Intermolecular Chelate Linkage Isomerism of the Hydroxyimino Group in the Nickel(II), Copper(II), and Palladium(II) Complexes of Quadridentate Schiff-base Ligands

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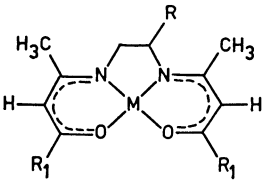
The C-nitrosation of bivalent quadridentate β-imino ketone complexes of nickel(II), copper(II), and palladium(II), with nitrosating reagents has been investigated. The chemical analysis and spectroscopic results reveal that one of the α-CH groups of the coordinated lignad undergoes selective nitrosation forming mono(hydroxyimino) derivative. The hydroxyimino group introduced coordinates through either N- or O- atom to metal(II) by dislodging the carbonyl group already coordinated. This gives rise to two linkage isomers, one with N-bonded and the other with O-bonded hydroxyimino group in the case of nickel(II) (except for **1d**) and palladium(II), and a single isomer with O-bonded hydroxyimino group in copper(II) complexes. The isomers obtained from **1b** and **1i** have been separated by column chromatography. In chloroform each of the isomers of nickel(II) isomerizes to give an equilibrium mixture of two isomers, but not those of copper(II) and palladium(II).

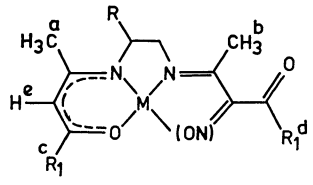
The α-CH proton of coordinated β-diketones[1–3] and β-imino ketones[4–9] can be substituted by a variety of electrophiles. However, reports on the nitrosation of these chelates are scanty.[10–12] Nitrosation reactions of coordinated β-diketones and its nitrogen analogs assume special importance, for in these reactions the α-CH group is generally converted into hydroxyimino group. The latter being potentially ambidentate can coordinate to metal(II) through either nitrogen or oxygen giving chelate linkage isomers.

The linkage isomers of monooximato complex have been isolated by nitrosation of [*N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediaminato]nickel(II) (**1a**) and a single isomer (hydroxyimino O-bonded) for the corresponding copper(II) complex.[13–14] The structure of the latter compound has been confirmed by X-ray diffraction studies.[15]

In continuation of our work on the linkage isomerism of the hydroxyimino group, we report here the preparation and characterization of a series of monooximato Ni(II), Cu(II), and Pd(II) complexes (**2b**—**2i**) from corresponding complexes of quadridentate β-imino ketones(**1b**—**1i**). The linkage isomers of the hydroxyimino group in Pd(II) complexes has been isolated for the first time.



1a — 1i



2a — 2i

	M(II)	R	R_1
1a	Ni	H	CH_3
1b	Ni	CH_3	CH_3
1c	Ni	CH_3	C_6H_5
1d	Ni	H	C_6H_5
1e	Cu	CH_3	CH_3
1f	Cu	H	C_6H_5
1g	Cu	CH_3	C_6H_5
1h	Pd	H	CH_3
1i	Pd	CH_3	CH_3

Schiff-base ligands of the monooximato complexes, **2a**—**2i** corresponding to **1a**—**1i** are listed below:

- **a, h:** 3-hydroxyimino-4,9-dimethyl-5,8-diaza-4,8-dodecadiene-2,11-dione
- **b, e, i:** 3-hydroxyimino-4,7,9-trimethyl-5,8-diaza-4,8-dodecadiene-2,11-dione
- **d, f:** 2-hydroxyimino-3,8-dimethyl-1,10-diphenyl-4,7-diaza-3,7-decadiene-1,10-dione
- **c, g:** 2-hydroxyimino-3,6,8-trimethyl-1,10-diphenyl-4,7-diaza-3,7-decadiene-1,10-dione.

Experimental

Materials and Physical Techniques. The quadridentate Schiff-base ligands and their complexes (**1b**—**1i**) were prepared by the reported methods.[16] Nitrogen monoxide was generated by the method of Blanchard.[17] Nickel(II) acetate tetrahydrate, copper(II) acetate monohydrate, sodium nitrite (A.R. grade) and palladium(II) chloride (Johnson Mathey, Ltd.) were used. Alumina (neutral, Brockmann activity,1) was obtained from National Chemical Laboratory, Poona, India. Silica gel (60—120 mesh, BDH) was used for chromatographic separation. All the organic solvents used were of A.R. grade.

