

## Coordination properties of vic-isonitrosoimines in their copper (II) and palladium (II) complexes

B P SUDHA, N S DIXIT and C C PATEL

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012

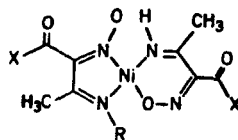
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**Abstract.** Preparation and structural characterization of palladium (II) complexes of ligands III-V and copper (II) complexes of III are reported. The elemental analyses of the complexes show that the metal: ligand ratio is 1 : 2. The electrical conductance in acetone shows the non-electrolytic nature of the complexes. The diamagnetic character suggests a gross square-planar geometry for the palladium (II) complexes. Copper (II) complexes are paramagnetic with  $\mu_{\text{eff.}} \sim 1.90$  B.M. Spectral data suggest that in all the complexes the ligand coordinates to the metal (II) symmetrically through isonitroso-nitrogen and imine-nitrogen, forming a five membered chelate ring. Amine-exchange reactions of the complexes are discussed and compared on the basis of their structures.

**Keywords.** Vic-isonitrosoimines; ambidentate; amine-exchange.

### 1. Introduction

Recently, considerable interest has been evinced in the coordination chemistry of isonitroso- $\beta$ -ketoimines, for the isonitroso group ( $\text{>C=NOH}$ ) of these ligands can function ambidentately forming coordination compounds having unusual structures. Nickel(II), for example, reacts with isonitrosoacetylacetoneimine(HIAD) forming an orange red diamagnetic complex for which structure I ( $\text{X}=\text{CH}_3$ ,  $\text{R}=\text{H}$ ) has been assigned (Lacey *et al* 1970; Bose 1970). The hybrid ring structure is retained when X is substituted by  $\text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$  or  $\text{NHC}_6\text{H}_5$  (Iyengar 1975). Further, the Ni(II) complexes of I react with primary aliphatic amines producing the mono-alkyl



- I  $\text{R}=\text{H}$ ,  $\text{X}=\text{CH}_3$ ,  $\text{OCH}_3$ , etc  
II  $\text{R}=\text{alkyl or aryl}$

complexes having the same asymmetric structure II ( $\text{R}=\text{alkyl}$ ) (Bose 1970; Iyengar *et al* 1975; Iyengar 1975). The novel structure of this type has been confirmed by x-ray single crystal analysis for the molecule II ( $\text{X}=\text{R}=\text{CH}_3$ ) (McConnel *et al* 1973). However, studies involving the coordination compounds of isonitroso- $\beta$ -ketoimines

Table 1\*

Ligand	M(II)	R	Abbrev.
III	Cu	H	CuL <sub>2</sub>
III	Pd	H	PdL <sub>2</sub>
III	Cu	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , <i>n</i> -C <sub>3</sub> H <sub>7</sub> , <i>n</i> -C <sub>4</sub> H <sub>9</sub> , <i>n</i> -C <sub>6</sub> H <sub>11</sub> , C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	Cu(R-L) <sub>2</sub>
III	Pd	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , <i>n</i> -C <sub>3</sub> H <sub>7</sub> , <i>i</i> -C <sub>3</sub> H <sub>7</sub> , <i>n</i> -C <sub>4</sub> H <sub>9</sub> , <i>i</i> -C <sub>4</sub> H <sub>9</sub> , <i>t</i> -C <sub>4</sub> H <sub>9</sub> , <i>n</i> -C <sub>6</sub> H <sub>11</sub> , C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	Pd(R-L) <sub>2</sub>
IV, V	Pd	H	PdL <sub>2</sub>
IV, V	Pd	CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , <i>n</i> -C <sub>3</sub> H <sub>7</sub> , <i>i</i> -C <sub>3</sub> H <sub>7</sub> , <i>n</i> -C <sub>4</sub> H <sub>9</sub>	Pd(R-L) <sub>2</sub>

\*The elemental analyses of the complexes show metal to ligand ratio to be 1 : 2.

ligands with other transition metals are meagre (Bose *et al* 1973; Dixit *et al* 1976). The present paper reports preparation and characterization of Cu(II) and Pd(II) complexes of ligands III, IV and V. The amine-exchange reactions of the complexes when R=H are discussed and compared on the basis of the proposed structure.

