

The $\nu\text{C}=\text{N}$ absorption of the pyridine ring^{8,17} appears at $1590 \pm 5 \text{ cm}^{-1}$ in the ligands and remains unaffected on complexation. In-plane and out-of-plane ring deformation modes of pyridine are observed at ~ 620 and 410 cm^{-1} respectively in the spectra of the ligands and their adducts, suggesting non-participation of the pyridine N atom in coordination¹⁸.

The bands appearing at 1605 and 1610 cm^{-1} in the spectra of the ligands Ic_1 and Ic_2 respectively may be attributed to the $\nu\text{C}=\text{N}$ (azomethine). In the spectra of the complexes these bands appear to be split into two strong peaks at $1645 \pm 20 \text{ cm}^{-1}$ and $1618 \pm 6 \text{ cm}^{-1}$, the former may be assigned mainly to $\nu\text{C}=\text{N}$ whilst the lower band may be due to $\nu\text{C}=\text{N}$ coupled with aromatic $\nu\text{C}-\text{C}$ stretch¹⁵. The shift of 20 to 60 cm^{-1} , towards higher frequency suggests coordination through the exocyclic N atom¹⁹⁻²².

It is concluded that the Schiff bases behave as monodentate ligand coordinating through azomethine N atom. An octahedral structure is suggested for the complexes in the solid state.

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Nitration & Bromination of Some Binary & Mixed Ligand Schiff Base Complexes of Cu(II)

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Nitration and bromination reactions have been carried out on Cu(II) complexes of Schiff bases derived from 2-hydroxybenzophenone and 2-hydroxy-1-naphthaldehyde. In the case of 2-hydroxybenzophenone, the electrophilic substitution takes place in the phenolic ring rather than in the substituent group attached to the azomethine carbon. Dinitration and dibromination take place on each of the ligands resulting in tetranitro and tetrabromo compounds. It is observed that in 2-hydroxy-1-naphthaldehyde moiety, only mono nitration takes place at C-6, and this results in dinitro products in the case of bis-(2-hydroxy-1-naphthalaldiminato)Cu(II) and N,N'-ethylenebis(2-hydroxy-1-naphthalaldiminato)Cu(II) but trinitro products in the case of (2-hydroxy-1-naphthalaldiminato)(salicylaldiminato)Cu(II) and N,N'-ethylene-(2-hydroxy-1-naphthalaldiminato)(salicylaldiminato)Cu(II) complexes. The complexes have been characterized on the basis of elemental analyses, spectral and magnetic studies.

REACTIONS of coordinated ligands have evoked considerable interest in recent years and a number of reports on halogenation, nitration, thiocyanation, acetylation and formylation reactions have appeared¹⁻¹⁹. In continuation of the work on nitration of Schiff base complexes derived from 2-hydroxyacetophenone, reported earlier from our laboratory²⁰, we report here the results of our investigation on nitration and bromination of some Schiff base complexes of Cu(II). Nitration reactions have been mostly performed on Cu(II) complexes, because they are more stable and the ligand does not break easily. The mild nitrating agent acetylnitrate used in the present reaction was formed *in situ* by the reaction of copper(II) nitrate with acetic anhydride. This reagent is especially useful in the case of coordinated ligands because unlike strong nitrating agents (N_2O_4 , HNO_3 and H_2SO_4), it does not cause the decomposition of the Schiff base complexes.

N-Bromosuccinimide was used as the brominating agent. It has been used by many workers for brominating coordinated ligands^{3,5,8-10}. The brominium ion (Br^+) produced *in situ* acts as an electrophile in the bromination reaction of coordinated ligands.

All the complexes used for the present reactions were prepared according to the published procedure^{21,22}. Acetic anhydride (BDH), copper(II) nitrate trihydrate (Riedel), sodium acetate (Pfizer) and N-bromosuccinimide (Riedel) were used as such.

Nitration reactions were carried out on the following Schiff base complexes.

(a) Bis(2-hydroxybenzophenoniminato)Cu(II), (b) N,N'-ethylenebis(2-hydroxybenzophenoniminato)Cu(II), (c) N,N'-propylenebis(2-hydroxybenzophenoniminato)Cu(II), (d) bis(2-hydroxy-1-naphthaldiminato)Cu(II), (e) N,N'-ethylenebis(2-hydroxy-1-naphthaldiminato)Cu(II), (f) (2-hydroxy-1-naphthaldiminato)(salicylaldiminato)Cu(II) and (g) N,N'-ethylene(2-hydroxy-1-naphthaldiminato)(salicylaldiminato)Cu(II).

