Reactions of Aminoalkanols with Some Copper(II) Complexes of the Mixed and Non-mixed Bis(Schiff base) Ligands

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(Received March 22, 1976; in revised form January 18, 1977)

Reactions of aminoalkanols have been carried out with mixed and non-mixed bis(Schiff base) complexes of copper(II). In these reactions one of the ligands combines with the aminoalcohol forming a tridentate ligand, wheras another ligand is removed. From the resulting complexes the tendency to form the Schiff base is found to be in the order 2-hydroxybenzophenone≈2-hydroxy-1-naphthaldehyde>salicylaldehyde>2-hydroxyacetophenone. The complexes formed have been characterized by analytical, spectral, and magnetic studies.

Tridentate Schiff bases of amino acids with salicylaldehyde, and other similar tridentate Schiff base ligands form 1 : 1 complexes with copper(II),[1-6] the fourth site being occupied by a water molecule[2,3]. Aminoalkanols are also known to form tridentate Schiff base with aromatic aldehydes or ketones.[7] It has been shown by X-ray studies that the tridentate ligand occupies three positions around the metal ion.[2] Chakravorty and co-workers[8] have recently observed that mixed-ligand complexes of copper(II) containing salicylaldehyde, and the Schiff base of *N,N*-diethylethylenediamine with salicylaldehyde react with acids to lose the salicylaldehyde part, and that a complex of tridentate Schiff base is formed with water at the forth position. These facts suggest that the tridentate Schiff bases have a great tendency to form stable copper(II) complexes. An attempt was, therefore, made to study the reactions of aminoalkanols with bis(bidentate Schiff base)complexes of copper(II), and to confirm the formation of copper(II) complexes with tridentate Schiff bases through an amine-exchange reaction.[9] The reactions were also carried out on the mixed Schiff base complexes of copper(II) reported by us earlier[10-12] to compare the relative reactivity among the tridentate ligands. The structures of the resulting tridentate Schiff base complexes have been discussed, and the machanism of the formation of the 1 : 1 complex has been suggested.

Experimental

All the complexes used for the reactions with aminoalkanols were prepared according to the published procedures.[10-16] Aminoalkanols used were 2-aminoethanol(mea) and 1-amino-2-propanol(ipa) of A. R. quality.

Reactions with Bis(imine) Complexes of Copper(II). The following bis-complexes have been used:

(a) Bis(salicylideneaminato)copper(II),
(b) bis(2-hydroxy-1-naphthylmethyleneaminato)copper(II),
(c) bis[1-(*o*-hydroxyphenyl)ethyleneaminato]copper(II),
(d) bis[α-(*o*-hydroxyphenyl)benzylideneaminato]copper(II).

The complexes (a), (b), (c), or (d) (1 g) was taken in suspension in ethanol (30 ml), and to this was added mea (2 ml) or ipa (2 ml), and the mixture was refluxed for 3 h. The reaction mixture was stirred well, and water was added when a solid separated out. It was filtered, washed and dried.

Reactions with the Mixed Schiff Base Complexes of Copper(II). The reactions were carried out with the following mixed complexes:

(a′) (Salicylideneaminato)(2-hydroxy-1-naphthylmethyleneaminato)copper(II),
(b′) (salicylideneaminato)[1-(*o*-hydroxyphenyl)ethylideneaminato]copper(II),
(c′) (salicylideneaminato)[α-(*o*-hydroxyphenyl)benzylideneaminato]copper(II),
(d′) (2-hydroxy-1-naphthylmethyleneaminato)[α-(*o*-hydroxyphenyl)benzylideneaminato]copper(II).

An ethanolic (30 ml) suspension of the complex (a′), (b′), (c′), or (d′) (1 g) was refluxed for 3 h with 2-aminoethanol (2 ml) or 1-amino-2-propanol (2 ml). The reaction mixture was stirred well and water was added to obtain the compound. The complex was filtered, washed, and dried.

The complexes have been analysed for metal, N, C, and H (in some cases). The results have been tabulated 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 on a Perkin Elmer 427 infrared grating spectrophotometer in the form of KBr pellets. The electronic spectra of the complexes in chloroform solutions 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 the LiF medium have been obtained for some of the complexes.

The molar conductances of all the copper(II) complexes in chloroform show them to be non-electrolytes. The magnetic and spectral data have been presented in Table 1. The important IR bands of some of the complexes are listed in Table 2.