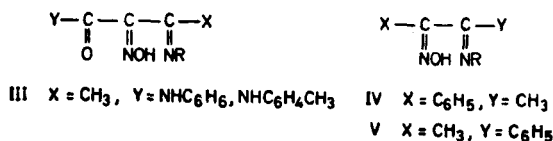


Table 1 lists the complexes prepared and the abbreviations mentioned therein are used throughout the text.

## 2. Experimental

### 2.1. Materials and physical measurements

Isonitrosoacetoacetanilide (Knorr 1887), isonitrosoacetoacet-*p*-toluidide (Knorr 1887), isonitrosobenzylmethylketone (Kolb 1896) and isonitrosopropiophenone (Hartung and Crossly 1943) were prepared by the reported methods. Copper(II) acetate monohydrate (AR) and palladium (II) chloride (Johnson-Mathey) were used as such. Liquor ammonia (LR, density, 0.88 g/ml), methylamine (33% aq.), ethylamine (50% aq.), *n*-propylamine, iso-propylamine, *n*-butylamine, iso-butylamine, tert-butylamine, *n*-hexylamine and benzylamine (all Riedel products) were used. Organic solvents were of Analar grade.

The conductivity of the complexes in acetone was determined with a Siemens conductivity bridge. Molecular weights of the complexes were determined by mass spectroscopy using Atlas Mat Breman Massen spectrometer CH4. Magnetic moments of the complexes were determined at room temperature by Gouy method

using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as a calibrant. IR spectra in Nujol mull were recorded on a Carl-Zeiss UR-10 spectrometer. Pmr spectra of the palladium(II) complexes in  $\text{CDCl}_3$  were taken on Varian T-60 and HA-100 spectrometers using TMS as an internal standard. Nitrogen 1s x-ray photoelectron spectra of a few palladium(II) complexes were recorded on a McPherson ESCA-36 photoelectron spectrometer, using aluminium  $K_\alpha$  x-ray ( $h\nu=1486$  eV) for the photoelectron excitation.

**2.1.1. Preparation of complexes:** All the Cu(II) and Pd(II) complexes listed in table 1 were prepared by a general procedure. According to this method, the required ligand was synthesised *in situ* by the reaction of vic-isonitroso ligand with an appropriate amine and the ligand was then complexed to the metal ion. In a typical procedure, a mixture of isonitrosoacetoacetanilide (0.002 mole) and ammonia ( $\sim 3$  ml) in methanol (30 ml) was stirred for about 20 min. To the resulting dark red solution, copper acetate monohydrate (0.001 mole) dissolved in the same solvent was added and the solution was stirred continuously for 4 hrs. A crystalline product formed was filtered, washed with methanol and recrystallized from chloroform. Yield, 90%.

**2.1.2. Amine-exchange reactions:** (a) Reactions of  $\text{PdL}_2$  ( $L=\text{IANI}$  or  $\text{IAPI}$ ) with  $\text{R-NH}_2$ , where  $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $i\text{-C}_3\text{H}_7$  or  $n\text{-C}_4\text{H}_9$ —A suspension of  $\text{PdL}_2$  (0.001 mole) in 50 ml chloroform-methanol mixture (1:1 v/v) or iso-propanol (30 ml) was treated with an appropriate amine (3-6 ml). The reaction mixture was refluxed over a water bath when the suspension slowly dissolved giving a clear yellow solution. The solution was then partially evaporated in vacuum when yellow crystals of the complexes (80-90%) were obtained. The time required for the completion of the reaction in chloroform-methanol mixture when  $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $i\text{-C}_3\text{H}_7$  and  $n\text{-C}_4\text{H}_9$ , was in the sequence of 10-12, 8-9.5, 5-6, 4-4.5 and 3-3.5 hr., respectively. The reaction times were 2-3 folds less in iso-propanol.

