

Reactions of coordinated bivalent tetradeятate schiff-base chelates of nickel (II) and palladium (II)

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Abstract. Reactions of N,N' -*n*-propylene-bis(acetylacetoneimino) metal (II), $M[n\text{-P-(AI)}_2]$, where $M=\text{Ni(II)}$ or Pd(II) , with nitrosating reagents have been investigated. Mono- and di-nitrosated complexes were obtained selectively, depending upon the concentration of the nitrosating reagents and the reaction time. In both the cases, the $\gamma\text{-CH}$ group is transformed to an ambidentate isonitroso group ($>\text{C=NOH}$), which coordinates to the metal ion by dislodging the already coordinated carbonyl group. The factors influencing the mode of binding of the isonitroso group have been discussed. The bromination reactions of the mono-nitrosated products of $M[n\text{-P-(AI)}_2]$ and Pd(II) complexes, $\text{Pd}[E/i\text{-P-(AI)}_2]$, where $E/i\text{-P-(AI)}_2$ is a dianion of ethylene/*i*-propylene-bis (acetylacetoneimine), are also reported. The reaction products have been characterized by elemental analyses, electrical conductivity, molecular weight determination, and ir, pmr and electronic spectral data.

Keywords. Factors affecting ambidentate coordination; chelate linkage isomers; nitrosation.

1. Introduction

In our previous paper (Dixit *et al* 1978a), we have shown that the mononitrosation of $M[E/i\text{-P-(AI)}_2]$ [$M=\text{Ni(II)}$, Cu(II) or Pd(II)] yields inter-molecular chelate linkage isomers depending upon the nature of the metal ion. On the other hand, the mode of coordination of the isonitroso group in the dinitrosated complexes has been shown to be dependent upon the electronic properties of the terminal substituents, in addition to the nature of the metal ion (Dixit *et al* 1978b). To examine further the factors modifying the ambidentate coordination of the isonitroso group, mono- and di-nitrosation of $M[n\text{-P-(AI)}_2]$ [$M=\text{Ni(II)}$ or Pd(II)] have been carried out and the reaction products characterized. The quasiaromatic property of the non-nitrosated chelate ring has been supported by the facile bromination of a series of mono-nitrosated Ni(II) and Pd(II) complexes. The details of the results of the above studies form the subject matter of this paper.

2. Experimental

2.1. Materials and physico-chemical techniques

$M[n\text{-P-(AI)}_2]$ [$M=\text{Ni(II)}$ or Pd(II)] (McCarthy and Martell 1967) and nitric oxide (Blanchard 1946) were prepared by the reported methods. The chelate linkage

isomeric (isonitroso-acetylacetoneimino-ethylene/i-propylene-acetylacetoneimino) palladium (II), $Pd(IAI-E/iP-AI)$ (mixture of N- and O- bonded isomers) were prepared and the isomers separated in the case of $Pd(IAI-i-P-AI)$ by the literature method (Dixit *et al* 1978a). Sodium nitrite, ammonium-acetate and organic solvents used were of analar grade. Bromine (Merck) was used as such. N-bromosuccinimide (NBS) (Riedel) was crystallized from water before use. The physico-chemical techniques employed for the characterization of the complexes are described elsewhere (Sudha *et al* 1977).

2.1(a). Reaction of $M[n-P-(AI)_2]$ with controlled quantities of nitrosating reagents

Method (i): An ice-cooled solution of $Pd[n-P-(AI)_2]$ in chloroform or benzene (0.001 mole in 100 ml) was degassed by bubbling nitrogen gas. Gaseous nitric oxide purified over sodium hydroxide pellets, was then bubbled through the above solution at the rate of ten bubbles per minute. The resulting solution was concentrated in vacuum to yield an yellow crystalline compound (80%). The compound was recrystallized from chloroform or benzene.

The reaction of Ni(II) complex, $Ni[n-P-(AI)_2]$ with nitric oxide was carried out by a method analogous to the one described above. The resulting dark red crystalline product was recrystallized from benzene. Yield 90%.

Method (ii): A solution of $M[n-P-(AI)_2]$ [$M=Ni(II)$ or $Pd(II)$] (0.001 mole in 100 ml of 80% aqueous methanol was treated with sodium nitrite (0.05 mole) and ammonium acetate (0.05 mole). The resulting mixture was stirred at room temperature for an hour. The yellow or red solution obtained yielded crystalline product after concentration in vacuum. The compound was collected by filtration, washed with water and recrystallized as before. Yield $\sim 85\%$. The reaction was found to be catalysed in presence of a few drops of glacial acetic acid.

