

Studies in Some Mixed Ligand Complexes: Part III— Mixed Ligand Complexes of Cu(II) with 2-Hydroxy- & 2-Hydroxy- 3-methylacetophenones as Primary Ligands & Acetylacetonone as Secondary Ligand

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Received 29 September 1975; accepted 3 August 1976

Mixed ligand complexes of the type $[CuLL']$, where $L = 2\text{-hydroxyacetophenone}$ or $2\text{-hydroxy-3-methylacetophenone}$ and $L' = \text{acetylacetonone}$, have been prepared. On treatment of $[CuLL']$ with ammonia, methyl amine or ethyl amine, only the acetophenone part forms the Schiff base giving the complexes IIa, b and IIIa-d. The above Schiff base complexes can also be prepared by treating the metal ammine complex with an equivalent amount of each of the two ligands. Amine exchange reactions are also possible. Treatment of Ia and Ib with ethylenediamine or propylenediamine results in the formation of the Schiff base complexes (IVa-d) in which diamine is condensed at one end with acetophenone and other end with acetylacetonone. IVa-d can also be prepared by the imine exchange reaction on IIa or IIb with the above diamines. The complexes have been characterized on the basis of elemental analyses, TLC, conductance, magnetic and spectral data.

IN continuation of our earlier studies on mixed ligand complexes¹⁻³, we report in this paper the preparation and reaction of mixed ligand complexes of the type $[MLL']$, where $M = Cu(II)$, $L = 2\text{-hydroxyacetophenone}$ or $2\text{-hydroxy-3-methylacetophenone}$ and $L' = \text{acetylacetonone}$. The complexes were characterized on the basis of elemental analyses, TLC, conductance, magnetic, UV and IR data.

Materials and Methods

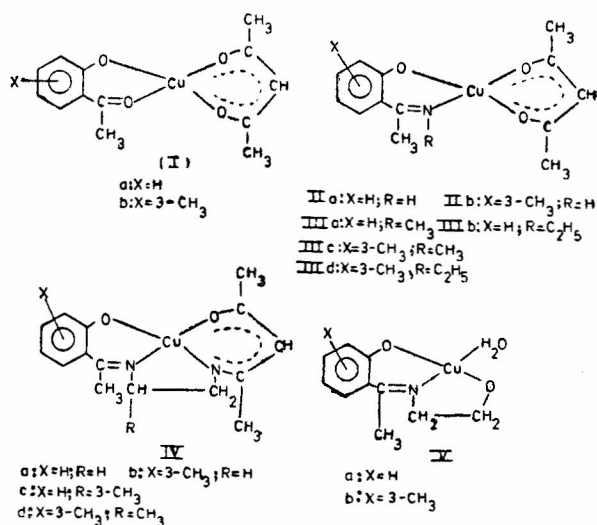
(2-Hydroxyacetophenonato)(acetylacetonato)Cu(II) (Ia) — It was prepared by adding 2-hydroxyacetophenone and acetylacetonone to the metal ion solution in 1:1:1 ratio, and raising the pH to ~5.5 with dil. ammonia. The mixture was stirred well and the solid separated was filtered, washed with water and 50% ethanol, and recrystallized from chloroform.

Similar reaction of 2-hydroxy-3-methylacetophenone and acetylacetonone with metal ion furnished the complex Ib.

The amine Schiff base complexes IIa and IIb were prepared using the following two methods:

Method (a) — The preformed mixed complex I was treated with an excess of ethanolic ammonia and refluxed on a water-bath with constant stirring. The solid separated was filtered, washed with water and 50% ethanol and recrystallized from chloroform.

Method (b) — To the metal ion solution an excess of ammonia was added till the precipitates formed redissolved. To this was added 2-hydroxyacetophenone and acetylacetonone such that the metal and the two ligands were in 1:1:1 molar ratio. After stirring, the precipitated complex was filtered, washed with water and 50% ethanol, and recrystallized from chloroform.



Alkylamine Schiff base complexes (IIIa-d) — The complexes IIIa-d were prepared either by the direct action of methyl amine or ethyl amine on Ia and Ib, or by treating the Schiff base complexes (IIa and IIb) with alkyl amine (methyl amine or ethyl amine). The complexes formed were filtered, washed with water and 50% ethanol, and recrystallized from chloroform.

