

Mixed Ligand Ni(II) Complexes of Isonitroso- β -Ketoimines, β -Ketoimines and Salicylaldimines and Some of Their Reactions; Importance of H-Bonding in the Stabilization of Isonitroso N-Bonded Isomer

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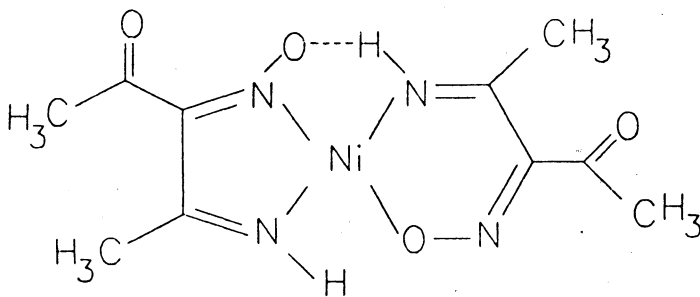
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A new series of diamagnetic nickel(II) complexes of isonitroso- β -ketoimines, β -ketoimines and salicylaldimines have been synthesised and characterised by analytical, IR, NMR, CMR and electronic spectral studies. Synthesis of this type of complexes has been achieved by chelate exchange method. The quasiaromatic character of acetylacetonimine moiety of mixed ligand complexes is confirmed by conducting nitrosation, bromination and phenyl isocyanation and the products have been characterised by elemental analyses, electronic and IR studies.

INTRODUCTION

Isonitrosoacetylacetone (HIAI, 4-imino-2,3-pentane-dione-3-oxime) or related compounds are versatile chelating ligands showing various modes of bonding to metal ions^{1,2}. The isonitroso moiety ($>C=NOH$) also referred to as hydroxyimino group in the literature) is potentially ambidentate coordinating either through nitrogen or oxygen atom producing chelate linkage isomers. For example HIAI reacts with aqueous solution of nickel(II) acetate tetrahydrate yielding bright red square planar complex for which Structure-I has been assigned on the basis of spectral studies^{3,4}.



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This structure has been confirmed in the case of $\text{Ni}(\text{CH}_3\text{-IAI})(\text{IAI}')^{5,6}$ where $\text{CH}_3\text{-IAI}$ is N-bonded N-methylisonitrosoacetylacetoneimine and IAI' is O-bonded isonitrosoacetylacetoneimine. The molecule is essentially planar with significant interaction between N—H proton of the six-membered chelate ring and the projecting oxygen of the N—O group which is *cis* to it. The N—O bond length (1.26 Å) of the five-membered chelate ring is much shorter than the average N—O bond length (1.36 Å) of the six-membered ring. The Ni—N distance (1.81 Å) of the six-membered chelate ring is significantly shorter (1.89 Å) than that of the five-membered chelate ring.

It is important to note that in Structure-I, one of the ligand molecules coordinates through imine-nitrogen and isonitroso-nitrogen while the other through imine-nitrogen and isonitroso-oxygen. This kind of isomerism wherein the dual modes of coordination of isonitroso group occurs in the same metal ion has been referred to as 'intramolecular chelate linkage isomerism'. Since the recognition of this type of novel structure, extensive studies have been carried out in this area mainly by Patel and his coworkers to understand the factors influencing the bifunctional coordination properties of the isonitroso group of isonitroso- β -ketoimines. In addition the reactivity of the coordinated imine groups with aliphatic primary amines and diamines, amine-exchange reactions have also been investigated. Several of these aspects have been reviewed¹. It has been shown that the coordination site of the $>\text{C}=\text{NOH}$ group is primarily governed by factors like the nature of the metal ion, substituent on the azomethine nitrogen, terminal substituent, steric hindrance, polarity of the solvent and temperature. However, surprisingly in all nickel(II) complexes of isonitroso- β -ketoimine complexes known so far, the ligand adopts N,N,N,O-asymmetric coordination sphere around the metal ion irrespective of any other factors. So far no satisfactory explanation has been offered for such an observation. It was, therefore, thought worthwhile to extend these studies to understand the coordination selectivity of isonitroso group in the case of nickel(II) complexes.

Synthesis and characterisation of mixed ligand nickel(II) complexes of isonitroso- β -diketone, acetylacetoneimine and salicylaldehydeimine are described in this paper. It has been shown from these studies that the hydrogen bonding between the two chelated ligands is the prime criterion in determining the bonding site of the isonitroso group. In addition, some of the characteristic reactions of acetylacetoneimine in the mixed ligand complexes of the type (isonitroso- β -ketoimino) (acetylacetoneimino) nickel(II) are also described.

RESULTS AND DISCUSSION

All the parent complexes isolated in the present study are of mixed ligand type and are represented by the general formula $[\text{Ni}(\text{R-L})(\text{L}_1)]$ where R-L = N-alkylisonitrosoacetylacetoneimine/N-alkylisonitrosoethylacetateimine (R-IAI) (R-IEI), N-alkyl = $-\text{C}_2\text{H}_5$, $-\text{n-C}_3\text{H}_7$, $-\text{i-C}_3\text{H}_7$ or $-\text{n-C}_4\text{H}_9$ and L = acetylacetoneimine (AI) or salicylaldehydeimine (SI).

All these complexes were prepared by two methods as described in the experimental section, both involving the chelate exchange mechanism. Generally,

the yields of the complexes obtained by method (II) were higher compared to the method (I). Tables 1 and 2 list the colours, melting points and analytical data of the complexes. All the complexes are non-electrolytes in acetone ($\Lambda_M < 1 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}$). All the complexes are diamagnetic which suggest square-planar geometry around nickel(II).