2.1b. Reactions of $M[n-P-(AI)_2]$ with excess of nitrosating reagents

These reactions were carried out by the methods (i) and (ii), using excess of sodium nitrite and ammonium acetate or by passing nitric oxide for a prolonged period (2-3 hr). Dark yellow or red crystals obtained were filtered, washed with methanol and recrystallized from chloroform. Yield 90%.

2.1c. Reactions of $Pd(IAI-E/i-P-AI)$ with Br_2 or NBS:

$Pd(IAI-E/i-P-AI)$ containing the N- and/or O- bonded chelate linkage isomers (0.001 mole) in methanol (50 ml) was treated with a freshly crystallized NBS (0.001 mole). The reaction mixture was stirred at room temperature for 2-3 hr. The yellow crystals separated were filtered and washed with ethanol to remove the succinimide formed in the reaction. The complex was recrystallized from a large volume of chloroform. Yield 70%.

The thin layer chromatography (tlc) experiments showed the presence of two isomers in the brominated complexes. However, the isomers could not be separated by column chromatography.

Bromination of the mono-nitrosated analogues of $M[n-P-(AI)_2]$ was carried out

by a method similar to the one described above. The products were purified from chloroform. Yields $\sim 75\%$.

2.2. Some general properties of the complexes

All the complexes are brilliantly coloured; Ni(II) complexes are bright red, while Pd(II) complexes are bright yellow. They are crystalline, air-stable compounds, decomposing above 270°C. The nitrosated complexes have good solubility in common organic solvents, whereas their brominated products have poor solubility.

All the complexes are non-electrolytes ($\Lambda_M < 1.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$). Their diamagnetic nature suggests square-planar stereochemistry around the metal ion.

3. Results and discussion

3.1. Structure of the nitrosated complexes

The elemental analyses (table 1) of the nitrosated products obtained in reactions *a* and *b* indicate the ratio $M[n\text{-P-(AI)}_2]$: NO to be 1:1 and 1:2, respectively. This suggests that under the experimental conditions employed, the $\gamma\text{-CH}$ groups undergo stepwise nitrosation. The mono and di- nitrosated complexes are formulated as $M[IAI\text{-n-P-AI}]$ and $M[IAI\text{-n-P-IAI}]$, respectively, where, $M=\text{Ni(II)}$ or Pd(II) ($IAI\text{-n-P-AI}$) = isonitrosoacetylacetoneimine-n-propylene-acetylacetoneimine and ($IAI\text{-n-P-IAI}$) = isonitrosoacetylacetoneimine-n-propylene-isonitrosoacetylacetoneimine.

