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Cu(II) & Ni(II) Complexes with Schiff Bases Derived from 2-Hydroxypropiophenone

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A series of mixed ligand complexes of the types ML_2 and MLL′ [M = Cu(II) or Ni(II); L = Schiff bases derived from 2-hydroxypropiophenone and L′ = Schiff bases derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde] have been prepared and characterized on the basis of analytical, magnetic moment and electronic and IR spectral data. Complexes have been assigned square-planar structures. Amine-exchange reactions have been carried out in some cases.

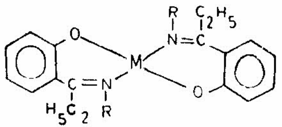
IN continuation of our work on the reactions of coordinated Schiff bases[1-5], we report here the preparation and reactions of binary and ternary complexes, containing Schiff bases derived from 2-hydroxypropiophenone.

The binary and mixed Schiff base complexes of the type ML_2 and MLL′ [M = Cu(II) or Ni(II), L = Schiff bases obtained from 2-hydroxypropiophenone and L′ = Schiff bases derived from salicylaldehyde or 2-hydroxy-1-naphthaldehyde] were prepared as described earlier[1-5]. The amine-exchange reactions with alkyl amines (mono and di) were also carried out. Reaction with 2-hydroxyalkyl amines were also carried out in the case of Cu(II) complexes by adding monoethanol amine or isopropanol amine (1 ml) to Cu(II) Schiff base complex (1 g) in 25 ml EtOH and refluxing the mixture for 2 hr on a water-bath with occasional stirring. The resulting blue solid was filtered, washed with ethanol, dried and finally analysed. All the complexes gave satisfactory metal and nitrogen analysis. The parent complexes were analysed for carbon content also.

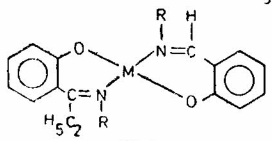
The parent Schiff base complex of the type ML_2, bis[N-1-(2′-hydroxyphenyl)propylideneimino] M(II), [(I), R=H], was prepared by the reaction of 2-hydroxypropiophenone with the metal ammine compound.

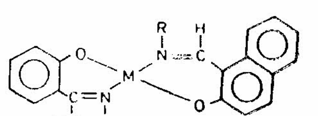
The parent mixed Schiff base complexes MLL′ have the structure (IIA) and (IIB) (R=H).

In the case of bis[N-1-(2-hydroxyphenyl)propylideneimine]M(II), the exchange of ammonia by alkyl amines was incomplete as shown by analysis, only exception being the complex (I) with R = CH_3 and M = Ni(II) (complex No. 9 in Table 1). This may be because the ethyl group in (I) causes the steric hindrance to the entry of alkyl amines.


(I)

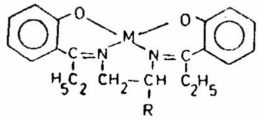
M = Cu(II) OR Ni(II)
R = H OR CH_3

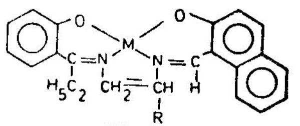

(IIA)

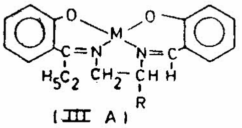

(IIB)

M = Cu(II) OR Ni(II)
R = H, CH_3 OR C_2H_5

Parent complexes (I), (IIA) and (IIB) (all with R = H), on reaction with concentrated ethylene diamine (en) or propylene diamine (pn), undergo amine-exchange reaction giving corresponding *cis* diamine Schiff base complexes (III), (IIIA) and (IIIB) respectively.

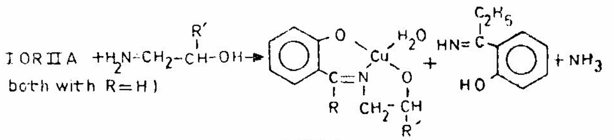

(III)


(III B)


(III A)

M = Cu(II) OR Ni(II)
R = H OR CH_3

Finally, when Cu(II) complexes of the type (I), (IIA) or (IIB) (all with R = H) were treated with monoethanol amine or isopropanol amine, interesting complexes of the type (IV) were obtained.



