

N⁴-COORDINATED ISOMER OF BIS (4-IMINO-2, 3-PENTANEDIONE-3-OXIME) PALLADIUM (II)

Miss B. P. SUDHA, N. S. DIXIT AND C. C. PATEL

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

ABSTRACT

The isomer Pd(IAI)₂ has been isolated for the first time either by refluxing the asymmetrically coordinated palladium complex, Pd(IAI) (IAI') (where, IAI and IAI' denote N-coordinated and O-coordinated isonitrosoacetylacetonate imine respectively) or by constituents combination method at elevated temperature for a long time. Magnetic and spectral data suggest that the complex has a square planar stereochemistry around the metal-ion with both the ligands coordinated through nitrogen of the isonitroso groups.

INTRODUCTION

ISONITROSO-β-KETO imine ligands constitute an interesting class of systems, because of their ability to form isomers with 'intramolecular' as well as 'intermolecular' chelate linkage. Isonitrosoacetylacetonate imine, for example, can form three chelate linkage isomers as shown in Fig. 1. These

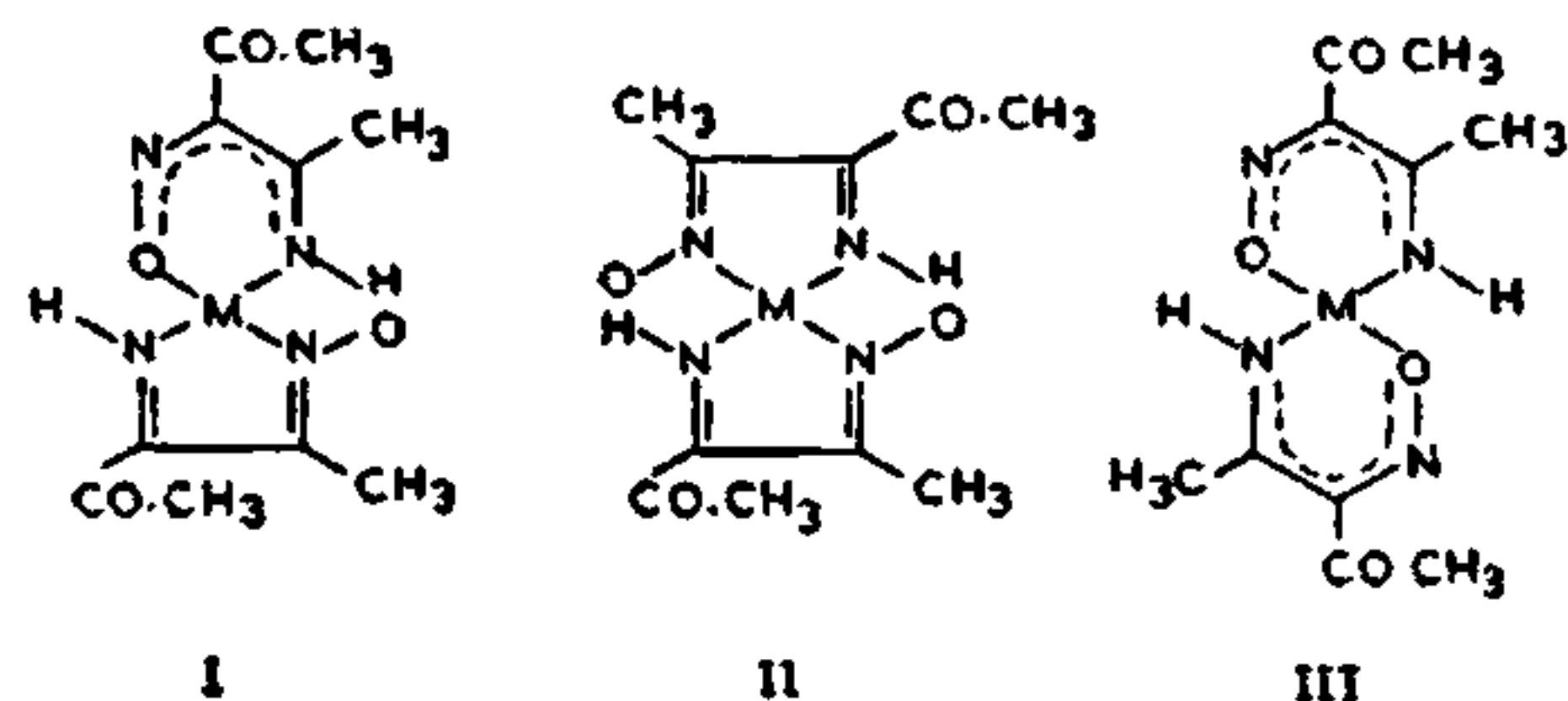


FIG. 1

isomers involve O- or N-donors of the isonitroso group and the imine nitrogen as coordination sites.

Nickel (II)¹, palladium (II)² and copper (II)³ are shown to form complexes of the type I with isonitrosoacetylacetonate imine. Recently, such a structure has been confirmed by x-ray diffraction studies⁴. There is no report so far, on the isolation of either of the isomers II or III. However, the possibility of formation of isomer II of palladium (II) in chloroform medium has been indicated spectroscopically. In this paper, we report the isolation and characterisation of the isomer of the type II for the first time with palladium (II).

EXPERIMENTAL

Isonitrosoacetylacetonate imine was prepared by the method of Wolff *et al.*⁵. Palladium (II) chloride was obtained from Arora-Methey, Ltd., Calcutta. Chloroform (A.R.), a B.D.H. product, was used without further purification. Bis (isonitrosoacetylacetonate imino) palladium (II) was prepared by the reported method⁵. Magnetic susceptibility of the complex was determined by the Gouy method using Hg [Co(NCS)₄] as the standard. I.R. spectra in Nujol mull were recorded on a Carl-Zeiss UR-10 spectrophotometer, equipped with LiF, NaCl

