Reactions of Metal $\beta$-Diketonates: Part II—Reactions of Bis(acetylacetonato)copper(II) Dihydrate with Chelating Ligands Containing at Least One Amino Group

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Reactions of bis(acetylacetonato)copper(II) dihydrate, Cu(acac)$_2$.2H$_2$O, [or its dehydrated form, Cu(acac)$_2$] with various chelating ligands, viz. ethylenediamine, 1,3-diaminopropane, 1,3-diaminopropan-2-ol, ethanolamine, glycine, o-aminophenol, anthranilic acid, semicarbazide, and thiosemicarbazide under different reaction conditions are described. Lewis acid-base adducts are formed when Cu(acac)$_2$ reacts with L-L (where L-L is a chelating ligand) in non-aqueous media, e.g. toluene, dichloromethane, dichloroethane, and o-dichlorobenzene. On the other hand, template Schiff base chelates (derived from acetylacetone and L-L) are formed when the reactions of Cu(acac)$_2$.2H$_2$O [or Cu(acac)$_2$] are performed in ethanol, methanol, aqueous ethanol or aqueous acetone. Possible mechanisms of these reactions are qualitatively discussed. The newly synthesized copper(II) complexes have been characterized with the help of elemental analyses, molar conductances, magnetic susceptibilities, infrared, ultraviolet and visible absorption spectral data.

The Lewis acid behaviour of bis(acetylacetonato)-metal(II), M$^{II}$(acac)$_2$, is revealed in the formation of 1:2 and 1:1 addition compounds$^8$ with nitrogen bases. A few reports are available concerning the reactions of bis($\beta$-diketonato)metal(II), M$^{II}$(d-dik), with chelating ligands$^9$. Many of these published work have reported the reactions of bis(hexafluoroacetato)copper(II), Cu$_2$(hfac)$_2$, with bidentate chelating ligands, e.g. ethylenediamine, o-phenanthroline, 2,2′-dipyridyl, ethylenediamine, N,N'-disubstituted ethylenediamines and N,N'-tetrasubstituted ethylenediamine and o-phenylenediamine. Not much work seems to have been done on the reactions of Cu$_2$(acac)$_2$ (B) with chelating ligands containing a $-\text{NH}_2$ group$^9$. We have, thus, undertaken a scheme to study the reactions of M$^{II}$(acac)$_2$ with various chelating ligands (containing at least one $-\text{NH}_2$ group) under different reaction conditions. We wish to report here our work was in progress, a note on the reactions of Ni(acac)$_2$ with ethylenediamine and N,N'-disubstituted ethylenediamines in toluene appeared$^9$, in which cis-octahedral Ni(acac)$_2$(en) and Ni(acac)$_2$(NN'-Me$_2$-en) were isolated. No template synthesis of Schiff base metal complexes were observed by these authors, contrary to which we had isolated several Schiff base nickel(II) complexes through template way by the reactions of Ni(acac)$_2$ with amines$^{10}$ in different solvent systems.

The following abbreviations for the Schiff bases of acetylacetone have been used in the present study: AEN$_2$-H$_2$ for the ligand (I, R = CH$_2$CH$_2$OH), AOAP$_2$-H$_2$ for the ligand in (I, R = o-C$_6$H$_4$OH), AGLY$_2$-H$_2$ for the ligand (I, R = CH$_3$COOH), ASC$_2$-H$_2$ for the ligand (I, R = NHCONH$_2$), and ATSC$_2$-H$_2$ for the ligand (I, R = NHCSNH$_2$).

**Materials and Methods**

Experimental details were the same as described previously$^{10}$, Cu(acac)$_2$.2H$_2$O (A) was dehydrated (when required) as described earlier$^{10}$ or by azeotropic distillation of water from toluene solution to get Cu(acac)$_2$(B).

Cu(acac)$_2$(en) (I) — A mixture of Cu(acac)$_2$ (1.3 g, 0.005 mol) and ethylenediamine (0.3 g, 0.005 mol) in dichloroethane (50 ml) was stirred for 30 min at room temperature. The blue solution was filtered and the filtrate on concentration, yielded a greenish blue crystalline compound, which was filtered, washed with ethanol and dried in vacuo. yield.


Results and Discussion

Reactions of Cu(acac)$_2$2H$_2$O (A) or Cu(acac)$_3$ (B) with chelating agents like en, ena-H, aa-H, gly-H, SOAP-H$_2$, SALEN-H$_2$, sc-H$_2$HCl and tsc-H in different solvents under reflux yielded variety of copper(II) chelates including a large number of mixed ligand complexes of copper(II) (Table 1). It is observed that when the reactions are carried out in non-aqueous solvents (e.g., dichloromethane or toluene) using anhydrous Cu(acac)$_3$, the mixed ligand complexes involving acetylacetonate anions and the corresponding chelating ligands are produced. No condensation of coordinated carbonyl group(s) with −NH$_2$ group, present in the chelating ligands used, is observed. On the other hand, it has been observed in several cases the carbonyl group(s) of acetylacetonate ion condenses with primary amine group(s) to generate an azomethine group if the reactions are carried out in refluxing ethanol, aqueous ethanol or aqueous acetone. It has been demonstrated earlier$^{13}$ and in the present work that coordinated acetylacetonate anion does not favour condensation with amine$^{11}$, ethylenediamine$^{12}$, substituted ethylenediamines$^{8}$, amino acids$^{8}$ and amino alcohols$^{8}$ when the reactions are carried out in non-aqueous media. In this context, the condensation of a carbonyl group of a coordinated acetylacetonate ion with −NH$_2$ group of a chelating ligand in some of our reactions is surprising. This can be explained by the fact that one or both the copper-oxygen bond(s) in Cu(acac)$_3$ may be cleaved during reflux, and the free Ce$^{3+}$ ion may then condense with the −NH$_2$ group leading to the template synthesis of Schiff base complexes. Another probability is that the coordination number of copper(II) in Cu(acac)$_3$ (if somehow generated in the medium) may be increased from 4 to 5 after the reaction with the chelating ligand. Under such conditions, this allows for the formation of Schiff base complexes.
circumstances the formation of a Schiff base complex will be facilitated (see later discussion).

