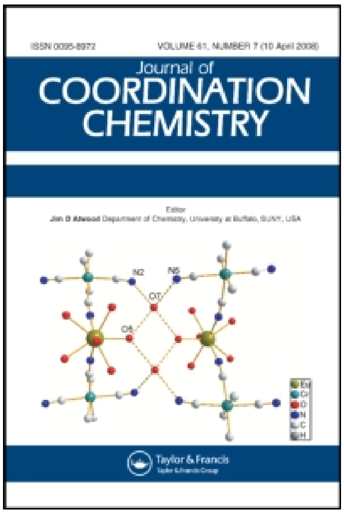

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BONDING ISOMERISM IN THE CHELATE-EXCHANGE REACTIONS OF ISONITROSO-β-KETO-IMINO ISOMERIC NICKEL(II) MIXED LIGAND COMPLEXES

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A novel chelate exchange reaction, leading to the formation of a series of N-alkyl substituent dependent mixed ligand isomeric complexes of the type Ni(R-AB)(AC′) and Ni(R-AC)(AB′) (Figure 1) are discussed. Here, AB and AC denote two different N-bonded isonitroso-β-keto-imino ligand moieties, while AB′ and AC′ are the corresponding O-bonded ligand moieties and R is an N-alkyl substituent. The isomeric complexes are suggested to be monomeric, neutral and diamagnetic with an asymmetric square planar geometry. The bonding isomerism of the isonitroso group in these complexes is discussed on the basis of the infrared and proton magnetic resonance spectral studies. A probable mechanism for the preparative route is also proposed.

INTRODUCTION

The chelate-exchange reaction,

$$\mathrm{MCh_n + n\ HCh' \rightleftharpoons MCh'_n + n\ HCh}$$

usually involves displacement of a chelated ligand (Ch) from the coordination sphere of a metal ion(M) by another ligand(HCh′) and thus produces its new metal complex.[1-4] However, a somewhat similar but comparatively novel chelate exchange reaction has been observed by us. In this, when two unstable metal chelate species in solution are made to react in a suitable solvent, it yields two moles of a new stable complex. Such a chelate exchange reaction seems to be quite unusual and rare. The importance of this reaction lies in the fact that isomeric pairs of mixed ligand complexes could be produced separately and only one at a time, by manipulating the initial reactants.

The previous studies[5-12] have established structures of a number of nickel(II) complexes containing isonitroso-β-keto-imino bidentate ligands, where both the ligand moieties in the planar complex are derived from the same isonitroso-β-keto-imine. However, isomeric nickel(II) complexes of analogous ligands, where each of the two ligand moieties in the complex is derived from two different isonitroso-β-keto-imines are quite uncommon. By adopting a specific mode of synthesis, it is possible to have a particular type of bonding (either through N- or O- coordination of the isonitroso group) of the ligands to get a desired isomer of the mixed ligands complex. A series of isomeric pairs of mixed ligand complexes of the type Ni(R–AB)(AC′) and Ni(R–AC)(AB′) are prepared, where AB and AC represent the isonitroso-β-keto-imino moiety of ligands HAB and HAC respectively, with N-bonded isonitroso groups; while AB′ and AC′ refer to the corresponding O-bonded ligand moieties. The ligands employed are: 4-imino-2,3-pentanedione 3-oxime (isonitrosoacetylacetoneimine, HIAI); 4-imino-1-phenyl-1, 3-butanedion 3-oxime (isonitrosobenzoylacetoneimine, HIBI) and 1-ethoxycarbonyl-2-imino-1-propanone oxime (isonitrosoethylacetoacetateimine, HIEAI). R is an N-alkyl substituent, derived from the corresponding N-alkylamine, R–NH$_2$. The details of the synthesis of the isomeric complexes and their spectral characterization are reported in this paper.

EXPERIMENTAL

Materials and Methods Employed

Nickel acetate tetrahydrate, isonitrosoacetylacetone (HIAA), isonitrosobenzoylacetone (HIBA) and

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isonitrosoethylacetoacetate (HIEAA) were prepared as reported earlier.[6,8] Similarly, bis(isonitrosoacetylacetoneimino)nickel(II), Ni(IAI)(IAI′); bis(isonitrosobenzoylacetoneimino)nickel(II), Ni(IBI)(IBI′) and bis(isonitrosoethylacetoacetateimino)nickel(II), Ni(IEAI)(IEAI′) were synthesised also as reported earlier.[6,8] Methylamine (Riedel, 33% aqueous solution), ethylamine (Riedel, 50% aqueous solution), n-propylamine (Fluka), n-butylamine (Riedel) and i-butylamine (Riedel) were used as such without further purification. Liquor ammonia used had a density of 0.89 g/ml. Acetone, chloroform, benzene, and other solvents used for the physicochemical measurements were guaranteed AR grade reagents. These were redistilled and dried according to the standard procedures.[13] Unless otherwise stated, all other solvents, like methanol, ethanol, etc., which were used in the preparative procedures, were of commercial grade and distilled before use.

