

Mode of Coordination of Isonitroso Group of 4-Iminopentane-2,3-dione-3-oxime in Cu(II) Complexes

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β - Isonitrosoacetylacetonimine(4 - iminopentane - 2,3 - dione - 3 - oxime, HIAI) complexes of copper(II) of the types $\text{Cu}(\text{IAI})(\text{IAI}')$, $\text{Cu}(\text{Me-IAI})(\text{IAI}')$ and $\text{Cu}(\text{Me-IAI})_2$, where IAI and IAI' represent anions of N- and O-coordinated isonitrosoacetylacetonimine respectively, have been prepared and characterized. The complexes are monomeric, non-electrolytic and paramagnetic. Spectroscopic evidences suggest that the ligands are coordinated through both nitrogen and oxygen of isonitroso groups in $\text{Cu}(\text{IAI})(\text{IAI}')$ and $\text{Cu}(\text{Me-IAI})(\text{IAI}')$, and through nitrogen in $\text{Cu}(\text{Me-IAI})_2$ giving a symmetric structure.

ABLOV and Zubarev¹ have reported the preparation of bis(isonitrosoacetylacetonimino)copper(II) and bis(N-methylisonitrosoacetylacetonimino)copper(II), but attempts to repeat their methods did not succeed. Further, these authors did not consider the possibility of chelate linkage isomerism in these complexes, the occurrence of which has recently been shown²⁻⁶ in Ni(II) and Pd(II) complexes of these ligands. Based on the structures of dimethylglyoxime complexes of Cu(II)⁷ and Ni(II)⁸, Ablov and Zubarev have assigned symmetric structures for the complexes with both the ligands, coordinated through nitrogen of the isonitroso group. In the present paper, we wish to report our studies on Cu(II) complexes of isonitrosoacetylacetonimine and its N-methyl derivative.

Materials and Methods

Isonitrosoacetylacetonimine was prepared by the method of Wolff *et al.*⁹. Copper acetate monohydrate (Riedel, AR), methyl amine (Riedel, 33% aq. solution) and aq. ammonia (density 0.88 g/ml) were used as such. Common solvents like methanol, chloroform (AR, BDH), etc., were used without further purification, while absolute alcohol and dry benzene were prepared by the standard procedures¹⁰.

Molecular weights of the complexes in benzene were determined cryoscopically. Conductivity measurements in acetone were carried out using Siemen's conductivity bridge. The magnetic susceptibilities of the complexes were determined by Gouy technique, using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. Infrared and electronic spectra were recorded on Carl-Zeiss UR-10 and Unicam 700-A spectrophotometers respectively.

Preparation of the complexes (i) Bis(isonitrosoacetylacetonimine)copper(II) [Cu(IAI)(IAI')] — Isonitrosoacetylacetonimine (2.2 g, ~ 0.0017 mole) dissolved in absolute alcohol (10 ml) was added slowly to a solution of copper acetate monohydrate (1 g, ~ 0.005 mole) and ammonia (3 ml, $\sim 28.0\%$) in absolute alcohol (80 ml). Red crystals of Cu(II) complex were obtained when the solution was kept

aside at room temperature for 4 hr. The crystals were filtered, dried over conc. H_2SO_4 and recrystallized from absolute alcohol as black needle shaped crystals, yield 1.2 g ($\sim 75\%$); $\mu_{\text{eff}} = 1.95$ B.M.; m.p. 360° .

(ii) *Bis(N-methylisonitrosoacetylacetonimino)copper(II) [Cu(Me-IAI)] —* Methanol (20 ml) solution containing isonitrosoacetylacetonimine (1.5 g, ~ 0.011 mole) and 33% aq. methyl amine (3 ml) was stirred for 30 min. To this, copper acetate monohydrate (1 g, ~ 0.005 mole) in methanol (50 ml) was added slowly with constant stirring when a brown complex separated out immediately. It was filtered, dried over conc. H_2SO_4 and recrystallized from chloroform, yield 1.5 g ($\sim 85\%$), $\mu_{\text{eff}} = 1.93$ B.M. m.p. 360° .

Attempts to prepare similar complexes using higher alkyl amines by the above method gave black oily material from which the desired complex could not be isolated.

(iii) *(N-Methylisonitrosoacetylacetonimine)(isonitrosoacetylacetonimine)copper(II) [Cu(Me-IAI)(IAI')] —* $\text{Cu}(\text{IAI})(\text{IAI}')$ (0.317 g, 0.001 mole) and $\text{Cu}(\text{Me-IAI})_2$ (0.345 g, 0.001 mole) were added to dry benzene (25 ml) and the resulting suspension stirred for 2 hr, when the solid complexes got dissolved giving a dark red solution. It was kept overnight and red crystals of the complex were obtained when benzene was removed under reduced pressure. It was recrystallized twice from dry benzene at room temperature. The complex was found to be a single component, as indicated by TLC, yield 0.4 g ($\sim 60\%$); $\mu_{\text{eff}} = 1.90$; B.M.; m.p. 172° .