Diamine Schiff base complexes (IVa-d) — These were prepared either by the direct treatment of the mixed ligand complex (I) with ethylenediamine (en) or propylenediamine (pn) or by carrying out the imine exchange reaction on II with diamine (ethylenediamine or propylenediamine) on a water-bath. The propylenediamine Schiff base complexes (IVc and IVd) have also been prepared by carrying out en to pn exchange reaction on the ethylenedi-

amine Schiff base complexes (IVa and IVb) with propylenediamine. The resulting solid was filtered, washed with water and 50% ethanol, and recrystallized from chloroform.

Reaction of II with ethanolamine: Formation of Va and Vb — The mixed Schiff base complex IIa or IIb was refluxed on a water-bath with an ethanolic solution of ethanolamine. The solid that separated on adding water to the reaction mixture was filtered, washed with water and 50% ethanol, and recrystallized from ethanol.

Results and Discussion

During the formation of II and III from I, the acetylacetonato moiety remained unaffected because coordinated acetylacetonates have very little tendency to undergo condensation with ammonia or alkyl amines⁴. However, coordinated 2-hydroxyacetophenone undergoes reaction with primary amines to give the Schiff base complexes.

The formation of diamine Schiff base complexes wherein diamine is condensed at one end with

2-hydroxyacetophenone and the other end with acetylacetonate, was supported by analytical and IR data. Formation of IV can be explained on the basis of the fact that diamines are more basic than the primary amines, and hence condense with β -diketones^{5,6}. It is interesting to note that ethylenediamine Schiff base complexes (IVa and IVb) when treated with propylenediamine undergo exchange reaction to give the propylenediamine complexes (IVc and IVd).

In order to find out coordinating tendencies of the two ligands, the mixed ligand imine complex was treated with ethanolamine. It was found that the 2-hydroxyacetophenone moiety reacted with one mole of ethanolamine to form a tridentate ligand which occupies three positions on the copper atom forming a monomeric complex (V), the acetylacetonate part being removed. TLC analysis shows the compound to be pure. The results of elemental analysis agree with the suggested composition. However, the mechanism of displacement is not very clear.

TABLE 1 — PHYSICAL DATA OF THE MIXED LIGAND AND MIXED SCHIFF BASE COMPLEXES OF Cu(II)

Complex	Name	% Calc. (Found) [§]		λ_{\max} (ϵ)	μ (BM)
		Cu	N		
I	[(2-OH-Acetophenonato-acetylacetonato)Cu(II)]	21.36 (21.57)	—	660 (55)	1.96
IIa*	[(2-OH-Acetophenoniminato-acetylacetonato)Cu(II)]	21.43 (21.43)	4.72 (4.61)	630 (74)	1.87
IIa*	[(2-OH-Acetophenoniminato-acetylacetonato)Cu(II)]	21.43 (21.37)	4.72 (4.58)	650 (76)	1.90
IIb	[(2-OH-3-Me-Acetophenoniminato-acetylacetonato)Cu(II)]	20.40 (20.31)	4.49 (4.42)	660 (72)	1.91
IIIa*	[(N-Methyl-2-OH-acetophenoniminato-acetylacetonato)Cu(II)]	20.46 (20.51)	4.51 (4.46)	640 (78)	1.88
IIIa†	[(N-Methyl-2-OH-acetophenoniminato-acetylacetonato)Cu(II)]	20.46 (20.73)	4.51 (4.39)	640 (76)	1.90
IIIb*	[(N-Methyl-2-OH-acetophenoniminato-acetylacetonato)Cu(II)]	19.58 (19.38)	4.31 (4.26)	630 (66)	1.86
IIIb†	[(N-Ethyl-2-OH-acetophenoniminato-acetylacetonato)Cu(II)]	19.58 (19.43)	4.31 (4.40)	630 (64)	1.89
IIIc†	[(N-Methyl-2-OH-3-Me-acetophenoniminato-acetylacetonato)- Cu(II)]	19.52 (19.36)	4.30 (4.25)	640 (79)	1.92
IIId†	[(N-Ethyl-2-OH-3-Me-acetophenoniminato-acetylacetonato)- Cu(II)]	18.72 (18.83)	4.12 (4.06)	630 (76)	1.89
IVa*	[N,N'-Ethylene(2-OH-acetophenoniminato-acetylacetoniminato)- Cu(II)]	19.76 (19.59)	8.71 (8.58)	560 (405)	1.82
IVa†	[N,N'-Ethylene(2-OH-acetophenoniminato-acetylacetoniminato)- Cu(II)]	19.76 (19.61)	8.71 (8.63)	560 (408)	1.82
IVb†	[N,N'-Ethylene(2-OH-3-Me-acetophenoniminato-acetylacetonimi- nato)Cu(II)]	18.89 (18.96)	8.32 (8.13)	560 (350)	1.83
IVc*	[N,N'-Propylene(2-OH-acetophenoniminato-acetylacetoniminato)- Cu(II)]	18.94 (18.78)	8.34 (8.29)	560 (407)	1.91
IVc†	[N,N'-Propylene(2-OH-acetophenoniminato-acetylacetoniminato)- Cu(II)]	18.94 (18.81)	8.34 (8.19)	560 (407)	1.94
IVc†	[N,N'-Propylene(2-OH-acetophenoniminato-acetylacetoniminato)- Cu(II)]	18.94 (18.71)	8.34 (8.21)	560 (403)	1.89
IVd†	[N,N'-Propylene(2-OH-3-Me-acetophenoniminato-acetylaceton- iminato)Cu(II)]	18.13 (18.26)	7.98 (7.83)	560 (135)	1.89
IVd†	[N,N'-Propylene(2-OH-3-Me-acetophenoniminato-acetylaceton- iminato)Cu(II)]	18.13 (18.08)	7.98 (7.78)	560 (135)	1.86
Va	[(N-Hydroxyethylene-2-OH-acetophenoniminato aquo)Cu(II)]	24.48 (24.37)	5.39 (5.08)	630 (85)	1.86
Vb	[(N-Hydroxyethylene-2-OH-3-Me-acetophenoniminato aquo)- Cu(II)]	23.15 (23.48)	5.09 (5.40)	630 (88)	1.89