(b) Reactions of  $\text{PdL}_2$  ( $L=\text{IPI}$ ,  $\text{IBMI}$ ) with  $\text{R-NH}_2$  ( $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $i\text{-C}_3\text{H}_7$  or  $n\text{-C}_4\text{H}_9$ ): These reactions were carried out following the same procedure as in (a) using  $\text{PdL}_2$  and an appropriate amine in iso-propanol. The products were recrystallised from chloroform. Yields, 70-95%. The time required for the completion of the reaction when  $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ , and  $n\text{-C}_4\text{H}_9$  was in the sequence of 3-4, 2.25-2.55, 1.5-2.2, 1.8 and 1-2 hr., respectively as indicated by the dissolution of  $\text{PdL}_2$ .

## 2.2. Analyses

Palladium in the complexes was estimated as its dimethylglyoximate, while copper was estimated iodometrically (Vogel 1951) after decomposing the complexes with a mixture of perchloric and sulphuric acids. C, H and N were estimated by micro-analytical methods.

## 3. Results and discussion

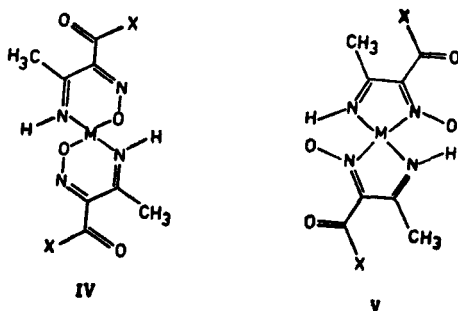
The results of the elemental analyses (not given) show that the metal: ligand ratio for all the complexes is 1 : 2. Pd(II) complexes are yellow, while those of Cu(II) show colours like red, brown and bluish green. In general, the complexes decompose

above 200°C. All the complexes except those with R=H, have good solubility in common organic solvents.

The complexes are non-electrolytes in acetone ( $\Lambda_M \sim 2 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ). The diamagnetism of the Pd(II) complexes suggests square-planar stereochemistry around metal, while those of Cu(II) are paramagnetic with  $\mu_{\text{eff}} \sim 1.90 \text{ B.M.}$ , a value expected for the monomeric Cu(II) complexes without magnetic interaction. The molecular weights, as obtained from the mass spectra of Pd(IANI)<sub>2</sub>, Pd(C<sub>2</sub>H<sub>5</sub>-IANI)<sub>2</sub>, Pd(IAPI)<sub>2</sub>, Pd(*n*-C<sub>3</sub>H<sub>7</sub>-IAPI)<sub>2</sub> and Pd(C<sub>2</sub>H<sub>5</sub>-IBMI)<sub>2</sub> are respectively, 514, 570, 542, 626 and 484, indicating their monomeric nature.

### 3.1. Structure of ML<sub>2</sub> (R=H) complexes

The ir spectra of ML<sub>2</sub> complexes [M = Cu(II), Pd(II); L = IANI, IAPI]\* in nujol mull display an intense band in the region 1650–1670 cm<sup>-1</sup> and a sharp band of medium intensity in the region 3320–3350 cm<sup>-1</sup>. These vibrational bands are assignable respectively, to the stretching frequencies of non-coordinated CO and coordinated NH. The occurrence of a single  $\nu_{\text{CO}}$  and a single  $\nu_{\text{NH}}$  is indicative of symmetric coordination of both the ligands as shown in IV and V.