(iv) *Amine-exchange reaction of Cu(IAI)(IAI') with methyl amine —* Methyl amine (0.3 ml) was added to $\text{Cu}(\text{IAI})(\text{IAI}')$ (0.180 g) dissolved in chloroform-methanol (1:1, 40 ml). It was kept for 1 hr at room temperature. Brown solid complex was obtained after partial removal of the solvents by passing dry air. The complex was filtered, dried over conc. H_2SO_4 and recrystallized from chloroform. It was found to be identical with that obtained by the direct method (ii), as indicated by their colour,

melting point, electronic and infrared spectra. Yield 0.15 g (~80%).

Results and Discussion

The complexes are monomeric in benzene, non-electrolytic in acetone ($\Lambda_M \approx 1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) and paramagnetic ($\mu_{\text{eff}} 1.90\text{--}1.95 \text{ B.M.}$). Characterization data of the complexes are given in Table 1. The molecular weight of $\text{Cu}(\text{Me-IAI})_2$ could not be determined because of its poor solubility in benzene.

The IR spectrum of $\text{Cu}(\text{IAI})(\text{IAI}')$ in mull shows two NH frequencies at 3280 (m, b) and 3240 cm^{-1} (m, sharp) and two C=O bands at 1680 (vs, b) and 1650 cm^{-1} (m). The spectrum in chloroform exhibits these bands at 3350, 3292 and 1685, 1666 cm^{-1} (sh) respectively. The occurrence of two NH and two C=O bands suggests asymmetric mode of coordination of the ligands to the metal, as in the case of $\text{Ni}(\text{IAI})(\text{IAI}')$ and $\text{Pd}(\text{IAI})(\text{IAI}')$.

The close similarity of the IR spectra of $\text{Cu}(\text{MeIAI})(\text{IAI}')$ and $\text{Ni}(\text{Me-IAI})(\text{IAI}')$ is indicative of structure (Ic) for the copper complex. The NH stretching frequency of $\text{Cu}(\text{Me-IAI})(\text{IAI}')$ in mull occurs at 3270 cm^{-1} and that in chloroform at 3260 cm^{-1} . Two distinct C=O bands are observed at 1680 (s) and 1668 cm^{-1} (s) in the mull spectrum and a broad band at 1689 cm^{-1} in chloroform spectrum. The presence of two C=O bands in the mull spectrum supports the asymmetric bonding in the $\text{Cu}(\text{II})$ complex. Out of the two C=O frequencies observed in these complexes, the higher frequency can be assigned to the O-coordinated and the lower frequency to the N-coordinated ligand. The occurrence of C=O stretch at higher frequency in the O-coordinated ligand compared to N-coordinated ligand, may be attributed to the greater contribution of the resonance form II to the structure of the former compared to the latter.

In $\text{Ni}(\text{IAI})(\text{IAI}')$, the two NH bands at 3229 (w, b) and 3365 cm^{-1} (m, sharp) in the chloroform solution spectrum have been assigned to the O- and N-coor-

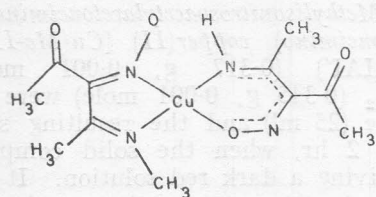
ordinated isonitroso groups of the ligands respectively. In $\text{Cu}(\text{IAI})(\text{IAI}')$ and $\text{Cu}(\text{Me-IAI})(\text{IAI}')$ the NH frequency of the O-coordinated ligand occurs at 3292 and 3260 cm^{-1} respectively. This may be due to the weak hydrogen bonding between the oxygen of the projecting NO and the imine proton which is in *cis* position. Possibly the larger ionic radius of $\text{Cu}(\text{II})$ (0.72 Å) compared to $\text{Ni}(\text{II})$ (0.68 Å) causes weak hydrogen bonding. In agreement with this, the observed bands are quite sharp in the chloroform solution spectrum.

The strong band occurring around 1210 cm^{-1} in both the copper complexes can be assigned to the O-coordinated NO frequency. Gurrien¹¹ *et al.* have assigned the band at a similar position to NO stretch in the metal complexes of 1-nitroso- and 2-nitroso-1-naphthol where the ligands are shown to be coordinated through isonitroso oxygen.

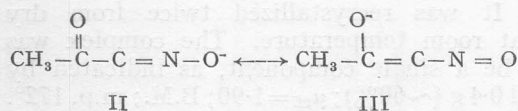
The structural identity of $\text{Cu}(\text{IAI})(\text{IAI}')$ and $\text{Cu}(\text{Me-IAI})(\text{IAI}')$ is further supported by the similarity in their electronic spectra in chloroform medium. The electronic bands in these complexes occur around 41,300 ($\epsilon = 24,000$), 37,600 (sh), 33,300 (sh) and 24,400 cm^{-1} ($\epsilon = 5970$). However, pure *d-d* bands could not be located, possibly due to their overlap by the charge transfer band at 24,400 cm^{-1} .

