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Synthesis of Reactivity of Mixed Ligand Copper(II) Complexes

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A series of paramagnetic mixed ligand copper(II) complexe, CuAB, where A = salicylaldehyde and B = β-diketone/β-ketoimine are subjected to phenylisocyanation, α-naphthylisocyanation, nitrosation and diamine condensation reactions. Phenylisocyanate and α-naphthylisocyanate attack the γ-CH of β-diketone/β-ketoimine moiety and after prototropic rearrangement form amido derivatives. The results are presented based on spectroscopic results. The structure of the chelates is proposed.

Key Words: Mixed ligand, Copper(II) chelates, Phenylisocyanation, α-Naphthylisocyanation, Nitrosation, Amine condensation.

INTRODUCTION

When two or more chelating ligand species are added to a solution containing a metal ion, it has been observed that the metal ion can form complex(es) with all the ligand molecules separately or singly as one species (one at the same time, depending upon various conditions). More importance, so far, has been given to the study of mixed ligand complexes of bivalent as well as trivalent metal ions[1–4]. Besides, the spectroscopic studies, the polarographic measurements have also shown the formation of a number of mixed ligand complexes[5]. Further, a number of mixed ligand complexes of the type [M(AL)] where A = dipyridyl or *o*-phenanthroline, and L = an amino acid, mercapto acid, aromatic aldehyde, polyphenol, oxalic acid or a tridentate Schiff base, etc. with metal ions like M = Cu(II), Ni(II) have been isolated and extensively studied[6]. The mixed ligand complexes of Cu(II) of the type M(AL) have been reported recently by Bhattacharya *et al.*[7], where A is 2,2′-dipyridyl or *o*-phenanthroline and L is a β-diketone. Further, a number of literature documentation of similar studies on mixed ligand metal chelates of the type MLL′ (L = salicylaldehyde, L′ = 2-OH acetophenone or its methyl derivatives)[8], CuLL′ (L = salicylaldehyde, L′ = acetyl acetone)[9], Co(EA)(L) (EA = dianion of N,N′-ethylene bis(acetyl-acetoneimine), L = anion of various isonitroso-β-ketoimine ligands)[10] have been reported.

Although in the above account of mixed ligand transition metal complexes, some of them contain the unsubstituted γ-CH of β-diketone as one of the ligand moieties of the mixed ligand chelates, reports regarding the synthesis of various types of γ-CH substituted β-diketone mixed ligand complexes appear to be rare[8, 11, 12].

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The first attempt of Fuji[13] on the halogenation of N,N′-ethylene bis(acetylacetoneiminato) acetylacetato cobalt(III) has indicated the possibility of electrophilic substitution at the γ-CH of the acetylacetonate moiety (but not those of the other two acetylacetoneimine moieties). A similar report of electrophilic γ-CH substitution is the nitration of N,N′-ethylene-bis (salicylaldehyde iminato) acetylacetonato cobalt(III) monohydrate[11] and the bromination of *cis*-Co(EA)(L)[12]. The above account of γ-CH substituted mixed ligand complexes reveals that much is to be achieved yet in this direction. It was felt worthwhile to carry out some γ-CH substitution reactions at the protons of mixed ligand complexes containing β-diketonates and β-ketoiminates (as one of the ligand moieties) under different environments. This paper deals with the synthesis of a series of mixed ligand complexes of the type Cu(LL′) (where L = salicyaldehyde and L′ = β-ketoester/β-ketoimine) by different synthetic routes wherever possible and their characterization based on several physico-chemical techniques. The complexes are also subjected to various reactions with reagents like phenylisocyanate, α-naphthylisocyanate, aliphatic amines, diamines, nitric oxide.

EXPERIMENTAL

The synthesis of Cu(LL′) (L = salicyaldehyde, L′ = -diketone, β-ketoester or β-ketoimine) and their reaction product with phenylisocyanate, α-naphthlisocyanate, primary amines, diamine, nitric oxide are described below.