TABLE-1
COLOUR, MELTING POINT AND ANALYTICAL DATA OF MIXED LIGAND
Ni-(R-IAI-IEI)(AI/SI) COMPLEXES

Complex (colour)	m.p. (°C)	Analytical data %			
		C	H	N	Ni
Ni(C ₂ H ₅ -IAI)(AI) (Red)	137	46.10 (46.18)	6.07 (6.15)	13.40 (13.47)	18.17 (18.81)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(AI) (Red)	112	47.72 (47.88)	6.39 (6.51)	12.85 (12.89)	17.98 (18.01)
Ni(<i>i</i> -C ₃ H ₇ -IAI)(AI) (Scarlet red)	105	47.74 (47.88)	6.43 (6.51)	12.83 (12.89)	17.99 (18.01)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(AI) (Dark red)	105	49.38 (49.44)	6.78 (6.83)	12.30 (12.36)	17.22 (17.26)
Ni(C ₂ H ₅ -IEI)(AI) (Dark red)	180	45.62 (45.65)	6.16 (6.20)	12.32 (12.29)	16.88 (17.16)
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI) (Rosy red)	132	47.19 (47.22)	6.48 (6.52)	11.76 (11.80)	16.05 (16.49)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI) (Red)	94	48.62 (48.67)	6.79 (6.82)	11.42 (11.36)	15.79 (15.86)
Ni(C ₂ H ₅ -IAI)(SI) (Reddish brown)	138	50.28 (50.33)	5.09 (5.14)	12.52 (12.58)	17.56 (17.58)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(SI) (Dark red)	113	51.71 (51.76)	5.46 (5.51)	12.03 (12.08)	16.84 (16.87)
Ni(<i>i</i> -C ₃ H ₇ -IAI)(SI) (Ruby red)	143 (Decomp)	51.74 (51.76)	5.47 (5.51)	12.01 (12.08)	16.85 (16.87)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(SI) (Red)	110	52.95 (53.07)	5.70 (5.86)	11.66 (11.88)	15.94 (16.21)
Ni(C ₂ H ₅ -IEI)(SI) (Reddish brown)	172	49.45 (49.48)	5.22 (5.27)	11.52 (11.55)	15.89 (16.13)
Ni(<i>n</i> -C ₃ H ₇ -IEI)(SI) (Scarlet red)	169	50.79 (50.83)	5.57 (5.61)	11.08 (11.12)	15.38 (15.53)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(SI) (Red)	140	51.95 (52.07)	5.88 (5.92)	10.67 (10.72)	14.81 (14.97)

R = C₂H₅, *n*-C₃H₇ or *n*-C₄H₉.

The theoretical values are given in parentheses below their observed values.

TABLE-2
 COLOUR, MELTING POINT AND ANALYTICAL DATA OF MIXED LIGAND
 COMPLEXES Ni(R-IAI-IEI)(AI·C₆H₅NCO/AI·Br/IAI')

Complex (colour)	m.p. (°C)	Analytical data %			
		C	H	N	Ni
Ni(C ₂ H ₅ -IAI)(AI·C ₆ H ₅ NCO) (Orange red)	240	52.99 (52.92)	5.25 (5.62)	13.13 (12.99)	13.54 (13.62)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(AI·C ₆ H ₅ NCO) (Reddish orange)	235	53.90 (53.95)	5.85 (5.90)	12.84 (12.59)	13.11 (13.19)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(AI·C ₆ H ₅ NCO) (Orange)	242	52.79 (54.92)	6.08 (6.16)	12.17 (12.20)	12.73 (12.78)
Ni(C ₂ H ₅ -IEI)(AI·C ₆ H ₅ NCO) (Orange red)	250	52.15 (52.08)	5.62 (5.69)	12.20 (12.15)	12.70 (12.73)
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI·C ₆ H ₅ NCO) (Yellowish red)	255	53.13 (53.07)	5.93 (5.95)	11.85 (11.79)	12.31 (12.35)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI·C ₆ H ₅ NCO) (Orange red)	245	53.92 (54.00)	6.14 (6.19)	11.49 (11.45)	11.96 (11.99)
Ni(C ₂ H ₅ -IAI)(AI·Br) (Reddish brown)	262	36.81 (36.87)	4.61 (4.65)	10.68 (10.75)	14.98 (15.02)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(AI·Br) (Reddish brown)	268	38.14 (38.55)	4.86 (4.99)	10.31 (10.38)	14.44 (14.50)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(AI·Br) (Reddish brown)	260	40.09 (40.13)	5.24 (5.30)	9.97 (10.03)	13.97 (14.50)
Ni(C ₂ H ₅ -IEI)(AI·Br) (Orange brown)	265	36.67 (37.09)	4.70 (4.79)	9.92 (9.98)	13.90 (13.95)
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI·Br) (Orange brown)	260	38.59 (38.65)	5.03 (5.11)	9.60 (9.66)	13.44 (13.50)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI·Br) (Orange brown)	258	40.06 (40.12)	5.34 (5.40)	9.31 (9.36)	13.02 (13.07)
Ni(C ₂ H ₅ -IAI)(IAI') (Reddish brown)	147	42.19 (42.26)	5.25 (5.33)	16.36 (16.43)	17.15 (17.21)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(IAI') (Yellow)	134	43.89 (43.97)	5.61 (5.69)	15.72 (15.78)	16.48 (16.53)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(IAI') (Yellowish brown)	178	45.48 (45.55)	6.14 (6.20)	15.12 (15.18)	15.87 (15.91)
Ni(C ₂ H ₅ -IEI)(IAI') (Yellow)	133	41.98 (42.07)	5.39 (5.44)	15.01 (15.10)	15.75 (15.82)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(IAI') (Orange)	114	43.60 (43.66)	5.74 (5.77)	14.50 (15.55)	15.19 (15.25)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(IAI') (Yellowish brown)	112	45.09 (45.14)	6.01 (6.07)	13.98 (14.04)	14.66 (14.71)

R = C₂H₅, *n*-C₃H₇ or C₄H₉.

The theoretical values are given in parentheses below their respective observed values.

In the UV region, generally three absorption bands are observed around 38000, 34000 and 29400 cm^{-1} . The high intensities of these bands suggest that they are due to spin allowed $\pi \rightarrow \pi^*$ transition. Electronic spectral data for representative complexes are given in Tables 3 and 4.