(IV)

R=H(FOR II A) OR C_2H_5(FOR I)
R′= H OR CH_3

Similar observation is also made in the case of mixed Schiff base complex of 2-hydroxypropiophenone and 2-hydroxy-1-naphthaldehyde (IIB, R = H), one of the ligands forms a tridentate Schiff base complex (IV) and another ligand is knocked out. It is seen that in the case of mixed Schiff base complexes, hydroxyalkylamine brings about amine-exchange on salicylaldimine or naphthaldimine forming a tridentate ligand and 2-hydroxypropiophenonimine is removed. Thus, a monomeric complex of Cu(II) involving the tridentate Schiff base and a water molecule at the fourth coordination position is formed. 2-Hydroxy-1-naphthaldehyde

TABLE 1 — ANALYTICAL AND PHYSICOCHEMICAL DATA OF BINARY AND TERNARY SCHIFF BASE COMPLEXES

No.	Complex*	Found (calc.), %		λmax (nm)	μeff (BM)
		M	N		
BIS SERIES DERIVED FROM 2-HYDROXYPROPIOPHENONE					
1	$Cu(C_9H_{10}ON)_2$† [I, R=H]	17·59 (17·67)	7·78 (7·78)	525	1·82
2	$Cu(C_{10}H_{11}ON)_2$ [III, R=H]	16·32 (16·48)	7·22 (7·26)	530	1·89
3	$Cu(C_{21}H_{24}O_2N_2)$ [III, R=CH_3]	15·66 (15·90)	6·69 (7·01)	530	1·92
4	$Cu(C_9H_{11}O_3N)$ [IV, R=C_2H_5 R=H]	26·18 (25·99)	5·38 (5·14)	625	1·92
5	$Cu(C_{12}H_{17}O_3N)$ [IV, R=C_2H_5 R=CH_3]	22·56 (22·17)	4·02 (4·88)	630	1·94
6	$Ni(C_9H_{10}ON)_2$† [I, R=H]	16·48 (16·54)	N=7·80 (N=7·89)	530	Diamagnetic
7	$Ni(C_{10}H_{11}ON)_2$ [III, R=H]	15·70 (15·42)	7·85 (7·35)	535	1·01
8	$Ni(C_{21}H_{24}O_2N_2)$ [III, R=CH_3]	14·44 (14·87)	6·67 (7·09)	540	Diamagnetic
9	$Ni(C_{10}H_{12}ON)_2$ [I, R=CH_3]	15·61 (15·34)	7·77 (7·32)	520	Partially paramagnetic
MIXED COMPLEX SERIES DERIVED FROM SALICYLALDEHYDE AND 2-HYDROXYPROPIOPHENONE					
10	$Cu(C_8H_8ON)_2$† [IIA, R=H]	18·68 (19·16)	N=8·44 (N=8·44)	525	1·83
11	$Cu(C_9H_9ON)_2$ [IIIA, R=H]	18·02 (17·77)	7·82 (7·83)	535	1·96
12	$Cu(C_{19}H_{20}O_2N_2)$ [IIIA, R=CH_3]	17·43 (17·10)	7·13 (7·54)	540	1·80
13	$Cu(C_9H_{10}ON)_2$ [IIA, R=CH_3]	17·50 (17·67)	7·87 (7·79)	520	1·95
14	$Cu(C_{10}H_{12}ON)_2$ [IIA, R=C_2H_5]	16·84 (16·39)	7·70 (7·23)	540	2·02
15	$Cu(C_9H_{11}O_3N)$ [IV, R=H]	25·80 (25·98)	5·87 (5·73)	630	1·65
16	$Cu(C_{10}H_{13}O_3N)$ [IV, R=CH_3]	24·18 (24·57)	5·91 (6·42)	630	1·60
17	$Ni(C_8H_8ON)_2$† [IIA, R=H]	18·09 (17·97)	N=8·56 (N=8·57)	530	Diamagnetic
18	$Ni(C_9H_9ON)_2$ [IIIA, R=H]	17·05 (16·64)	7·52 (7·94)	530	do
19	$Ni(C_{19}H_{20}O_2N_2)$ [IIIA, R=CH_3]	16·30 (16·01)	8·06 (7·64)	535	do
20	$Ni(C_9H_{10}ON)_2$ [IIA, R=CH_3]	16·13 (16·55)	8·13 (7·89)	530	1·12
21	$Ni(C_{10}H_{12}ON)_2$ [IIA, R=C_2H_5]	15·59 (15·13)	6·86 (7·32)	540	Partially paramagnetic
MIXED COMPLEX SERIES DERIVED FROM 2-HYDROXY-1-NAPHTHALDEHYDE AND 2-HYDROXYPROPIOPHENONE					
22	$Cu(C_{10}H_9ON)_2$† [IIB, R=H]	16·21 (16·65)	N=6·55 (N=7·33)	530	1·87
23	$Cu(C_{11}H_{10}ON)_2$ [IIIB, R=H]	15·29 (15·59)	6·84 (6·87)	535	1·89
24	$Cu(C_{23}H_{22}O_2N_2)$ [IIIB, R=CH_3]	15·11 (15·07)	6·66 (6·64)	540	1·91
25	$Cu(C_{11}H_{11}ON)_2$ [IIB, R=CH_3]	16·00 (15·51)	7·21 (6·83)	520	1·75
26	$Cu(C_{23}H_{24}O_2N_2)$ [IIA, R=C_2H_5]	14·97 (14·52)	6·71 (6·40)	530	2·00
27	$Cu(C_{13}H_{13}O_3N)$ [IV, R=H]	21·36 (21·57)	5·30 (4·75)	620	1·72
28	$Cu(C_{14}H_{15}O_3N)$ [IV, R=CH_3]	21·06 (20·59)	4·70 (4·54)	625	1·66
29	$Ni(C_{10}H_9ON)_2$† [IIB, R=H]	15·72 (15·58)	N=7·29 (N=7·43)	525	Diamagnetic
30	$Ni(C_{11}H_{10}ON)_2$ [IIIB, R=H]	14·62 (14·57)	6·96 (6·95)	530	Partially paramagnetic
31	$Ni(C_{23}H_{22}O_2N_2)$ [IIIB, R=CH_3]	14·46 (14·08)	7·14 (6·72)	525	Partially paramagnetic
32	$Ni(C_{11}H_{11}ON)_2$ [IIB, R=CH_3]	14·95 (14·50)	6·58 (6·91)	530	0·78
33	$Ni(C_{23}H_{24}O_2N_2)$ [IIA, R=C_2H_5]	14·00 (13·56)	6·96 (6·47)	530	0·82