and KBr optics. The electronic spectra of the complexes in mull were recorded on a Unicam 700-A recording spectrophotometer.

PREPARATION OF THE COMPLEX

The complex, Pd (IAI)₂, was prepared by the following two methods.

Method I.—The asymmetrically coordinated red palladium complex, Pd (IAI) (IAI') (0.2 g), was taken in chloroform (400 ml) and refluxed over a water-bath for about 16 hours when the solid suspension slowly dissolved to yield a yellow solution, which on cooling gave a brown complex. It was filtered, washed with chloroform and dried in air.

Method II.—Palladium (II) chloride (0.2 g), isonitrosoacetylacetonate (0.2 g) and ammonia (5 ml) were taken in 500 ml chloroform and refluxed over a water-bath for about 50–55 hours. The resulting yellow solution on cooling gave a brown complex. It was filtered, washed with chloroform and dried in air.

The complex prepared by both the methods was shown to be identical as indicated by their colour, infrared spectra and chemical analysis.

RESULTS AND DISCUSSION

The diamagnetic nature of the complex suggests square planar stereochemistry of the complex around palladium (II). The I.R. spectrum of the asymmetrically coordinated palladium (II) complex, Pd (IAI) (IAI') shows two non-coordinated C=O bands at 1684 cm⁻¹ and 1655 cm⁻¹ and two N-H bands at 3280 cm⁻¹, 3210 cm⁻¹ (sh). The brown complex obtained by refluxing this compound in chloroform shows a single carbonyl and N-H stretching bands at 1655 cm⁻¹ and 3260 cm⁻¹ respectively in its infrared spectra. This observation suggests the intramolecular linkage isomerisation to symmetrically coordinated isomer either II or III. In deciding between these two isomers, the positions of carbonyl and N-H bands are important since these bands are shown to vary considerably depending upon the mode of coordination of the isonitroso group. The position of the carbonyl

