

Mononitrosated and phenylamido substituted chelate linkage isomers of quadridentate Schiff base copper(II) complexes

V BALASUBRAMANIAN, R R IYENGAR and C C PATEL
Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India

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Abstract. The nitrosation of monophenylamido substituted quadridentate Schiff base complexes of copper(II) are observed to adopt N-bonded isonitroso coordination whereas the phenylisocyanation of the corresponding mononitrosated quadridentate complexes are found to prefer O-bonded isonitroso coordination.

Keywords. Quadridentate Schiff base complexes ; copper(II) complexes ; copper(II) linkage isomers ; chelate linkage isomers.

1. Introduction

The hetero group electrophilic substitution reactions of β -ketoimines (*i.e.* γ -C-X/Y, where $X \neq Y \neq H$), appear to be much less investigated compared to the corresponding reactions of β -diketonates and β -ketoesters (Collman 1966). The only fruitful attempt has been (Collman *et al* 1962) to isolate the complexes with hetero groups at the γ -CH ring protons in the case of tris(acetylacetonate) cobalt (III), to understand the influence of the hetero group/s substituent on the quasi aromatic properties of the chelate ring/s (Collman *et al* 1962). Similarly, though the electrophilic substitution reactions of transition metal complexes of monovalent β -diketones are quite well studied (Collman 1966), not many of the corresponding analogous reactions of bivalent tetradentate metal β -ketoimines are known. The bromination and nitration of (4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dionato)-copper(II) (Dixit 1976) and the mononitrosation of bivalent quadridentate Schiff base metal chelates derived from β -diketones and 1,2-diamines, namely, $M[en/ipn(Al)_2]$ (where $M = Ni(II), Cu(II)$ or $Pd(II)$, etc.) (Sudha and Patel 1978) seem to be the only few known examples of the electrophilic substitution reactions of bivalent tetradentate β -ketoimino Schiff base complexes. An interesting feature of the latter type of reaction (mononitrosations) is that the substitution products display an intermolecular chelate linkage isomerism. In respect of this, an ambidentate hetero group γ -CH substitution in either or both the chelate rings can be expected to change the coordination of the already present

(ambidentate) γ -CH substituent. Monophenylamido substituted bivalent tetradentate Schiff base copper(II) chelates are, therefore, subjected to nitrosation, in the present study. Similarly phenylisocyanation of some of the mononitrosated quadridentate Schiff base complexes of copper(II) were also investigated from the point of view of their coordination properties. The results of these reactions and their substitution products have been discussed in terms of the spectral characteristics of the end products in this paper.

2. Experimental

2.1. Materials and physico-chemical measurements

The bivalent tetradentate Schiff base complexes namely, N, N'-ethylene/isopropylene-bis(acetylacetonimine)copper(II), $\text{Cu}[\text{en/ipn}(\text{Al})_2]$ were prepared by the known methods (Struss and Martin 1963). Monophenylamido substituted N, N'-ethylene/isopropylene-bis(acetylacetonimine)copper(II), $\text{Cu}(\text{Al} \cdot \phi\text{NCO-en/ipn-AX})$ were prepared by a modified procedure (Balasubramanian *et al* 1979). Mononitrosated N, N'-ethylene/isopropylene-acetylacetonimine)copper(II) were prepared by the reported procedure (Dixit *et al* 1978). Phenylisocyanate was a Fluka product and used as such while the organic solvents used for the preparation and purification of the complexes were purified by standard methods.

The conductivity of the complexes in acetone was determined with a Siemens conductivity bridge. Molecular weights of the complexes were determined by mass spectroscopy using Atlas Mat Bremen Massen Spectrometer CH4. Magnetic moments of the complexes were determined by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. IR spectra in Nujol mull were recorded on a Carl-Zeiss UR-10 spectrometer, while the optical absorption spectra were obtained on a Unicam-700 A spectrometer (as Nujol mull smear).

2.1a. *Nitrosation reactions.* The parent monophenylamido tetradentate copper(II) Schiff base complex, $\text{Cu}(\text{Al} \cdot \phi\text{NCO-en/ipn-Al})$ (0.002 mole) was dissolved in chloroform (80 ml) and nitric oxide purified over NaOH pellets, was bubbled vigorously through this solution for about an hr, when the colour of the solution changed from violet to dark brown. The reaction vessel was then closed and left aside at room temperature for several hr with intermittent shaking. The solution was then concentrated in vacuum to obtain violet brown crystals. They were filtered, washed with methanol and recrystallized from chloroform. Yield, 85%.