TABLE-3
ELECTRONIC ABSORPTION SPECTRAL DATA OF THE MIXED LIGAND
COMPLEXES Ni(R-IAI/R-IEI)(AI) IN CHLOROFORM

Complex	Absorption maxima in cm^{-1}			
Ni(C ₂ H ₅ -IAI)(AI)	38400 (2.33×10^4)	34000 (1.00×10^4)	28500 (0.78×10^4)	20400 (0.2×10^4)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(AI)	38400 (2.59×10^4)	34000 (1.18×10^4)	28500 (0.98×10^4)	20400 (0.26×10^4)
Ni(<i>i</i> -C ₃ H ₇ -IAI)(AI)	37600 (1.43×10^4)	34200 (1.43×10^4)	28500 (0.55×10^4)	20400 (0.19×10^4)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(AI)	38700 (1.94×10^4)	34400 (0.86×10^4)	28500 (0.74×10^4)	20400 (0.19×10^4)
Ni(C ₂ H ₅ -IEI)(AI)	39700 (2.24×10^4)	35200 (1.06×10^4)	20800 (0.21×10^4)	
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI)	40000 (1.51×10^4)	33100 (1.18×10^4)	22200 (0.17×10^4)	
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI)	39700 (1.84×10^4)	36000 (0.89×10^4)	20800 (0.16×10^4)	

ϵ ($1 \text{ mole}^{-1} \text{ cm}^{-1}$) values in parentheses; R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇, or *n*-C₄H₉.

TABLE-4
ELECTRONIC ABSORPTION SPECTRAL DATA OF THE MIXED LIGAND
COMPLEXES Ni(R-IAI/E-IEI)(SI) IN CHLOROFORM

Complex	Absorption maxima in cm^{-1}		
Ni(C ₂ H ₅ -IAI)(SI)	37000 (2.84×10^4)	32200 (0.66×10^4)	20400 (0.1×10^4)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(SI)	37000 (2.64×10^4)	32200 (0.68×10^4)	20400 (0.25×10^4)
Ni(<i>i</i> -C ₃ H ₇ -IAI)(SI)	38000 (1.14×10^4)	32200 (0.64×10^4)	20400 (0.3×10^4)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(SI)	38000 (2.14×10^4)	33000 (0.78×10^4)	21600 (0.28×10^4)
Ni(C ₂ H ₅ -IEI)(SI)	39200 (2.6×10^4)		20800 (0.35×10^4)
Ni(<i>n</i> -C ₃ H ₇ -IEI)(SI)	38700 (2.6×10^4)		20800 (0.22×10^4)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(SI)	37800 (2.3×10^4)		21000 (0.22×10^4)

ϵ ($1 \text{ mole}^{-1} \text{ cm}^{-1}$) values in parentheses. (R in same is in Table-3).

The important IR frequencies along with their assignments are given in Tables 5 and 6 for the parent complexes. From the data (Table-5) it is clear that the spectra of (R-IAI/IEI)(AI) complexes show an intense band around 1660 cm^{-1} which is assignable to non-coordinated carbonyl group of $-\text{COCH}_3$ moiety. It is now generally accepted that the position of ν_{CO} can be used to determine the bonding site of the ambidentate isonitroso group. It has been reported that in most of the nickel(II) complexes with isonitrosoacetylacetonimine, the ν_{CO} of the isonitroso-N-coordinated ligand appears in the region $1670\text{--}1650\text{ cm}^{-1}$.^{1,2} The ν_{CO} observed in the present complexes is comparable with this value. It is therefore evident that R-IAI/R-IEI is coordinated to nickel(II) through isonitroso-N and imine-N atoms. The occurrence of a band of variable intensity around 1210 cm^{-1} (ν_{NO}) is also an indication of isonitroso-N-coordinated linkage^{1,2}. The

TABLE-5
CHARACTERISTIC IR FREQUENCIES (cm^{-1}) OF Ni(R-IAI-IEI)(AI) COMPLEXES

Complex	R-IAI/R-IEI			AI				
	ν_{NO}	ν_{CO} (Non-coord.)	ν_{CN}	π_{CH}	δ_{CO}	ν_{CO} (Coord.)	ν_{CN}	ν_{NH}
Ni(C ₂ H ₅ -IAI)(AI)	1210 w	1660 vs	1610 s	840 s	1200 w	1530 s	1590 m	3250 m,b
Ni(<i>n</i> -C ₃ H ₇ -IAI)(AI)	1220 w	1655 vs	1605 s	840 s	1200 w	1530 s	1590 m	3255 m,b
Ni(<i>i</i> -C ₃ H ₇ -IAI)(AI)	1220 m	1680 s	1605 s	815 s	1210 w	1540 s	1590 m	3260 m,b
Ni(<i>n</i> -C ₄ H ₉ -IAI)(AI)	1215 m	1660 s	1600 s	840 s	1200 w	1535 s	1590 m	3265 m,b
Ni(C ₂ H ₅ -IEI)(AI)	1230 w	1660 s	1590 s	835 s	1200 m	1525 s	1580 m	3250 m,b
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI)	1228 w	1670 s	1590 s	835 s	1200 m	1525 s	1585 m	3258 m,b
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI)	1220 w	1700 s	1600 s	830 s	1200 m	1530 s	1590 m	3258 m,b

R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇ or *n*-C₄H₉.