Preparation of mixed ligand (salicylaldehydato/β-diketonato) complexes, Cu(LL′)

L = Salicyaldehyde (Sal) and L′ = acetylacetone acac/methylacetoacetates (MAA)/ethylacetoacetate (EAA). The above-mentioned complexes were prepared by adding an alcoholic solution of salicylaldehyde [L = Sal] and β-diketone (L′ = acac/MAA/EAA) to a copper acetate solution in alcoholic medium (50 mL) in the 1 : 1 : 1 mole ratio. After mixing, the pH was raised by dilute ammonia to *ca.* 5.5; the mixture was stirred well at room temperature for a period of 1 h when a coloured crystalline solid separated out. The solid was filtered and washed with water, followed by 50% alcohol.

The yields of alcohol-recrystallized and vacuum dried respective mixed ligand (salicylaldehydato) (β-diketonato/β-ketoester) Cu(II) complexes varied from 85 to 90%. Diamine condensation reactions of mixed ligand salicylaldehydato ethylene/isopropylene-acetylacetoiminato) was prepared by the reported procedure[9].

Cu (Sal-en/ipn-acac)

Phenylisocyanation and α-napthylisocyanation reactions of mixed ligand complexes:

Cu(Sal)(acac/MAA/EAA·C_6H_5NCO),
Cu(Sal)(acac/MAA/EAA, α-naphthyl NCO),
Cu (Sal-en/ipn-acac·C_6H_5NCO)
Cu (Sal-en/ipn-acac. α-napthyl NCO)

The mixed ligand copper(II) complex, CuLL′, prepared as above and phenylisocyanate/α-naphthylisocyanate was taken in 1 : 1 mole ratio in dry benzene (50 mL). The mixture was then refluxed on a water bath in extremely dry condition until a greenish brown precipitate was obtained. The precipitate was filtered, washed with benzene, followed by chloroform. The yields of the recrystallised mixed ligand reacted complexes from benzene varied from 80–90%.

Amine condensation reaction of mixed ligand (salicylaldehydato) (phenyl or α-naphthylamido) β-diketo/β-ketoester) copper(II):

(i) Cu(Sal-NR) (L″)
(ii) Cu(Sal-en/ipn L″)

R = H or CH^3, L = acac·C_6H_5NCO or naphthyl NCO/MAA·C_6H_5NCO or naphthyl NCO/EAA·C_6H_5NCO or naphthyl NCO

An alcoholic (50 mL suspension of the (salicylaldiminato), (phenylamido or α-naphthylamido-β-diketonato) Cu(II); a parent complex, prepared by the procedure described above, was treated with an excess (5 mL) of diluted mono or diamine (in alcohol, 10 mL) (CH_3NH_2 or ethylenediamine/isopropylene diamine) and refluxed gently on a water bath for about 30–45 min. The precipitate was filtered, washed with water and finally with 50% alcohol. The respective yields and products were recrystallized from hot ethanol.

Nitrosation reaction of N,N′-ethylene/isopropylene nitric oxide, NO

This was produced by a slow and continuous addition of aqueous sodium nitrite solution to an acidified solution of ferrous sulphate heptahydrate[14]. (Salicylaldiminato-acetylacetoneiminato) Cu(II), Cu(Sal-en)/ipn-IAI), IAI = isonitroso-acetylacetone imine and one mole of N-N′-ethylene/isopropylene (salicylaldiminato-acetylacetone iminato) Cu(II).

The diamine-condensed product of Cu(Sal-en/ipn-acac) was taken in chloroform (40 mL) and nitrogen gas was bubbled at room temperature for about 25 min to remove oxygen. This was followed by bubbling dry gaseous nitric oxide through the solution with occasional shaking. After 1 h, the colour of the solution changed from parrot green to reddish green, when the bubbling of NO gas was stopped. Excess of NO was driven out by passing nitrogen gas. The solution was concentrated in vacuum where upon shining dark greenish red crystals of N,N′-en/ipn (salicylaldiminato-isonitroso acetylacetone iminato) Cu(II) were deposited. They were filtered and recrystallized from benzene, yield 35%.

