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Studies on Some Mixed Schiff's Base Complexes. V.

Rakesh Kumar KOHLI and P. K. BHATTACHARYA
Department of Chemistry, M. S. University, Baroda, 390002, India

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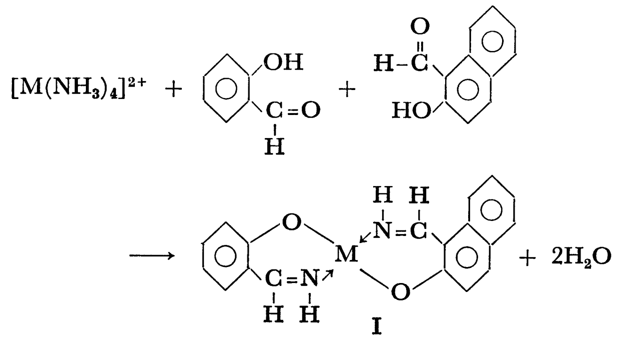
As regards the preparation and characterization of some new mixed complexes of the type MLL′ where M= Cu(II), Ni(II); L=salicylaldimine and L′=(*o*-hydroxybenzyl)(ethylideneamine) or *o*-hydroxydiphenylenethyleneamine or their derivatives, we have carried out the preparation of a few similar types of complexes where L′=2-hydroxy-1-naphthylmethyleneamine. The mixed imine Schiff's base complexes have been prepared by treating the metal ammine complex with an equivalent amount of salicylaldehyde and 2-hydroxy-1-naphthaldehyde. Amine exchange reactions were also been carried out by treatment of mixed imine Schiff's base complex with ethylenediamine(en) or propylenediamine(pn). The complexes of new Schiff's base were formed where diamine have salicylaldehyde condensed at one end and 2-hydroxy-1-naphthaldehyde at the other end. The complexes have been characterized by elemental analysis, TLC analysis, conductance measurements, magnetic measurements, and spectral analysis.

The preparation of the compound of the type ML$_2$ where L=salicylaldehyde and their reactions with ammonia leading to the formation of the Schiff's base complexes have been reported.[1–5] Reactions of bis-salicylaldehyde complexes with ethylenediamine[6] and aniline[7] have also been reported. Transamination and transamidation reactions have been performed on the Schiff's base complexes.[3–8] The study of reactions of amines with bis 2-hydroxy-acetophenone or bis-2-hydroxy benzophenone complexes of Cu(II) and Ni(II) have also been prepared.[9–10] The possibility of the formation of Mixed-Schiff's base complexes has been indicated by Chakravorty and Holm,[11] on the basis of NMR studies. However, such complexes were not been isolated in solid state. Schiff's base formation reaction of mixed ligand complexes of the type MLL′, where L= salicylaldineamine and 1(*o*-hydroxyphenyl)ethylideneamine[12] or *o*-hydroxydiphenylmethyleneamine and their derivatives have been reported. The present paper deals with the preparation and reactions of a series of mixed ligand complexes of general formula MLL′ where M=Cu(II) or Ni(II), L=salicylideneamine, L′=2-hydroxy-1-naphthyleneamine.

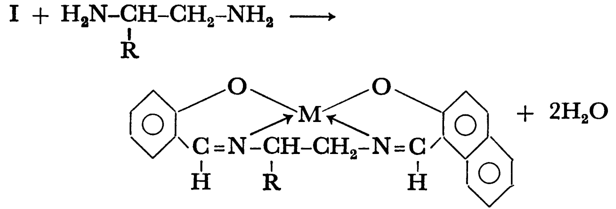
The mixed Schiff's base complex was prepared by treating the metal ammine complex with one equivalent of salicylaldehyde and another of 2-hydroxy-1-naphthaldehyde.



I

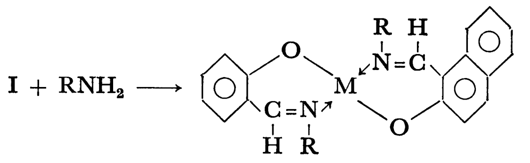
M=Cu(II) or Ni(II)

Complex(I) was treated with ethylenediamine(en) or propylenediamine(pn), leading to the formation of new Schiff's base complexes with the diamine condensed to one end with salicylaldehyde and at the other end with 2-hydroxy-1-naphthaldehyde.



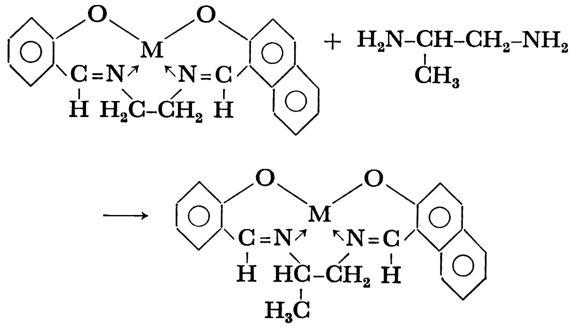
R=-H or -CH$_3$
M=Cu(II) or Ni(II)

Similar reactions were also carried out with methyl and ethyl amine and the following type of mixed complexes were obtained.