TABLE-6
CHARACTERISTIC IR FREQUENCIES (cm^{-1}) OF Ni(R-IAI/R-IEI)(SI) COMPLEXES

Complex	R-IAI/R-IEI			SI		
	ν_{NO}	ν_{CO} (Non-coord.)	ν_{CN}	ν_{CO} (Phenolic)	ν_{CN}	ν_{NH}
Ni(C ₂ H ₅ -IAI)(SI)	1200 m	1660 s	1615 s	1320 m	1580 m	3220 m,b
Ni(<i>n</i> -C ₃ H ₇ -IAI)(SI)	1230 s	1655 s	1610 s	1305 m	1590 m	3230 m,b
Ni(<i>i</i> -C ₃ H ₇ -IAI)(SI)	1210 s	1650 s	1620 s	1320 m	1605 m	3235 m,b
Ni(<i>n</i> -C ₄ H ₉ -IAI)(SI)	1220 m	1660 s	1620 s	1320 m	1585 m	3240 m,b
Ni(C ₂ H ₅ -IEI)(SI)	1200 m	1660 s	1600 s	1320 m	1585 m	3220 m,b
Ni(<i>n</i> -C ₃ H ₇ -IEI)(SI)	1230 s	1655 s	1620 s	1320 m	1585 m	3230 m,b
Ni(<i>n</i> -C ₄ H ₉ -IEI)(SI)	1220 m	1660 s	1620 s	1320 m	1585 m	3250 m,b

R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇ or *n*-C₄H₉

square planar geometry around nickel(II) is completed by the coordination of AI or SI moiety through its nitrogen and oxygen. The coordinated AI shows characteristic frequencies around 840, 1200, 1530 and 3250 cm^{-1} assignable to ν_{CH} , δ_{CH} , ν_{CO} (coordinated) and ν_{NH} respectively. The NH stretching frequency appears as a broad band suggesting that NH proton is H-bonded with oxygen of N—O group. Further the position of ν_{NH} shows slight dependence on the chain length of the alkyl group. As the chain length of the alkyl group increases, the band position of NH decreases indicating an increase in hydrogen bond length. A probable explanation for the observation is that as the chain length of alkyl group increases oxygen atom goes above/below the coordination plane. Consequently the —NO — — NH— distance decreases with the chain length of the alkyl group, thereby accounting for the increase in hydrogen bond strength with increase in chain length of the alkyl group.

As indicated in Table-6, the IR spectra of all Ni(R-IAI/IEI) (SI) complexes show intense bands around 1660–1650, 1230–1200 and 1605–1580 cm^{-1} which are assignable to non-coordinated ν_{CO} , ν_{NO} and ν_{CN} of the R-IAI/R-IEI ligand moiety^{1,2,7,8} respectively. Further the bands ν_{CO} and ν_{NO} are indicative of the N-coordinated isonitroso ligand moiety^{1,2,7,8}. It is therefore suggested that the ligand R-IAI is coordinated to Ni(II) through isonitroso-N and imine nitrogen formed a five-membered ring.

The coordinated salicylaldimine shows characteristic vibrational frequencies at 1320–1305, 1605–1580 and 3250–3220 cm^{-1} assignable to ν_{CO} (phenolic), $\nu_{\text{C=N}}$ and ν_{NH} respectively^{9,10}. Here again the NH stretching band appears as a broad absorption suggesting that it is H-bonded with the oxygen of N—O group of the five-membered ring. As the chain length of the alkyl group increases, the NH stretching frequency decreases, indicating increased H-bond strength.

The ¹H NMR spectral data of the complexes are given in Tables 7 to 10. The ¹H NMR spectra of Ni(R-IAI/R-IEI)(AI) complexes show four methyl signals in the region 2.38–0.97 δ and those of Ni(R-IAI/R-IEI)(SI) complexes show two signals corresponding to methyl group in the region 2.39–2.20 δ . It can be seen that the methyl protons of R-IAI/R-IEI are deshielded compared to those of AI. This may be due to the ring current effect of AI in the case of Ni(R-IAI/R-IEI)(AI) complexes, which have quasiaromatic character. The NH proton signal is quite broad in the NMR spectra of all the complexes which also indicates that it is H-bonded. Further NH proton is progressively deshielded as the chain length of R increases. The γ -CH proton of AI moiety in Ni(R-IAI)(R-IEI)(AI) appears as a doublet around 5.02 δ probably due to the 'meta-like coupling' with —NH proton as in benzene¹¹. The signals around 7.0 δ are assignable to phenyl protons of the salicylaldimine residue in the NMR spectra of Ni(R-IAI)(SI) complexes.

The ¹H assignments made above have also been confirmed by the ¹³CMR spectra of the complexes (Tables 11 and 12). The ¹³CMR assignments of all the mixed ligand complexes have been made by comparing with the ¹³C chemical shift data of related complexes⁸. These assignments have been verified by off resonance spectra in the case of Ni(n-C₃H₇-IAI)(AI) complex. From the data presented it is clear that —CO and —CN carbon chemical shifts lie in the region

TABLE-7
PMR DATA (δ ppm) OF Ni(R-IAI)(AI) COMPLEXES ALONG WITH THEIR ASSIGNMENTS IN CDCl₃

Complex	Signals of R-IAI			Signals of AI							
	—COCH ₃ of IAI moiety	=NCCH ₃	*N-R	N—CH ₂	—CH ₂	—CH ₂	—CH ₃	—NC(CH ₃)	—OC(CH ₃)	γ -CH	NH
Ni(C ₂ H ₅ -IAI)(AI)	2.38 (s,3)	2.23 (s,3)	3.43 (q,2)	1.2 (t,3)	1.90 (s,3)	2.07 (s,3)	5.02 (d,1)	5.02 (d,1)	6.60 (b,1)		
Ni(<i>n</i> -C ₃ H ₇ -IAI)(AI)	2.35 (s,3)	2.25 (s,3)	3.31 (t,2)	0.98 (t,3)	1.91 (s,3)	2.05 (s,3)	5.01 (d,1)	5.01 (d,1)	6.63 (b,1)		
Ni(<i>i</i> -C ₃ H ₇ -IAI)(AI)	2.32 (s,3)	2.20 (s,3)		1.46† (d,6)	1.92 (s,3)	2.07 (s,3)	5.02 (d,1)	5.02 (d,1)	6.65 (b,1)		
Ni(<i>n</i> -C ₄ H ₉ -IAI)(AI)	2.36 (s,3)	2.20 (s,3)	3.35 (t,2)	1.58 (m,2)	1.91 (s,3)	2.06 (s,3)	5.02 (d,1)	5.02 (d,1)	6.68 (b,1)		

*R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇ or *n*-C₄H₉

†The —CH proton of the isopropyl group occurs as a multiplet centered at 4.01 δ .

Abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, b: broad.