The conductivity, magnetic susceptibility, and spectral measurements of the complexes were carried out according to the reported procedure.[18] The molecular weights of the nickel(II) complexes which are soluble in benzene were determined by cryoscopic method, while those of Pd(II) complexes were determined by mass spectrometry using an Atlas Mat Breman Massen CH4 spectrometer. ESR spectra of the Cu(II) complexes in chloroform were recorded at 28 °C on a spectrometer, constructed at TIFR, Bombay, operating at 9.52 GHz klystron frequency. Proton probe was used to measure the magnetic field.

Palladium and nickel in their complexes were estimated as their dimethylglyoximates, and copper(II) by iodometry.[19] C, H, and N were analyzed by microanalytical methods.

Preparation of Complexes. All the complexes (Table 1) were prepared by two methods. In both methods, limited quantities of nitrosating reagents were used to avoid the formation of dioximato complexes, indicated by their precipitation due to low solubility as compared to that of monooximato complexes. Qualitatively, the rate of nitrosation of the complexes was found to be in the order Ni>Cu>Pd.

Method I. A solution of a Schiff-base complex (**1b**—

TABLE 1. COLORS, MELTING POINTS, MAGNETIC MOMENTS (μ_{eff}), AND ANALYTICAL DATA OF THE COMPLEXES

Metal	Complex	Color	Mp °C	μ_{eff}. BM	Found (%)			
					C	H	N	Metal
Ni	**2d**							
	Isomer A	Dark red	174	Dia.	48.12 (48.18)	6.01 (5.91)	12.81 (12.96)	18.02 (18.11)
	Isomer B	Red	179	Dia.	48.10 (48.18)	6.82 (5.91)	12.79 (12.96)	17.79 (18.11)
Ni Ni	**2d** **2c**	Red	150	Dia.	60.82 (60.86)	4.59 (4.87)	9.52 (9.67)	13.41 (13.52)
	Isomer(A+B)	Red	—	Dia.	61.69 (61.64)	5.11 (5.17)	9.25 (9.37)	13.02 (13.10)
Pd	**2h** Isomer(A+B)	Bright yellow	—	Dia.	40.33 (40.29)	4.56 (4.76)	11.66 (11.75)	29.71 (29.77)
Pd	**2i**							
	Isomer A	Yellow	300 (dec)	Dia.	41.98 (42.00)	4.89 (5.10)	11.26 (11.31)	28.61 (28.65)
	Isomer B	Orange yellow	300 (dec)	Dia.	41.89 (42.00)	4.82 (5.10)	11.18 (11.31)	28.55 (28.65)
Cu	**2e**	Red violet	188	1.90	47.36 (87.48)	5.79 (5.82)	12.62 (12.77)	19.15 (19.22)
Cu	**2f**	Chocolate red	235	1.91	60.08 (60.19)	4.73 (4.82)	9.52 (9.57)	14.41 (14.47)
Cu	**2g**	Chocolate red	200 (dec)	1.90	60.92 (60.89)	4.98 (5.11)	9.15 (9.27)	13.98 (14.02)

Abbreviations: dec=decomposes; Dia.=diamagnetic.
Calculated analytical values are in the parentheses.

1i) in 100 ml chloroform was degassed at 0 °C by bubbling nitrogen. Gaseous nitrogen monoxide, dried over sodium hydroxide pellets was then passed through the above solution for 30—50 min at a rate of 10 bubbles per minute. The resulting solution was concentrated *in vacuo* to obtain a crystalline product. The crystals were separated by filtration, washed with ether or benzene to remove the unreacted compound. The complexes were recrystallized from benzene, methanol, or chloroform. Yields, 80—90%.

Method II. A solution containing copper(II) acetate, or nickel(II) acetate or palladium(II) chloride (0.01 mol) and sodium nitrite (0.5 mol) in 150 ml water was treated with an appropriate Schiff-base ligand (10 mmol). The reaction mixture was stirred at ambient temperature for about 1 h in the case of Ni(II) and Cu(II) complexes, and 2—3 days in the case of Pd(II) complexes. The crystals of the complexes (80—95%) deposited were filtered, washed with water and recrystallized as before. The rate of nitrosation was found to be catalyzed in the presence of a few drops of glacial acetic acid.

Preliminary TLC experiments showed the presence of two components for Ni(II) and Pd(II) complexes of **1b**, **1c**, **1h**, and **1i** indicating the presence of two isomers, and a single component in the Ni(II) complex of **1d** and all the Cu(II) complexes.

