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Heterosubstitution Reactions on Coordinated Bivalent Quadridentate Ligands of Nickel(II) and Copper(II)

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Studies on properties of the isonitroso-β-diketones are conducted. Reactivity of coordinated ligands of bivalent quadridentate chelates of Ni(II) and Cu(II) is studied. Diazo coupling reactions on metal Schiff bases are conducted. Selective nature of the diazo coupling reactions is demonstrated by the isolation of monodiazo coupled products. To prove quasiaromaticity, iodination and α-naphthylisocyanation reactions are conducted on monoaryldiazo bivalent tetradentate β-ketoimine complexes of Ni(II) and Cu(II) and the products are characterised by analytical, magnetic, IR, NMR and ESR techniques.

INTRODUCTION

Studies on coordinating properties of the isonitroso-β-diketones are interesting since isonitroso group (>C═NOH) can function ambidentately yielding chelate linkage isomers[1–3]. It has been shown that hydroximino group exhibits its dual modes of coordination, depending on the metal ion, the electronic properties of the substituents, azomethine-nitrogen and isonitroso-carbon. Electrophilic substitution reactions at the γ-carbon of the coordinated β-diketones and a few β-ketoimines have been well studied[4–11]. The nature of substitution largely centres around halogenation, nitration, thiocyanation, acylation, formylation, chloromethylation, aminomethylation and nitrosation reactions. However, very little information is available in the study of diazo coupling reactions of coordinated ligands. Balakrishnan *et al.*[12] have reported that the diazo coupling reactions proceed readily leading to well defined products. It was shown by Hirsch *et al.*[13] that when the Schiff bases derived from acetylacetone and 1,2-diamine are reacted with diazonium salts, they give rise to products which are formulated as 3,10-bishydrazone derivatives. They have suggested that the protons which are involved in hydrogen bonding may be replaced by divalent metal ions, giving rise to stable metal chelates. This led Balakrishnan *et al.*[12] to investigate whether the products formed from the diazo coupling reaction of metal Schiff bases can be formulated as glyoxal hydrazoneimine (I) derivative or aryl diazo substituted compounds (II).

To prove the quasiaromatic character of Schiff base complexes of type (III), heterosubstitution reactions were carried out. The selective nature of the diazo coupling reaction is demonstrated by the isolation of monodiazo coupled products.

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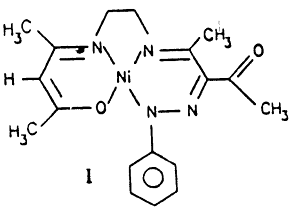

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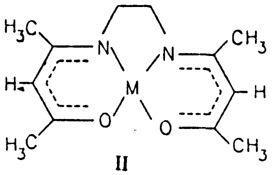

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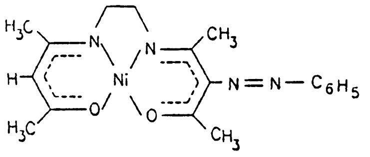


M = Cu(II) or Ni(II)

(III)

This is achieved only through the diazo coupling reactions of bivalent tetradentate β-ketoimine complexes of nickel(II) and copper(II). Hence in this paper iodination and α-naphthylisocyanation reactions are studied and reported on monoaryldiazo bivalent tetradentate β-ketoimine complexes of nickel(II) and copper(II).

RESULTS AND DISCUSSION

All heterosubstituted complexes are crystalline in nature and are sparingly soluble in common organic solvents. The analytical data of the complexes are shown in Table 1. The neutral nature of these complexes is shown by their electrolytic nature in acetone (Λ_M *ca.* 2×10^{-2} ohm^{-1} in 10^{-3} M solution). The square-planar geometry of the nickel(II) complexcs is evident from the diamagnetic nature of the complexes[12].