TABLE-8
PMR DATA (δ ppm) OF Ni(R-IEI)(AI) COMPLEXES ALONG WITH THEIR ASSIGNMENTS IN CDCl₃

Complex	Signals of R-IAI			Signals of AI						
	—COCH ₃ of IEI moiety	=NCCH ₃	*N-R	N—CH ₂	—CH ₂	—CH ₃	—NC(CH ₃)	—OC(CH ₃)	γ -CH	NH
Ni(C ₂ H ₅ -IEI)(AI)	4.20 (q,2)	1.27 (m,6)	2.14 (s,3)	3.47 (m,2)	†	1.90 (s,3)	2.03 (s,3)	5.03 (d,1)	6.65 (b,1)	
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI)	4.31 (q,2)	1.33 (m,6)	2.28 (s,3)	3.31 (q,2)	1.67 (m,2)	†	1.90 (s,3)	2.01 (s,3)	5.01 (d,1)	6.70 (b,1)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI)	4.27 (q,2)	0.97 (m,6)	2.16 (s,3)	3.33 (t,2)	1.47 (m,2)	†	1.90 (s,3)	2.00 (s,3)	5.00 (d,1)	6.80 (b,1)

*R = C₂H₅, *n*-C₃H₇ or *n*-C₄H₉

†Signal overlaps with the signal —OCH₂—CH₃

Abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, b: broad.

TABLE-9
PMR DATA (δ ppm) of Ni(R-IAI)(SI) COMPLEXES ALONG WITH THEIR ASSIGNMENT IN CDCl₃

Complex	Signals of R-IAI				Signals of AI					
	—COCH ₃ of IAI moiety	=NCCH ₃	N—CH ₂	*N-R	—CH ₂	—CH ₂	—CH ₃	—C ₆ H ₄	—N=CH	NH
Ni(C ₂ H ₅ -IAI)(SI)	2.37 (s,3)	2.26 (s,3)	3.15 (q,2)	1.23 (t,3)	—	—	—	7.03 (m,4)	8.01 (s,1)	9.28(b,1)
Ni(<i>n</i> -C ₃ H ₇ -IAI)(SI)	2.39 (s,3)	2.27 (s,3)	3.42 (t,2)	1.03 (q,3)	—	—	—	7.04 (m,4)	8.03 (s,1)	9.31 (b,1)
Ni(<i>i</i> -C ₃ H ₇ -IAI)(SI)	2.37 (s,3)	2.26 (s,3)	—	1.01 (d,6)	†	—	—	7.02 (m,4)	8.03 (s,1)	9.33 (b,1)
Ni(<i>n</i> -C ₄ H ₉ -IAI)(SI)	2.30 (s,3)	2.20 (s,3)	3.37 (t,2)	1.50 (m,4)	0.93 (q,3)	—	—	6.90 (m,4)	8.00 (s,1)	9.34 (b,1)

*R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇ or *n*-C₄H₉.

†The —CH proton of the isopropyl group occurs as a multiplet centred at 4.01 δ .

Abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, b: broad.

TABLE-10
PMR DATA (δ ppm) OF Ni(R-IEI)(SI) COMPLEXES ALONG WITH THEIR ASSIGNMENTS IN CDCl₃

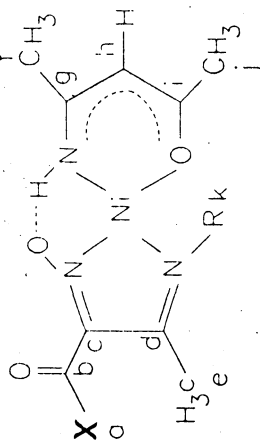
Complex	Signals of R-IAI				Signals of AI							
	—COCH ₃ of IEI moiety	—OCH ₂	—CH ₃	—NCCH ₃	N—CH ₂	*N-R	—CH ₂	—CH ₂	—CH ₃	—C ₆ H ₄	—N=CH	NH
Ni(C ₂ H ₅ -IEI)(AI)	4.27 (q,2)	1.27 (m,3)	—	2.20 (s,3)	—	—	3.47 (q,2)	†	—	7.00 (m,4)	8.01 (s,1)	9.33 (b,1)
Ni(<i>n</i> -C ₃ H ₇ -IEI)(AI)	4.37 (q,2)	1.36 (m,3)	—	2.23 (s,3)	—	—	3.47 (q,2)	1.63 (m,2)	1.03 (t,3)	7.05 (m,4)	8.06 (s,1)	9.53 (b,1)
Ni(<i>n</i> -C ₄ H ₉ -IEI)(AI)	4.24 (q,2)	1.33 (m,6)	—	2.20 (s,3)	3.33 (q,2)	1.70 (m,4)	—	—	1.03 (t,3)	7.05 (m,4)	7.96 (s,1)	9.53 (b,1)

*R = C₂H₅, *n*-C₃H₇ or *n*-C₄H₉

†Signal overlaps with the signal —OCH₂—CH₃.

Abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, b: broad.

TABLE-II
 ^{13}C -NMR SPECTRAL DATA (δ ppm) OF Ni(R-IA/R-IE)D(Al) COMPLEXES IN CDCl_3



Complex	a	b	c	d	e	f	g	h	i	j	k
Ni(C_2H_5 -IA)D(Al) X = CH_3 , R = C_2H_5	31.96	191.31	166.97	154.01	24.64	25.39	171.65	98.21	176.71	16.62	15.06 α 41.17 β
Ni(<i>n</i> - C_3H_7 -IA)D(Al) X = CH_3 , R = C_3H_7	31.96	192.00	166.97	154.11	24.55	25.39	171.78	98.21	176.58	16.62	11.63 α 18.48 β 48.39 γ
Ni(<i>i</i> - C_3H_7 -IA)D(Al) X = CH_3 , R = <i>i</i> - C_3H_7	31.65	193.60	166.80	152.40	25.30	23.93	170.00	97.84	176.00	17.08	*
Ni(<i>n</i> - C_4H_9 -IA)D(Al) X = CH_3 , R = C_3H_7	32.49	192.30	166.97	154.14	25.27	24.58	171.68	98.18	176.61	16.86	13.98 α 18.54 β 20.64 γ 46.63 δ