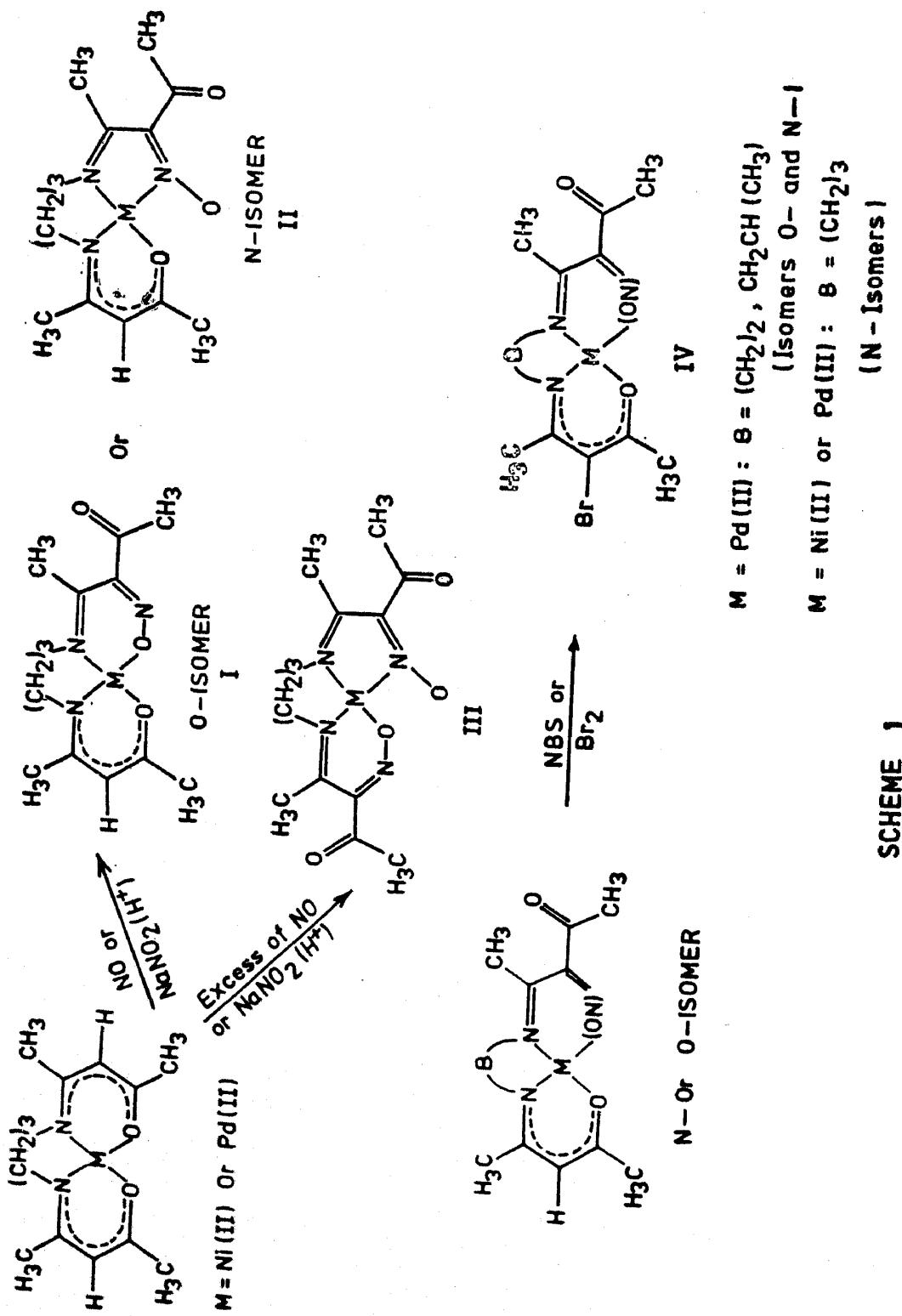
The tlc experiments indicated the presence of a single isomer in the mono- and di- nitrosated complexes.

The molecular weight determinations for the representative complexes by cryoscopy [$\text{Pd}(IAI\text{-n-P-AI})$: Calc. for $\text{C}_{13}\text{H}_{18}\text{N}_3\text{O}_3\text{Pd}$ 371.4, found 367; $\text{Pd}(IAI\text{-n-P-IAI})$: Calc. for $\text{C}_{13}\text{H}_{18}\text{N}_4\text{O}_4\text{Pd}$ 400.4, found 395] indicate that they are monomeric.

3.2. Spectra and bonding in mono-nitrosated complexes

Their spectra of the mono-nitrosated complexes display characteristic bands around 765, 1195, 1525 and 1580 cm^{-1} , which are assignable, respectively to π_{CH} , δ_{CH} , co-ordinated ν_{CO} and co-ordinated ν_{CN} . In addition, a new band is observed in the region 1648-1660 cm^{-1} . This band is in the region expected for the non-coordinated acetyl CO group [Lacey *et al* 1973; Sudha 1977]. This observation implies that the isonitroso group introduced at the $\gamma\text{-CH}$ position coordinates to the metal ion by dislodging one of the coordinated carbonyl groups. Since the isonitroso group is ambidentate in nature, the structures I and II are possible for the mono-nitrosated complexes (see scheme 1). However, the position of the non-coordinated ν_{CO} corresponds to that of the isonitroso N-bonded isomer of $M(IAI\text{-E/i-P-AI})$ [$M=\text{Ni(II)}$ or Pd(II)] (Sudha *et al* 1978a). Structure II has, therefore, been assigned to the mono- nitrosated complexes $M(IAI\text{-n-P-AI})$.