The positions of CO and NH vibrational bands which are significantly modified by the mode of coordination of the isonitroso group and the substituent X may be used as a probe to distinguish the chelate linkage isomeric structures IV and V. In Ni(II) (Lacey *et al* 1970; Bose 1970; Iyengar 1975; Iyengar *et al* 1975; Bose *et al* 1973) complexes of a series of isonitroso- $\beta$ -ketoimines it has been rationalised that  $\nu_{\text{CO}}$  of isonitroso N-bonded ligand appears at lower wave numbers than that of isonitroso O-bonded ligand and vice-versa for the coordinated  $\nu_{\text{NH}}$ . In bis (isonitrosoacetoacetanilideimino) nickel(II) (Iyengar 1975), Ni(IANI)(IANI'), which is suggested to have an asymmetric structure, for example,  $\nu_{\text{CO}}$  and  $\nu_{\text{NH}}$  of O-bonded ligand (IANI') occur at 1683 and 3208 cm<sup>-1</sup> respectively, while those of N-bonded ligand (IANI) occur at 1669 and 3365 cm<sup>-1</sup>. The vibrational frequencies due to CO and NH observed in the present complexes are comparable with the isonitroso N-bonded ligand of Ni(IANI)(IANI'). These results are consistent with the trans-symmetric structure V(X = NHC<sub>6</sub>H<sub>5</sub>, NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) for the present complexes. Furthermore, the complexes exhibit an intense band around 1200 cm<sup>-1</sup>,

\*Abbreviations: IANI, IAPI, IPI and IBMI represent anions of isonitrosoacetoacetanilideimine, isonitrosoacetoacet-*p*-toluidideimine, isonitrosopropiophenoneimine and isonitrosobenzylmethyl-ketoimine and R-L denotes corresponding alkyl/aryl derivatives.

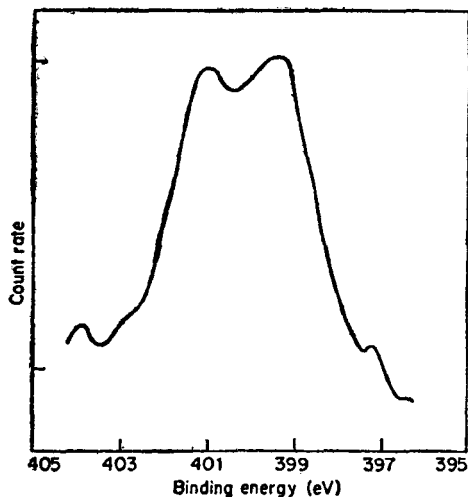


Figure 1. N 1s x-ray photoelectron spectrum of Pd(IBMI)<sub>2</sub>.

which is characteristic of coupled isonitroso N-bonded NO (Lacey *et al* 1970). This evidence also supports the symmetric structure. Structure of the type V has been assigned for Pd(IBMI)<sub>2</sub> and Pd(IPI)<sub>2</sub>. The ir spectra of these complexes show  $\nu_{\text{NH}}$  and  $\nu_{\text{NO}}$ , respectively, around 3300 and 1150 cm<sup>-1</sup>. The position and shape of the  $\nu_{\text{NH}}$  band indicate the absence of H-bond.

The nitrogen 1s x-ray photoelectron spectrum of Pd(IBMI)<sub>2</sub> (figure 1) shows two photoelectron peaks of almost equal intensities. The peaks at 399.4 and 401.0 eV have been assigned to azomethine nitrogen and isonitroso nitrogen coordinated to Pd(II), respectively. The binding energies are in excellent agreement with the coordinated nitrogens of isonitroso- $\beta$ -ketoimine ligands (Swartz-private communication). These results also confirm the Pd-N<sub>4</sub> coordination in Pd(IBMI)<sub>2</sub>.

### 3.2. Structure of Pd(R-L)<sub>2</sub> complexes

The ir pattern in the region 400-1800 cm<sup>-1</sup> of Pd(R-L)<sub>2</sub> complexes (R=alkyl, aryl and L=IANI, IAPI) are similar to those of the corresponding PdL<sub>2</sub> complexes, except for the absence of coordinated  $\nu_{\text{NH}}$  in the former complexes. The  $\nu_{\text{CO}}$  and  $\nu_{\text{NO}}$  in the complexes occur in the 1650-1670 cm<sup>-1</sup> and 1150-1200 cm<sup>-1</sup> regions respectively. These results indicate symmetric structure of the type V for the present complexes. The structure of this type has been confirmed (Dixit *et al* 1977) by single crystal x-ray analysis for the molecule bis(N-ethyl isonitrosoacetylacetoneimino) palladium (II). Pd(R-L)<sub>2</sub> complexes (L=IBMI, IPI) are also suggested to have a similar structure. The characteristic isonitroso N-coordinated  $\nu_{\text{NO}}$  of these complexes appears in the 1145-1170 cm<sup>-1</sup> region. The ir data indicate structure V for all Cu(R-L)<sub>2</sub> complexes.