TABLE-1

ANALYTICAL DATA OF THE HETEROSUBSTITUTED M^{II} (AI·N_2Ph-en-AI) COMPLEXES(M^{II} = Cu or Ni)

Complex	Colour	Analytical data, found/(calcd.), %			
		C	H	N	Ni
Ni(AI·N_2Ph-en-AI·I)	Dark red	42.15	4.27	10.99	11.41
		(42.22)	(4.33)	(10.95)	(11.47)
Ni(AI·N_2Ph-en-AI·$C_{10}H_7$NCO)	Reddish brown	62.78	5.21	12.59	10.52
		(62.84)	(5.27)	(12.64)	(10.59)
Cu(AI·N_2Ph-en-AI·I)	Purple	41.76	4.22	10.88	12.34
		(41.83)	(4.29)	(10.84)	(12.29)
Cu(AI·N_2Ph-en-AI·$C_{10}H_7$NCO)	Brown	62.23	5.18	12.46	11.30
		(62.29)	(5.23)	(12.53)	(11.36)

All the complexes do not show any definite melting point and decompose above 280°C.

The copper(II) complexes are paramagnetic with μ_{eff} = 1.88 B.M. (Table-1) which is as expected for copper(II) complexes without any magnetic interaction.

Addition of silver nitrate to a methanolic solution of the iodinated nickel(II) complex did not yield any precipitate of silver iodide. This shows that iodine is not present in the complex in the ionic form. The diamagnetic nature of nickel(II) complexes rules out 5-coordination of nickel(II) with iodine as an axial ligand. No solution studies are possible for the α-naphthylisocyanation reaction products owing to their sparingly soluble nature in common organic solvents.

The electronic absorption spectra of iodinated complexes and the corresponding monodiazo coupled nickel(II) β-ketoimine complexes are very similar. A band around 21050 cm^{-1} is observed in the visible region and it is assigned to a charge transfer band overlapping d-d transition. The resemblance of the electronic spectra of the iodinated and the starting monodiazo coupled complexes shows their structural similarity.

Monodiazo coupled products are obtained only through the diazo coupling reactions of bivalent tetradentate β-ketoimine complexes of nickel(II)/copper(II). These monodiazo coupled products exhibit linkage isomerism. It can be visualised as 3-aryldiazo substituted β-ketoimines (II), while the other isomer is produced due to intramolecularly rearranged glyoxal hydrazoneimine derivative (I).

Bonding of the monoaryl diazo chelates

The IR spectra of the complexes show four main bands in the region 1700–1500 cm^{-1} (Table-2). The assignments of these bands are made in comparison with the position of ν(CO) and ν(CN) in the parent complexes.[12, 14] On this basis, the bands at 1660 and 1565 cm^{-1} are assignable to ν(CO) and ν(CN) of the glyoxal hydrazoneimine part and the 1520 and 1600 cm^{-1} bands to the ketoimine part. Further out-of-plane and in-plane vibrations of γ-CH are assignable to bands at 790–780 and 1200–1190 cm^{-1} respectively[15].

TABLE-2

CHARACTERISTIC IR FREQUENCIES (cm^{-1}) OF HETEROSUBSTITUTED $M^{II}(AI{\cdot}N_2Ph\text{-}en\text{-}AI)$ COMPLEXES (M^{II} = Cu or Ni)

Complex	Ketoimine moiety					Glyoxalhydrazone imine moiety	
	$\pi_{(CH)}$	$\delta_{(CH)}$	$\nu_{(CO)}$ (amido)	$\nu_{(NH)}$ (amido)	$\nu_{(CO)}$ coordinated	$\nu_{(CO)}$	$\nu_{(CN)}$
$Ni(AI{\cdot}N_2Ph\text{-}en\text{-}AI)$	790 s	1180 s	—	—	1525 s	1660 s	1565 m
$Ni(AI{\cdot}N_2Ph\text{-}en\text{-}AI{\cdot}I)$	—	—	—	—	1509 s	1647 m	1563 m
$Ni(AI{\cdot}N_2Ph\text{-}en\text{-}AI{\cdot}C_{10}H_7NCO)$	—	—	1708 s	3000–3400 m, b	1511 s	1635 m	1554 m
$Cu(AI{\cdot}N_2Ph\text{-}en\text{-}AI)$	780 s	1200 s	—	—	1520 s	1600 s	1565 m
$Cu(AI{\cdot}N_2Ph\text{-}en\text{-}AI{\cdot}I)$	—	—	—	—	1525 s	1665 m	1560 m
$Cu(AI{\cdot}N_2Ph\text{-}en\text{-}AI{\cdot}C_{10}H_7NCO)$	—	—	1685 s	3000–3300 m, b	1511 s	1645 m	1555 m