2.1b. *Phenylisocyanation reactions.* To a benzene solution (50 ml) of freshly crystallized and vacuum dried $\text{Cu}(\text{Al} \cdot \text{en/ipn-Al})$ (0.01 mole) complex, phenyl isocyanate (0.01 mole) was added dropwise in an anhydrous condition with thorough mixing. The reaction mixture was then stirred magnetically for about 14 hr at room temperature and then refluxed for about 12 hr. The dark violet precipitate formed was filtered, washed with benzene and dried under vacuum over conc. H_2SO_4 . Yield, 75%.

2.2. Analyses

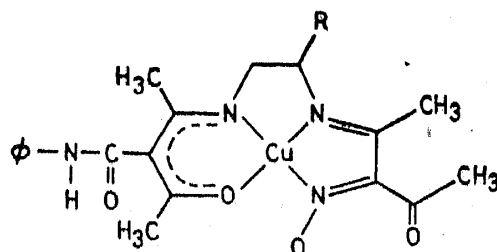
Copper in the complexes was estimated iodometrically (Vogel 1978) after decomposing the complexes with a mixture of perchloric and sulphuric acids. C, H and N were estimated by microanalytical methods. The stoichiometry of the complexes were observed to be in good agreement with the expected values.

3. Results and discussion

The brightly coloured nitrosated and phenylisocyanated tetradentate Schiff base copper(II) complexes are all crystalline, air stable and decompose above 250°C while melting. All these complexes have very poor solubility in common organic solvents. They are non-conducting in acetone ($\Lambda_M \sim 1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$), indicating their non-electrolytic nature. The magnetic moments of these complexes vary from 1.89 to 1.91 BM. These values are well within the range expected for magnetically dilute square planar copper(II) complexes (Hathaway and Thomlinson 1970). Further the nujol mull smear electronic spectra show bands at 15,380 cm^{-1} corresponding to the expected *d-d* transition of the square planar geometry (Dixit 1976).

3.1. Structure of $\text{Cu}(\text{AI} \cdot \phi\text{NCO-en/ipn-IAI})$

The IR spectra of the $\gamma\text{-CH}$ nitrosated complexes show presence of two new strong bands in the regions 1640-1645 and 1215-1230 cm^{-1} and a total disappearance of πCH of the parent reactant complexes (table 1). A careful examination of these two new frequencies reveals that the former could be due to the ketonic carbonyl and the latter due to the NO functionality (Dixit 1976; Dixit *et al* 1978; Iyengar 1975). A comparison with the parent IR spectra and their structures suggests that the carbonyl frequency in the nitrosated product can be considered to have arisen due to the dislodgement of one of the already coordinated CO's of the parent complex resulting in the appearance of the free acetyl carbonyl. As a result, the newly introduced NO substituent can enter into coordination with the metal ion either as N- or O-bonded NO. In comparison with the reported N- and O-bonded frequencies of NO for the isonitroso- β -ketoimine metal chelates, (Dixit 1976; Dixit *et al* 1978; Iyengar 1973, 1974) the observed NO at 1215-1230 cm^{-1} appears to be, in all probability due to the N-bonded oximino NO. Based on these data the following most tentative structure (structure 1) could,



R = H, $\text{Cu}(\text{AI} \cdot \phi\text{NCO} - \text{en} - \text{IAI})$

R = CH_3 , $\text{Cu}(\text{AI} \cdot \phi\text{NCO} - \text{ipn} - \text{IAI})$

Structure 1

Table 1. Characteristic infrared frequencies (in cm^{-1}) of the reaction products: $[\text{Cu}(\text{AI} \cdot \phi\text{NCO-en/ipn-IAI})]$ and $[\text{Cu}(\text{IAI}'\text{-en/ipn-AI} \cdot \phi\text{NCO})]$ complexes in nujol mull.

Reaction product complex	ν_{CO} (Coordinated)	$\nu_{\text{C-N}}$	ν_{CO} acetyl non-coordinated	ν_{NO} (O-bonded)	ν_{NO} (N-bonded)	Amide	
						ν_{CO}	ν_{NH}
$\text{Cu}(\text{AI} \cdot \phi\text{NCO-en-IAI})$	1520 s	1610 s	1645 s	..	1215 m	1670 s	3250 m, b
$\text{Cu}(\text{AI} \cdot \phi\text{NCO-ipn-IAI})$	1520 s	1610 s	1645 s	..	1230 m	1680 s	3300 m, b
$\text{Cu}(\text{IAI}'\text{-en-AI} \cdot \phi\text{NCO})$	1525 s	1610 s	1660 s	1140 s	..	1670 s	3230 m, b
$\text{Cu}(\text{IAI}'\text{-ipn-AI} \cdot \phi\text{NCO})$	1515 s	1610 s	1665 s	1145 s	..	1670 s	3230 m, b

IAI = isonitrosoacetylacetoneimine-N-bonded. IAI' = isonitrosoacetylacetoneimine-O-bonded. Abbreviations: s = strong; m = medium; b = broad.