*Separation of the Isomers of the Reaction Product of **1i**.* A concentrated solution of the nitrosation product of **1i** (250 mg) dissolved in a chloroform–methanol mixture (9 : 1 v/v) was poured into a silica gel column. Elution with the same solvent mixture gave a rapidly moving yellow band followed by a slowly moving orange yellow band. Collection of yellow and orange-yellow eluates and removal of the solvent at room temperature yielded yellow (isomer A) and orange-yellow (isomer B) crystals, respectively. The crystals were recrystallized from cold benzene.

The isomers obtained from **1b** were separated by the same procedure using an alumina column instead of silica gel column. Isomer A was more rapidly eluted than the isomer B. Attempts to separate the isomers derived from **1c** and **1h** were not successful. However, isomer A of oximato nickel complex from **1c** was obtained in pure form by fractional crystallization from ethanol.

Results and Discussion

Colors, melting points, and analytical data of the complexes are given in Table 1. The elemental analyses of the complexes indicate that they are monooximato complexes (**2b**—**2i**). The molar conductances ($\Lambda_M < 1\ \Omega^{-1}\ cm^2\ mol^{-1}$) in acetone show that they are non-electrolytes. The complexes with $R_1=CH_3$ are more soluble in common organic solvents as compared to those with $R_1=C_6H_5$. Molecular weights of the isomers of nickel complex **2b** in benzene [calcd for $NiC_{13}H_{19}O_3N_3$ 328; found 324] indicate their monomeric nature. The mass spectra of the isomer A or B of palladium complex **2i** and the mixture of isomers of **2h** show ion peaks at m/e=371 and 357 corresponding to the parent molecular ions $C_{13}H_{19}N_3O_3Pd^+$ and $C_{12}H_{17}O_3N_3Pd^+$, respectively. Insufficient solubility of the remaining complexes in benzene preclude their molecular weight determination by cryoscopic method. Ni(II) and Pd(II) complexes are diamagnetic suggesting square-planar geometry around the metal(II), while Cu(II) complexes are paramagnetic with $\mu_{eff} \approx 1.90$ B.M., a value expected for monomeric Cu(II) complexes without any magnetic coupling.

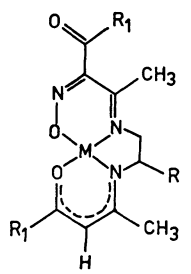
Table 2. Principal IR bands[a] (in cm^{-1}) of the monooximato Cu(II), Ni(II), and Pd(II) complexes in Nujol mull and in chloroform

Metal	Complex	$\nu_{C=O}$ (bonded)	$\nu_{C=O}$ (non-bonded)		ν_{N-O} (O-bonded)
			In mull	In $CHCl_3$	
Cu	**2e**	1520(s)	1680(s)	1680(s)	1162(s)
Cu	**2f**	1520(s)	1650(s)	1650(s)	1165(s)
Cu	**2g**	1520(s)	1652(s)	1650(s)	1160(s)
Ni	**2b**				
	Isomer A	1520(s)	1682(s)	1680(s)	1180(s)
	Isomer B	1520(s)	1645(s)	1644(s)	—
Ni	**2d**	1510(s)	1650(s)	1650(s)	1152(s)
Ni	**2c**				
	Isomer A	1522(s)	1658(s)	1650(s)	1160(s)
	Isomer B	1522(s)	1640(s)	1635(s)	—
Pd	**2h**				
	Isomer A	1515(s)	1690(s)	1688(s)	1125(s)
	Isomer B	1515(s)	1665(s)	1660(s)	—
Pd	**2i**				
	Isomer A	1512(s)	1688(s)	1688(s)	1135(w)
	Isomer B	1512(s)	1665(s)	1650(s)	—

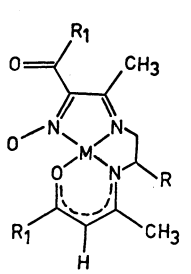
a) Abbreviations: s=strong; w=weak.

The electronic absorption spectra of isomers of the Ni(II) complexes in chloroform display a shoulder around 23300 cm^{-1}, assignable to the d-d transition of the square-planar Ni(II) complexes. Similarly Cu(II) complexes exhibit a broad absorption band in the 18000—25000 cm^{-1} region (ε=400—500 l mol^{-1} cm^{-1}). The isomers of Pd(II) complexes, on the other hand, show an intense band at 25000 cm^{-1}. Since the intensity of this band (ε=4000—6000 l mol^{-1} cm^{-1}) is rather high, it appears to be a charge-transfer transition, which has obsured the possible d-d transition of the planar Pd(II) complexes.