*Prepared from mixed complex.

†Prepared by imine exchange reaction.

‡Prepared by en to pn exchange reaction.

§The complexes also gave satisfactory analyses for C and H.

Similar reaction of ethanolamine on bis-salicylal-diminato Cu(II) and bis-2-hydroxyacetophenoniminato Cu(II), carried out in our laboratory, indicated that one of the salicylaldehyde or 2-hydroxyacetophenone moiety reacts with ethanolamine to form a tridentate ligand which occupies three positions on the copper atom forming a monomeric complex. Such replacement of one of the ligand has also been observed in other tridentate Schiff base complexes of Cu(II)⁷.

All Schiff base complexes obtained were insoluble in water and soluble in organic solvents. They were found to be non-conducting indicating non-electrolyte nature. The Cu(II) complexes were paramagnetic having magnetic moments corresponding to one unpaired electron. The visible spectra showed a broad band at ~ 560 or ~ 650 nm corresponding to a combination of ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_{1g}$ transitions^{8,9} in the D_{4h} symmetry, most probably square planar in these cases.

The IR spectra of I-IV showed no bands around 3400 cm^{-1} indicating that the hydroxyl group of 2-hydroxyacetophenone or the Schiff base is involved in the complex formation. In the case of I, the band $\sim 1625\text{ cm}^{-1}$ corresponded to the chelated ketonic C=O, and that around 1580 cm^{-1} to the C...O of acetylacetone. In the case of Schiff base complexes II and III, $\nu_{C=O}$ band at 1625 cm^{-1} was replaced by a new band around 1600 cm^{-1} corresponding to $\nu_{C=N}$. The band corresponding to diketone C...O around 1580 cm^{-1} was, however, retained indicating that only 2-hydroxyacetophenonato moiety underwent condensation with ammonia or alkylamines. The spectra also showed a ν_{N-H} around 3300 cm^{-1} which was, however, found to be absent in the case of III and IV. This shows that the

formation of IV involved condensation of both the NH_2 groups of the diamine. In IV the band at 1580 cm^{-1} $\nu_{C...O}$ was replaced by a $\nu_{C...N}$ band around 1540 cm^{-1} . The IR spectra of [(N-hydroxyethylene) (2-hydroxyacetophenoniminato) aquo Cu(II)] (Va) and [(N-hydroxyethylene) (2-hydroxy-3-methylacetophenoniminato) (aquo) Cu(II)] (Vb) showed a broad band in the region $3400\text{--}3300\text{ cm}^{-1}$ indicating the presence of a water molecule. This confirms a square planar structure for V. Thus, the tridentate ligand occupies three positions on the copper atom, the fourth being occupied by a water molecule.

Acknowledgement

The authors are grateful to Prof. K. N. Trivedi, Head, Department of Chemistry, M.S. University of Baroda, for providing necessary laboratory facilities, and to the UGC, New Delhi for the award of a junior research fellowship to one of them (U.D.).

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