*Entries inside the brackets refer to structural formulae.
†Satisfactory carbon and hydrogen analyses were also obtained.

has been shown earlier to have greater Schiff base forming tendency than salicylaldehyde[6]. Thus the order of Schiff base forming tendency is: 2-hydroxy-1-naphthaldehyde > salicylaldehyde > 2-hydroxypropiophenone.

This is in keeping with expectations based on inductive effect. This study also supports the mixed ligand nature of the complexes (II) and (III). If the compound would have been a mixture instead of a mixed ligand complex, a mixture of two tridentate complexes should have been obtained.

The magnetic moment, electronic and IR spectra of bidentate Schiff base complexes are comparable with those of the complexes reported earlier and can be interpreted accordingly[1-5].

The tridentate Schiff base complexes of Cu(II) (Nos. 4 and 5, Table 1) exhibit magnetic moments (~1·90 BM) corresponding to the presence of one unpaired electron and square-planar structure. Slightly reduced moments (~1·65 BM) of complexes (Nos. 15, 16, 27 and 28; Table 1), obtained from mixed ligand Schiff base complexes (Nos. 10 and 22, Table 1), suggest the possibility of partial dimerization leading to Cu-Cu interaction and reduction in magnetic moment values. The electronic spectra of Cu(II) complexes in benzene solution show a broad band around 630 nm which supports a planar structure in solution. The IR spectra of Cu(II) complexes exhibit a broad band at 3400 cm^{-1} showing the presence of water. A band at 885 cm^{-1} corresponding to OH out-of-plane deformation mode is also present indicating the presence of a coordinated water molecule.

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Studies in Tautomeric Equilibrium Schemes: 3-Amino-5-sulpho- & 5-Amino-3-sulpho-salicylic Acids

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The pK values of dissociation of the various groups in 3-amino-5-sulpho- and 5-amino-3-sulphosalicylic acids have been determined at 30° and $\mu = 0{\cdot}1M$ ($NaClO_4$) in aqueous medium by Calvin-Bjerrum potentiometric titration technique. The pK_1, pK_2 and pK_3 were ascribed to the dissociation of the —COOH, —NH_3^+ and —OH groups respectively. A tautomeric equilibrium scheme is drawn for the dissociation of the various species and the equilibrium constants for these steps have been calculated with the help of the Hammett's relationship. The dissociation of the —COOH group prior to the NH_3^+ is confirmed. Attempt has been made to understand the possible hydrogen bonding in the various species formed.