Results and Discussion

The reactions of 2-aminoethanol with the complexes (a), (b), (c), and (d) gave the products (A), (B), (C), and (D), respectively. Similar reactions take place with 1-amino-2-propanol and, the products obtained are (E), (F), (G), and (H). The reaction schemes proposed are as follows:

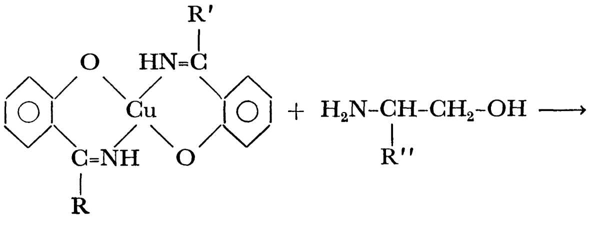
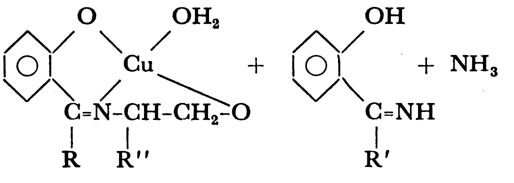


Table 1. Analytical data

Sample	Complex	Metal % Calcd	Metal % Found	C and H % Calcd	C and H % Found	N% Calcd	N% Found	λ_{max} (nm)	μ_{eff} (B.M)
(A)	[*N*-(Hydroxyethyl)salicylideneaminato]Cu(II)H_2O	25.98	25.58	39.25 4.49	39.15 4.25	5.72	5.85	610	1.50
(B)	[*N*-(2-Hydroxyethyl)-2-hydroxy-1-naphthylmethyleneaminato]Cu(II)H_2O	21.57	21.25	—	—	4.75	4.85	630	1.72
(C)	[*N*-(2-Hydroxyethyl)-1-(*o*-hydroxyphenyl)ethylideneaminato]Cu(II)H_2O	24.54	24.62	41.77 5.02	41.52 4.92	5.41	5.54	600	2.01
(D)	[*N*-(2-Hydroxyethyl)-α-(*o*-hydroxyphenyl)benzylideneaminato]Cu(II)H_2O	19.82	19.69	56.16 4.68	55.82 4.48	4.37	4.40	620	1.97
(E)	[*N*-(2-Hydroxy-1-methylethyl)salicylideneaminato]Cu(II)H_2O	24.58	24.21	—	—	5.41	5.81	610	1.44
(F)	[*N*-(2-Hydroxy-1-methylethyl)-2-hydroxy-1-naphthylmethyleneaminato]Cu(II)H_2O	19.88	19.50	—	—	4.38	4.52	620	1.75
(G)	[*N*-(2-Hydroxy-1-methylethyl)-1-(*o*-hydroxyphenyl)-ethylideneaminato]Cu(II)H_2O	23.22	23.00	—	—	5.11	5.24	610	1.95
(H)	[*N*-(2-Hydroxy-1-methylethyl)-α-(hydroxyphenyl)benzylideneaminato]Cu(II)H_2O	18.99	18.75	—	—	4.18	3.85	620	1.90
(A')	[*N*-(2-Hydroxyethyl)-2-hydroxy-1-naphthylmethyleneaminato]Cu(II)H_2O	21.57	21.32	—	—	4.75	5.41	620	1.78
(B')	[*N*-(2-Hydroxyethyl)salicylideneaminato]Cu(II)H_2O	25.98	25.70	—	—	5.72	5.30	600	1.52
(C')	[*N*-(2-Hydroxyethyl)-α-(*o*-hydroxyphenyl)benzylideneaminato]Cu(II)H_2O	19.82	19.58	—	—	4.37	4.50	620	1.96
(D')	[*N*-(2-hydroxy-1-methylethyl)-2-hydroxy-1-naphthylmethyleneaminato]Cu(II)H_2O	19.88	19.60	—	—	4.38	4.80	620	1.74
(E')	[*N*-(2-hydroxy-1-methylethyl)salicylideneaminato]Cu(II)H_2O	24.58	24.56	—	—	5.39	5.50	610	1.50

Table 2. IR spectral data

	Complex	C=N stretch (cm^{-1})	O–H stretch (cm^{-1})	O–H deformation mode (cm^{-1})
(A)	[*N*-(2-Hydroxyethyl)salicylideneaminato]Cu(II)H_2O	1600	3350	900
(B)	[*N*-(2-Hydroxyethyl)-2-hydroxy-1-naphthylmethyleneaminato]Cu(II)H_2O	1600	3400	880
(C)	[*N*-(2-Hydroxyethyl)-1-(*o*-hydroxyphenyl)-ethylideneaminato]Cu(II)H_2O	1600	3300	890
(D)	[*N*-(2-Hydroxyethyl)-α-(*o*-hydroxyphenyl)-benzylideneaminato]Cu(II)H_2O	1600	3400	900
(E)	[*N*-(2-Hydroxy-1-methylethyl)salicylideneaminato]Cu(II)H_2O	1600	3400	910
(F)	[*N*-(2-Hydroxy-1-methylethyl)-2-hydroxy-1-naphthylmethyleneaminato]Cu(II)H_2O	1590	3400	880
(G)	[*N*-(2-Hydroxy-1-methylethyl)-1-(*o*-hydroxyphenyl)-ethylideneaminato]Cu(II)H_2O	1600	3400	900
(H)	[*N*-(2-Hydroxy-1-methylethyl)-α-(*o*-hydroxyphenyl)-benzylideneaminato]Cu(II)H_2O	1590	3400	880



R=R'=H, CH_3, or C_6H_5
R''=H or CH_3

Thus it is observed that the aminoalkanols replace ammonia from of the Schiff base molecule, and the resulting tridentate Schiff base occupies three positions around the metal ion, the other Schiff base molecule being removed. The fourth position may be occupied by a water molecule.