All the present Cu(II) chelates are crystalline solids, paramagnetic in the solid state with \( \mu_{eff} \) values in the range 1.78 to 1.93 BM (Table 1) showing the presence of bivalent copper atom. Elemental analyses support their formulations.

The observed magnetic moments suggest either square planar or tetragonally distorted octahedral geometry for the present Cu(II) mixed chelates.

The electronic absorption spectral data of the complexes are given in Table 1. The present complexes do not exhibit any absorption band in the characteristic, low frequency region (8000-11030 cm\(^{-1}\)) of tetrahedral or pseudotetrahedral Cu(II) complexes\(^{16,17}\). This militates against a tetrahedral or pseudotetrahedral stereochemistry for the copper(II) complexes under discussion. Instead, the band positions \( \lambda_{max} \) in cm\(^{-1}\) for II are found to be 18000 and 11800 (sh) for the complex Cu(en)\(_2\)Cl\(_2\) in the medium. The molar conductance of 1.85 \( \times 10^{4} \) M solution of II is found to be 195 ohm\(^{-1}\) cm\(^{2}\) mol\(^{-1}\) which also suggests extensive dissociation in this medium to generate (possibly) [Cu(en)]\(^{2+}\) and acetylacetonate anions.

The complex Cu(acac)\(_2\)(ena-H) (V), with \( \mu_{eff} \) = 1.86 in a solution of II is found to be 18000 and 11800 (sh), can also be considered to be square planar or distorted octahedral in structure as proposed for I above.

The electronic spectral data (Table 1) and the magnetic moment values of the other Cu(II) complexes of the present series also suggest square planar or distorted octahedral structures for all of these complexes. It is not possible to assign the absorption bands on the basis of present studies.

It is interesting to note that the reactions of Cu(acac)\(_2\) with ena-H, oap-H, sc-HCl and tsc-H in refluxing ethanol, aqueous ethanol, or aqueous acetone yielded complexes of the types Cu(AENA-H)(acac)\(_2\)H\(_2\)O (III), Cu(ACOAP)(acac)H\(_2\)O (VI), Cu(ASC-H)\(_2\) (XIV), and Cu(ATSC)H\(_2\)O (XV) respectively.

In all of these chelates, as demonstrated by IR spectral data, coordinated imine groups are found to be present. It is thus clear that the condensation of a coordinated carbonyl group of acetylacetonate residue with the \(-\text{NH}_2\) group of ena-H, oap-H, sc-HCl, or tsc-H has occurred during the course of the reaction, although it has been demonstrated...
earlier\textsuperscript{8} that coordinated $\beta$-diketonate anion does not favour such condensation. The presence of $\nu$C=N group in III, VI, XIV and XV is revealed by the appearance of bands at 1630, 1585, 1625 and 1629 respectively in their IR spectra. Some of the important bands of the chelates III, V and VI along with their tentative assignments, are given in Table 2.

The IR spectral data of the complex (III) support the structural formula IIIa or IIIb. The presence of a neutral acetylacetone molecule (coordinated) in the complex (VI) is inferred from IR spectral data and this complex can be represented by the probable structure VIa or VIb. Although we prefer the neutral ketonic acetylacetone to coordinate with the Cu(II) ion as a bidentate ligand as in VIa, the presence of enolic molecule of acetylacetone coordinated to Cu(II) ion as a unidentate ligand as in VIb cannot, however, be ruled out.

The infrared spectral data of Cu(ASC-H)$_2$ (XIV) support the structure (XIV) of the complex, where two molecules of acetylacetonesemicarbazone coordinated with the Cu(II). The IR absorption bands of the complex have been compared with those of the free ligand\textsuperscript{33}. The assignment of the IR bands has been made on the basis of the assignment of the bands of Ni(II) and Co(II) complexes\textsuperscript{30} with this ligand. The free ligand shows bands at 3461 ($\nu$NH), 3334, 3184 (bonded $\nu$NH), 1695 ($\nu$CO, amide-I), 1665 ($\nu$C=N). There is no shift in free $\nu$NH in the ligand. The shift in $\nu$NH (bonded), $\nu$CO and $\nu$C=N in the complex to 3300-3200, 1695 and 1665 respectively supports the coordination of imine-nitrogen and amide-oxygen of the hydrazine moiety of the ligand to the central metal atom. The third point of attachment of the ligand is the enolized oxygen of the acetylacetone part. Thus, the ligand ASC-H$_2$ functions as a monobasic tridentate ligand in the complex (XIV) as shown in the structure (XIV) for this complex.

On the other hand, the reaction of Cu(acac)$_2$ with the semicarbazide in refluxing ethanol yields a complex Cu(ATSC)H$_2$O, (XV). In this complex the ligand acetylacetone thiocarbaryone functions as a dibasic tridentate ligand (no $\nu$C=S band in the range 1000-1200 cm$^{-1}$\textsuperscript{34} as shown in structure (XV).
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References