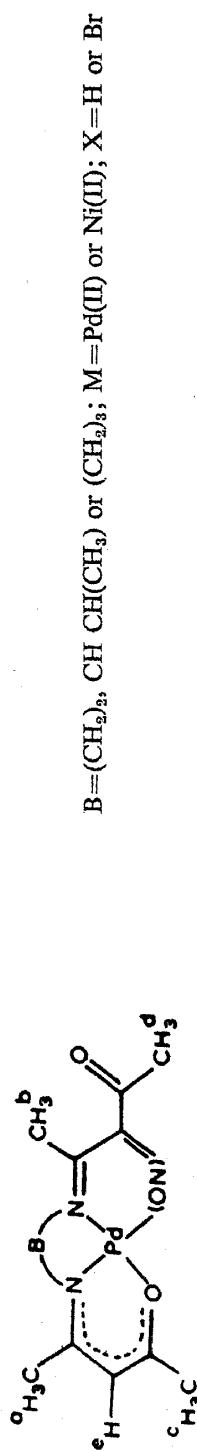
The pmr spectra of the present complexes show a singlet proton signal in the region 5.10-5.02 δ with an integrated intensity corresponding to one proton, in agreement with the fact that only one of the two $\gamma\text{-CH}$ groups is nitrosated. Further, four dis-



SCHEME I

Table 1. Elemental analyses of the mono-nitrosated, di-nitrosated and brominated complexes
(analytical data in percentage)

	Calculated				Found			
	C	H	N	Metal	C	H	N	Metal
Pd(IAI- <i>n</i> -P- <i>Al</i>)	42.00	5.12	11.31	28.65	41.91	4.88	11.20	28.60
Ni(IAI- <i>n</i> -P- <i>Al</i>)	48.19	5.87	12.97	18.13	47.99	5.68	12.79	18.04
Pd(IAI- <i>n</i> -P-IAI')	38.96	4.49	13.98	26.57	38.91	4.42	13.92	26.52
Ni(IAI- <i>n</i> -P-IAI')	44.32	5.11	15.92	16.67	44.25	4.99	15.68	16.58
Pd(IAI- <i>E</i> -BrAl) isomers (N+O)	33.0	3.67	9.62	24.38	32.4	3.42	9.51	24.23
Pd(IAI- <i>i</i> -P-BrAl) isomers (N+O)	34.64	3.99	9.33	23.62	34.54	3.62	9.51	23.20
Ni(IAI- <i>n</i> -P-BrAl)	38.74	4.47	10.43	14.58	38.68	4.32	10.29	14.42

Table 2. Pmr spectral data (δ , ppm) of mono-nitrosated and their brominated complexes in CdCl_3 

Complex	a	b	c	d	diamine protons* (B)	
					CH ₂	CH
Pd(Al-i-P-Al)						
Ni(Al-i-P-Al)						
Pd(Al-i-P-BrAl)						
Ni(Al-n-P-BrAl)						

Abbreviations: s = singlet and m = complex multiplet.

f signals not observed due to poor solubility of the complexes.

* methyl proton resonances of the diamine skeleton (B) in the O- and N-isomers of Pd(Al-i-P-Al) occur as doublets ($J=6.50$ Hz) at 1.28 and 1.40 δ

**Central methylene proton signals of the n-propylene diamine skeleton.

Distinct methyl proton signals appear in the region 2.46-2.05 δ , which confirm the presence of a single isomer in the complexes. The pmr spectral data for the complexes along with their assignments are given in table 2. The $-\text{CH}_2\text{CH}_2\text{CH}_2-$ proton signals of $\text{Ni}(IAI-n\text{-P-}AI)$ appear at higher fields than those of the Pd(II) analogue. This may be ascribed to the difference in the steric strain imposed on the ring comprising the *n*-propylene bridge; it is more for the Ni(II) complex due to the smaller ionic size of Ni(II) (0.68 Å) than for the Pd(II) analogue with a larger Pd(II) ion (1.24 Å).

The formation of a single isomer (N-bonded) in the case of $M(IAI-n\text{-P-}AI)$ complexes, while a mixture of two isomers (N- and O- bonded) in $M(IAI-E/i\text{-P-}AI)$ may be attributed to the size of the ring comprising the diamine skeleton. In the former case, the *n*-propylene bridge forms a six-membered ring, which may stabilize only one isomer. However, this explanation does not account for the formation of the N-bonded isomer, in particular. This may be due to steric reasons.

The mono-nitrosated complexes were refluxed in various organic solvents to examine the possibility of chelate linkage isomerization in solution. However, they do not isomerize but retain their structural identity. This observation is contrary to the one made in the case of $\text{Ni}(IAI-E/i\text{-P-}AI)$, which isomerize in chloroform (Sudha *et al* 1978a). The failure of the present complexes to undergo isomerization in solution may be attributed to the preferential stability of the N-bonded isomer.