RESULTS AND DISCUSSION

The analytical data of the various mixed ligand complexes and the reacted chelates are in good agreement with their proposed formulae (Tables 1–4). TLC analyses of all these complexes showed them to be pure single species. Among the reacted complexes, phenylamido and α-naphthylamido substituted mixed ligand complexes (Cu(Sal)acac/MAA/EAA/C_6H_5NCO or α-$C_{10}H_7NCO$) are less soluble in organic solvents while the parent mixed ligand complexes are soluble in common organic solvents. The magnetic susceptibility measurements indicate that all the complexes including the parent complexes, as paramagnetic (μ_{eff} = 1.91 to 1.94 BM) corresponding to square-planar geometry around copper(II). The visible absorption spectra of the unsubstituted mixed ligand parent complexes in chloroform reveal one band around 1900 cm^{-1} confirming the characteristic square planar geometry of the complexes[8, 9]. The mull absorption electronic spectra of the phenylamido substituted amine condensed complexes with a broad band around 1900 cm^{-1} show the same geometry.

The parent mixed ligand complexes Cu(Sal)(acac)[9], Cu(Sal)(MAA) and Cu(Sal)(EAA) exhibit characteristic vibrational frequencies in the range 1630–1620, 1340–1315,[9, 11] 830–760, 1220–1200 and 1580–1565 cm^{-1} (Tables 5 and 6)[8, 9].

TABLE-1.1
ANALYTICAL AND MAGNETIC DATA OF Cu(LL′) AND THEIR PHENYLAMIDO SUBSTITUTED DERIVATIVES

Complex (colour)	m.p. (°C)	μ_{eff} (B.M.)	Analytical data, %†			
			C	H	N	Cu
Cu(Sal)(acac) (Pale green)	—	1.91	50.72 (50.79)	4.22 (4.30)	—	22.32 (22.39)
Cu(Sal)(acac·C_6H_5NCO) (Brown)	>220	1.90	56.59 (56.63)	4.20 (4.26)	3.42 (3.48)	15.70 (15.77)
Cu(Sal)(MAA) (Dark green)	200	1.91	48.16 (48.08)	3.99 (4.04)	—	21.11 (21.20)
Cu(Sal)(MAA·C_6H_5NCO) (Yellowish green)	195	1.90	54.41 (54.47)	4.01 (4.10)	3.28 (3.34)	15.12 (15.17)
Cu(Sal)(EAA) (Green)	190	1.91	49.70 (49.75)	4.46 (4 51)	—	20.18 (20.25)
Cu(Sal)(EAA·C_6H_5NCO) (Greenish yellow)	222	1.90	55.41 (55.48)	4.38 (4.43)	3.17 (3.24)	14.62 (14.68)
Cu(Sal)(C_6H_5AI) (Brown)	208	1.93	50.90 (50.96)	4.58 (4.64)	4.90 (4.95)	22.41 (22.47)
Cu(Sal)(AI·C_6H_5NCO) (Greenish brown)	217	1.91	56.71 (56.77)	4.41 (4.52)	6.91 (6.97)	15.75 (15.81)
Cu(Sal)(C_6H_5AI) (Brown)	210	1.96	0.16 (60.23)	4.71 (4.78)	3.82 (3.90)	17.61 (17.70)

*L = salicylaldehyde (Sal)

L′ = acetylacetone (acac)/methylacetoacetate (MAA)/ethylacetoacetate (EAA)/acetylacetoneimine (AI)/acetylacetonephenylimine (C_6H_5AI).

†The theoretical values are given in parentheses below their respective observed values.

TABLE-2

COLOUR, MELTING POINT, MAGNETIC MOMENT OF MONOAMINE CONDENSED SCHIFF BASE COMPLEXES OF PHENYLAMIDO SUBSTITUTED COPPER (II) MIXED LIGAND DERIVATIVES