Molecular weights, magnetic susceptibilities and conductivity measurements together with ir, electronic and pmr spectral data of the complexes were collected as done in our earlier publications.[6-8]

Preparation of the Complexes

In all, two different sets (I and II) of isomeric pairs, with different isonitroso-β-keto-imine ligands and varying N-alkyl substituent, R, are prepared. Complex (a) of set I is isomeric with complex (c) of set II. Similarly the complexes (b) and (d) are isomeric.

Set I. *Ni(R–AB)(AC′)*: (a) Ni(R–IBI)(IAI′) and (b) Ni(R–IBI)(IEAI′).

Set II. *Ni(R–AC)(AB′)*: (c) Ni(R–IAI)(IBI′) and (d) Ni(R–IEAI)(IBI′).

The preparative details are in general described below.

The desired alkylamine (R–NH_2, 0.80 ml) was added to a mixture of nickel acetate tetrahydrate (0.50 g, ~ 0.002 mole) and an isonitroso-β-ketone of HAB/HAC† (~ 0.004 mole) in a 50 ml solvent mixture of 1:1 methanol (AR) and chloroform (AR). The reaction mixture was stirred for about an hour at room temperature. To this solution, powdered bis(isonitroso-β-ketoimino)nickel(II), Ni(AC)(AC′)/Ni(AB)(AB′)† (parent complex of HAC/HAB,† ~ 0.002 mole) was added slowly with stirring, when the latter complex went into solution. The mixture was then left aside at room temperature for 12–16 hours with occasional shaking. The solvent was next removed under vacuum till 10–15 ml of the solution was left over. Water was next added dropwise and very slowly with vigorous shaking to induce crystal formation.

Sufficient water could then be added to get a maximum possible yield of the complex. It was noted that in most of the cases, rapid addition of water, even on vigorous stirring produces a pasty or oily mass which is difficult to crystallize. Many a time, the oily mass had to be dissolved in a minimum amount of alcohol and allowed to evaporate slowly at room temperature either by passing dry air or leaving aside, when crystals separate out. The crystalline precipitate was next filtered, washed 4–5 times with water, followed by quick repeated washings with cooled 2:1 water-alcohol mixture. It was recrystallised from 3:1 alcohol-water mixture and dried in vacuum over concentrated H_2SO_4. The yields of the complexes are given below:

a) Ni(R–IBI)(IAI′): when R = Me, 88%; Et, 85%; n-Pr, 93%; n-Bu, 94%; and i-Bu, 86%.

b) Ni(R–IBI)(IEAI′): when R = Me, 85%, Et, 94%; n-Pr, 92%; and n-Bu, 88%.

c) Ni(R–IAI)(IBI′): when R = Me, 85%; Et, 87%; n-Pr, 89%; n-Bu, 86%; and i-Bu, 80%.

d) Ni(R–IEAI)(IBI′): when R = Me, 91%; Et, 89%; n-Pr, 79%; and i-Bu, 83%.

Analyses

The carbon, hydrogen, and nitrogen contents in the complexes were determined by micro-combustion method through the kind courtesy of micro-analytical laboratory, BARC, Bombay – 400 085, India; while nickel(II) was estimated as bis(dimethylglyoximato)-nickel(II) after decomposing the complexes with a mixture of H_2SO_4, HNO_3 and $HClO_4$ acids.

RESULTS AND DISCUSSION

All the complexes are bright coloured, crystalline solids and highly stable under atmospheric conditions. They have got a good solubility in almost all common

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†In the case of (a): ligand HAB ≡ HIBA and the parent complex of HAC, i.e., Ni(AC)(AC′) ≡ Ni(IAI)(IAI′), while, in the case of (c): ligand HAC ≡ HIAA and the parent complex of HAB, i.e., Ni(AB)(AB′) ≡ Ni(IBI)(IBI′); similarly, in the case of (b): ligand HAB ≡ HIBA and the parent complex of HAC, i.e., Ni(AC)(AC′) ≡ Ni(IEAI)(IEAI′), while, in the case of (d): ligand HAC ≡ HIEAA and the parent complex of HAB, i.e., Ni(AB)(AB′) ≡ Ni(IBI)(IBI′).