The PMR studies of nickel complexes are helpful in arriving at the structure of the complexes proposed for monodiazo coupled products. The presence of a signal at 4.9 δ is due to γ-CH in the complexes. This suggests the monosubstituted nature of these complexes. The PMR signals for structure II would give rise to two sets of signals (ring CH_3 protons). These signals may not be significantly different from one another. However, structure I is expected to give four methyl signals, three belonging to the chelate ring and one to the terminal part of the molecule. The signal at 1.86 δ is similar to that of β-ketoimine complexes and therefore it has been assigned to (CH_3—C=N—) of the non-substituted ring while the signal at 1.33 δ is assignable to (CH_3—C—O—) group. The above assignments are reasonable since the neighbouring phenyl ring induces high field shift in methyl protons, because they are oriented in the shielding zone of the phenyl ring[12]. This behaviour is expected for structure II and, therefore, I is the most probable structure for the intramolecularly rearranged glyoxal hydrazoneimine derivative. The signals of the bridging and phenyl protons occur at different fields compared to disubstituted products. Therefore this effect arises from unsymmetrical π-conjugation operating in the monosubstituted products.

TABLE-3

PMR DATA (δ ppm) OF HETEROSUBSTITUTED Ni(AI·N_2Ph-en-AI) COMPLEXES

Complex	Ring —CH_3	Terminal —CH_3	γ-CH	Diamine group	Phenyl	α-Naphthyl	Amido NH
Ni(AI·N_2Ph-en-AI)	1.33 (s, 3) 1.93 (s, 3)	2.43 (s, 6)	4.9 (s, 1)	3.26 (sextet, 4)	7.4 (m, 5)	—	—
Ni(AI·N_2Ph-en-AI·I)	1.30 (s, 3) 1.90 (s, 3)	2.46 (s, 6)	—	3.20 (sextet, 4)	7.4 (m, 5)	—	—
Ni(AI·N_2Ph-en-AI·$C_{10}H_7$NCO)	1.30 (s, 3) 1.90 (s, 3)	2.46 (s, 6)	—	3.20 (sextet, 4)	7.4 (m, 5)	7.4–7.8 (m, 7)	8.39 (b, 1)

The reaction of aryl diazonium chloride with nickel(II) complexes of β-ketoimines generally yields hydrazoneimine derivatives. The reaction of metal β-ketoimine with aryl diazonium chloride proceeds through the cleavage of M—O bond followed by the formation of hydrazoneimine and then the coordination of the α-N to the metal ion may occur resulting in the formation of hydrazoneimine derivatives. The fact that the products bis(glyoxalhydrazoneimine) complexes of nickel(II) are obtained by both direct and indirect methods suggests that they exist in the stable hydrazoneimine form (I) rather than the aryl diazo form (II).

IR and PMR Spectra of Heterosubstituted Chelates

The quasiaromatic and selective nature of the reactions of tetradentate Schiff base complexes of nickel(II) and copper(II) is further evidenced by the heterosubstitution reactions such as iodination and α-naphthylisocyanation. The α-naphthylisocyanated product exhibits two new bands around 1708–1685 cm^{-1} and a broad band centred around 3400–3000 cm^{-1}. Further, the products also show the absence of bands due to π(CH) and δ(CH) indicating the substitution at γ-CH. The new bands around 1708–1685 and 3400–3000 cm^{-1} are characteristic of amido CO and amido NH respectively[18–20]. It is believed that α-naphthyl isocyanate attacks the methine proton and after prototropic rearrangement forms α-naphthyl amido substituent[19, 20]. These results are further substantiated by PMR spectra. In nickel(II) chelates, the signal around 4.8–4.9 δ which is characteristic of methine proton disappears after α-naphthylisocyanation. Further, a broad medium signal found around 8.39 δ corresponds to NH proton. Therefore it appears that α-naphthyl isocyanate adds on to methine proton and after prototropic rearrangement forms α-naphthylamido substituent. The heterosubstituted product formed is another evidence to show the quasiaromatic character of quadridentate Schiff base chelates. The IR spectra of all iodo substituted complexes of nickel(II) and copper(II) chelates exhibit no bands due to π(CH) and δ(CH). By comparing with the IR spectra of monoaryl diazo substituted β-ketoiminates of nickel(II) and copper(II) which exhibit the presence of bands due to π(CH) and δ(CH), iodo substitution is confirmed. Qualitative tests also confirmed the presence of iodine in the complexes. Further the PMR spectra of iodo derivative of nickel(II) complex exhibit no signal due to γ-CH in the region 4.9δ.

