν_{NH} region, which do not differ significantly from that of the ligand. However shifting by $20\text{--}30\text{ cm}^{-1}$ is difficult to explain. The presence of a strong band at 3000 cm^{-1} in the parent complex suggests that the coordinate bond to metal would have been formed by sharing lone pair of oxygen of the OH and not by replacement of its proton. The presence of a strong band at 1320 cm^{-1} in the parent complex indicates the absence of $\text{C}=\text{N}^2$. These results suggest that HAT would have behaved as neutral tridentate ligand in the parent complex. The absence of a band around 3000 cm^{-1} in the adducts indicates the removal of proton of the hydroxy group during complexation. It also shows the shifting of band at 1310 cm^{-1} to higher frequencies, suggesting the presence of $\text{C}=\text{N}^2$ (Cavalca *et al* 1962). This indicates the presence of mercapto form, from which proton would have been removed on complex formation. Thus in adducts HAT would have behaved as a doubly charged tridentate ligand.

The diffuse reflectance spectra (table 2) of high spin (2.99 BM) NiL_2Cl_2 show three pseudo-octahedral ligand field bands (Lever 1968). They can be assigned to the ν_1 , ν_2 and ν_3 transitions. To confirm the assignment band fitting procedures (Konig 1971) have been used and the average value of $B = 597\text{ cm}^{-1}$ has been determined. The $Dq = \nu_1/10$ is found to be 1111 cm^{-1} . The value of B in complex is found to be considerably reduced, compared to the free ion value of 1041 cm^{-1} indicating the appreciable amount of covalent character in the bonds.

Reflectance spectra of the diamagnetic and presumably planar adducts show (table 2) a strong band around 18000 cm^{-1} and a shoulder around 25000 cm^{-1} , probably on a tail of charge transfer band (Drago 1968; Maki 1958).

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