TABLE I
Some general physical properties of Ni(R–AB/R–AC)(AC′/AB′)[a] complexes and their analytical data

				Analytical data[b], %			
Complex	Colour	Melting point, °C	Molecular weight[b]	Ni	C	H	N
Ni(Me–IBI)(IAI′)	Golden yellow	183.0	380 (389)	14.99 (15.09	49.40 49.39	4.90 4.67	14.88 14.40)
Ni(Et–IBI)(IAI′)	Bright yellow	180.5	400 (403)	14.55 (14.56	50.22 50.65	5.07 5.01	13.87 13.90)
Ni(n–Pr–IBI)(IAI′)	Yellow	182.5	412 (417)	14.10 (14.07	52.20 51.82	5.23 5.33	13.90 13.43)
Ni(n–Bu–IBI)(IAI′)	Bright yellow	149.5	426 (431)	13.54 (13.62	52.90 52.92	5.60 5.62	12.85 13.00)
Ni(i–Bu–IBI)(IAI′)	Yellow	173.0	437 (431)	13.60 (13.62	53.13 52.92	5.67 5.62	12.84 13.00)
Ni(Me–IAI)(IBI′)	Orange (mustard)	161.0	401 (389)	15.11 (15.09	49.23 49.39	4.45 4.67	14.36 14.40)
Ni(Et–IAI)(IBI′)	Orange yellow	154.0	386 (403)	14.52 (14.56	50.52 50.65	4.80 5.01	14.07 13.90)
Ni(n–Pr–IAI)(IBI′)	Yellow	156.0	405 (417)	14.20 (14.07	52.10 51.82	5.43 5.33	13.49 13.43)
Ni(n–Bu–IAI)(IBI′)	Red	135.5	426 (431)	13.65 (13.62	53.40 52.92	5.35 5.62	12.78 13.00)
Ni(i–Bu–IAI)(IBI′)	Orange	150.5	435 (431)	13.60 (13.62	53.20 52.92	5.60 5.62	12.85 13.00)
Ni(Me–IBI)(IEAI′)	Orange yellow	176.5	407 (419)	14.09 (14.01	48.30 48.71	4.90 4.82	13.33 13.37)
Ni(Et–IBI)(IEAI′)	Golden yellow	161.5	428 (433)	13.98 (13.55	49.90 49.91	5.60 5.13	13.25 12.94)
Ni(n–Pr–IBI)(IEAI′)	Yellow	165.0	440 (447)	13.10 (13.13	51.29 51.03	5.81 5.42	12.63 12.53)
Ni(i–Bu–IBI)(IEAI′)	Red	153.0	466 (461)	13.01 (12.73	52.41 52.08	5.60 5.69	12.41 12.15)
Ni(Me–IEAI)(IBI′)	Orange	155.0	426 (419)	14.11 (14.01	48.70 48.71	4.70 4.82	13.86 13.37)
Ni(Et–IEAI)(IBI′)	Deep orange	168.5	427 (433)	13.25 (13.55	49.70 49.91	5.70 5.13	13.13 12.94)
Ni(n–Pr–IEAI)(IBI′)	Deep orange	157.0	452 (447)	13.60 (13.13	51.50 51.03	5.60 5.42	12.33 12.53)
Ni(n–Bu–IEAI)(IBI′)	Yellow	160.5	450 (461)	12.60 (12.73	52.20 52.08	6.21 5.69	11.71 12.15)

[a] R = Me, Et, n–Pr, n–Bu or i–Bu.
[b] The theoretical values are given in parentheses below their respective observed values.

organic solvents, the solubility being maximum in chloroform. The complexes are all found to be non-electrolytic in nature ($\Lambda_M \sim 0.5$ to 1.5 ohm^{-1} cm^2 mole^{-1}), monomeric and diamagnetic having a square planar geometry around nickel(II). The molecular weights of the complexes (determined cryoscopically in benzene) together with their melting points, colour and the analytical data are given in Table I.

The electronic spectra of the complexes in chloroform and a few in n-heptane give bands in the region 40,000 to 10,000 cm^{-1} at, more or less, the same frequencies in both the solvents. Three to four

TABLE II

Characteristic infrared frequencies (in cm^{-1}) of Ni(R–AB/R–AC)(AC′/AB′)[a] complexes