The complexes were nitrated by taking (a), (b), (c), (d), (e), (f) or (g) (0.5 g) and acetic anhydride (15 ml) in a flask fitted with calcium chloride guard tube and stirring for 15 min at 0° (ice-bath). Powdered Cu(NO₃)₂·3H₂O (0.80 g) was added in small portions over a period of 30 min. The ice-bath was removed after 5 hr; but the stirring was continued for five more hours. The resulting green coloured substance was decomposed by pouring into ice-cold water (150 ml) containing sufficient amount of sodium acetate. The contents were stirred for 2 hr and the precipitate thus obtained was filtered, washed, first with water and then with 50% ethanol.

Bromination of (a), (b) and (c) was performed as follows: To a solution of (a), (b) or (c) (0.5 g) in DMF (20 ml), a stoichiometric amount of N-bromosuccinimide in DMF (15 ml) was added. After stirring the mixture for 1 hr at room temperature, it was poured into 300 ml of cold distilled water. The resulting yellow coloured precipitate was filtered, washed with water, 50% ethanol and dried.

The complexes were analysed for metal, nitrogen, carbon, hydrogen (in some cases) and bromine (Table 1). Conductivity measurements were carried out in chloroform using Toshniwal conductivity bridge CLO1/01A. 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. The electronic spectra of the complexes were recorded (in chloroform) on a DU-2 Beckman spectrophotometer in the range 400-1000 nm.

Analytical data of the complexes are in agreement with the molecular formulae assigned to them (Table 1). The molar conductances of all the complexes in chloroform or DMF show that they are non-electrolytes.

Nitration of (a), (b), (c), (d), (e), (f) and (g) gave the products, bis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II), N,N'-ethylenebis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II), N,N'-propylenebis(2-hydroxy-3,5-dinitrobenzophenoniminato)Cu(II), bis(2-hydroxy-6-nitro-1-naphthaldiminato)Cu(II), N,N'-ethylenebis(2-hydroxy-6-nitro-1-naphthaldiminato)Cu(II), (2-hydroxy-6-nitro-1-naphthaldiminato)(3,5-dinitrosalicylaldiminato)Cu(II) and N,N'-ethylene(2-hydroxy-6-nitro-1-naphthaldiminato)(3,5-dinitrosalicylaldiminato)Cu(II), respectively.

The products isolated after bromination of (a), (b) and (c) were bis(2-hydroxy-3,5-dibromobenzophenoniminato)Cu(II), N,N'-ethylenebis(2-hydroxy-3,5-dibromobenzophenoniminato)Cu(II) and N,N'-propylenebis(2-hydroxy-3,5-dibromobenzophenoniminato)Cu(II) respectively.

As expected 3,5-dinitro derivatives are formed, the electrophilic substitution taking place in *ortho* and *para* positions to the hydroxy group. The -OH group has the mesomeric effect directing the incoming nitro group to *ortho* and *para* positions. A similar behaviour is observed in the case of the coordinated 2-hydroxybenzophenonimin complexes also. Dinitration takes place on each ligand resulting in compounds with four nitro groups. Even when excess of nitrating agent was used, nitration in the phenyl substituent (on the azomethine carbon) could not be brought about.

It is known that electrophilic substitution takes place only at C-6 in the free 2-hydroxy-1-naphthaldehyde²³. We find that in the case of coordinated