Complex	a	b	c	d	e	f	g	h	i	j	k
Ni(C ₂ H ₅ -IEI)(Al) X = OC ₂ H ₅ , R = C ₂ H ₅	15.59 —OCH ₂ CH ₃	179.06	166.72	145.20	25.27	24.58	170.00	98.18	176.46	16.41	14.26 α 41.51 β
	61.92 —OCH ₂ CH ₃										
Ni(<i>n</i> -C ₃ H ₇ -IEI)(Al) X = OC ₂ H ₅ , R = C ₃ H ₇	14.23 —OCH ₂ CH ₃	179.04	164.80	144.80	25.60	23.68	169.94	98.16	174.80	16.31	11.59 α 18.48 β 48.55 γ
	61.29 —OCH ₂ CH ₃										
Ni(<i>n</i> -C ₄ H ₉ -IEI)(Al) X = OC ₂ H ₅ , R = C ₄ H ₉	15.45 —OCH ₂ CH ₃	178.02	162.42	142.70	24.82	23.58	171.50	98.47	175.52	15.64	11.65 α 14.15 β 23.72 γ 48.12 δ
	62.31 —OCH ₂ CH ₃										

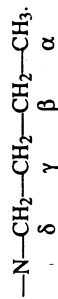
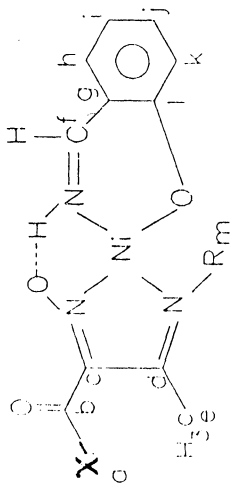
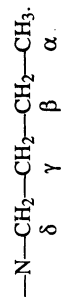


TABLE-12
 ^{13}C -NMR SPECTRAL DATA (δ ppm) OF $\text{Ni}(\text{R}-\text{IAI}/\text{R}-\text{IEI})(\text{SI})$ COMPLEXES IN CDCl_3



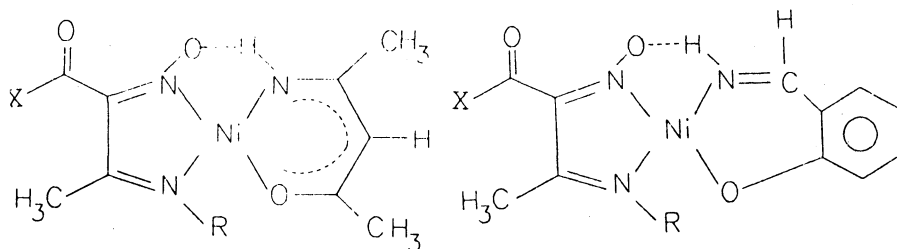
Complex	a	b	c	d	e	f	g	h	i	j	k	l	m
$\text{Ni}(\text{C}_2\text{H}_5\text{-IAI})(\text{SI})$ $\text{X} = \text{CH}_3, \text{R} = \text{C}_2\text{H}_5$	31.96	192.05	163.41	154.23	18.45	172.49	120.90	115.88	121.99	132.90	134.27	164.21	15.07 α 41.17 β
$\text{Ni}(\text{n-C}_3\text{H}_7\text{-IAI})(\text{SI})$ $\text{X} = \text{CH}_3, \text{R} = \text{C}_3\text{H}_7$	31.99	192.00	163.50	148.10	18.51	172.40	120.04	115.91	121.96	132.93	134.36	164.00	11.72 α 23.68 β 42.36 γ
$\text{Ni}(\text{i-C}_3\text{H}_7\text{-IAI})(\text{SI})$ $\text{X} = \text{CH}_3, \text{R} = \text{C}_3\text{H}_7$	31.90	192.01	163.52	147.10	18.52	172.50	120.04	115.80	121.96	133.10	134.70	164.10	*
$\text{Ni}(\text{n-C}_4\text{H}_9\text{-IAI})(\text{SI})$ $\text{X} = \text{CH}_3, \text{R} = \text{C}_4\text{H}_9$	32.80	192.80	164.00	148.80	18.80	172.80	121.20	116.40	122.40	133.50	134.80	164.80	14.4 α 17.2 β 20.8 γ 46.8 δ

Complex	a	b	c	d	e	f	g	h	i	j	k	l	m
Ni(C ₂ H ₅ -IEI)(SI) X = OC ₂ H ₅ , R = C ₂ H ₅	18.48 —OCH ₂ CH ₃	170.59	163.28	145.10	15.74	170.41	120.99	115.79	121.89	132.96	134.11	164.06	15.12 α 41.48 β
	61.01 —OCH ₂ CH ₃												
Ni(<i>n</i> -C ₃ H ₇ -IEI)(SI) X = OC ₂ H ₅ , R = C ₃ H ₇	20.74 —OCH ₂ CH ₃	175.60	163.28	144.80	15.97	170.01	120.08	115.82	121.87	132.96	134.23	163.36	14.04 α 35.52 β 46.87 γ
	61.04 —OCH ₂ CH ₃												
Ni(<i>n</i> -C ₄ H ₉ -IEI)(SI) X = OC ₂ H ₅ , R = C ₄ H ₉	18.51 —OCH ₂ CH ₃	170.54	160.04	145.24	15.97	164.00	121.03	115.83	121.83	132.96	134.17	163.28	11.72 α 14.23 β 23.72 γ 48.67 δ
	61.04 —OCH ₂ CH ₃												



of 192.05–150.01 δ , while the carbon chemical shifts of the alkyl groups resonate in the high field region, 48.67 to 11.59 δ .

Based on the spectroscopic evidences discussed above, the complexes can be assigned the following general Structures II and III.