	C=O str.[b] in		N–H str. of AC′/AB′ moiety in		N–O str. in nujol mull of	
Complex	Nujol mull	Chloroform (CCl_4)	Nujol mull	Chloroform (CCl_4)	N-coordinated (R–AB/R–AC) moiety	O-coordinated (AC′/AB′) moiety
Ni(Me–IBI)(IAI′)	1657 vs **1685** vs	1670 vs **1699** vs	3145 mb	3180 mb	1195 s	1140 s
Ni(Et–IBI)(IAI′)	1650 vs **1685** vs	1669 vs **1700** vs	3138 mb	3160 mb	1185 s 1195 s	1140 s
Ni(n–Pr–IBI)(IAI′)	1640 vs **1692** vs	1667 vs **1696** vs	3170 mb	3180 mb	1190 s	1135 s
Ni(n–Bu–IBI)(IAI′)	1655 vs **1690** vs	1665 vs **1696** vs	3133 mb	3160 mb	1196 s	1140 s
Ni(i–Bu–IBI)(IAI′)	1652 vs **1691** vs	1655 vs **1696** vs	3150 mb	3160 mb	1196 s	1135 s
Ni(Me–IAI)(IBI′)	1665 vs,b **1665** vs,b	1666 vs **1656** sh	3154 mb	3163 mb	1192 vs	1128 s 1151 s
Ni(Et–IAI)(IBI′)	1665 vs **1660** sh	1675 vs,b **1675** vs,b	3165 mb	3185 mb	1198 s	1128 s 1150 s
Ni(n–Pr–IAI)(IBI′)	1680 vs **1665** sh	1675 vs,b **1675** vs,b	3173 mb	3165 mb	1185 s	1121 s 1151 s
Ni(n–Bu–IAI)(IBI′)	1665 sh **1660** vs	1670 vs,b **1670** vs,b	3190 mb	3165 mb	1190 s	1128 s 1151 s
Ni(i–Bu–IAI)(IBI′)	1669 vs **1653** vs	1675 vs,b **1675** vs,b	3180 mb	3185 mb	1185 s	1120 s 1150 s
Ni(Me–IBI)(IEAI′)	1652 vs **1720** vs	1668 vs **1722** vs	3170 mb	3165 mb	1199 s 1235 s	1100 s 1139 s
Ni(Et–IBI)(IEAI′)	1655 vs **1720** vs	1665 vs **1725** vs	3170 mb	3165 mb	1200 s 1230 s	1098 s 1135 s
Ni(n–Pr–IBI)(IEAI′)	1650 vs **1720** vs	1666 vs **1725** vs	3170 mb	3165 mb	1200 s 1232 s	1100 s 1120 s
Ni(i–Bu–IBI)(IEAI′)	1655 vs **1722** vs	1670 vs **1725** vs	3175 mb	3170 mb	1200 s 1230 s	1100 s 1125 s
Ni(Me–IEAI)(IBI′)	1710 vs **1660** vs	1715 vs (1710 vs) **1670** vs **(1675** vs)	3175 mb	3165 mb (3160 mb)	1190 s 1214 s	1130 s 1152 s
Ni(Et–IEAI)(IBI′)	1696 vs **1665** vs	1714 vs (1708 vs) **1670** vs **(1669** vs)	3170 mb	3162 mb (3160 mb)	1198 s 1210 s	1130 s 1151 s
Ni(n–Pr–IEAI)(IBI′)	1689 vs **1665** vs	1715 vs **1670** vs	3164 mb	3165 mb	1200 s 1210 s	1130 s 1150 s
Ni(n–Bu–IEAI)(IBI′)	1710 vs **1660** vs	1710 vs **1670** vs	3170 mb	3160 mb	1195 s 1210 s	1130 s 1150 s

[a] R = Me, Et, n–Pr, n–Bu or i–Bu.

[b] The C=O stretching frequencies due to AC′/AB′ (O-coordinated) moiety are in bold type, while those in ordinary type belong to R–AB/R–AC (N-coordinated) moiety.

intense high energy bands, observed in the region 41,000 to 27,000 cm^{-1} are probably due to $\pi-\pi^*$ ligand transitions, while the shoulder around 25,500 cm^{-1} may be attributed to the characteristic d–d transition confirming the square planar stereochemistry of the complexes.

The nature of the metal-donor bonding in these complexes could best be arrived at by comparing the ir and pmr spectral evidences of the isomeric pairs between themselves and with those of the analogous / related ones; since in these isomeric complexes, we have two different ligand moieties bonded to the same metal ion and they have two different modes of coordination of the isonitroso group in the same molecule. Thus by this approach it would be possible to characterise the common and/or uncommon ir bands and pmr signals; and hence the identification of the coordination of ligand moieties.

As regards the N–H ir band or pmr signal, in both the simple mono N-alkylated derivatives – Ni(R–AB)(AB′) and Ni(R–AC)(AC′) and mixed ligand isomeric pairs – Ni(R–AB)(AC′) and Ni(R–AC)(AB′), the assignment can be done in a straightforward way by comparison with the parent complexes, Ni(AB)(AB′) and Ni(AC)(AC′). This is evident, since the parent complex exhibits two N–H bands; whereas in the corresponding mono N-alkylated or mixed ligand isomeric complexes only one N–H frequency is observed. [6,7,9] The disappearance of one of the N–H bands/signals of Ni(AB/AC)(AB′/AC′) in Ni(R–AB/R–AC)(AB′/AC′) and Ni(R–AB/R–AC)(AC′/AB′) makes it easy to identify and assign the N–H frequency/signal that appears in the N-alkyl complexes.