The pmr spectral data of representative complexes are given in table 2. The spectrum of Pd(C<sub>2</sub>H<sub>5</sub>-IANI)<sub>2</sub> shows only one set of proton signals due to CH<sub>3</sub>, NHC<sub>6</sub>H<sub>5</sub> and NHC<sub>6</sub>H<sub>5</sub> respectively, at 7.28, 2.50 and -1.55 $\tau$ . The protons due to  $\text{>C=N-(C}_2\text{H}_5\text{)}$  moiety display a characteristic triplet and quartet pattern. Similarly

**Table 2.** Proton magnetic resonance signals (in  $\tau$ , ppm) of a few palladium (II) complexes along with their assignments\*

Complex	-CH <sub>3</sub>	-C <sub>6</sub> H <sub>5</sub>	-NHC <sub>6</sub> H <sub>5</sub>	-NHC <sub>6</sub> H <sub>5</sub>	N-R	
					-CH <sub>2</sub>	-CH <sub>3</sub>
Pd(C <sub>2</sub> H <sub>5</sub> -IAND) <sub>2</sub>	7.28(s, 6)		2.50(m, 10)	-1.55(s, 2)	5.97(q, 4)	8.78(t, 6)
Pd(CH <sub>3</sub> -IBMI) <sub>2</sub>	7.94(s, 6)	2.74(m, 10)				6.50(s, 6)
Pd(C <sub>2</sub> H <sub>5</sub> -IBMI) <sub>2</sub>	7.97(s, 6)	2.67(m, 10)			6.02(q, 4)	8.84(t, 6)
Pd(CH <sub>3</sub> -IPI) <sub>2</sub>	8.32(s, 6)	2.64(m, 10)				6.67(s, 6)
Pd(C <sub>2</sub> H <sub>5</sub> -IPI) <sub>2</sub>	8.39(s, 6)	2.65(m, 10)			6.52(q, 4)	8.79(t, 6)

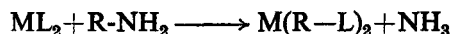
\*Abbreviations: s=singlet; t=triplet, q=quartet and m=multiplet. Integrated intensities and complexities of the signals are given in parenthesis.

the spectra of Pd(R-IBMI)<sub>2</sub> and Pd(R-IPI)<sub>2</sub>, where R=CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, also exhibit single resonances due to CH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub> of the chelate ring around 8.00 and 2.70 $\tau$ , respectively.

The N 1s x-ray photoelectron spectra of Pd(C<sub>2</sub>H<sub>5</sub>-IPI)<sub>2</sub> and Pd(*n*-C<sub>3</sub>H<sub>7</sub>-IAPI)<sub>2</sub> show two peaks around 399.0 and 401.0 eV, which are assignable to coordinated azomethine nitrogen and isonitroso nitrogen, respectively. However, the intensity of the signal at 401.0 eV in the spectrum of Pd(*n*-C<sub>3</sub>H<sub>7</sub>-IAPI)<sub>2</sub> is twice that of the lower energy peak. This suggests the merging of N 1s signal of the nitrogen of NHC<sub>6</sub>H<sub>5</sub> moiety with that of the isonitroso nitrogen. This observation may be ascribed to very small difference in their ionization potentials. The pmr as well as N 1s spectral data coupled with ir data therefore, confirm the trans-symmetric structure with Pd-N<sub>4</sub> coordination sphere for all the di-alkyl complexes.

