# Nitration of Binary and Ternary Schiff Base Complexes of Cu(II)

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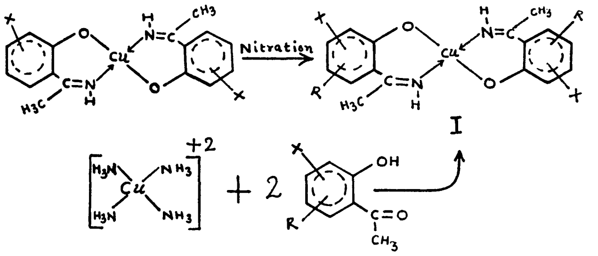
(Received November 18, 1975)

Nitration of the coordinated ligands in the complexes bis[1-(2-hydroxyphenyl)ethylideneamine or its methyl derivative]Cu(II) and *N,N'*-ethylene or propylene bis[1-(2-hydroxyphenyl)ethylideneaminato]Cu(II) have been carried out. Similar nitration reactions of mixed diamine Schiff base complexes of Cu(II) have also been carried out. The substitution products have been characterized by elemental analyses, comparison with authentic samples in case of binary complexes and by means of magnetic moments, electronic and IR spectral studies. The orientation of incoming substituents in the chelates is found to be the same as that in uncomplexed 2-hydroxyacetophenone or methyl substituted 2-hydroxyacetophenone. Nitration reactions in case of mixed ligand complexes confirm the structure.

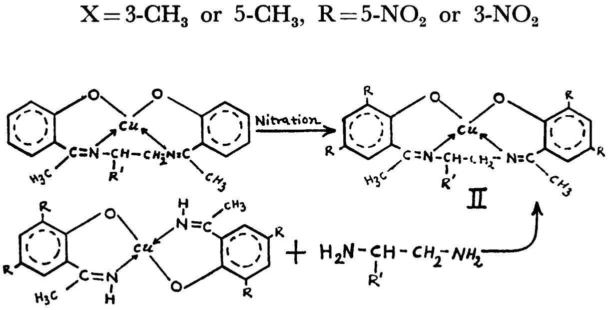
Nitration of metal salicylaldehyde and metal acetylacetonates using different nitrating agents such as $N_2O_4$, a mixture of copper nitrate, beryllium nitrate in acetic anhydride[1-3] or $N_2O_4 \cdot BF_3$[4] has been reported earlier. This paper describes the substitution of nitro groups in Schiff base present in binary and ternary Cu(II) complexes. The mild nitrating agent, acetyl nitrate used in the present reactions is formed *in situ* by the reaction of copper nitrate with acetic anhydride. This mild reagent has been used for many nitration reactions and in the case of coordinated ligands the reagent seems to have many advantages over other strong nitrating agents such as $N_2O_4$, $HNO_3$, and $H_2SO_4$ which cause decomposition of the Schiff base complexes. The mechanism of electrophilic substitution over a benzene ring in a coordinated ligand has been reported by Singh *et al.*[2]

In the present investigation nitrated compounds have been prepared by direct substitution of nitro groups, into the appropriate unsubstituted Schiff base complexes. These derivatives were characterized by comparison with authentic samples obtained by complexing appropriate nitrated 2-hydroxyacetophenone or methyl substituted 2-hydroxyacetophenone.



I

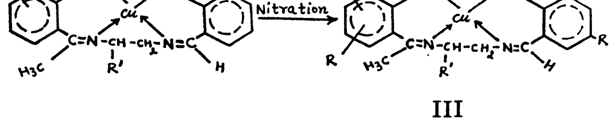
X=H or 4-$CH_3$, R=3-$NO_2$ and 5-$NO_2$
X=3-$CH_3$ or 5-$CH_3$, R=5-$NO_2$ or 3-$NO_2$



II

R=3-$NO_2$ and 5-$NO_2$
R'=H or -$CH_3$

The nitration reactions were further extended to the mixed Schiff base complexes reported by us earlier.[5] The reaction can be shown as follows:



III

X=H or 4-$CH_3$, R=3-$NO_2$ and 5-$NO_2$
X=3-$CH_3$ or 5-$CH_3$, R=5-$NO_2$ or 3-$NO_2$
R'=H or -$CH_3$

## Experimental

*Material Used.* Bis[1-(2-hydroxyphenyl)ethylideneamine or its methyl derivative]Cu(II), *N,N'*-ethylene or propylene bis[1-(2-hydroxyphenyl)ethylideneaminato]Cu(II) and mixed ligand *N,N'*-ethylene or propylene [salicylideneaminato, 1-(2-hydroxyphenyl)ethylideneaminato or its methyl derivative]Cu(II) were prepared as reported earlier.[5,6] Acetic anhydride (BDH), cupric nitrate trihydrate (Riedell, pure, Germany), and sodium acetate crystal (Pfiezer) were used. Ethanol was of analytical grade.

*Method and Apparatus.* The magnetic susceptibilities of the Cu(II) complexes were determined at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. TLC was carried out for most of the complexes. Infrared spectra in KBr disc were recorded on a Perkin Elmer model 427 infrared grating spectrophotometer in the range 4000—625 $cm^{-1}$. The reflectance spectra of the complexes have been taken on a DU2 Beckman Spectrophotometer.

Synthesis of bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneamine]Cu(II), bis[1-(2-hydroxy-3,5-dinitro-*p*-tolyl)ethylideneamine]Cu(II), bis[1-(6-hydroxy-5-nitro-*m*-tolyl)ethylideneamine]Cu(II), bis[1-(2-hydroxy-5-nitro-*m*-tolyl)ethylideneamine]Cu(II), *N,N'*-ethylene or propylene bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II), *i.e.*, I and II R=3-$NO_2$ and 5-$NO_2$, R'=H or $-CH_3$, X=H, 3-$CH_3$, 4-$CH_3$, or 5-$CH_3$. 0.5 g of bis[1-(2-hydroxyphenyl)ethylideneamine or its methyl derivative]Cu(II) or *N,N'*-ethylene or propylene bis[1-(2-hydroxyphenyl)ethyleneaminato]Cu(II) Schiff base and acetic anhydride (14 ml) were taken in a 250 ml conical flask fitted with a calcium chloride drying tube and stirred magnetically over an ice bath for half an hour. Powedred $Cu(NO_3) \cdot 3H_2O$ (0.82 g) was added in small portions over a period of 30 min. The ice bath was removed after 4 h but the stirring was continued for additional 4 h. The resulting green substance was decomposed by pouring into 150 ml of ice-cold water containing sufficient amount of sodium acetate and stirring for 2 h. The precipi-

TABLE 1. ELECTRONIC SPECTRAL BANDS, MAGNETIC MOMENTS AND ELEMENTAL ANALYSIS OF NITRATED BINARY IMINE, DIAMINE, AND MIXED DIAMINE Cu(II) SCHIFF BASE COMPLEXES