As an illustration, let us consider the case of the isomeric complexes Ni(R–IBI)(IAI′) and Ni(R–IAI)(IBI′) (Table II). In the former set, the N–H stretching frequency occurs in the range 3130–3170 cm^{-1} in the solid state (nujol mull) and around 3160–3180 cm^{-1} in the chloroform solution as a medium broad band; while in the latter set the same are observed around 3155–3190 cm^{-1} in the solid state and 3165 cm^{-1} in solution respectively. The position, medium intensity and broad nature of this band is well comparable with the corresponding N–H stretch of the O-coordinated ligand in Ni(IAI)(IAI′), Ni(R–IAI)(IAI′) [3190 cm^{-1} in mull and $CHCl_3$][6] and Ni(IBI)(IBI′), Ni(R–IBI)(IBI′) [3160 cm^{-1} in mull and 3165 cm^{-1} in $CHCl_3$], [8,9] respectively. Similar correspondence is also observed with Ni(R–IEAI)(IAI′),[14] and Ni(R–IEAI)(IBI′) complexes, respectively. In the comparable analogous systems, our previous studies[6,9] have established that the N–H is present in the O-bonded ligand moiety. It is, therefore, suggested that the N–H of the isomeric sets **belongs to the O-coordinated ligand moiety. Hence, the IAI′ of Ni(R–IBI)(IAI′) and IBI′ of Ni(R–IAI)(IBI′) are O-coordinated ligand moieties.**

This N–H band is broad, suggesting that it is hydrogen bonded to the oxygen of N-coordinated N–O cis to it, as shown in Figure 1. This type of H-bonding requires N-coordinated N–O cis to NH, suggesting that R–IAI/R–IBI has N-bonded isonitroso moiety.

This mode of metal ligand coordination can also be supported by the carbonyl band positions. Reference to Table II shows that the carbonyl band observed for R–IBI in Ni(R–IBI)(IAI′) [1650 (mull), 1660 ($CHCl_3$) cm^{-1}] and IBI′ in Ni(R–IAI)(IBI′) [1665 (mull), 1666 ($CHCl_3$) cm^{-1}], correspond to the corresponding ligand parts of Ni(IBI)(IBI′) [1665 (mull), 1670 ($CHCl_3$) cm^{-1}],[8] Ni(R–IBI)(IBI′) [1665 (mull), 1670 ($CHCl_3$) cm^{-1}],[9] respectively and also to other analogous complexes. Similarly, those observed for R–IAI [1670 (mull), 1658 ($CHCl_3$) cm^{-1}] and IAI′ [1685 (mull), 1700 ($CHCl_3$) cm^{-1}] moieties in the isomeric pair correspond to those of Ni(IAI(IAI′) [1660–1670 (mull), 1670–1675 ($CHCl_3$) cm^{-1}],[6] Ni(R–IAI)(IAI′) [1695–1700 (mull), 1695 ($CHCl_3$) cm^{-1}],[6] and to analogous ones.[14,15] Here, it is assumed that the position of the carbonyl band of a particular ligand is essentially determined by its mode of coordination. This assumption is justified from the chloroform solution spectra. In the solid state, however, there may be some deviation from this assumption, due to the presence of intermolecular interactions like hydrogen bonding, local environment effects, etc. The occurrence of the two C=O frequencies [although in a few cases, due to the overlap of two closely spaced bands, only one broad band is observed as in the case of Ni(Me–IAI)(IBI′)] indicates that each of the ligands present in these complexes has a different mode of coordination.

A similar approach can be extended to the assignment of pmr signals as well (Table III and the published data).[6–9,14,15] It may be pointed out that care need be exercised when there are two or more very closely occurring pmr signals. This is expecially true for signals such as those due to the phenyl groups where they usually appear as complex multiplets.

In this way, a comparison of the spectra of **Ni(R–IEAI)(IBI′), Ni(R–IBI)(IEAI′), Ni(R–IEAI)(IEAI′) and Ni(R–IBI)(IBI′) and analogous ones[6–9;14,15] allows one to assign the ir bands and pmr signals separately to each of the ligands and to any**

TABLE III
Proton magnetic resonance signals (in τ ppm) of Ni(R–AB/R–AC)(AC′/AB′)[a] complexes in $CDCl_3$ and their assignments[b]

