

Reactions of mononitrosated Schiff base complexes of nickel(II). A study on chelate linkage isomerism

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Abstract

Phenyl isocyanation reaction of the isomers of mononitrosated tetradentate (N, N'-en/ipn/npn-bisacetylacetonimine)nickel(II) gives a mixture of O- and N-bonded isonitrosophenylamido substituted isomers.

Keywords: Phenylisocyanation, schiff bases - nickel(II) complexes - chelate linkage isomerism, prototropic rearrangement.

1. Introduction

The electrophilic substitution reactions of transition metal complexes of monovalent β -diketones are well known^{1–4}. Except for bromination and nitration⁵ of (4, 9-dimethyl-5, 8-diazadodeca-4, 8-diene-2, 11-dionato)copper(II), no detailed investigation has been made on the reactions involving complexes of bivalent quadridentate Schiff bases derived from β -diketones and 1,2-diamines or partially nitrosated Schiff-base complexes. Bromination of intermolecular chelate linkage isomers of 3-oximino-4, 8-dimethyl-(or 4, 7, 9-trimethyl)-(5, 8-diazadodeca-4, 8-diene-2, 11-dionato)nickel(II) has been reported. In this paper, phenylisocyanation reactions of mononitrosated tetradentate N, N'-en/ipn/npn-bis(acetylacetonimine)nickel(II) are reported, where en, ipn and npn are, respectively, ethylenediamine, isopropylenediamine and *n*-propylenediamine⁶.

2. Experimental

2.1. Materials

Nickel acetate, ferrous sulphate, sodium nitrite and sodium hydroxide used were of BDH origin. Organic solvents used were purified by standard methods⁷. The Schiff bases and their nickel(II) complexes Ni(baen), Ni(bapn) and Ni(baipn) were synthesised according to known methods⁸. They were recrystallised from methanol and used. All the chelate linkage isomeric mononitrosated complexes were prepared and separated by column chromatography on alumina by the reported procedure^{8–10}. Their purity was checked by elemental analysis and melting point.

2.2. Preparation of the heterosubstituted chelates

Preparation of C-phenylamido-substituted complexes of mononitrosated tetradentate ethylenediamine/isopropylene/isopropylenebis(acetylacetonimine)-nickel(II), Ni(IAI/IAI'-en/npn/ipn-AI) is given below.

IAI — isonitrosoacetylacetonimine N-bonded isomer (isomer A)

IAI' — isonitrosoacetylacetonimine O-bonded isomer (isomer B)

AI — acetylacetonimine.

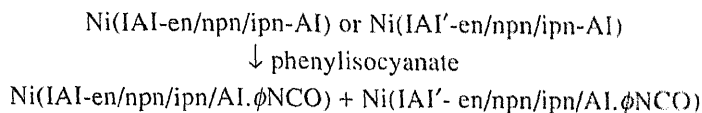
To a solution containing Ni(IAI/IAI'-en/npn/ipn-AI) isomer A with N-bonded isonitroso group or isomer B with O-bonded isonitroso group (0.01 mole) in dry benzene (50 ml), phenylisocyanate (0.01 mole) was added. The mixture was stirred in a dry atmosphere, when a deeply coloured precipitate appeared. Stirring was continued for 12 h for the completion of the reaction and the solution was filtered; the precipitate was washed with 50 ml of chloroform dried under vacuum. Yield ~80%. Preliminary TLC spotting of all the phenylamido-substituted complexes indicated the presence of two compounds.

2.3. Techniques employed

Conductivity measurements were made using a Siemen's conductivity bridge at room temperature. Magnetic measurements were made by Gouy technique using mercury(II)tetrathiocyanatocobaltate(II) as the calibrant. Electronic spectra of the complexes were recorded on a Beckmann model-25 and the IR spectra on a Perkin-Elmer UR-10 automatic double-beam spectrometer equipped with LiF, NaCl and KBr optics. The IR spectra of the solid complexes were recorded as nujol mulls and KBr discs. The PMR spectra of the complexes in CDCl_3 were recorded on a Bruker WH-270 MHz spectrometer using tetramethylsilane (TMS) as the internal standard. The amount of nickel(II) in the complexes was estimated using conventional procedure¹¹.