| No. | Complex | Analytical data % | | | | | | | | $\lambda_{max}$ in nm | $\mu_{eff.}$ in B.M. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcd | | | | Found | | | | | |
| | | Cu | C | H | N | Cu | C | H | N | | |
| 1 | Bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneamine]Cu(II) | 12.42 | 37.53 | 2.34 | 16.41 | 12.75 | 37.97 | 2.66 | 16.29 | 530 | 1.88 |
| 1a | Bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneamine]Cu(II) | 12.42 | 37.53 | 2.34 | 16.41 | 12.30 | 37.40 | 2.52 | 15.98 | — | 1.90 |
| 2 | Bis[1-(2-hydroxy-5-nitro-*m*-tolyl)ethylideneamine]Cu(II) | 14.13 | 48.05 | 4.00 | 12.45 | 13.70 | 47.80 | 4.42 | 11.99 | 530 | 1.82 |
| 2b | Bis[1-(2-hydroxy-5-nitro-*m*-tolyl)ethylideneamine]Cu(II) | 14.13 | — | — | 12.45 | 14.08 | — | — | 12.00 | — | 1.86 |
| 3 | Bis[1-(6-hydroxy-5-nitro-*m*-tolyl)ethylideneamine]Cu(II) | 14.13 | 48.05 | 4.00 | 12.45 | 13.85 | 47.94 | 4.06 | 13.00 | — | 1.89 |
| 3c | Bis[1-(6-hydroxy-5-nitro-*m*-tolyl)ethylideneamine]Cu(II) | 14.13 | 48.05 | 4.00 | 12.45 | 13.92 | 48.65 | 3.64 | 12.23 | 550 | 1.92 |
| 4 | Bis[1-(2-hydroxy-3,5-dinitro-*p*-tolyl)ethylideneamine]Cu(II) | 11.77 | 40.03 | 2.95 | 15.56 | 11.75 | 39.74 | 2.94 | 15.05 | 590 | 1.92 |
| 4d | Bis[1-(2-hydroxy-3,5-dinitro-*p*-tolyl)ethylideneamine]Cu(II) | 11.77 | — | — | 15.56 | 11.50 | — | — | 15.15 | — | 1.90 |
| 5 | *N*,*N*′-ethylene bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II) | 11.82 | 40.18 | 2.60 | 15.62 | 12.19 | 40.68 | 2.67 | 16.12 | 540 | 1.84 |
| 5e | *N*,*N*′-ethylene bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II) | 11.82 | — | — | 15.62 | 11.98 | — | — | 15.82 | — | 1.85 |
| 6 | *N*,*N*′-propylene bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II) | 11.52 | 41.33 | 2.90 | 15.23 | 11.69 | 40.97 | 2.68 | 15.40 | 550 | 1.80 |
| 6f | *N*,*N*′-propylene bis[1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II) | 11.52 | — | — | 15.23 | 11.42 | — | — | 15.15 | — | 1.78 |
| 7 | *N*,*N*′-ethylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II) | 12.13 | 38.96 | 2.29 | 16.04 | 12.00 | 38.75 | 2.21 | 15.95 | 560 | 1.94 |
| 8 | *N*,*N*′-propylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II) | 11.82 | 40.18 | 2.60 | 15.62 | 11.78 | 40.00 | 2.52 | 15.42 | 560 | 1.95 |
| 9 | *N*,*N*′-ethylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-5-nitro-*m*-tolyl)ethylideneaminato]Cu(II) | 12.90 | — | — | 14.21 | 12.75 | — | — | 14.02 | 560 | 1.86 |
| 10 | *N*,*N*′-propylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-5-nitro-*m*-tolyl)ethylideneaminato]Cu(II) | 12.54 | — | — | 13.82 | 12.42 | — | — | 13.50 | 560 | 1.91 |
| 11 | *N*,*N*′-ethylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-3,5-dinitro-*p*-tolyl)ethylideneaminato]Cu(II) | 11.82 | — | — | 15.62 | 11.65 | — | — | 15.25 | 550 | 1.84 |
| 12 | *N*,*N*′-propylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-3,5-dinitro-*p*-tolyl)ethylideneaminato]Cu(II) | 11.52 | — | — | 15.23 | 11.48 | — | — | 15.00 | 550 | 1.82 |
| 13 | *N*,*N*′-ethylene[3,5-dinitrosalicylideneaminato, 1-(6-hydroxy-5-nitro-*m*-tolyl)ethylideneaminato]Cu(II) | 12.90 | 43.85 | 3.04 | 14.21 | 12.62 | 43.55 | 3.00 | 14.00 | 550 | 1.87 |
| 14 | *N*,*N*′-propylene[3,5-dinitrosalicylideneaminato, 1-(6-hydroxy-5-nitro-*m*-tolyl)ethylideneaminato]Cu(II) | 12.54 | 45.01 | 3.35 | 13.82 | 12.35 | 44.98 | 3.23 | 13.52 | 550 | 1.89 |

a, b, c, and d prepared from nitrated ligand. e and f prepared from imine nitrated complex.

tate thus obtained was filtered, washed with water, then with ethanol.