Complexes	Ni(R–IBI)(IAI′)[a]					Ni(R–IAI)(IBI′)[a]				
Proton signals R	Me	Et	n–Pr	n–Bu	i–Bu	Me	Et	n–Pr	n–Bu	i–Bu
a) $\underline{H_3C}-\overset{\prime}{C}=N-$										
N-coord. moiety (R–AB/R–AC)	7.84	7.83	7.84	7.85	7.85	7.69	7.69	7.68	7.67	7.65
O-coord. moiety (AC′/AB′)	7.55[d]	7.55[d]	7.54[d]	7.56[d]	7.57[d]	7.58[d]	7.58[d]	7.58[d]	7.56[d]	7.57[d]
b) $\underline{X/Y^e}-\overset{O}{\overset{\|}{C}}-\underset{\mid}{C}=N-$										
N-coord. moiety (R–AB/R–AC)	2.54[c] 2.27[c]	2.50[c] 2.25[c]	2.50[c] 2.25[c]	2.50[c] 2.25[c]	2.53[c] 2.28[c]	7.61	7.62	7.60	7.60	7.65
$\underline{Y/X^e}-\overset{O}{\overset{\|}{C}}-\underset{\mid}{C}=N-$										
O-coord. moiety (AC′/AB′)	7.46	7.45	7.45	7.45	7.47	2.52[c] 2.16[c]	2.53[c] 2.17[c]	2.51[c] 2.15[c]	2.50[c] 2.15[c]	2.53[c] 2.17[c]
c) $H_3C-\overset{\mid}{C}=N-\underline{R}$										
N-coord. moiety (R–AB/R–AC)	6.84 (CH_3)	8.88[t] (CH_3) 6.56[q] (CH_2)	8.93[t] (CH_3) 8.48[s] (CH_2) 6.63[t] (CH_2)	9.93[t] (CH_3) 8.42[s] ($2CH_2$) 6.52[t] (CH_2)	8.96 (CH_3) 8.88 (CH_3) 6.72 (CH) 6.62 (CH_2)	6.93 (CH_3)	8.80[t] (CH_3) 6.51[q] (CH_2)	9.02[t] (CH_3) 8.34[s] (CH_2) 6.58[t] (CH_2)	9.06[t] (CH_3) 8.48[c] ($2CH_2$) 6.54[t] (CH_2)	8.98 (CH_3) 8.91 (CH_3) 6.68 (CH) 6.61 (CH_2)
d) $H_3C-\underset{\mid}{C}=\underline{NH}$										
O-coord. moiety (AC′/AB′)	1.20	1.16	1.19	1.20	1.22	1.00	0.97	0.97	0.96	1.01

[a] R = Me, Et, n–Pr, n–Bu or i–Bu ; [b] Key: d = doublet, t = triplet, q = quartet, s = sextet and c = complex multiplet.

[e] When $X = C_6H_5$, $Y = CH_3 \longrightarrow$ Ni(R–IBI)(IAI′); $X = CH_3$, $Y = C_6H_5 \longrightarrow$ Ni(R–IAI)(IBI′).
$X = C_6H_5$, $Y = OC_2H_5 \longrightarrow$ Ni(R–IBI)(IEAI′); $X = OC_2H_5$, $Y = C_6H_5 \longrightarrow$ Ni(R–IEAI)(IBI′).

other isomeric complexes as well. This general approach with reference to Tables II and III, thus leads to the following conclusions regarding the nature of metal–ligand bonding as:

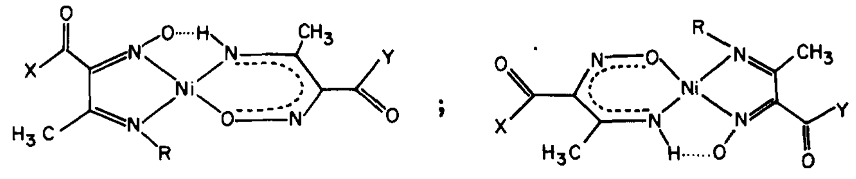
1) In Ni(R–IBI)(IAI′) the R–IBI and IAI′ ligand moieties are respectively N- and O-coordinated; while in their isomeric Ni(R–IAI)(IBI′) complexes R–IAI and IBI′ moieties are N-and O-coordinated respectively.

2) Similarly, in Ni(R–IBI)(IEAI′) complexes, the R–IBI and IEAI′ moieties are N- and O-coordinated respectively; whereas the reverse is true for their isomeric pairs, Ni(R–IEAI)(IBI′).

The following general asymmetric structure (Figure 1) can, therefore, be suggested.

TABLE III (continued)

