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Reactions of Aminoalkanols with Some Ni(II) Complexes of the Mixed and *Bis* (Schiff Base) Ligands

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Reactions of aminoalkanols have been carried out with mixed and *bis* (Schiff base) complexes of nickel(II). In these reactions both the ligands combine with the aminoalkanol forming tridentate ligand, here -H of the -OH group is not removed. Therefore, both the ligands are retained and they behave as bidentate ligands. From the resulting nickel(II) complexes the tendency to form the Schiff base in the coordinated ligand is found to be similar for salicylideneamine, 2-hydroxy-1-naphthyl methyleneamine and 1-(2-hydroxy phenyl) ethylideneamine. The complexes formed have been characterized by analytical, spectral and magnetic studies.

A good number of examples of complexes formed by potential tridentate Schiff base ligands have been summerized by Goodwine[1,2]. The Schiff base, N-hydroxy ethylsalicylideneamine was found to act as a tridentate ligand with nickel (II)[3] and titanium (IV)[4] ions. This tridentate Schiff base ligand form 1 : 2 complexes with nickel(II), the alcoholic hydroxyl group of the ligand was presumed to coordinate through its oxygen atom, but the $-$OH proton remained undissociated[3,5]. This fact suggests that tridentate Schiff bases have a great tendency to form stable nickel (II) complexes having 1 : 2 composition. An attempt was, therefore made to study the reactions of aminoalkanols with *bis* (bidentate Schiff base) complexes of nickel (II), and to confirm the formation of nickel (II) complexes with tridentate Schiff bases through amine exchange reaction. The reactions were also carried out on mixed imine Schiff base complexes of nickel (II) which are reported earlier[6,7]. The structures of the resulting Schiff base complexes have been discussed, and the mechanism of the formation of the 1 : 2 and 1 : 1 : 1 has been suggested in case of *bis* and mixed complexes respectively.

Experimental

All the six complexes used for the reactions with aminoalkanols were prepared according to the published procedures[6-8].

(i) *Reactions with bis [1-(2-hydroxyphenyl) ethylideneamine] Ni(II)* :

A solution of mono ethanol amine (mea) or isopropanol amine (ipa) (3 ml) in 30 ml of ethanol was added to a suspension of (1g) title imine-complex in 50 ml of ethanol. Well stirred reaction mixture was refluxed for 1 hr. and water was added in order to get the solid compound. It was filtered, washed with water and ethanol and air dried.

(ii) *Reactions with the mixed Schiff base complexes of nickel (II)* :

The reactions were carried out with the following mixed compounds :

(a) [Salicylideneamine, 1-(2-hydroxyphenyl) ethylideneamine] Ni(II).

(b) [2-Hydroxy-1-naphthyl methyleneamine, 1-(2-hydroxypnenyl)-ethylideneamine] Ni (II).

A solution of mea or ipa (3 ml) in 30 ml of ethanol was added to a suspension of the complex (a) or (b) (lg) in 50 ml of ethanol.

The reaction mixture was refluxed for 1hr. The reaction mixture was stirred well and water was added to obtain the solid compound. The solid compound obtained in each case was filtered, washed successively with water and ethanol and air dried.

The complexes have been analysed for metal, N, C and H (in some cases). The results are reported in Table 1. Conductivity measurements were carried out in chloroform using a Toshniwal conductivity bridge type CLOI/OIA. The magnetic susceptibilities of the complexes were determined at room temperature by the Gouy method using Hg[CO $(NCS)_4$] as the calibrant. Infrared Spectra of the complexes were recorded in the form of KBr pellets. The electronic spectra of the complexes in chloroform solution were taken on a Beckman DU-2 spectrophotometer at room temperature using 1 cm quartz cells in the range of 400-1000 nm. The reflectance spectra in LiF medium have been obtained for some of the complexes.

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TABLE 1—ANALYTICAL, ELECTRONIC SPECTRAL BAND AND MAGNETIC MOMENT OF *bis* AND MIXED AMINOALKANOL SCHIFF BASE COMPLEXES OF Ni(II)

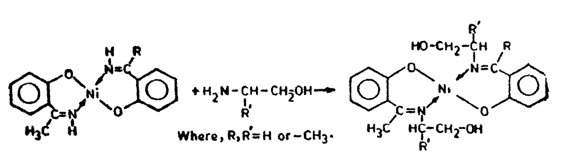
No.	Complex	Found (Calculated) %								λ_{max} (nm)	$\mu_{eff.}$ (B.M.)
		Ni		C		H		N			
1.	*Bis* [N-Hydroxyethyl-1-(2-hydroxy phenyl) ethylideneaminato] Ni(II).	14.15	14.25	-	-	-	-	6.75	6.85	620	3.12
2.	N-Hydroxyethyl [(salicylidene-aminato), (2-hydroxyphenyl)-ethylideneaminato] Ni(II).	14.72	15.14	-	-	-	-	6.98	7.00	650	3.08
3.	N-Hydroxyethyl [(2-hydroxy-1-naphthyl-methyleneaminato), 1-(2-hydroxyphenyl) ethylideneaminato] N(II).	13.02	12.90	61.23	61.02	5.32	5.22	6.21	6.00	750 820	3.03
4.	*Bis* [N-Hydroxy-iso-propyl-1-(2-hydroxyphenyl) ethylideneaminato) Ni(II).	13.26	13.50	-	-	-	-	6.32	6.50	630	3.04
5.	N-Hydroxy-iso-propyl-[salicylideneaminato, 1-(2-hydroxy phenyl) ethylideneaminato] Ni(II).	13.63	13.48	58.53	59.02	6.50	6.15	6.50	6.25	650	3.10
6.	N-Hydroxy-iso-propyl-[2-hydroxy-1-naphthylmethyleneaminato, 1-(2-hydroxyphenyl) ethylideneaminato] Ni(II).	12.26	12.16	-	-	-	-	5.85	5.63	650	3 14