R=-CH$_3$ or -C$_2$H$_5$
M=Cu(II) or Ni(II)

When the en Schiff's base is treated with pn, en is slowly replaced by pn, as shown in the following equn.



M=Cu(II) or Ni(II)

Experimental

Material. Ligand of AR quality and nickel nitrate and cupric chloride of Analar grade were used.

Preparation of Amine Schiff's Base Complex. (Salicylaldeneaminato)(2-hydroxy-1-naphthylmethyleneaminato)Cu(II) or Ni(II): To the metal chloride solution was added an excess of ammonia till the hydroxide formed dissolved resulting in the formation of metal ammine complex. To this was added one equi-

TABLE 1. ANALYTICAL DATA

	Name of compound	Metal %		C, H %		Nitrogen %		λ_{max} nm	ε	μ Effective in B.M.
		Calcd	Found	Calcd	Found	Calcd	Found			
1a″	(Salicylideneaminato)(2-hydroxy-1-naphthylmethyleneaminato)Ni(II)	16.83	16.28	C=61.94 H= 4.01	C=62.37 H= 4.40	8.02	7.56	550	303	Diamagnetic
2a′	{*N*,*N*′-Ethylene(salicylaldeneaminato-2-hydroxy-1-naphthylmethyleneaminato)}Ni(II)	15.66	16.10			7.47	7.30	530	418	Partially paramagnetic
3a′	{*N*,*N*′-Propylene(salicylaldeneaminato-2-hydroxy-1-naphthylmethyleneaminato)}Ni(II)	15.10	14.90			7.20	6.50	550	343	0.956 Partially paramagnetic
4a′	(*N*-Methylsalicylaldeneaminato)(*N*-methyl-2-hydroxy-1-naphthylmethyleneaminato)Ni(II)	15.58	15.44			7.43	6.60	560 590	213 213	Partially paramagnetic
5a′	(*N*-Ethylsalicylaldeneaminato)(*N*-ethyl-2-hydroxyl-1-naphthylmethyleneaminato)Ni(II)	14.50	14.91	C=65.23 H= 5.43	C=66.40 H= 5.46	6.91	6.48	520 570 596	318 275 275	Partially paramagnetic
6a″	(Salicylideneaminato)(2-hydroxy-1-naphthylmethyleneaminato)Cu(II)	17.97	17.78			7.91	7.29	530 550	123 123	1.83
7a′	{*N*,*N*′-Ethylene(salicylaldeneaminato-2-hydroxy-1-naphthylmethyleneaminato)}Cu(II)	16.74	16.36	C=63.23 H= 4.74	C=63.45 H= 4.28	7.37	6.90	560	410	1.83
8a′	{*N*,*N*′-Propylene(salicylaldeneaminato-2-hydroxy-1-naphthylmethyleneaminato)}Cu(II)	16.10	15.80			7.00	6.70	490 550	319 478	1.83
9a′	(*N*-Methylsalicylaldeneaminato)(*N*-methyl-2-hydroxy-1-naphthylmethyleneaminato)Cu(II)	17.65	17.52			7.33	6.33	530 570	252 213	1.86
10a′	(*N*-Ethylsalicylaldeneaminato)(*N*-ethyl-2-hydroxy-1-naphthylmethyleneaminato)Cu(II)	16.51	15.99			6.83	6.12	490	533	1.98
11a‴	{*N*,*N*′-Propylene(salicylaldeneaminato-2-hydroxy-1-naphthylmethyleneaminato)}Cu(II)	16.10	16.32			7.00	6.72	490	320	1.89

a′=Ammine exchange; a″=compound found from metal amine; a‴=en to pn exchange.

valent each of alcoholic solution of salicylaldehyde and 2-OH-1-naphthaldehyde. The mixture was refluxed (75 min) and stirred. The compound obtained was filtered, washed with water and finally with 50% alcohol. The compound was recrystallized from chloroform and analyzed.

Preparation of Methyl and Ethyl Amino Schiff's Base Complexes. Imine Schiff's base complex(I) was treated with methyl or ethylamine solution (0.5 M) and refluxed gently on a water-bath for 3—4 h. Green crystalline solids were obtained. They were washed with water and 50% alcohol, dried and recrystallized from chloroform and analyzed. Ethylamine compound could be obtained in about 3—4 h, whereas refluxing had to be carried out for about 6—7 h in the case of methyl amine reaction.