AMINOSULPHOSALICYLIC acids have four dissociable groups. It is very well known[1] that the —SO_3H group dissociates at $pH < 1{\cdot}0$. Above this pH, aminosulphosalicylic acid is, therefore, expected to exhibit a zwitterion type structure. Under these circumstances it would be interesting to examine the priority of the dissociating groups. In amino acids, the dissociation of the —COOH group prior to that of NH_3^+ has been confirmed by Laidler and Bunting[2]. We have carried out such a study to examine the equilibrium constants of various equilibria, including the tautomeric one, through which the system passes at various pH values. This study is an extension of our earlier work on the pK values of substituted salicylic acids in aqueous medium[3].

The ligands 3-amino-5-sulphosalicylic acid (3-A-5-SSA) and 5-amino 3-sulphosalicylic acid (5-A-3-SSA) were of AR grade (Schuchardt Munchen).

The details regarding the instrumentation and the procedure of the Calvin-Bjerrum potentiometric titrations are given in an earlier communication[4].

The mathematical expressions adopted to calculate pK values are given earlier[4]. The accuracy of the pK values was 0·03 to 0·05.

The pK of the —SO_3H group being nearly 1·0, an increase in [H^+] on the addition of the ligand to free perchloric acid ($\sim 10^{-3}M$) was expected. Actually the initial pH for the acid and acid + ligand solutions, without any addition of alkali, were identical. This means that H^+ ions liberated from the —SO_3H group have combined with the basic —NH_2 group to form a zwitterion.

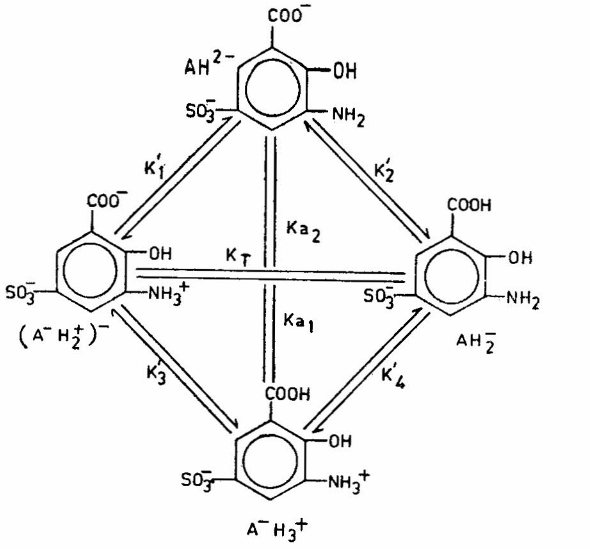

Fig. 1 — The tautomeric equilibrium scheme for 3-A-5-SSA

The pK values 2·58, 4·38 and 15·75 of 3-A-5-SSA and 2·26, 4·23 and 16·17 of 5-A-3-SSA are due to the dissociations of the —COOH, —NH_3^+ and —OH groups. The values of 15·75 and 16·17 are certainly due to —OH group. The remaining two values, therefore, need to be fixed. Whether the pK_1 is due to the —COOH or —NH^+ was initially decided by comparing the experimental values with the theoretically expected ones. The pK_1 expected for 3-A-5-SSA on the basis of the Hammett's relation is 2·45 (pK_{COOH} for 5-SSA is 2·49 and $\sigma_{m\text{-}NH_2}$ is $-0{\cdot}04$)[5]. The observed value 2·58 being in good agreement with the expected one, the dissociation of —COOH prior to —NH_2 group was anticipated. This speculation was further confirmed by studying the tautomeric equilibrium of the various possible species. A total of seven equilibrium constants can be defined in this system, as shown in Fig. 1. The constants are related by the mathematical expression:

$$K_T = \frac{K_1'}{K_2'} = \frac{K_4'}{K_3'}$$

and

$$K_{a1} \times K_{a2} = K_2'.K_4' = K_1.K_3'$$

The values of K_1', K_2', K_3' and K_4 can be predicted from the knowledge of Hammett's substituent constants σ and the reaction constants ρ. Literature survey revealed that the σ values for the various substituting groups of benzoic acid are known while the reliable values of σ for aniline dissociation are not available. The constants K_2' and K_1' were, therefore, calculated mathematically and were further utilized to get K_1' and K_4' by the expressions given above.

The calculated pK_3' is 1·8 ($\sigma_{o-HO} = 1{\cdot}22$, $\sigma_{m-NH_3^+} = 1{\cdot}13$, $\sigma_{m=SO_3} = 0{\cdot}05$ and ρ for benzoic acid is $1{\cdot}0$)[5]. The magnitude of pK_2' was 3·0. The values of K_T thus obtained are presented in Table 1.