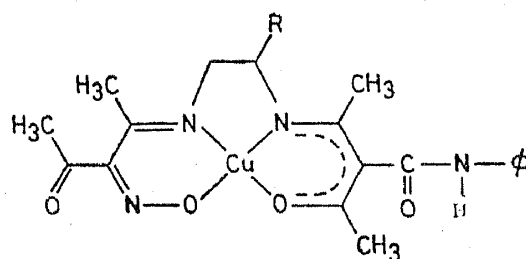
therefore, be assigned to the nitrosated γ -CH hetero group substituted N, N'-ethylene/isopropylene-bis(acetylacetonimine)copper(II).

3.2. Structure of $\text{Cu}(\text{IAI}'\text{-en/ipn-AI} \cdot \phi\text{NCO})$

The IR spectral data (table 1) of the starting mononitrosated O-bonded N, N'-ethylene/isopropylene-bis(acetylacetonimine)copper(II), $\text{Cu}(\text{IAI}'\text{-en/ipn-AI})$ exhibits its metal-donor environment (Dixit 1976) as :

- (i) Coordinated ν_{CO} at $1520\text{--}1525\text{ cm}^{-1}$,
- (ii) Non-bonded ν_{CO} at $1652\text{--}1688\text{ cm}^{-1}$,
- (iii) π -CH and δ -CH of γ -CH at 770 and 1180 cm^{-1} respectively,
- (iv) Bonded ν_{CN} at 1605 cm^{-1} and
- (v) O-bonded ν_{NH} at $1160\text{--}1167\text{ cm}^{-1}$.

On the other hand, the phenylisocyanated product of the above mononitrosated complex displays IR characteristic bands (table 1) at 1670 and 3230 cm^{-1} , assignable to free ν_{CO} and ν_{NH} of phenylamido group (Howells *et al* 1976; Balasubramanian *et al* 1978, 1979), respectively. Besides, the bands due to the O-bonded NO, free (*i.e.*, non-coordinated) acetyl ν_{CO} of oximino moiety, coordinated ν_{CO} of AI moiety and bonded ν_{CN} of IAI' and AI moieties more or less appear in the same region (with $\sim \pm 5\text{--}10\text{ cm}^{-1}$ shift) as those of their respective parent complexes. Further, the phenylamido substituted complex also indicates total absence of γ -CH IR vibrational frequencies. These observations, therefore, suggest that γ -CH proton gets substituted by the phenylisocyanate substituent which further undergoes prototropic rearrangement forming the hetero group γ -CH phenylamido substituted O-bonded (isonitroso-ethylene/isopropylene-acetylacetonimine)copper(II), $(\text{IAI}'\text{-en/ipn-AI} \cdot \phi\text{NCO})\text{Cu}(\text{II})$ complex. The following most probable structure 2, hence could be proposed for these complexes.



R=H, $\text{Cu}(\text{IAI}'\text{-en-AI} \cdot \phi\text{NCO})$

R=CH₃, $\text{Cu}(\text{IAI}'\text{-ipn-AI} \cdot \phi\text{NCO})$

Structure 2

Repeated failures to prepare the N-bonded mononitrosated N, N'-ethylene/isopropylene bis(acetylacetonimine)copper(II), for its phenylisocyanation γ -CH substitution reaction precluded this study. However, in conclusion, it seems worthwhile to note the fact that when the nitrosation of $(\text{AI} \cdot \phi\text{NCO}\text{-en/ipn-AI})\text{-Cu}(\text{II})$ is carried out only the N-bonded isonitroso hetero group substituted complex is obtained whereas the O-bonded isonitroso hetero group substituted

complex of the same could be prepared only *via* the phenylisocyanation of the O-bonded Cu(IAl-en/ipn-Al). Thus in this case the synthesis of intermolecular linkage isomers is possible only *via* adopting different routes. Although, rationalization of the factors influencing the bifunctional coordination of the isonitroso group is difficult, it appears that the mode of preparation dictates the mode of linkage of the isonitroso group.

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