Structure of Nickel(II) and Palladium(II) Complexes. Since the hydroxyimino group can coordinate to a metal ion ambidentatively, two structures, **2A** and **2B**, are expected for the monooximato complexes. The relevant IR frequencies along with their assignments are given in Table 2. The IR spectra of all the complexes show an intense band in the region 1645—1690 and 1520 cm^{-1}, assignable to the non-coordinated and coordinated CO vibrations, respectively. They further show the characteristic bands around 760(s) and 1185(vw) cm^{-1} attributable to the out-of-plane and in-plane vibrations of α-CH, respectively.



2A



2B

The position of the non-coordinated ν_{CO}, sensitive to the bonding site of the hydroxyimino group, has been used as a probe for differentiating the structures **2A** and **2B**.[13-14] For example, ν_{CO} of N- and O-bonded isomers of nickel complex **2a** occurs at 1644 and 1684 cm^{-1}, respectively. The IR spectra of isomers A of **2b**, **2h**, and **2i** are very close to that of the hydroxyimino O-bonded isomer of Ni(II) complex **2a** and corresponding Cu(II) complex. Based on these results, the structure of type **2A** has been assigned to the isomers A. Similar structures have been suggested for nickel complex **2d** and isomer A of **2c**. The IR spectra of these complexes display the non-coordinated ν_{CO} around 1658 cm^{-1}. Furthermore, the occurrence of an intense band in the 1125—1180 cm^{-1} region, which is characteristic of coupled O-bonded ν_{CO} vibration[13] also supports the hydroxyimino O-coordination for the isomers A.

The IR spectra of isomers B of **2b**, **2c**, **2h**, and **2i** display the non-bonded ν_{CO} in the range expected for the hydroxyimino N-bonded moiety.[13-14] The structure of type **2B** has thus been proposed for the isomer B. However, it has not been possible to identify the N-bonded ν_{CO}. It is evident that isomers A and B differ only in bonding site of the hydroxyimino group. The dual modes of bonding of donor atoms of the hydroxyimino group are displayed in two different molecules. The isomerism of this type has been referred to as "intermolecular chelate linkage isomerism."

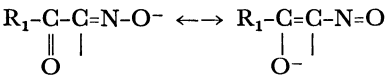
The available spectroscopic data of the isomers of the complexes led us to draw a significant conclusion about the non-bonded ν_{CO} vibrational frequency. For a given isomeric pair, the ν_{CO} of isomer A appears at a higher frequency (by $\approx$25—30 cm^{-1}) than that of isomer B. However, the dependence of ν_{CO} on the mode of attachment of hydroxyimino group is not yet clear. It is plausible that the resonance form **3A** contributes more to the structure of isomer

TABLE 3. PMR SIGNALS[a] (δ, in ppm) OF THE MONOOXIMATO COMPLEXES ALONG WITH THEIR ASSIGNMENTS

Metal	Complex	a	b	c	d	e	Diamine skeleton protons		
							CH_3	CH_2	CH
Ni	**2b**								
	Isomer A	1.88(s, 3)	2.00(s, 3)	2.18(s, 3)	2.38(s, 3)	4.98(s, 1)	1.18(d, 3) (J=6.0 Hz)	3.45(m, 4)	4.00(m, 1)
	Isomer B	1.94(s, 3)	2.04(s, 3)	2.30(s, 3)	2.48(s, 3)	5.02(s, 1)	1.36(d, 3) (J=6.0 Hz)	3.40(m, 2)	4.05(m, 1)
Ni	**2c**								
	Isomer A	1.97(s, 3)	2.06(s, 3)	2.68(m, 5)	2.56(m, 5)	5.80(s, 1)	8.61(d, 3) (J=6.0 Hz)		
	Isomer B	2.01(s, 3)	2.10(s, 3)	2.27(m, 5)	2.16(m, 5)	5.95(s, 1)	8.55(d, 3) (J=6.0 Hz)		
Pd	**2h**								
	Isomer A	2.03(s, 3)	2.26(s, 3)	1.95(s, 3)	2.38(s, 3)	4.85(s, 1)		3.70(m, 4)	
	Isomer B	2.03(s, 3)	2.32(s, 3)	1.97(s, 3)	2.54(s, 3)	4.90(s, 1)		3.42(m, 4)	
Pd	**2i**								
	Isomer A	2.05(s, 3)	2.23(s, 3)	1.96(s, 3)	2.40(s, 3)	4.86(s, 1)	1.31(d, 3) (J=6.0 Hz)	3.40(m, 2)	4.10(m, 1)
	Isomer B	2.05(s, 3)	2.35(s, 3)	2.00(s, 3)	2.43(s, 3)	4.92(s, 1)	1.40(d, 3) (J=6.0 Hz)	3.38(m, 2)	4.02(m, 1)

a) Key: s=singlet; d=doublet; m=complex multiplet.
Complexity and relative peak intensities of the signals are in parentheses.