II

III

X = CH₃ or OC₂H₅, R = C₂H₅, n-C₃H₇, i-C₃H₇ or n-C₄H₉

Probable mechanism of formation of mixed ligand complexes

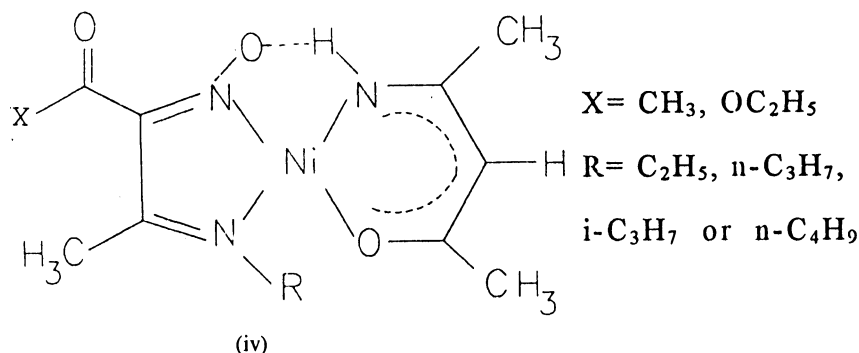
All the mixed ligand complexes have been prepared by two independent methods. Method I involves ligand exchange between an unstable complex and a chelating ligand and method II involves ligand exchange between two chelates. The following mechanism has been suggested for the formation of the complexes.

In the first step, the isonitroso- β -diketone reacts with added alkylamine to form a Schiff base (N-alkylisonitroso- β -ketoimine). In the second step, the unstable N-alkylisonitroso- β -ketoimine complexes react with nickel(II) forming bis-(N-alkylisonitroso- β -ketoimine)-nickel(II). The latter complex is stable only in solution. Its existence in the solution having a *trans* symmetric structure has been confirmed by ¹H NMR studies *in situ*¹². In the third step, the ligand AI/SI displaces one of the R-IAI of the unstable Ni(R-IAI)₂/(R-IEI)₂ complex forming a stable complex. If Ni(AI)₂ or Ni(SI)₂ is added to the solution of the unstable complex Ni(R-IAI)₂/(R-IEI)₂, chelate exchange occurs between the unstable complex and Ni(AI/SI)₂, forming the stable mixed ligand Ni(R-IAI/R-IEI)(AI/SI). The yield of the complexes obtained by method II are higher compared to that of method I. This may be attributed to the partial hydrolysis of HAI/SAI. In fact, β -ketoimines and salicylaldimines are known to hydrolyse in aqueous medium¹³.

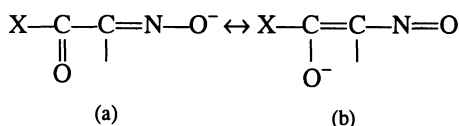
Reaction of mixed ligand complexes

It is well known that the coordinated β -diketones undergo several reactions at γ -CH position which are characteristic of aromatic nuclei. However, studies on such a reaction in the case of coordinated β -ketoimines are meagre¹. It was therefore thought worthwhile to examine the reactivity of coordinated AI in the present mixed ligand complexes. Nitrosation, bromination and phenyl isocyanation reactions were conducted on Ni(R-IAI/R-IEI)(AI) complexes.

Nitrosation: Reactions of Ni(R-IAI/R-IEI)(AI) with gaseous nitric oxide yielded coloured nitrosated crystalline complexes. The following asymmetric structure has been proposed for the nitrosated complexes (IV).



The asymmetric coordination is revealed by the IR spectra. The IR spectra (Table-13) of nitrosated complexes show two distinct bands for the non-coordinated CO (1720–1660 cm⁻¹). Of the two CO frequencies in the complex, the higher frequency has been assigned to the N-coordinated and the lower to O-coordinated ligand¹. The shift of the CO stretching to higher frequency in the O-coordinated compared to the N-coordinated one is attributed to the larger contribution of the resonance form (a) than (b) to the structure of the former than that of the latter.



The N- and O-bonded stretching frequencies of NO are observed around 1230–1100 cm⁻¹. The higher frequencies are assignable to N-bonded and lower frequencies to O-bonded NO stretch¹.

The PMR spectra of the nitrosated complex are identical with those of the same type of complexes obtained by the usual procedure^{2, 4, 11, 14}. The complexes obtained by this procedure have higher purity than those obtained by the routine methods.

Bromination: Ni(R-IAI/R-IEI)(AI) react readily with bromine or N-bromo-succinimide giving γ -substituted complexes. All the complexes are coloured crystalline solids and are sparingly soluble in common organic solvents. All the complexes have square planar geometry as indicated by their diamagnetic nature. The IR spectra (Table-14) of the complexes showed the absence of π_{CH} and δ_{CH} frequencies suggesting the γ -CH substitution by bromine. Rest of the spectral features are similar to those of parent complexes.

Phenylisocyanation: Ni(R-IAI/R-IEI)(AI) react with phenyl isocyanate giving γ -phenylamido substituted complexes. All the complexes are coloured crystalline solids and are sparingly soluble in common organic solvents. They have square planar geometry evidenced from their diamagnetic nature. The absence of π_{CH} and δ_{CH} bands and the appearance of new bands corresponding to γ_{CH} vibrations in the IR spectra (Table-14) of the complexes confirm the substitution at γ -CH position by the phenylamido group. Rest of the spectral features are same as those of the parent complexes.

TABLE-13
CHARACTERISTIC IR FREQUENCIES (IN cm^{-1}) OF Ni(R-IAI/R-IEI)(IAI') COMPLEXES

Complex	5-Membered ring			6-Membered ring		
	ν_{NO} N-bonded	ν_{CO} Non-coordinated	$\nu_{\text{C=N}}$	ν_{NO} O-bonded	ν_{CO} Non-bonded	ν_{NH}
Ni(C_2H_5 -IAI)(IAI')	1225 m	1660 s	1600 s	1110 m	1720 s	3190 m,b
Ni(n - C_3H_7 -IAI)(IAI')	1220 w	1670 s	1600 s	1130 m	1730 s	3185 m,b
Ni(n - C_4H_9 -IAI)(IAI')	1220 w	1700 s	1610 s	1135 m	1740 s	3180 m,b
Ni(C_2H_5 -IEI)(IAI')	1230 w	1670 s	1610 s	1115 m	1725 s	3195 m,b
Ni(n - C_3H_7 -IEI)(IAI')	1228 w	1680 s	1610 s	1135 m	1730 s	3190 m,b
Ni(n - C_4H_9 -IEI)(IAI')	1225 w	1710 s	1620 s	1135 m	1730 s	3190 m,b

R = C_2H_5 , n - C_3H_7 or n - C_4H_9 .