The molar conductance of all the nickel (II) complexes in chloroform show them to be non-electrolytes. The magnetic and spectral data have also been presented in Table 1.

Results and Discussion

The reactions of mea with *bis* and mixed imine complexes gave the amine-exchange products (1), (2) and (3), respectively. Similar reactions take place with ipa and the products obtained are (4), (5) and (6).

In nickel (II) complexes, however, the solid obtained corresponds to the composition [Ni—L_2] or [Ni—L—L^1], where L=N-hydroxyethyl or isopropyl-1-(2-hydroxyphenyl) ethylideneamine and L'=N-hydroxyethyl or isopropyl-salicylideneamine or 2-hydroxy -1-naphthyl methyleneamine. In *bis* and mixed nickel (II) complexes both the ligand molecules react with mea or ipa to form tridentate ligands. The reaction schemes proposed are as follows :



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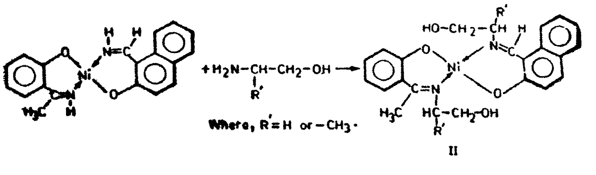

II

Thus it is observed that the Schiff base of aminoalkanols with aldehyde and ketone acts as bidentate ligand and the -OH group of the Schiff base remains uncoordinated. This is because the Schiff base with a double bond cannot occupy two equitorial and two axial positions[9,10]. If the -OH groups would have coordinated, losing the proton, the complex would have been ionic. But it is observed that compounds are insoluble in water and soluble in organic solvents. The conductivities of their solutions show them to be non-electrolytes. Simliar structures of *bis* tridentate Schiff base complexes of nickel (II) with non-coordinated -OH groups have been reported earlier[3,5].

The structure can be explained by the analogy with *bis* (N-hydroxy ethyl-salicylideneaminato) Ni(II) complex, prepared by Yamada and coworkers[3] and Poddar *et al*[5] by direct action of the metal salt with N-hydroxy ethyl salicylideneamine. They have found an octahedral configuration of the Ni(II) complexes on the basis of electronic absorption spectra and both in the solid state and in solution and magnetic moment value ($\mu_{eff.}$=2 95 B.M.).

Present *bis* and mixed nickel(II) Schiff base complexes are mastared and green in colour. These complexes show magnetic moment values between 3.1 to 3.28 B.M. This suggests that the complexes have an octahedral configuration. Since, the two ligands are bidentate there should be a tetra coordinated square planar structure. However, the octahedral geometry may be due to partial coordination between metal and oxygen atom of alcoholic -OH group, or it may be due to the polymerization. This situation occurs when the distortion from the square arrangement of the donor atoms with respect to metal atom arises from nonplanarity of the ligand molecules. This nonplanarity of the ligand molecule probably arises from steric interaction[1,11]. The solubility of the compounds in water and other organic solvents is very low indicating that the compounds may be polymeric.

The electronic absorption spectra, both in the solid state and in solutions of Ni(II) *bis* and mixed Schiff base complexes show a broad band between 600 to 650 nm. There is an increase in optical density after 800 nm. This shows that the compounds have an octahedral structure in the solid state.

The ir spectra of 1 : 2 and 1 : 1 : 1 nickel(II) Schiff base complexes shows a broad band in the range 3600-3300 cm^{-1} corresponding to O-H stretching frequency indicating the undissociated hydrogen of OH group. *Bis* and mixed-imine Schiff base complexes of nickel (II) show a band at 3300 cm^{-1} corresponding to -N-H stretching frequency. The disappearance of the 3300 cm^{-1} band after amine exchange reaction can be attributed to the replacement of the N-H hydrogen in nickel *bis* and mixed imine Schiff complexes by an alkanol amine group. The two weak bands observed at 2920 and 2860 cm^{-1} correspond to C—H stretching frequency due to $-CH_3$ group and aldehydic C—H, respectively. In nickel(II) complexes (Structure-I) the C=N stretching band appears at 1650 cm^{-1} while in nickel(II) complexes (Structure II) it appears at 1620 cm^{-1}. All these complexes show a band at 1450 cm^{-1} due to C—H bending. In all the complexes there is a band near 1300 cm^{-1} corresponds to C—O stretching. The band observed at 820 cm^{-1} in all the complexes is due to the O—H bending.

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