The above bis complexes were also prepared by direct treatment of tetra ammine Cu(II) salt with nitrated 2-hydroxyacetophenone or its methyl derivatives. 2-Hydroxy-3,5-dinitroacetophenone, 2-hydroxy-5-methyl-3-nitroacetophenone, 2-hydroxy-3-methyl-5-nitroacetophenone were prepared as described in the literature.[7] These nitrated 2-hydroxyacetophenone were converted into above shown Cu(II) Schiff base complexes by treating Cu–ammine solutions with 2 moles of appropriate ethanolic solutions of nitrated 2-hydroxyacetophenone or its methyl derivatives. The mixture was refluxed for half an hour. The precipitate thus obtained was filtered, washed with water, then with ethanol.

The above nitrated ethylideneamine and propylenediamine complexes were also prepared by direct treatment of nitrated imine Schiff base complex with ethylenediamine or propylenediamine.

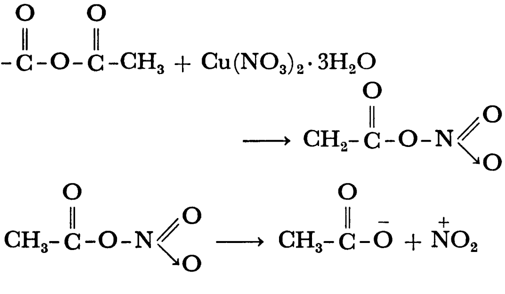
Synthesis of mixed *N,N'*-ethylene or propylene[3,5-dinitrosalicylideneaminato, 1-(2-hydroxy-3,5-dinitro-*p*-tolyl) or (2-hydroxy-3,5-dinitrophenyl)ethylideneaminato]Cu(II), *N,N'*-ethylene or propylene[3,5-dinitro salicylideneaminato, 1-(2-hydroxy-5-nitro-*m*-tolyl)ethyleneaminato]Cu(II) and *N,N'*-ethylene or propylene[3,5-dinitro salicylideneaminato, 1-(6-hydroxy-5-nitro-*m*-tolyl)ethyleneaminato]Cu(II), *i.e.*, III R= $3\text{-}NO_2$ and $5\text{-}NO_2$, R'=H or $-CH_3$ and X=H, $3\text{-}CH_3$, $4\text{-}CH_3$ or $5\text{-}CH_3$. The procedure is the same as that for binary Schiff base complexes.

*Analysis.* Cu(II) in the complexes was analyzed iodometrically, after the complexes had been decomposed in nitric acid. Carbon, hydrogen, and nitrogen were determined by the micro analytical method. The analytical data are given in Table 1.

The solubilities of nitrated binary and mixed Schiff base complexes of Cu(II) in organic solvents are very low. TLC of all the compounds have been carried out on silica gel G(Sichem) using chloroform: acetone (6 : 4) mixture as the solvent. Only one dot is obtained for dinitro and mononitro complexes indicating that the complex formed is a single compound.