IAI = N-bonded isonitrosoacetylacetonimine moiety.

IAI' = O-bonded isonitrosoacetylacetonimine moiety.

TABLE-14
CHARACTERISTIC IR FREQUENCIES (IN cm^{-1}) OF Ni(R-IAI/R-IEI)(IAI') COMPLEXES

Complex	R-IAI/R-IEI			AI		
	ν_{NO}	ν_{CO} Non-coordinated	ν_{CN}	ν_{NO} Coordinated	ν_{CN}	ν_{NH}
Ni(C_2H_5 -IAI)(AI·Br)	1225 w	1665 s	1590 s	1520 s	1575 m	3240 m,b
Ni(n - C_3H_7 -IAI)(AI·Br)	1220 w	1680 s	1590 s	1520 s	1580 m	3250 m,b
Ni(n - C_4H_9 -IAI)(AI·Br)	1220 w	1690 s	1590 s	1525 s	1585 s	3522 m,b
Ni(C_2H_5 -IEI)(AI·Br)	1235 w	1675 s	1595 s	1530 s	1580 m	3250 m,b
Ni(n - C_3H_7 -IEI)(AI·Br)	1225 w	1685 s	1600 s	1530 s	1585 m	3255 m,b
Ni(n - C_4H_9 -IEI)(AI·Br)	1220 w	1690 s	1600 s	1535 s	1585 s	3260 m,b

R = C_2H_5 , n - C_3H_7 or n - C_4H_9 .

EXPERIMENTAL

Isonitrosoacetylacetone (HIAA)¹⁵, isonitrosoethylacetoacetate (HIEA)¹⁶, acetylacetoneimine (AI) and salicylaldimine (SI)¹⁷ were prepared by the reported procedures. Bis(acetylacetoneimino)nickel(II)¹⁸ and bis(salicylaldimino) nickel (II)¹⁹ were also prepared according to the known method.

Preparation of mixed ligand complexes

(N-alkylisonitrosoacetylacetoneimino) (acetylacetoneimino / salicylaldimino)-nickel(II) complexes were prepared by two methods.

Method I: A mixture of nickel(II)-acetate tetrahydrate (0.001 mole), isonitrosoacetylacetone (0.002 mole) and the amine (1 mL) in 90% aqueous ethanol (30 mL) was stirred till a clear solution was obtained. To the resulting reddish brown solution, powdered acetylacetoneimine (0.002 mole) or salicylaldimine (0.002 mole) was added and the stirring continued for 2–4 h. An orange yellow or red solution obtained was concentrated in vacuum to obtain crystals of the complex. In some cases a paste was obtained. It was dissolved in ethanol twice and concentrated to obtain the crystals of the complexes.

Method II: The procedure employed in this method was similar to that of the first method, except that bis(acetylacetoneimine)nickel(II) (0.002 mole) was added instead of acetylacetoneimine. An ethanolic solution (90% aqueous) containing nickel(II)acetate tetrahydrate (0.001 mole), isonitrosoacetylacetone (0.002 mole) and amine (1 mL) was stirred till a clear solution was obtained. To this solution powdered bis(acetylacetoneimino)nickel(II) or bis(salicylaldimino) nickel(II) was added with constant stirring. Crystals of the complexes were obtained after concentrating the resulting solution in vacuum. The yield of the complex obtained by this procedure was generally higher as compared to method I.

(N-Alkylisonitrosoethylacetoacetateimino) (acetylacetoneimino/salicylaldimino)nickel(II) complexes were prepared by an analogous procedure adopted for Ni(R-IAI)(AI/SI) except that HIEA was employed in place of HIAA. The complexes were recrystallised from benzene or diethyl ether or benzene-diethyl ether mixture (1 : 1 by volume).

Substituted complexes of Ni(R-IAI/R-IEI)(AI)

Nitrosation: The nitrosation of the complexes was carried out with nitric oxide. An ice-cooled solution of the complex (0.001 mole) in chloroform (40 mL) was degassed by bubbling nitrogen gas. Nitric oxide, purified over sodium hydroxide pellets, was bubbled vigorously through the above solution for about 15 min, to obtain a reddish yellow solution. It was concentrated in vacuum to obtain reddish brown crystals. The complexes were recrystallised from benzene or benzene-chloroform mixture (1 : 1 by volume).

Bromination: Brominated complexes were obtained by two methods.

To an ice-cold solution of the complex (0.001 mole) in benzene, liquid bromine (0.001 mole) was added slowly with constant stirring. After the addition of bromine, the solution was stirred at 0–5°C for about 15 min. A crystalline

precipitate which results was filtered, washed repeatedly with benzene followed by chloroform.

To a solution of the complex (0.001 mole) in chloroform (40 mL) powdered N-bromosuccinimide (0.001 mole) was added. The resulting solution was stirred for 2–3 h. The crystalline precipitate obtained was filtered, washed with warm ether to remove the succinimide formed during the reaction.

Yield was higher when N-bromosuccinimide was used as a brominating agent. The complex could not be purified further because of their poor solubility in common organic solvents.

Phenylisocyanation: A solution of the complex (0.001 mole) and phenyl isocyanate (0.001 mole) in dry benzene (50 mL) was stirred vigorously for about 30 min. During stirring, the reaction container was closed with CaCl₂ guard tube to prevent atmospheric moisture. A crystalline product that was obtained was filtered and washed with benzene followed by ether. Low solubility of the complexes in common organic solvents prevented their further purification.

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