

## Role of Nucleophiles in Schiff Base Interaction with Nickel Ions

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Schiff base, *N*-2-methylthiophenyl-2'-hydroxybenzylideneimine [ $\text{CH}_3\text{S}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$  (SMe-N-OH)] on heating for 2-3 hr with nickel acetate or propionate in a molar ratio of 2:1 provides the bis compound  $\text{Ni}(\text{SMe-N-O})_2$ . The same compound has been obtained instantaneously at room temperature in the presence of *t*-butylamine, diethylamine and triethylamine. In the presence of ammonia, however, the ligand splits to form *o*-methylthioaniline and salicylaldehyde, the latter forming bis(salicylaldehyde)nickel(II) complex. Some properties of both the complexes have been studied.

TRANSITION metal ions combine with tridentate Schiff bases containing sulphur, oxygen and nitrogen atoms to form stable complexes<sup>1,2</sup>. 2-Acetylpropylideneamino-*o*-methylthiobenzene, a Schiff base of the above class has, however, been found to decompose in the presence of copper and nickel chlorides to provide complexes of *o*-methylthioaniline<sup>3</sup> only. Reaction of nickel(II) acetate or propionate with the Schiff base *N*-2-methylthiophenyl-2'-hydroxybenzylideneimine (SMe-N-OH) (I) in the presence of primary (*t*-butylamine), secondary (diethylamine) and tertiary (triethylamine) and ammonia has now been carried out to examine the behaviour of the system.

### Materials and Methods

The Schiff base (I) was prepared by heating for 1 hr an equimolar mixture of *o*-methylthioaniline with salicylaldehyde in an oil-bath maintained at 110°. The mixture was cooled and the solid thus formed was filtered and crystallized twice from ethanol to give yellow needles, m.p. 53° (Found: C, 68.40; H, 5.25; N, 5.66; S, 12.98.  $\text{C}_{14}\text{H}_{13}\text{NOS}$  requires C, 69.13; H, 5.35; N, 5.76; S, 13.17%).

*Preparation of complexes*—A solution of nickel (II) acetate or propionate in ethanol was treated with Schiff base (I) in 1:2 molar ratio and the mixture refluxed for 2 to 3 hr when a precipitate was formed. Precipitate appeared almost instantly at room temperature if *t*-butylamine or diethylamine or triethylamine was added to the reaction mixture. The yellowish brown complex was filtered, washed first with ethanol and then with ether and recrystallized from tetrahydrofuran or from methylene chloride-*n*-pentane and finally dried under vacuum;

m.p. 258°. It is soluble in methanol, acetone, nitromethane, nitrobenzene but very soluble in methylene chloride (Found: C, 61.53; H, 4.34; N, 4.94; Ni, 10.28; S, 11.25.  $\text{C}_{28}\text{H}_{24}\text{N}_2\text{NiO}_2\text{S}_2$  requires C, 61.91; H 4.42; N, 5.16; Ni, 10.81; S, 11.79%).

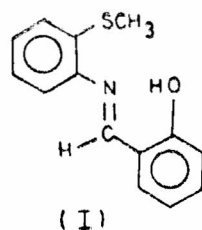
However, if small amount of ammonia was added to the above reaction mixture, the brown colour of the solution changed slowly into orange red with subsequent precipitation of an orange shining complex. It was filtered and washed with ethanol and ether and then purified by sublimation between 150 and 160° at  $10^{-3}$  torr; m.p. 325°. The compound was devoid of sulphur (Found: C, 55.94; H, 4.06; N, 9.17; Ni, 19.37;  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{NiO}_2$  requires C, 56.24; H, 4.01; N, 9.37; Ni, 19.65%). This complex is insoluble in water but slightly soluble in ethanol methanol, acetonitrile, acetone, nitromethane, nitrobenzene, dioxane, methylene chloride and chloroform. It is soluble in dimethylformamide, dimethyl sulphoxide, hexamethylphosphoramide and pyridine.

The complex was repeatedly heated with conc.  $\text{HNO}_3$  and then with conc. HCl and nickel estimated complexometrically by titration against EDTA using murexide as indicator.

*Physical measurements*—Magnetic susceptibility was measured by Gouy method employing  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as standard. Molar conductance was determined on a conductivity bridge type CL 01/01. The infrared spectra were recorded as nujol mull and as KBr pellet on Perkin-Elmer grating spectrophotometer 325. The electronic spectra were measured on a Spectromom 204. Mass spectra were recorded at  $145^\circ/10^{-5}$  torr on a Varian CH 7 in Munich, FRG.