### 3.3. Amine-exchange reactions of the complexes

A large excess of amine is used in the preparation of M(R-L)<sub>2</sub> complexes by the reaction of ML<sub>2</sub> with R-NH<sub>2</sub> (eq. 1). Qualitatively, the time required for the reaction (eq. 1) decreases in the order CH<sub>3</sub>>C<sub>2</sub>H<sub>5</sub>>*n*-C<sub>3</sub>H<sub>7</sub>>*i*-C<sub>3</sub>H<sub>7</sub>>*n*-C<sub>4</sub>H<sub>9</sub>. This sequence roughly corresponds to the reverse order of the basicities of the amines.



M=Pd(II), Cu(II); R=straight or branched chain alkyl.

These observations illustrate that in the present examples high concentration and basicities of the substituting amine are the driving forces of the amine-exchange reactions. These results are in agreement with those reported by Verter and Frost (1960) and Olzewski and Martin (1965) in their studies on the amine-exchange reactions of bis(salicylaldimino) Cu(II).

In contrast to PdL<sub>2</sub>, the ligands in CuL<sub>2</sub> do not undergo amine-exchange with isopropylamine. The difference in the reactions of CuL<sub>2</sub> and PdL<sub>2</sub> may be attributed to the steric hindrance between the protruding >N-O and >N-R in cis positions. This is expected due to the smaller size of Cu(II) (0.72Å) as compared to that of Pd(II) (1.24Å). However, Pd(II) complexes with R=*i*-C<sub>4</sub>H<sub>9</sub> could not be prepared by the

amine-exchange reactions. This suggests that even in the case of Pd(II) complexes, steric factors are operative when R is sufficiently bulky. However, these complexes are obtained in low yields by the direct method.

A significant feature of the present studies is that the ligands coordinate symmetrically to the metal ions investigated, irrespective of the nature of substituents on the azomethine nitrogen (R) and carbonyl carbon (X). This is in contrast to isonitrosoacetylacetonimine, which forms asymmetric complexes with Ni(II) (Bose 1970, Bose *et al* 1973) Cu(II) (Dixit *et al* 1976) and symmetric (Pd-N, N, N, N) as well as asymmetric (Pd-N, N, N, O) with Pd(II) (Bose *et al* 1973). Further, N-alkyl isonitrosoacetylacetonimine produces symmetric complexes with Cu(II) (Dixit *et al* 1976) and Pd(II) (Bose *et al* 1973) and such complexes are not formed by Ni(II).

Although, rationalization of the factors influencing the bifunctional coordination of the isonitroso group is difficult, it appears that the electron acceptor and/or donor properties of X and R dictate the mode of linkage of the isonitroso group.

## References

- Bose K S 1970 Ph.D. Thesis, Indian Institute of Science, Bangalore  
Bose K S, Sharma B C and Patel C C 1973 *Inorg. Chem.* **72** 720  
Dixit N S, Bose K S and Patel C C 1976 *Indian J. Chem.* **A14** 507  
Dixit N S, Manohar H and Patel C C *J. Inorg. Nucl. Chem. Lett.* (in press)  
Hartung and Crossley 1943 *Org. Syntheses Coll. Vol. 2* 363  
Iyengar R R 1975 Ph.D. Thesis, Indian Institute of Science, Bangalore  
Iyengar R R, Bose K S and Patel C C 1975 *J. Inorg. Nucl. Chem.* **37** 75  
Van L Knorr 1887 *Ann.* **236** 80  
Kolb 1896 *Ann.* **291** 280  
Lacey M J, Macdonald C G, Shannon T S and Collin P J 1970  
*Aust. J. Chem.* **23** 2279  
McConnel J F, Lacey M J, Macdonald C G and Shannon T S 1973 *Acta. Cryst.* **B29** 2477  
Olszewski E J and Martin D F 1965 *J. Inorg. Nucl. Chem.* **27** 345  
Veter H S and Frost A E 1960 *J. Am. Chem. Soc.* **82** 85  
Vogel A I 1951 *A text book of quantitative analysis* (New York: Longmans-Green) II ed. p. 349  
Sudha B P, Dixit N S and Patel C C 1975 *Curr. Sci.* **44** 651  
Swartz W I private communication