Preparation of Diamine Schiff's Base Complexes in Case of Cu(II) or Ni(II). {N,N-*Ethylene or Propylene(salicylideneaminato-2-hydroxy-1-naphthylmethyleneaminato)*}*Cu(II) or Ni(II)*: The complexes were obtained by substitution reactions. The preformed mixed imine Schiff's base complexes of Cu(II) or Ni(II) (2 g) were refluxed (3 h) with en (2 ml) or pn (2 ml) in ethanol (25 ml). The reaction mixture was stirred thoroughly to obtain the compounds. It was filtered, washed, dried and recrystallized from chloroform and analyzed.

General Properties of Complexes. All the complexes were found to be crystalline, stable in atmosphere and insoluble in water. All the compounds are soluble in organic solvents.

In order to characterize and determine the structures of complexes the following studies were undertaken.

Analysis. Cu was estimated by complexometric titration against standard EDTA disodium salt solution, using Fast Sulphon Black F as an indicator. Ni was estimated gravimetrically as dimethylglyoximate. The results of metal, carbon, hydrogen, and nitrogen analyses are presented in the table.

TLC Anslysis. TLC analyses of all the complexes were carried out on a silica gel G(Sichen) using a mixture of chloroform–ether (6:4) as a solvent. The solvent was selected after several trials. A mixture of 1:1 bis(salicylaldeneaminato)M-(II) and bis(2-hydroxy-1-naphthylmethyleneaminato)Ni(II) complexes was prepared. On subjecting it to TLC analysis, the mixture was found to give two spots whereas the mixed ligand complex is pure and a single compound rather than the mixture of bis complexes of the two ligands.

Magnetic Measurements. Magnetic measurements were carried out at room temperature (28 °C) using Guoy balance.

Conductance. Conductivity measurements were carried out in chloroform using Toshniwal Conductivity Bridge Type C LO/O1A.

Spectrophotometric Measurements. The visible spectra of all the complexes were a studied in chloroform solution, on a DU2 Beckman Spectrophotometer at room temperature (30 °C) using 1 cm quartz cell in the range 300—1000 nm.

IR Measurements. IR spectra was recorded in Nujol in the range 4000—625 cm^{-1} on a Perkin-Elmer Model 427.

None of the complexes had adequate solubility in the solvents for NMR studies.

Results and Discussion

The molar conductance of all the complexes in chloroform show them to be non electrolytes.

Structure of Cu(II) Complexes. All the Cu(II) complexes are paramagnetic showing the presence of one unpaired electron. The values of μ expected for one unpaired electron is 1.73 B.M., the slightly higher value obtained for the present complexes can be attributed to spin-orbit coupling.[13] The visible spectra show a broad band at ≈590 or ≈520 nm; and agree with the square planar geometry. The Cu(II) imine Schiff's base complex shows a band around ≈550 nm ($\varepsilon=123$) and the en and pn Schiff's base complexes exhibit at ≈560 ($\varepsilon=410$) and at ≈550 ($\varepsilon=478$), respectively. The spectrum of complex {*N,N′*-ethylene(salicylideneaminato-2-hydroxy-1-naphthylmethyleneaminato)}Cu(II) (No. 7) was compared with that of (bis-ethylene salicylideneaminato)Cu(II) and (bis-ethylene 2-hydroxy-1-naphthylmethylenediaminato)Cu(II) complexes. The complex (No. 7) shows one peak falling between the two bis compounds. This indicates the mixed nature of these complexes.

Structure of Ni(II) Complexes. All the complexes were recrystallized until constant magnetic susceptibility was obtained. They exhibit some paramagnetism. Anomalous magnetic behavior of Ni(II) Schiff's base complexes were studied and interpreted in detail.[14,15] The visible spectra of the imine Schiff's base complex in chloroform solution shows a shoulder at ≈550 nm with ($\varepsilon=274$). A similar spectrum was obtained in the case of en and pn Schiff's base complexes, the shoulder shifting to ≈530 nm and ≈550 nm with ($\varepsilon=418$) and ($\varepsilon=343$), respectively. The absence of bands beyond 600 nm confirms square geometry for the complexes.

In the IR spectra of all the compounds bands in the range ≈3400 cm^{-1} are absent indicating that O–H hydrogen of the aldehyde or the Schiff's base get dissociated after complexation. In the spectra of Cu(II) and Ni(II) complexes(I) a band at 1600 cm^{-1} corresponding to C=N stretch appears. There is a strong band at ≈3200 cm^{-1} corresponding to N=H stretching frequency. This is absent in the en and pn diamine Schiff's base and also in methyl and ethyl amines compounds showing the absence of free =NH group.

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