TABLE 1 — ANALYTICAL, ELECTRONIC SPECTRAL AND MAGNETIC MOMENT DATA OF THE NITRATED AND BROMINATED SCHIFF BASE COMPLEXES

Complexes	Found (Calc.), %		λ_{\max} (nm)	μ_{eff} (BM)
	Metal	N		
Bis-(2-hydroxy-3,5-dinitrobenzophenoniminato) Cu(II)*	9.84 (9.99)	12.83 (13.21)	575, 585	1.75
N,N'-Ethylenebis-(2-hydroxy-3,5-dinitrobenzophenoniminato) Cu(II)	9.25 (9.60)	12.26 (12.69)	550, 590	2.03
N,N'-Propylenebis-(2-hydroxy-3,5-dinitrobenzophenoniminato) Cu(II)	9.12 (9.41)	11.97 (12.43)	555, 590	1.99
Bis-(2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II)	12.60 (12.87)	11.34 (11.34)	565	1.85
N,N'-Ethylenebis-(2-hydroxy-6-nitro-1-naphthaldiminato) Cu(II)	12.10 (12.23)	10.81 (10.77)	560	1.90
(2-Hydroxy-6-nitro-1-naphthaldiminato)(3,5-dinitrosalicylaldiminato) Cu(II)	12.90 (13.00)	13.64 (14.32)	570	1.92
N,N'-Ethylene-(2-hydroxy-6-nitro-1-naphthaldiminato)(3,5-dinitrosalicylaldiminato) Cu(II)	12.09 (12.34)	12.97 (13.60)	555	1.88
Bis-(2-hydroxy-3,5-dibromobenzophenoniminato) Cu(II)*†	7.83 (8.24)	3.58 (3.63)	555	1.79
N,N'-Ethylenebis-(2-hydroxy-3,5-dibromobenzophenoniminato) Cu(II)*†	7.72 (7.97)	3.42 (3.51)	560	1.92
N,N'-Propylenebis-(2-hydroxy-3,5-dibromobenzophenoniminato) Cu(II)†	7.52 (7.83)	3.26 (3.45)	555	1.96

*Satisfactory C, H analyses were also obtained.

†Satisfactory Br analyses was obtained.

2-hydroxy-1-naphthaldehyde also, nitration takes place at C-6. Nitration of bis(2-hydroxy-1-naphthaldehydato)Cu(II) complexes gives dinitro compound.

Nitration of the mixed Schiff base complex (2-hydroxy-1-naphthaldiminato)(salicyldiminato)Cu(II) gave trisubstituted product. This is because, in 2-hydroxy-1-naphthaldehyde moiety only mono nitration occurs. This reaction also proves the mixed-ligand nature of the complex.

The bromination reaction has been carried out using N-bromosuccinimide. This reagent is normally known to bring about bromination through free radical mechanism. However, under the conditions of the present study using polar solvent (DMF), N-bromosuccinimide acts as an electrophilic reagent. The electrophile Br^+ attacks the two phenolic rings of the ligand molecule at the *ortho* and *para* positions, as in the case of nitration. Tetrabromo Schiff base complexes were thus obtained, in the case of 2-hydroxybenzophenone complexes. The substitution does not take place in the phenyl group attached to the azomethine carbon. This can be explained on the same lines as in the case of nitration reaction. The nitrated or brominated, Cu(II) Schiff base complexes are paramagnetic indicating the presence of one unpaired electron. The visible spectra exhibit a broad band around 565 nm for the nitrated monoamine Schiff base complexes and around 550 nm for the nitrated diamine Schiff base complexes. The bands for the corresponding bromo compounds are observed at 560 and 550 nm respectively.

From magnetic and spectral studies, it is inferred that these complexes have a square-planar geometry. Substitution does not affect the absorption spectra and magnetic properties.

The IR spectra of the substituted compounds show bands similar to those present in unsubstituted Schiff base complexes. In the IR spectrum of the substituted monoamine Schiff base complex, a band around 3200 cm^{-1} corresponds to free $=\text{N}-\text{H}$ group. This band is, however, absent in the substituted diamine Schiff base complexes. In both the monoamine and diamine Schiff base complexes, a band around 1620 cm^{-1} corresponds to $\nu\text{C}=\text{N}$. In all the compounds a band is observed around 1260 cm^{-1} which may be assigned to $\nu\text{C}-\text{O}$. The nitrated compounds show a strong band near 1550 cm^{-1} due to asymmetrical stretch of NO_2 group while a band appears around 1340 cm^{-1} due to symmetric stretch of NO_2 group.

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Formation Constants of Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Er(III) & Yb(III) Chelates of Salicylhydroxamic Acids

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The thermodynamic stability constants of Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Er(III) and Yb(III) complexes with salicylhydroxamic acid (SHA) and 5-chloro-, 5-bromo-, 5-nitro-, 4-chloro- and 4-bromo-salicylhydroxamic acids have been determined in 50% (v/v) aq dioxane at $\mu=0.1\text{M}$ (NaClO_4) and 30° using Calvin-Bjerrum potentiometric titration technique. The ionic nature of these chelates has been predicted from the examination of the Born equation and the relation $\log K = a \text{p}K + b$.

IN continuation of our work on the formation constants of transition metal chelates of salicylhydroxamic acid (SHA) and its substituted derivatives¹⁻³, we report in this note the results of our studies on some rare earth chelates with these ligands.

Rare earth oxides, obtained from Bhabha Atomic Research Centre, Bombay, were converted into the corresponding perchlorates and were estimated as oxalates. The details regarding the reagents, instrumentation and the calibration of glass electrode in the mixed solvent have been reported earlier⁴.