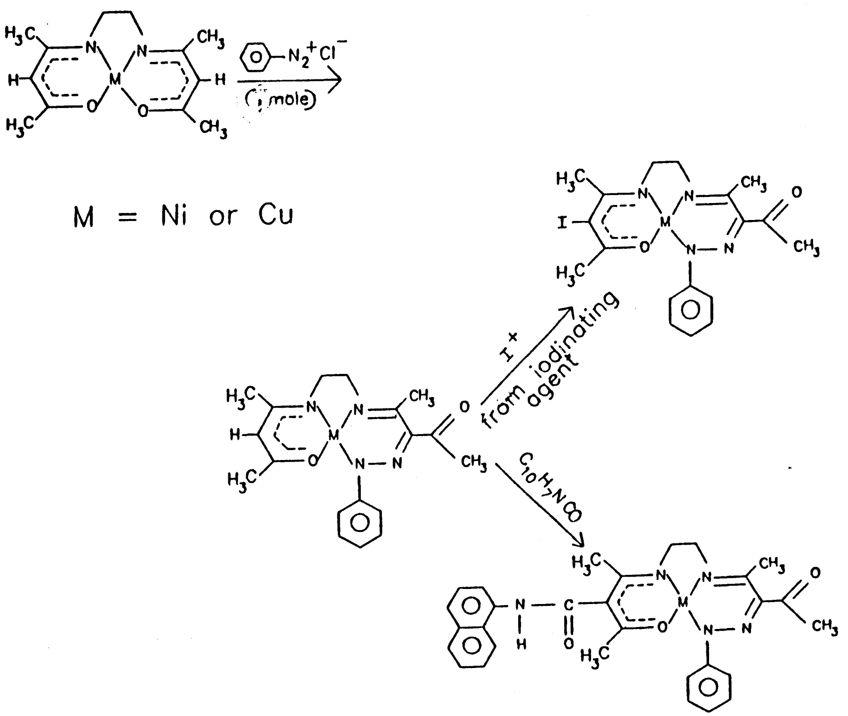
The ESR spectra of the copper(II) complexes exhibit the expected ligational environment around copper(II) in monoaryl diazonium substituted complexes of ethylene bis(acetylacetoneimino) copper(II). The changes in the ligational environment as a result of change in the mode of coordination can be seen from the hyperfine splitting in the ESR spectra of copper(II) complexes. The first derivative ESR spectrum of the copper(II) complex shows nearly equally spaced four main peaks. This is due to the hyperfine interaction of the unpaired electron with $^{63}Cu(I = 3/2)$. The high field line is split into seven lines in the spectra of monoaryl diazonium copper(II) complexes. This clearly reveals that the existence of ligational environment is (CuN_3O) chromophore in monoaryl diazo substituted complexes.

The α-naphthylamido and iodo aryl diazonium substituted complexes of copper(II) exhibit similar ESR spectra. Hence α-naphthylisocyanation and iodination do not affect the ligational environment as found in monoaryl diazonium substituted complexes. Scheme 1 confirms the mode of bonding in the heterosubstituted complexes.

The ESR parameters of the complexes are given in Table-4 and they are in the range expected for square-planar copper(II) complexes. The α^2, which is a measure of the covalency in the metal-ligand bonding, falls in a range which is very close to that observed for some copper(II) Schiff base complexes[21].

TABLE-4
ESR DATA OF HETEROSUBSTITUTED $Cu(AI\cdot N_2PH\text{-}en\text{-}AI)$ COMPLEXES

Complex	g	A_{Cu} (gauss)	A_N (gauss)	α^2
$Cu(AI\cdot N_2Ph\text{-}en\text{-}AI)$	2.070	89.45	11.78	0.790
$Cu(AI\cdot N_2Ph\text{-}en\text{-}AI\cdot I)$	2.073	87.60	11.63	0.791
$Cu(AI\cdot N_2Ph\text{-}en\text{-}AI\cdot C_{10}H_7NCO)$	2.081	88.72	11.80	0.792