### Results and Discussion

The instantaneous formation of  $\text{Ni}(\text{SMe-N-O})_2$  in the presence of primary, secondary or tertiary amines can be explained as follows: these nucleophiles do not attack the imine carbon nor coordinate with the nickel ions but make the elimination of phenolic proton easy, thereby helping in the formation of a covalent bond between nickel and oxygen. The compound  $\text{Ni}(\text{SMe-N-O})_2$  has a magnetic



moment of 3.23 BM at room temperature which supports the expected octahedral geometry. This is further confirmed by its electronic spectrum in DMF. Four bands have been observed at 940 ( $\epsilon=29$ ), 570 (sh), 450 (6800) and 330 nm (4500). These bands are characteristic of octahedral nickel(II) compounds<sup>4-6</sup>. It is a nonelectrolyte in nitromethane ( $\Lambda_{1000}=7.3 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ , 25°). The infrared spectrum shows a strong band at 1530  $\text{cm}^{-1}$  which has been assigned on literature<sup>2</sup> analogy to phenolic CO band. It further shows the absence of any oxobridging in the complex<sup>7</sup>. The  $\nu\text{N}=\text{C}$  has been observed at 1605  $\text{cm}^{-1}$ .

Ammonia, on the other hand, reacts differently and solution changes colour from brown to orange red with subsequent appearance of shining needles. The pure ligand I shows a medium intensity band at 3405  $\text{cm}^{-1}$  attributed to  $\nu\text{OH}$ . This band vanishes and a strong intensity band at 1553  $\text{cm}^{-1}$  due to phenolic CO appears in the spectrum of the complex. The position of this band indicates the absence of any oxobridging in the complex as the spectra of bi- and trinuclear oxobridged complexes show  $\nu\text{C}-\text{O}$  beyond 1545  $\text{cm}^{-1}$  (ref. 7). Band at 1610  $\text{cm}^{-1}$  in the ligand and the complex is due to  $\nu\text{C}=\text{N}$ . In addition, the complex shows a sharp band at 3305  $\text{cm}^{-1}$ . This absorption is associated with  $\nu\text{NH}$ . New bands appearing in the complex at 500, 467 and 405  $\text{cm}^{-1}$  fall in the metal-oxygen and metal-nitrogen stretching regions.

The isolated complex has a bright orange red colour typical of square planar nickel(II) compounds and this geometry is further supported by its diamagnetic nature. The complex in DMF provides an orange red solution which does not change its colour even on keeping for many weeks, thereby indicating that no appreciable amount of solvated six-coordinated species exist even in a basic solvent like DMF. The electronic spectrum in DMF shows bands at 548 ( $\epsilon=99$ ), 408 (3000), 340 (3500) and 255 nm (4000). In analogy with literature<sup>4,5</sup> bands at 548 and 408 nm are characteristic of square planar nickel(II) complexes. The band at 340

nm is reminiscent of diamagnetic nickel(II) (ref. 6) confirming further the square planar geometry.  $\Lambda_{1000}$  in nitromethane is 1.9  $\text{cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$  at 25°C. This suggests almost nonpolar nature of the complex in the solvent.

The mass spectrum of the complex at 145°/10<sup>-5</sup> torr shows a molecular weight of 298 with <sup>58</sup>Ni. The elemental analysis of the complex further shows that it does not contain any sulphur which indicates that the Schiff base decomposes to provide a complex devoid of sulphur.

The interaction of the nickel ion with the Schiff base(I) causes an electronic shift away from the azomethine carbon —N=C< atom but as has been observed<sup>8</sup> in the complexes of ligand (I) with nickel, copper and cobalt salts, the formation of the chelate ring stabilizes the system and pull on azomethine carbon is sufficiently balanced. This system has been found to be stable in the presence of primary, secondary and tertiary amines but susceptible to nucleophilic attack of ammonia. The interaction of ammonia at imine carbon in the presence of nickel ions causes the splitting of the Schiff base (I) into salicylaldimine and *o*-methylthioaniline. Out of the two, salicylaldimine forms square planar complex bis(salicylaldiminato)nickel (II) (ref. 9).

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