Complex	Colour	m.p. (°C)	μ_{eff} (B.M.)	Analytical data, %*			
				C	H	N	Cu
Cu(Sal-NH) (acac·C_6H_5NCO)	Dark brown	150	1.91	56.70 (56.77)	4.49 (4.52)	5.92 (6.97)	15.78 (15.81)
Cu(Sal-N-CH_3) (acac·C_6H_5NCO)	Yellowish brown	172	1.91	57.69 (57.75)	4.80 (4.86)	6.69 (6.74)	15.21 (15.28)
Cu(Sal-NH) (MAA·C_6H_5NCO)	Brown	180	1.91	54.53 (54.60)	4.28 (4.35)	6.62 (6.70)	15.14 (15.21)
Cu(Sal-N-CH_3) (MAA·C_6H_5NCO)	Dark brown	160	1.93	55.53 (55.61)	4.61 (4.68)	6.42 (6.49)	14.65 (14.71)
Cu(Sal-NH) (EAA·C_6H_5NCO)	Brown	152	1.94	55.51 (55.61)	4.59 (4.68)	6.43 (6.49)	14.67 (14.71)
Cu(Sal-N-CH_3) (EAA·C_6H_5NCO)	Brownish yellow	165	1.93	56.49 (56.55)	4.92 (4.98)	6.20 (6.28)	14.19 (14.25)

*The theoretical values are given in parentheses below their respective observed values.

TABLE-3

COLOUR, MELTING POINT, MAGNETIC MOMENT AND ANALYTICAL DATA OF DIAMINE CONDENSED SCHIFF BASE COMPLEXES OF PHENYLAMIDO SUBSTITUTED COPPER(II) MIXED LIGAND DERIVATIVES

Complex	Colour	m.p. (°C)	μ_{eff} (B.M.)	Analytical data, %*			
				C	H	N	Cu
Cu(Sal-en-acac·C_6H_5NCO)	Dark brown	200	1.91	58.98 (59.07)	4.92 (4.97)	9.82 (9.84)	14.81 (14.88)
Cu(Sal-en-MAA·C_6H_5NCO)	Brown	225	1.91	56.89 (56.93)	4.72 (4.79)	9.42 (9.49)	14.30 (14.34)
Cu(Sal-en-EAA·C_6H_5NCO)	Light brown	238	1.92	57.74 (57.81)	5.01 (5.08)	9.11 (9.20)	13.81 (13.90)
Cu(Sal-ipn-acac·C_6H_5NCO)	Brown	195	1.91	59.84 (59.91)	5.19 (5.27)	9.47 (9.53)	14.36 (14.41)
Cu(Sal-ipn-MAA·C_6H_5NCO)	Greenish brown	189	1.93	57.74 (57.81)	5.01 (5.08)	9.13 (9.20)	13.82 (13.90)
Cu(Sal-ipn-EAA·C_6H_5NO)	Brown	191	1.94	58.59 (58.64)	5.29 (5.36)	8.84 (8.92)	13.42 (13.49)

*The theoretical values are given in parentheses below their respective observed values.

TABLE-4
COLOUR, MELTING POINT, MAGNETIC MOMENT AND ANALYTICAL DATA OF NITROSATED DIAMINE SCHIFF BASE COMPLEXES OF COPPER(II) MIXED LIGAND DERIVATIVES

Complex	Colour	m.p. (°C)	μ_{eff} (B.M.)	Analytical data, %*			
				C	H	N	Cu
Cu(Sal-en-IAI)	Greenish red	140	1.91	49.84 (49.91)	4.43 (4.50)	12.44 (12.48)	18.80 (18.86)
Cu(Sal-ipn-IAI)	Greenish red	162	1.91	51.29 (51.34)	4.83 (4.89)	11.93 (11.98)	18.03 (18.11)

*The theoretical values are given in parentheses below their respective observed values.