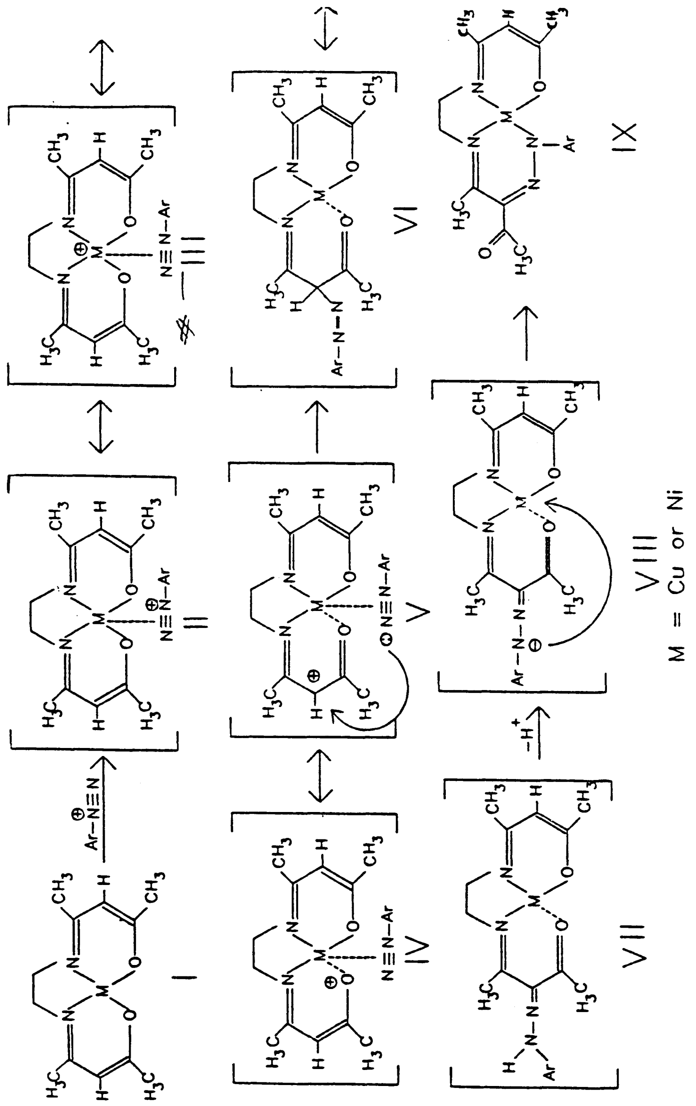


Scheme-1. Heterosubstitution of monoaryl diazo substituted ethylene bis(acetylacetone-imino) metal(II) complexes

Proposed Mechanism for the Formation of Monodiazo Coupled Complexes

On the basis of the structure assigned to the monodiazo coupled complexes, a probable mechanism, depicted in Scheme-2, is proposed. The primary step of the reaction is envisaged as the formation of a transient species II in which the aryl diazonium ion (Ar—N_2^+) is coordinated to the metal ion. Though there is no direct evidence for the formation of this intermediate, examples are known for such coordination in the literature[22–24]. The formation of II can be described in terms of the three resonance forms III, IV and V in which the positive charge is delocalised. Subsequent to this step the coordinated aryl diazonium ion attacks the γ-CH carbon forming a diazo derivative VI. The diazo derivative can exist in a tautomeric form VII. From VII the proton of the α-nitrogen is abstracted by CH_3COO^- and this is accompanied by metal-oxygen bond cleavage and subsequently the α-nitrogen of the hydrazone coordinates to the metal ion to form IX. Thus, the proposed mechanism is that the aryl diazonium ion attacks the organic chelate through the coordination sphere of the metal ion.

Interestingly, unlike the conventional electrophilic substitution reactions, the diazo coupling reaction is accompanied by change in the ligational environment around the metal ion. This behaviour seems to be characteristic of the diazo coupling reaction and may be attributed to the tendency of the diazo to tautomerise to the hydrazone form which coordinates strongly to the metal ion in preference to the already coordinated carbonyl group.



Scheme-2. Proposed mechanism for the monodiazo coupling reaction

Comparison of the Reactivity of Copper(II) and Nickel(II) Chelates

It is known that monoaryl diazo substituted acetylacetoneimine complexes of nickel(II) and copper(II) undergo electrophilic substitution reaction at γ-CH position. Qualitative comparisons of the rates of these reactions have been made by noting the time required for the reactions to occur. It is found that the reaction proceeds relatively faster for the copper(II) complexes.