Complexes	Ni(R–IBI)(IEAI′)^a					Ni(R–IEAI)(IBI′)^a				
Proton signals R	Me	Et	n–Pr	n–Bu	i–Bu	Me	Et	n–Pr	n–Bu	i–Bu
a) $\underline{H_3C}-\overset{|}{C}=N-$										
N-coord. moiety (R–AB/R–AC)	7.86	7.83	7.86	–	7.83	7.73	7.72	7.72	7.73	–
O-coord. moiety (AC′/AB′)	7.59^d	7.58^d	7.58^d	–	7.58^d	7.60^d	7.59^d	7.60^d	7.61^d	–
b) $\underline{X/Y^e}-\overset{O}{\overset{\Vert}{C}}-\underset{|}{C}=N-$										
N-coord. moiety (R–AB/R–AC)	2.50^c 2.26^c	2.50^c 2.25^c	2.50^c 2.27^c	–	2.52^c 2.29^c	8.67^t (CH_3) 5.69^q (CH_2)	8.65^t (CH_3) 5.69^q (CH_2)	8.66^t (CH_3) 5.70^q (CH_2)	8.65^t (CH_3) 5.70^q (CH_2)	– –
$\underline{Y/X^e}-\overset{O}{\overset{\Vert}{C}}-\underset{|}{C}=N-$										
O-coord. moiety (AC′/AB′)	8.63^t (CH_3) 5.64^q (CH_2)	8.63^t (CH_3) 5.63^q (CH_2)	8.64^t (CH_3) 5.63^q (CH_2)	– –	8.63^t (CH_3) 5.63^q (CH_2)	2.53^c 2.17^c	2.52^c 2.17^c	2.50^c 2.16^c	2.53^c 2.18^c	– –
c) $H_3C-\overset{|}{C}=N-\underline{R}$										
N-coord. moiety (R–AB/R–AC)	6.87 (CH_3)	8.83^t (CH_3) 6.58^q (CH_2)	8.92^t (CH_3) 8.48^s (CH_2) 6.64^t (CH_2)	– – –	8.99 (CH_3) 8.89 (CH_2) 6.73 (CH) 6.61 (CH_2)	6.93 (CH_3)	8.79^t (CH_3) 6.53^q (CH_2)	9.01^t (CH_3) 8.35^s (CH_2) 6.65^t (CH_2)	9.04^t (CH_3) 8.50^c $(2CH_2)$ 6.58^t (CH_2)	– –
d) $H_3C-\underset{|}{C}=\underline{NH}$										
O-coord. moiety (AC′/AB′)	1.16	1.14	1.15	–	1.16	0.91	0.88	0.95	0.95	–



Ni(R-AB/R-AC)(AC′/AB′)

FIGURE 1

Here when, $X = CH_3$, $Y = C_6H_5$; $X = OC_2H_5$, $Y = C_6H_5$; $X = C_6H_5$, $Y = CH_3$; and $X = C_6H_5$, $Y = OC_2H_5$; R = Me, Et, n-Pr, n-Bu or i-Bu and $X \neq Y$.

The N-alkyl isonitroso-β-keto-imine moiety always coordinates to nickel(II) through the isonitroso and imino nitrogens; while the isonitroso-β-keto-imine (the other moiety) through the isonitroso oxygen and imino nitrogen.

Factors Governing the Ambidentate Coordination

The present complexes form a unique series of mixed ligand isomeric complexes in which an interchange in the imine substituent between the two coordinated ligands is accompanied by an interchange in their mode of coordination. The formation of these mixed ligand complexes reveals certain factors determining the ambidentate coordination. Specifically, the dependence of the mode of coordination of the ligand on the imine substituent can be due to two factors; one electronic and the other steric.

As one goes from Ni(R–AB)(AC′) to its isomeric complex Ni(R–AC)(AB′), the imine N–H of one ligand and the N–R substituent of the other ligand get exchanged. This in fact, is followed by a change in the mode of coordination as well, i.e., one of the ligands (containing the imine N–H) changing from O- to N- and the other (having N–R) from N- to O-coordination of the isonitroso group. This change in