A than of isomer B.



3A **3B**

As expected the PMR spectra of **2b**, **2h**, and **2i** show four distinct methyl signals of the chelate ring, the assignments of which are given in Table 3. It can be seen that the proton signals of isomer A except $COCH_3$ protons and α-CH proton of isomer A are more shielded than those of isomer B. Similar spectral features are found in the isomers of nickel complex **2c**.

Chelate Linkage Isomerization. In the solid state, isomer A of **2b** is hydroxyimino O-bonded, while isomer B is hydroxyimino N-bonded. In chloroform at 40 °C, each of these isomerizes giving an equilibrium mixture of A and B isomers. The transformation is irreversible. This is due to the fact that

$$\text{Nickel complex } \mathbf{2b} \text{ isomer A or B} \xrightarrow[40\,^\circ C]{CDCl_3} \text{isomers(A+B)} \qquad (1)$$

the IR as well as PMR spectra of the complexes obtained by refluxing each isomer in chloroform at 40 °C, corresponded to those containing mixture of the isomers A and B. Similarly isomer A of **2c** also isomerizes in $CDCl_3$. Its room temperature PMR spactrum displays two methyl signals and a complex multiplet due to phenyl protons with intensity ratio of 3 : 3 : 10, respectively. However, the spectrum of

$$\text{Nickel complex } \mathbf{2c} \text{ isomer A} \xrightarrow[50\,^\circ C]{CDCl_3} \text{isomers(A+B)} \qquad (2)$$

isomer A, which was previously refluxed at 50 °C in $CHCl_3$, showed a pattern corresponding to the mixture of isomers A and B. In Eqs. 1 and 2, the isomers are produced by the reorganization in the donor sites of the hydroxyimino group of the same ligand. This phenomenon may be referred to as "chelate linkage isomerization," the occurrence of which is rare in organic chelating ligands. It is, however, common in the case of inorganic ligands, particularly the complexes of chalcogenocyanates.[20] The isomerization is not favoured in **2d** (hydroxyimino O-bonded), Pd(II) and Cu(II) complexes under similar conditions. Probably, the high activation energies associated with these complexes appear to be responsible for their failure to isomerize.

Structure of the Copper(II) Complexes. In contrast to Ni(II) and Pd(II) complexes, a single isomer is obtained by nitrosation of the Cu(II) Schiff-base complexes. The ν_{CO} (non-bonded) and ν_{NO} in the Cu(II) complexes appear in the region 1650—1680 cm^{-1} and at 1160 cm^{-1}, respectively. The positions of these bands are compatible with those of the corresponding isomer A of the Ni(II) complexes. Hence, the bonding of the hydroxyimino group in all the Cu(II) complexes is suggested to be through oxygen.

The first derivative ESR spectra of the Cu(II) complexes consist of four main groups of equally spaced lines, which result from the coupling of ^{63}Cu (I=3/2) with the unpaired electron. The hyperfine structure of the first two high field signals consists of five peaks of intensity ratio 1 : 2 : 3 : 2 : 1. These peaks result from the splitting by two nitrogens (I=1) of the diamine skeleton. Thus, the hyperfiine structure of the main peaks suggests that the coordination sphere around Cu(II) is N_2O_2. This conclusion is in line

with that derived from IR data. The average values of ESR parameters are 2.07(g), 90.0 G (A_{Cu}), 12.5 G (A_N) and 7.6 (covalency factor α^2). These values are compatible with the square-planar Cu(II) complexes with N_2O_2 ligational environment.[21-24]

In conclusion, nitrosation of **1b—1i** gives monooximato complexes under the experimental conditions employed, unlike the conventional substitution reactions. Further, the hydroxyimino group introduced at the ring CH carbon dislodges the coordinated carbonyl group and coordinates to metal ion either through nitrogen or oxygen, giving rise to chelate linkage isomers. The preferential mode of coordination of the hydroxyimino group essentially depends upon the metal ion.

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