3. Results and discussion

Phenylisocyanation of isonitroso N-bonded isomer A or isonitroso O-bonded isomer B gave a mixture of two isomers as indicated by TLC experiments.



The complexes are diamagnetic and hence a square planar geometry around nickel(II)⁹ is expected.

The electronic spectra of phenylamido-substituted complexes are almost identical with those of the corresponding mononitrosated complexes and show, in chloroform, a single band around $21,500 \text{ cm}^{-1}$ ($\epsilon \sim 500 \text{ mol}^{-1} \text{ cm}^{-1}$) which is characteristic of square planar oximinob- β -ketoiminonickel(II) complexes and is assignable to d-d-transition^{12,13}. Other strong transitions in the ultraviolet region around 28,000, 32,000 and 39,000 cm^{-1} are

Table I
Characteristic infrared stretching frequencies (ν) in cm^{-1} of Ni(IAI/IAI'-en/npn- $\text{Al}\phi\text{NCO}$) complexes

Complex	νCO	νCO (not bonded)	νNO	νCO (amido)	νNH (amido)
Ni(IAI'-en- $\text{Al}\phi\text{NCO}$)	1520 s	1690 s	1135 m	1635 s	3330 m, b
Ni(IAI-en- $\text{Al}\phi\text{NCO}$)	1510 s	1640 s	1190 m	1635 s	3330 m, b
Ni(IAI'-ipn- $\text{Al}\phi\text{NCO}$)	1520 s	1690 s	1130 m	1640 s	3270 m, b
Ni(IAI-ipn- $\text{Al}\phi\text{NCO}$)	1525 s	1660 s	1190 m	1630 s	3270 m, b
Ni(IAI'-nnp- $\text{Al}\phi\text{NCO}$)	1540 s	1680 s	1145 m	1640 s	3310 m, b
Ni(IAI-nnp- $\text{Al}\phi\text{NCO}$)	1535 s	1640 s	1190 m	1620 s	3310 m, b

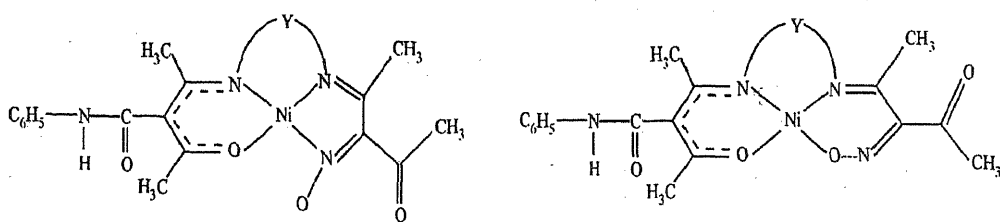
IAI' = isonitrosoacetylacetoneimine O-bonded isomer; IAI = isonitrosoacetylacetoneimine N-bonded isomer. Abbreviation: s : strong; m : medium; b : broad

possibly due to $\pi \rightarrow \pi^*$ transitions of the coordinated ligand. The electronic spectra of the complexes (in CHCl_3) exhibit a shoulder in the range 21,000–26,000 cm^{-1} which is probably due to d-d transition of the square planar complexes¹⁴. The resemblance of the spectra of phenylamido-substituted and the parent mononitrosated complexes show their structural similarity.

As already reported^{8,9,13}, mononitrosated nickel(II) complexes display characteristic IR frequencies due to ring $\gamma\text{-CH}$ in the region 762–755 cm^{-1} , due to out-of-plane CH bending, and near 1180–1200 cm^{-1} due to in plane CH bending. These bands are absent in the infrared spectra (Table I) of the phenylamido-substituted complexes suggesting substitution of the phenylamido group at $\gamma\text{-CH}$. The absence of ring $\gamma\text{-CH}$ proton signals in the PMR spectra (Table II) of the phenylamido-substituted complexes also supports the substitution of the $\gamma\text{-CH}$ by phenylamido substituent.

It can be seen that the free C = O stretching (1690–1680 cm^{-1} for isomer A and at 1640–1620 cm^{-1} for isomer B) in the phenylamido-substituted complexes is nearly at the same frequency as in the corresponding mononitrosated complexes. The new frequencies in the region 1660–1635 and 3300–3270 cm^{-1} may be assigned to amido CO and NH stretching modes of the phenylamido substituent^{9, 10, 15, 16, 17}. It indicates the attack of phenylisocyanate at the $\gamma\text{-CH}$ position and after protropic rearrangement forms phenylamido group substituent¹⁶. The bands near 1190 and 1145–1130 cm^{-1} are due to N-bonded isonitroso and at 1230 cm^{-1} due to O-bonded N-O groups^{17–19}. The band around 1610–1600 cm^{-1} is assignable to C = N stretching^{13, 17, 18}.