3.3. Spectra and bonding in the di-nitrosated complexes

The ir spectra of the di-nitrosated complexes show two intense bands in the region 1668-1698 cm^{-1} due to the non-coordinated ν_{CO} . The two vibrational bands occurring in range 1140-1240 cm^{-1} are assignable to two coordinated ν_{NO} . These results indicate that both the $\gamma\text{-CH}$ groups are transformed into isonitroso groups, which coordinate to the metal ion by dislodging the already bonded carbonyl groups. The occurrence of two ν_{CO} and two ν_{NO} bands is indicative of asymmetric chelation of the isonitroso groups as shown in III(scheme 1). The complexes are, therefore, formulated as $M(IAI-n\text{-P-}IAI')$ where, IAI and IAI' denote N- and O- coordinated isonitroso ligand moieties, respectively. Recently, structure of the type III has been confirmed by x-ray single crystal diffraction studies for the molecule $\text{Ni}(IAI-E-IAI')$ (Dixit *et al* unpublished).

In agreement with the proposed structure, the pmr spectra of the $M(IAI-n\text{-P-}IAI')$ [$M=\text{Ni(II)}$ or Pd(II)] complexes show four distinct methyl proton signals. The CH_3 and COCH_3 , signals of the five-membered chelate ring appear around 82.32 and 2.40 respectively. The corresponding signals associated with the six-membered chelate ring are observed around 82.37 and 2.42, respectively. The terminal and central methylene protons of the *n*-propylene bridge appear as complex multiplets centered at respectively, 4.32 and 2.05 δ .

3.4. Structure and bonding in brominated complexes

All the mono-nitrosated complexes undergo facile bromination at the $\gamma\text{-CH}$ position of the non-nitrosated chelate ring. This is confirmed by the absence of the vibrational bands due to π_{CH} and δ_{CH} in the ir spectra as well as the absence of the $\gamma\text{-CH}$ proton signal in the pmr spectra of the brominated products. Bromination of the individual

Table 3. Principal ir frequencies (ν , cm^{-1}) of the brominated complexes in nujol mull.

Complex	ν_{CO} (non-bonded)	ν_{CO} (bonded)	ν_{CN}	ν_{NO} (O-bonded)
Pd(IAI-E-BrAI)				
N-isomer	1650 s	1515 s	1595 s	
O-isomer	1685 s	1520 s	1600 s	1128 m
Pd(IAI-i-P-BrAI)				
N-isomer	1655 s	1512 s	1605 s	
O-isomer	1690 s	1520 s	1600 s	1130 w
Pd(IAI-n-P-BrAI)				
N-isomer	1655 s	1525 s	1580 s	
Ni(IAI-n-P-BrAI)				
N-isomer	1650 s	1520 s	1590 s	

Abbreviations: s = strong; m = medium and w = weak.

chelate linkage isomer of Pd(IAI-i-P-*AI*) (N- or O- bonded) yielded a mixture of the γ -bromo substituted isomers. This indicates that the bromination occurs through a dissociative mechanism. Two isomers were obtained in the case of Pd(IAI-E-BrAI) also. However, these isomers could not be separated due to their poor solubility in common organic solvents. In contrast, a single isomer was obtained in the case of *M*(IAI-n-P-BrAI) [*M*=Ni(II) or Pd(II)].

The relevant ir frequencies of the brominated complexes are given in table 3. It can be seen that the vibrational bands associated with ν_{CO} (coordinated), ν_{CO} (non-coordinated) and ν_{NO} appear at almost the same frequencies as in the corresponding mono-nitrosated complexes. The pmr spectral data of the brominated derivatives are presented in table 2. Based on these results, structure IV (scheme 1) has been assigned for all the brominated complexes.

The electronic spectra of the nitrosated and brominated complexes in chloroform display a single band around $25,000 \text{ cm}^{-1}$. The high intensity of this band ($\epsilon \sim 1000 \text{ l. mole}^{-1} \text{ cm}^{-1}$) suggests that it is possibly a charge-transfer band enveloping the expected *d-d* transition.

In conclusion, the results of the present investigation show that the ambidentate coordination of the isonitroso group depends on the size of the ring comprising the diamine skeleton. However, this is true only in the mono-nitrosated complexes, since in all the di-nitrosated compounds, the two isonitroso groups are asymmetrically coordinated to the metal ion. Further, the γ -CH proton of the mono-nitrosated complexes undergo facile bromination, producing the corresponding γ -bromo derivatives. This demonstrates the quasi-aromatic property of the non-nitrosated β -ketoimine chelate ring, in spite of its heteroatomic nature.

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