The reaction can be explained by analogy with the Schiff base copper(II) complex of *N*,*N*-diethylethylenediamine.[8] It can be considered that the OH of the aminoalkanol liberates on coordination the H^+ ion which attacks the phenolic-O of the other Schiff base molecule reforming OH, and that a Schiff base molecule is detached.

The reactions of 2-aminoethanol with the mixed complexes (a′), (b′), and (c′) gave the products (A′), (B′), and (C′), respectively, salicylideneamine or 1-(*o*-hydroxyphenyl)ethylideneamine being removed. Similar reactions take place with 1-amino-2-propanol. Reactions of 1-amino-2-propanol with (c′) gave no definite compound. The reactions can be shown by the same scheme as above where R is H and R′ is CH_3.

Thus it is observed that for the mixed ligand complexes also aminoalkanol replaces ammonia from one of the ligands forming a tridentate Schiff base and another ligand molecule is removed.

The above reaction is a confirmation of the fact that the mixed Schiff base complex (CuLL′) is really a mixed ligand complex. If it were a mixture of the two bis-compounds, CuL_2 and CuL_2', a mixture of complexes of tridentate Schiff base from both the ligands (L and L′) would have been obtained. In the cases of reactions of mea and ipa on mixed Schiff base complexes, it is also interesting to observe which ligand forms the tridentate Schiff base, and which one is displaced. For the copper(II) complexes (b′), salicylaldehyde is retained, and 1-(*o*-hydroxyphenyl)ethylideneamine is removed. This shows that salicylaldehyde has a stronger tendency to form the Schiff base. For the complex (c′), 2-hydroxybenzophenone is retained, and salicylideneamine is removed. It is indicated that 2-hydroxybenzophenone has a stronger tendency to form the Schiff base than salicylaldehyde. Thus the order found is as follows:

2-hydroxybenzophenone > salicylaldehyde >
2-hydroxyacetophenone.

Similarly with complex (a′), 2-hydroxy-1-naphthaldehyde is retained, salicylideneamine being removed. For the complex (d′), no definite compound was obtained on reaction with 2-aminoethanol. The composition of the compound obtained is very close to the complex in which both 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzophenone form Schiff bases and remain with copper(II). This shows that 2-hydroxy-1-naphthaldehyde and hydroxybenzophenone have similar tendencies to form a Schiff base. Thus the order of forming Schiff base is 2-hydroxybenzophenone ≈ 2-hydroxy-1-naphthaldehyde > salicylaldehyde > 2-hydroxyacetophenone

This is expected from theoretical considerations also. Schiff base formation or amine exchange is due to the nucleophilic attack of an amine on the positively charged carbonyl carbon atom.[17] Attachment of a methyl group with the +I effect lowers the positive charge on the carbon atom, reducing the nucleophilic attack. Thus 2-hydroxyacetophenone is less susceptible to Schiff base formation. The attachment of a phenyl group with the −I effect to C=O group increases the possibility of the nucleophilic attack of 2-hydroxybenzophenone. Similarly the naphthalene ring in 2-hydroxy-1-naphthaldehyde makes the carbonyl carbon atom more positive.

Above reactions with mixed and non-mixed Schiff base complexes show that copper(II) prefers to form a 1 : 1 complex with the tridentate Schiff base. All the copper(II) complexes formed are paramagnetic, corresponding to the nearly spin-only value of one unpaired electron. This shows that a water molecule is in the coordination sphere, and it is a monomeric complex. In some copper(II) complexes the magnetic moment is slightly lower than the spin-only value of one unpaired electron. This may be due to the fact that the complexes are anhydrous and dimeric, leading to the Cu–Cu interaction and the lowering of paramagnetism.[18] The electronic spectra of all the copper (II) complexes are similar and show a peak at ≈620 nm expected for the $Cu(N)(O)_3$ type complexes[19]. This broad band is a combination of three bands corresponding to

$$^2B_{1g} \longrightarrow 2A_{1g},\ ^2B_{1g} \longrightarrow {}^2B_{2g} \text{ and}$$
$$^2B_{1g} \longrightarrow {}^2E_g \text{ transitions.}^{20)}$$

The IR spectra of copper(II) complexes exhibit a broad band at 3400 cm^{-1} showing the presence of water. Since there is a band at 900 cm^{-1} corresponding to the O–H out-of-plane deformation mode, this suggests the coordinated water molecule[21]. The absence of the N–H stretching frequency at about 3300 cm^{-1} is also in keeping with the structure of the complexes.

Authors' thanks are due to Prof. S. M. Sethna, former Head, Department of Chemistry, for providing all the laboratory facilities. Two of the authors (V.B.M) and (R.K.K) are also grateful to M. S. University, Baroda, and U.G.C. New-Delhi for providing fellowships.

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