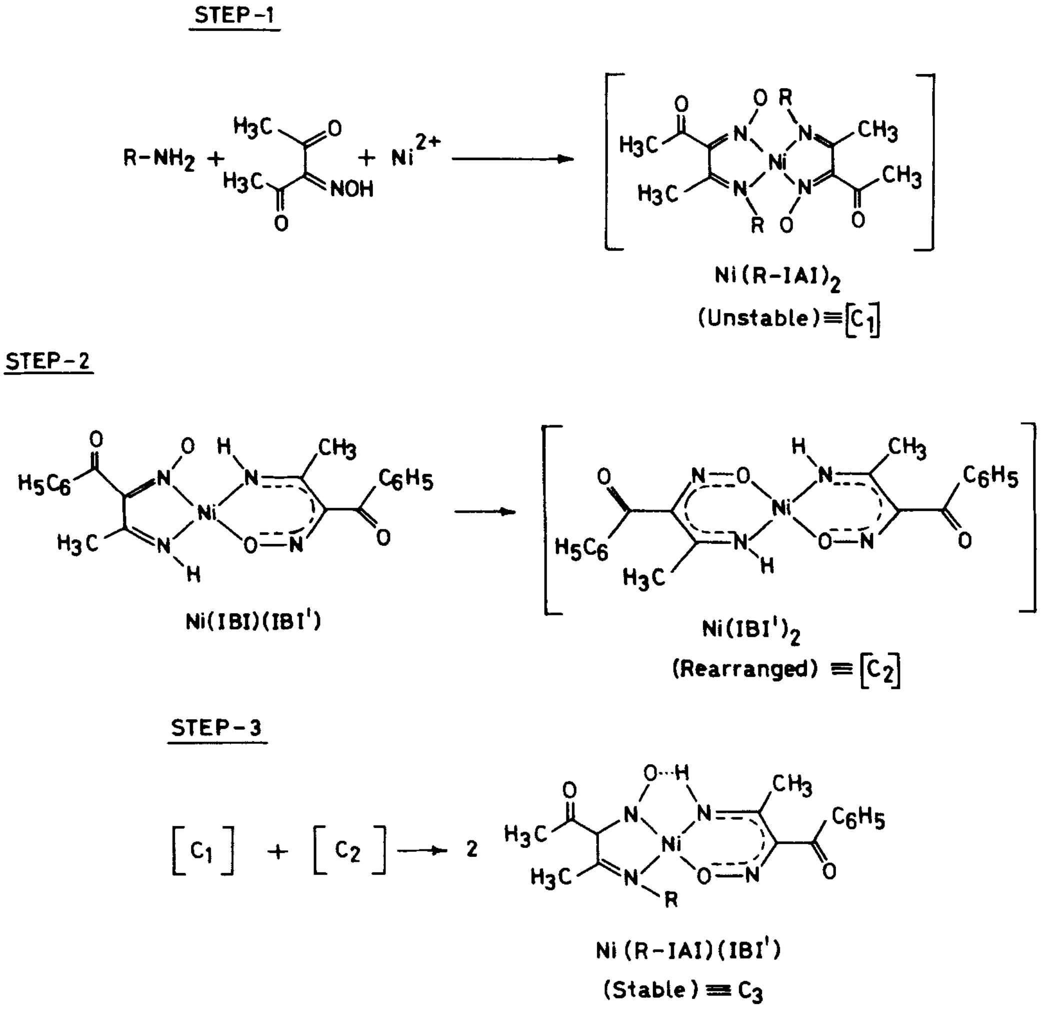


FIGURE 2

the mode of coordination which is dependent on the imine substituent appears to be determined essentially by the steric reasons. The N-alkyl substituted five membered ring ligand adopts an O-coordinated NO in the six membered ring due to steric reasons, as soon as the N–R is replaced by N–H. On the other hand, the N–O group which was O-coordinated previously (in the six membered ring ligand moiety) now changes to the N-coordination as the steric hindrance gets eliminated. Thus, this change in the bonding between the two ligand moieties is simultaneously accompanied by a change in the ring size. The essential difference between the two mixed ligand isomeric complexes, thus seems to be due to the imine substituent as far as the chemical configuration is concerned.

Electronic factors also appear to have some significant influence on the ambidentate coordination of the isonitroso group in the present complexes. It has been observed that the N-alkyl substituted ligands are always N-coordinated[5,7,9] while the unsubstituted ligand moieties can coordinate either through the nitrogen or oxygen of NO.[5,6,8] Thus, the electron donating character of R appears to be responsible for the invariable N-coordination of NO of the N-alkyl substituted ligands.

The formation of only mono alkyl derivatives, Ni(R–AB)(AB′) on amine-exchange of Ni(AB)(AB′), and the non-formation of complexes of the type, Ni(R–AB)$_2$ have been explained as due to the steric hindrance provided by the projecting N–O group cis to the imine (or alkylimine) group.[5,7,9] The same explanation holds good for the present complexes also. In the present case, the formation of the mixed ligand complexes as well as the interchange in the ligand coordination (to cause isomeric pairs) thus appears to be determined by the major contribution of similar steric effects. This steric strain would not have been present, if both the ligand moieties, whether same or different would have adopted the O-coordination of the isonitroso groups.

Probable Mechanism of the Formation of the Complexes

It is found that when one mole of Ni(R–IAI) (IAI′) and one mole of Ni(R–IBI)(IBI′) are mixed together, it is not possible to get either of the isomeric complexes Ni(R–IAI)(IBI′) or Ni(R–IBI)(IAI′). The isolation of the latter type of complexes in the solid state is possible, only when one molecule of an unstable complex [C$_1$] existing in solution reacts with another complex added to it in the finely powdered solid state, which consequently dissolves and undergoes a rearrangement transforming to an unstable O-bonded symmetric complex [C$_2$]. The two species [C$_1$] and [C$_2$] finally undergo ligand exchange by double decomposition to form two moles of the stable isomeric complex (C$_3$), which can be isolated in the solid state. This is explained with reference to the formation of Ni(R–IAI)(IBI′) in Figure 2.

Thus in the isomeric mixed ligand complex, the five membered N-alkyl substituted ring is provided by the constituent combination method while the six membered ring by the rearrangement of the added parent complex. In an analogous way the formation of its isomer, Ni(R–IBI)(IAI′) and other isomeric pairs can be explained.

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