TABLE-5
CHARACTERISTIC INFRARED FREQUENCIES (IN cm^{-1}) OF COPPER(II) MIXED LIGAND COMPLEXES AND THEIR PHENYLAMIDO DERIVATIVES IN NUJOL MULL

Complex	Sal		β-diketone·φNCO/β-ketoester·C_6H_5NCO/ β-ketoimine.C_6H_5NCO (B)					
			CO			Amide		
	ν(CO) phenolic	ν(C=O) aldehydic	π(CH)	δ(CH)	ν (coordinated)	ν(NH)	ν(CO)	ν(NH)
Cu(Sal)(acac)	1320 s	1625 m	830 m	1200 m	1580 s	—		—
Cu(Sal) (acac·C_6H_5NCO)	1315 s	1625 m	—	—	1570 s	—	1650 s	3200–3350 m,b
Cu(Sal)(MAA)	1340 s	1630 m	760 m	1200 m	1570 s	—	—	—
Cu(Sal) (MAA·C_6H_5NCO)	1340 s	1630 m	—	—	1570 s	—	1660 s	3200–3350 m,b
Cu(Sal)(EAA)	1330 s	1620 m	830 m	1210 m	1565 s	—	—	—
Cu(Sal) (EAA·C_6H_5ONCO)	1330 s	1620 m	—	—	1565 s	—	1660 s	3200–3350 m,b
Cu(Sal)(AI)	1330 s	1620 m	830 m	1210 m	1530 s	3340 m	—	—
Cu(Sal) (AI·C_6H_5NCO)	1330 s	1620 m	—	—	1535 s	3340 m	1650 s	3150–3350 m,b

TABLE-6

CHARACTERISTIC INFRARED FREQUENCIES (IN cm^{-1}) OF Cu(Sal·NR) (β-DIKETONE/β-KETOESTER)* COMPLEXES IN NUJOL MULL

Complex†	Sal-NR		β-diketone·φNCO/β-ketoester·φNCO/ β-ketoimine·φNCO (B)			
	ν(CO) phenolic	ν(C=N)	ν(NH)	ν(CO) (coordinated)	Amide	
					ν(CO)	ν(NH)
Cu(Sal-NH) (acac·φNCO)	1320 m	1615 m	3460 s	1570 s	1650 s	3350 (m, b)
Cu(Sal-NCH$_3$) (acac·φNCO)	1320 m	1610 m	—	1575 s	1650 s	3350 (m, b)
Cu(Sal-NH) (MAA·φnco)	1320 m	1610 m	3450 s	1560 s	1650 s	3360 (m, b)
Cu(Sal-NCH$_3$) (MAA·φNCO)	1320 m	1605 m	—	1560 s	1640 s	3350 (m, b)
Cu(Sal-NH) (EAA·φNCO)	1310 m	1600 m	3460 s	160 s	1640 s	3355 (m, b)
Cu(Sal-NCH$_3$) (EAA.φONCO)	1320 m	1605 m	—	1565 s	1655 s	3355 (m,b)

*R = H or CH$_3$

†The frequencies due to ν(C=O) (aldehydic), π(CH) and δ(CH) are absent in all these complexes.

From the absence of the IR band around 3400 cm^{-1}, characteristic of phenolic OH of salicylaldehyde[9, 11] indicates that phenolic OH is involved in bonding with the metal ion acceptor. This is substantiated by the presence of coordinated phenolic ν(CO) (1340–1315 cm^{-1})[9, 11].

Further, the presence of two different vibrational stretching frequencies in the region characteristic of carbonyl group can be attributed to aldehydic CO (1630–1620 cm^{-1}) and β-diketone CO (1580–1565 cm^{-1})[9, 11] respectively. The lower shift of 40–30 cm^{-1} as compared to their corresponding free ligand bands suggests coordination through the CO to the metal ions[9], in which there is delocalization of π electron. The presence of γ-CH group of β-diketone and its derivatives is indicated by π(CH) (830–760 cm^{-1}) and δ CH (1220–1200 cm^{-1}) bands. The above IR data suggest the presence of both coordinated salicyaldehydato and β-diketonato ligand moieties in the metal complexes.

Metal donor bonding of phenylisocyanated and α-naphthylisocyanated mixed ligand chelates

The phenylisocyanated and α-naphthylisocyanated mixed ligand chelates show the characteristic bands for the coordinated β-diketones and coordinated salicylaldehydato moieties.