Reactions of this type at the methine position of 2,4-pentanedione complexes are believed to be electrophilic[25]. The base-catalysed methine proton exchange in [Co(Baen)X_2] suggests similar behaviour for these complexes[26]. Elfring and Rose[27], and Martin and Cumings[28] have found that the pKa's for the reactive methine hydrogens of 13 and 14-membered tetraaza macrocyclic complexes of Ni(II) are 3 units less than those of the corresponding Cu(II) complexes. The replacement of Ni(II) by Cu(II) in both the 13- and 14-membered systems results in a 100-fold decrease in acidity. Therefore, if these reactions are electrophilic, it is not surprising that the copper compounds react faster than the nickel compounds.

It is of interest to note here the assumptions made by Nelson *et al.*[29] to explain the enhanced reactivity of Cu(baen) complexes towards isocyanates. The electron rich methine carbon affords suitable site of attack for the electrophiles and this is due to the interaction of the pseudo-aromatic π-system with the π-cloud of the aryl diazonium ion. This interaction is governed by the polarisation of the ligand by the metal ion, providing a qualitative explanation for the influence of the metal ion upon the rate. The enhanced electron density at the methine carbon is expected from the extent of possible π-back bonding arising from metal to the ligand. This will be higher in the case of Cu(II) (d^9) than that of Ni(II) (d^8). It provides an explanation for the qualitative observation that Cu(II) complexes react faster than those of nickel(II).

EXPERIMENTAL

Preparation of aryl diazonium chloride

Freshly prepared aqueous solution of aryl diazonium chloride was used for the reactions. It was prepared by the diazotisation of the aromatic amine according to the following procedure. Aniline (0.01 mole) was suspended or dissolved in 8–10 mL of 5 N HCl at 0°C. The mixture of the amine and acid was cooled in an ice-salt mixture to a temperature between 0°C and –10°C. An aqueous solution of sodium nitrite (0.9 g, 0.01 mole) was then added slowly so that the temperature did not rise above 10°C. Any excess of nitrous acid produced in the medium was destroyed by adding small amounts of urea. The presence of urea did not interfere with subsequent reactions.

Preparation of monoaryl diazo substituted complexes of ethylene bis(acetylacetoneimino) nickel(II)/copper(II)

The parent complexes were prepared according to the reported procedure[14]. The parent complex (0.01 mole) was dissolved in 200 mL of methanol containing

10 g of sodium acetate and kept stirring at 5°C. The aqueous phenyl diazonium chloride (0.01 mole) was added dropwise to the methanolic solution over a period of 10 min, when a red crystalline solid precipitated out. It was filtered, washed with 1 : 2 alcohol-water mixture and dried in vacuum over conc. H_2SO_4. The complex was recrystallised from 1 : 1 methanol-chloroform mixture. Yield *ca.* 90%.

Heterosubstitution

Preparation of iodinated monodiazo coupled tetradentate ethylene bis(acetylacetoneimino) nickel(II)/copper(II),

$M^{II}(AI\cdot N_2Ph\text{-}en\cdot AI.I)$, M^{II} = Ni(II) or Cu(II)

To a solution of the complex (0.001 mole) in methanol (50 mL), a solution of monopyridineiodine(I) chloride in methanol (40 mL) was added. The resulting solution was stirred for about 3 h. The precipitate obtained was filtered, washed with ethanol and recrystallised from benzene. Yield 70%.

Preparation of α-naphthylamido substituted monodiazo coupled tetradentate ethylene bis(acetylacetoneimino) metal(II) complexes

$M^{II}(AI\cdot N_2Ph\text{-}en\text{-}AI\cdot C_{10}H_7NCO)$, M^{II} = Ni(II) or (Cu(II)

To a solution of the monodiazo coupled complex (0.005 mole) in dry benzene (30 mL), α-naphthyl isocyanate (0.005 mole) was added. The mixutre was stirred in a dry atmosphere when a deeply coloured precipitate was obtained. Stirring was continued for another 12 h for the completion of the reaction. The solution was filtered, and the precipitate was washed with 50 mL of chloroform and dried under vacuum. Yield 65%.

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