The PMR spectra of these complexes show eight proton signals due to β -ketoinmine chelate ring (Table II) and the data suggest the existence of two isomers. Phenyl proton signals are in the region 7.71–7.1 δ while the NH signals are in the region 8.39–7.71 δ ^{9, 10, 19}. The methyl proton signals of the isopropylene group are in the range 1.26–1.24 δ a value expected for δ -gauche conformation. Thus the conformation of the diamine skeleton remains unaltered even after phenylisocyanation. Based on the above arguments, the following structures (Fig. 1) have been assigned for the isomer A (N-bonded) and isomer B (O-bonded) of Ni(IAI/IAI'-en/npn/ipn- $\text{Al}\phi\text{NCO}$), respectively.



Isomer A

Y = (CH₂)₂, (CH₂)₃ or -CH₂CH(CH₃)

Isomer B

FIG. 1.

Table II

PMR data (δ ppm) of phenylamido-substituted nickel(II) complexes [Ni(IAI/IAI'-en/ipn/npn-Al. ϕ NCO)]*

Complex	a	b	c	d	e	f	g** CH ₂	CH
Ni(IAI/IAI'-en-Al. ϕ NCO)								
isomer B (IAI')	2.50 (s, 3)	2.17 (s, 3)	2.31 (s, 3)	2.07 (s, 3)	7.71 (b, 1)	7.12 to	3.17 (m, 4)	
isomer B (IAI)	2.41 (s, 3)	2.24 (s, 3)	2.39 (s, 3)	2.10 (s, 3)	8.39 (b, 1)	7.68 (m, 10)	3.38 (m, 4)	
Ni(IAI/IAI'-ipn-Al. ϕ NCO)								
isomer B (IAI')	2.51 (s, 3)	2.41 (s, 3)	2.28 (s, 3)	2.03 (s, 3)	7.89 (b, 1)	7.12 to	3.25 (m, 2)	4.13 (m, 1)
isomer A (IAI)	2.41 (s, 3)	2.20 (s, 3)	2.33 (s, 3)	2.13 (s, 3)	8.20 (b, 1)	7.60 (m, 10)	3.55 (m, 2)	(3.80) (m, 1)
Ni(IAI/IAI'-nnpn-Al. ϕ NCO)								
isomer B (IAI')	2.48 (s, 3)	2.24 (s, 3)	2.31 (s, 3)	2.04 (s, 3)	8.10 (b, 1)	7.14 to	1.92-3.17 (m, 2)(m, 4)	
isomer A (IAI)	2.40 (s, 3)	2.29 (s, 3)	2.34 (s, 3)	2.18 (s, 3)	8.37 (b, 1)	7.71 (m, 10)	1.99-3.39 (m, 2)(m, 4)	***

* Isomer B (IAI') oximino-O-bonded
Isomer A (IAI) oximino-N-bonded** Methyl proton resonance of Y (diamine skeleton) in the isomers of A and B of Ni (IAI/IAI'-ipn-Al. ϕ NCO) occurs as a doublet at 1.24 and 1.26, respectively, with J = 6.40 Hz

*** Central methylene proton signals: splitting and intensities of the signals are given in parentheses Abbreviations: s: singlet; m: multiplet; b: broad

As discussed above, the spectra of phenylamido-substituted tetradentate nickel(II) complexes show that each of the isomers of Ni(IAI/IAI'-en/npn/ipn-AI) on phenylisocyanation gives a mixture of isomers of O- and N-bonded isonitrosophenylamido-substituted isomers. Since structurally the relation between isomers A and B involves the rearrangement of the bonding site of oximino group of the same ligand molecule, this property may be referred to as intramolecular chelate-linkage isomerisation. Although isomerisation involving inorganic ambidentate ligands, especially thiocyanate anion, is well known⁴, it seems that only a few examples involving chelating organic ligands are known^{18,20,21}.

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