They show characteristic bands for the coordinated β-diketone, with prominent absence of δ(CH) (1220–1200 cm^{-1})[14, 15] observed in the Cu(Sal)(acac/MAA/EAA) complexes indicating the substitution of γ(CH) proton of the β-diketone ligand moiety by a substituent. The presence of two new additional bands in the regions 1660–1650 cm^{-1} and 3350–3100 cm^{-1} in all probability can be attributed to the amido CO and amido NH respectively[15–19], indicating the presence of ν(CO) and γ(NH) of phenylamido and α-naphthylamido group and the absence of ν(CH) frequencies suggests the electrophilic addition at γ(CH) followed by prototropic rearrangement. Bonding mode of the amine condensed mixed ligand phenylamido and α-naphthylamido substituted copper(II) chelates. As discussed in the previous presentation, the phenylamido substituted derivatives of Cu(Sal) (acac/MAA/EAA·C_6H_5NCO or α-$C_{10}H_7NCO$) exhibit

(a) coordinated phenolic hydroxyl oxygen,
(b) coordinated aldehydic carbonyl, and
(c) coordinated β-diketone carbonyl.

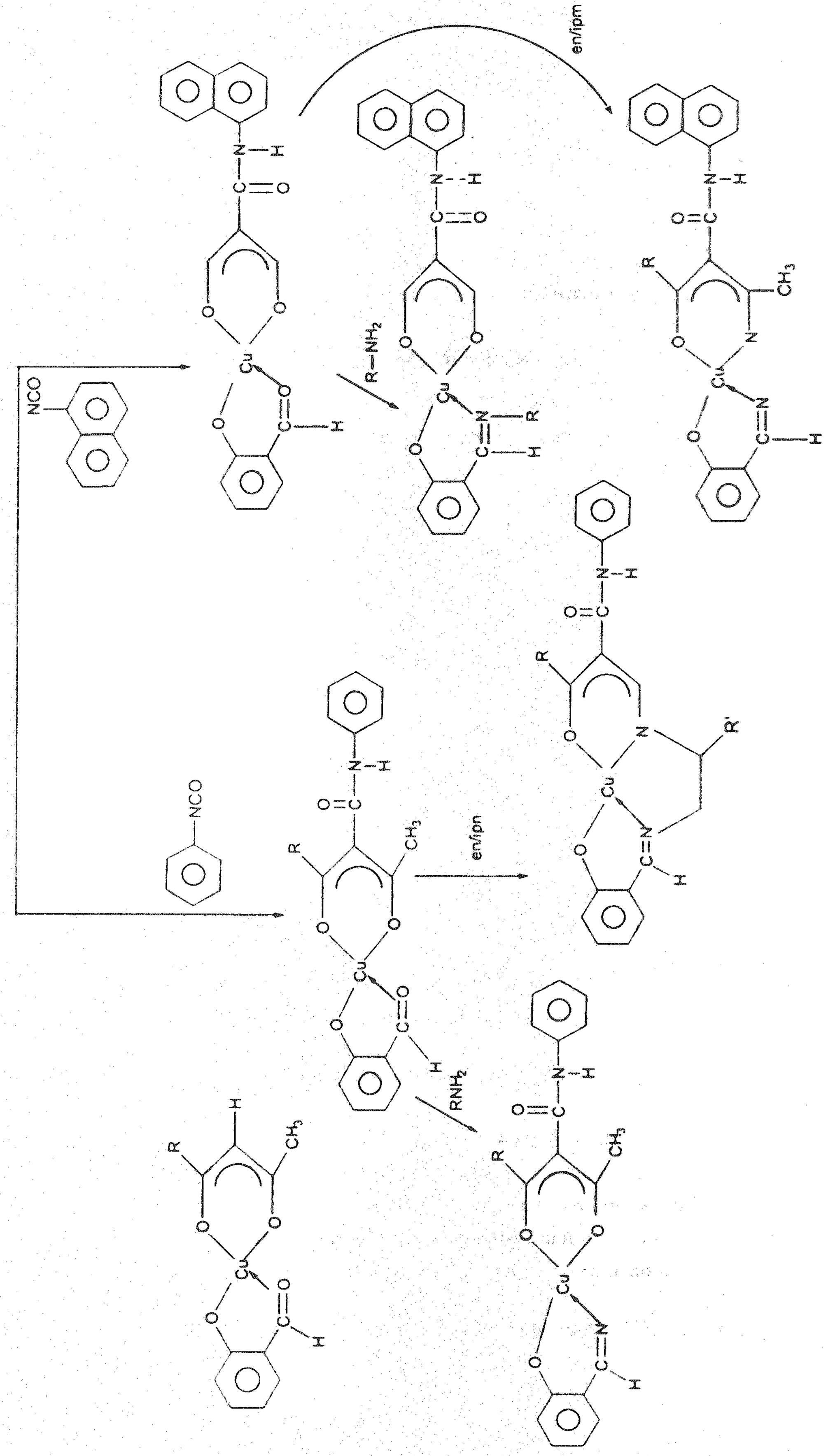
It is well known that Schiff base coordination always involves either aldehydic or ketonic oxygen[20]. One can without much difficulty anticipate, more or less, the same geometry with changes in the aldehydic CO or ketonic CO or both. The present set of complexes exhibits almost all the frequencies of the corresponding Cu(Sal) (acac/MAA/EAA·C_6H_5NCO or α-$C_{10}H_7NCO$) (Table-2), except for the prominent absence of aldehydic $>C{=}O<$ around 1625 cm^{-1} (observed in the former set) and its replacement with a new frequency around 1615–1600 cm^{-1} can very well be attributed to the presence of azomethine $>C{=}N<$ group in place of the aldehydic group. In ammonia condensation derivatives, the band around 3460–3450 cm^{-1} due to imine NH stretching frequency[8].