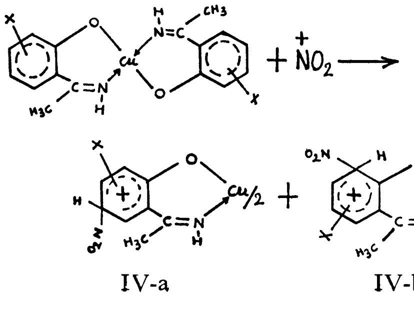
## Results and Discussion

In these reactions the nitronium ions produced from the acetyl nitrate act as electrophile to form two stable σ-complex intermediates (IV-a and b) (V-a and b) as follows:

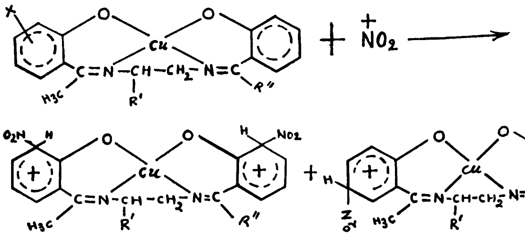


$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + Cu(NO_3)_2\cdot 3H_2O \longrightarrow CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-O-}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$$

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-O-}N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{-}{O} + \overset{+}{N}O_2$$



IV-a   IV-b



V-a   V-b

X=H, $3\text{-}CH_3$, $4\text{-}CH_3$ or $5\text{-}CH_3$  R'=R''=H or $-CH_3$

The proton is removed from each of these intermediates and the dinitro chelates further react with the $NO^+_2$ ion in the same manner resulting in the formation of the di-, tri, or tetranitro compounds I, II, or III. In the case of 3-methyl and 5-methyl substituted binary imine complexes, however, only mononitro complexes were formed, one of the positions 3 or 5 being already occupied by the methyl group. This shows that the nitration reaction takes place over benzene ring at positions 3 and 5 rather than positions 4 and 6. This is due to *ortho*, *para* orienting effect of phenolic O and *meta* directing effect of –C=N–. Thus the orientation of incoming substitutions in the binary Schiff base complexes is found to be the same as that for the uncomplexed 2-hydroxyacetophenone or methyl substituted 2-hydroxyacetophenone. The nitration reaction, however, requires a long time of refluxing. This shows that the electrophilic substitution reaction is retarded on the coordination of the ligand with the metal.

The analysis, magnetic moments and spectral properties of the above binary nitrated complexes and the corresponding binary complexes obtained by the reaction of metal with nitrated Schiff base are found to be similar.

In the case of complexes of ethylenediamine Schiff base coordinated at two ends with 2-hydroxy-4-methyl- or 2-hydroxyacetophenone and salicylaldehyde, tetranitro complexes were formed. Both salicylaldehyde and 2-hydroxy-4-methyl or 2-hydroxyacetophenone get nitrated at positions 3 and 5. In the case of diamine Schiff base, complexes of 2-hydroxy-3-methyl or 5-methyl acetophenone and salicylaldehyde trinitrated complexes were formed, since salicylaldehyde gets nitrated at positions 3 and 5 while 2-hydroxy-3-methyl and 5-methyl acetophenone gets nitrated only at positions 5 and 3, respectively, the other position being already occupied by the methyl group.

TLC shows only one dot indicating that nitro compounds are single compounds. This confirms the proposed structure[5] for these new Schiff base complexes with ethylenediamine condensed at two ends with aldehyde and ketone.

All nitrated Cu(II) Schiff base complexes are paramagnetic ($\mu$=1.8 to 2.0 B.M.) indicating the presence of one unpaired electron. There is no change in the paramagnetic value of nitrated compounds of Cu(II) Schiff base complexes from those without nitro substitution. The reflectance spectra of nitrated compounds exhibit one broad band at ≈550 nm as expected for a square planar structure. This shows that the square planar structure of the complex is retained even after the substitution of the nitro groups.

The IR spectra of the nitrated compounds show bands similar to those of unsubstituted Schiff base complexes.5,6) However, there is a broadening in the bands showing the presence of nitro groups. The IR spectra of the nitro compounds obtained by the two methods are also almost superimposable indicating that the complexes are identical. Nitration of the coordinated ketone and aldehyde is thus confirmed.

Thanks are due to Prof. S. M. Sethna, Head, Department of Chemistry, M. S. University, Baroda, for providing necessary laboratory facilities.

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