band observed in the brown complex corresponds to the lower band at 1650 cm^{-1} of Pd (IAI) (IAI'). This band has been assigned to the N-coordinated isonitroso- β -keto imine. It is important to note here that the $\text{C}=\text{O}$ frequency of the O-coordinated isonitroso- β -keto imine ligand occurs at a higher frequency compared to the N-coordinated isonitroso- β -keto imine ligand. The band at 3260 cm^{-1} assigned to N-H stretching mode of Pd (IAI)₂ agrees well with the higher frequency band observed in the I.R. spectra of the asymmetrically coordinated palladium (II), nickel (II) and copper (II) complexes of the same ligand. This band is also assigned to the N-coordinated isonitroso- β -keto imine ligand. These evidences suggest that both the ligands are coordinated to palladium (II) through nitrogen donors of the isonitroso groups in the brown complex.

The proposed structure for the complex is further supported by comparing its electronic spectrum with that of Pd (IAI) (IAI') in the solid state. The assignment of the electronic spectral bands of Pd (IAI)₂ are given in Table I.

Unlike Pd (IAI)₂, which shows four bands in the visible region, Pd (IAI) (IAI') shows a broad shoulder around 21200 cm^{-1} , which may possibly be the expected *d-d* transition. The differences in

the electronic spectra of the two complexes also support the proposed structure for the former complex.

TABLE I
Electronic spectral bands of Pd (IAI)₂ in mull

ν in cm^{-1}	Assignment
22700	Possibly a charge transfer band
20600	$1_{A_{1g}} \rightarrow 1_{E_{1g}} (\text{sh})$
18500	$1_{A_{1g}} \rightarrow 1_{B_{1g}}$
17000	$1_{A_{1g}} \rightarrow 1_{A_{2g}}$

The isolation of the present complex shows that the kind of chelate linkage isomer formed by the isonitroso- β -keto imine ligands depends upon the physical conditions like temperature, solvent, etc.

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3, 5-DICHLORO-2-HYDROXYACETOPHENONE OXIME AS A CHELATING AGENT: STUDIES ON ITS PALLADIUM(II) CHELATE

KEEMTI LAL AND S. P. GUPTA

Chemistry Department, D.N. College, Meerut-250 002

ABSTRACT

3, 5-Dichloro-2-hydroxyacetophenone oxime (DCHAO) has been found to be a good reagent for gravimetric estimation of palladium and for its separation from other ions. The composition and structure of the chelate are studied by microanalysis, pH metric titration, I.R. and Electronic spectra.

O-HYDROXY keto-oximes have been successfully used as chelating reagents. The gravimetric and spectrophotometric studies of the metal chelates in solution have been reported by several workers¹⁻⁴. Gupta and Lal⁵⁻⁷ have reported the physico-chemical studies on the chelates of Cu (II), Ni (II) and Co (II) with 3, 5-dichloro-2-hydroxyacetophenone oxime (DCHAO). In this communication, we report DCHAO as a gravimetric reagent for Pd (II). The composition and structure of Pd (II) chelate has been determined on the basis of micro-analysis, pH metric titration, I.R. and Electronic spectra.

EXPERIMENTAL

DCHAO was prepared as reported earlier⁵. An ethanolic solution (0.5%) of the ligand was

employed for the gravimetric studies. A solution of palladium chloride was prepared from B.D.H. (A.R.) sample in 0.05 M HCl and standardised gravimetrically. Solutions of other ions were prepared from reagent grade samples. NaOH solution (0.05 M) was used for the pH titration using systronic pH meter (type 322).

Determination of Palladium (II)

Metal ion solution ($\sim 20\text{ mg}$) is diluted to 100–125 ml and the pH adjusted (1.0 to 5.0) with hydrochloric acid and ammonium hydroxide buffer, heated to 60–70° and treated with (0.5%) ethanolic solution of DCHAO dropwise with constant stirring (about double the theoretical amount). The precipitate (yellow) was digested on water-bath