With the above arguments for the monoamine condensed products, all the phenylamido and α-naphthylamido diamine Schiff base mixed ligand complexes, besides the absence of aldehydic carbonyl, also exhibit the absence of ν(CO) of coordinated β-diketone moiety. Further the presence of new band around 1540 cm^{-1} suggests that, besides the presence of azomethine $>C{=}N—$ in place of aldehydic $>C{=}O$ (discussed above), there is a similar $>C{=}O$ band the place of coordinated carbonyl group[1-10].

Hence these findings lead to the conclusion that both NH_2 groups of ethylenediamine/isopropylene diamine undergo condensation with $>C{=}O$ of the salicylaldehyde moiety and that of the phenyl/amido/α-naphthyl/amido β-diketone moiety[9].

Metal donor bonding of the nitrosated product of N,N′-ethylene/isopropylene-(salicylaldimine-acetylacetone imino) Cu(II)

Bhattacharya *et al.*[9] reported the structural aspects of Cu(Sal-en/ipn-acac)[9]. From the reported structures, all the amine condensed derivatives have coordinated phenolic CO (1315 cm^{-1}) $>C{=}O$, coordinated $>C{=}N$ azomethine (1600 cm^{-1}), coordinated -C—N (1540 cm^{-1}) δ(CH) (1200 cm^{-1}) and π(CH) (795 cm^{-1}) and coordinated CO (1575 cm^{-1}). Besides the appearance of the common characteristic IR frequencies of the salicylaldehydato moiety, the nitrosated product of Bhattacharya complex displays certain new additional bands due to the nitrosated part of the β-diketone moiety. These are 1645 cm^{-1} due to acetyl CO and 1210 cm^{-1} characteristic of N-bonded NO[21]. They also show the



Schemes I and II

disappearance of the π(CH) (795 cm^{-1}) and δ(CH) (1200 cm^{-1}) and coordinated carbonyl 1575 cm^{-1} of the non-nitrosated product. All these evidences show that nitrosation has occurred at γ(CH) and the substituted nitroso group is coordinated to the metal ion through isonitroso nitrogen, dislodging the already coordinated carbonyl CO (absence of 1570 cm^{-1} and appearance of 1645 cm^{-1} bands). Similar results have also been observed in the nitrosation reactions of a quadridentated β-ketoimine complexes[22–24].

Considering the above discussion the molecular structure of parent complexes, phenyl and naphthyl amido substituted complexes, amine/diamine condensed products are given in **Scheme-1** and nitrosated products are given in **Scheme 2.**

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