The complex $\text{Cu}(\text{Me-IAI})_2$ shows a single sharp C=O stretch at 1667 cm^{-1} in its mull spectrum and at 1676 cm^{-1} in the chloroform solution spectrum, suggesting symmetric coordination of both the ligand molecules. The position of the C=O band corresponds to the lower band observed in the $\text{Cu}(\text{IAI})(\text{IAI}')$ and $\text{Cu}(\text{Me-IAI})(\text{IAI}')$. This suggests that both the ligands are coordinated through the nitrogen of the isonitroso group in $\text{Cu}(\text{Me-IAI})_2$. Such symmetrical structures have been assigned to analogous $\text{Pd}(\text{R-IAI})_2$ complexes, where R is nonbulky monoalkyl group⁶. Recently, this type of structure in one of the $\text{Pd}(\text{II})$ complexes, with $\text{R} = \text{C}_2\text{H}_5$, has been confirmed by X-ray crystal structure in our laboratory¹².

The absence of O-coordinated NO stretching frequency around 1210 cm^{-1} in $\text{Cu}(\text{Me-IAI})_2$ also suggests the different type of bonding of isonitroso group in this complex. The strong band around 1150 cm^{-1} in $\text{Cu}(\text{Me-IAI})_2$ can be assigned to NO stretch of N-coordinated isonitroso group. Bands at similar position have been assigned to the NO group in the $\text{Pd}(\text{II})$ complexes of isonitrosoethylmethylketoimine and its alkyl derivatives where the ligands are coordinated through isonitroso nitrogen¹³. Further, this assignment compares well with a recent assignment of N-coordinated NO band in the region 1130 cm^{-1} of dimethylglyoxime complexes of $\text{Pd}(\text{II})$ and $\text{Ni}(\text{II})$ for which normal



I



II

III

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES

| Complex | Calc. (%) | | | | Found (%) | | | |
|---|-----------|-------|------|-------|-----------|-------|------|-------|
| | Metal | C | H | N | Metal | C | H | N |
| $\text{Cu}(\text{IAI})(\text{IAI}')$ | 19.99 | 37.79 | 4.44 | 17.63 | 20.17 | 37.60 | 4.43 | 16.88 |
| $\text{Cu}(\text{Me-IAI})_2$ | 18.37 | 41.67 | 5.24 | 16.20 | 18.47 | 41.40 | 5.20 | 16.21 |
| $\text{Cu}(\text{Me-IAI})(\text{IAI}')$ | 19.14 | 39.81 | 4.86 | 16.88 | 19.00 | 40.00 | 5.23 | 17.01 |

coordinate analysis has been done¹⁴. However, it should be noted that the NO frequency always occurs as a coupled vibration^{2,15}. The electronic spectrum of Cu(Me-IAI)₂ exhibits bands at 39,700 ($\epsilon = 17,000$) and 31,200 cm⁻¹ ($\epsilon = 8950$). The simplicity of this spectrum as compared to that of the asymmetrically coordinated Cu(II) complexes also supports the symmetric structure of Cu(Me-IAI)₂.

One of the peculiarity of the present system is that Ni(II) forms complexes of the type Ni(R-IAI)(IAI') with monoalkyl or aryl substituents but does not form dialkylated or diarylated complexes of the type Ni(R-IAI)₂. Pd(II), on the other hand, forms complexes of the type Pd(R-IAI)₂ with nonbulky alkyl groups and Pd(R-IAI)(IAI') with bulky alkyl or aryl substituents. Cu(II), however, forms both Cu(Me-IAI)(IAI') and Cu(Me-IAI)₂ with methyl substituent.

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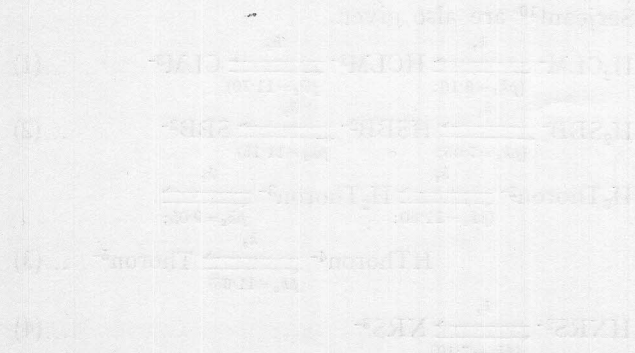
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The electronic spectra of the complexes were recorded in 10% aqueous solution. The absorption maxima were observed at 39,700 and 31,200 cm⁻¹. The molar absorptivity values were 17,000 and 8,950 respectively. The simplicity of the electronic spectrum of Cu(Me-IAI)₂ as compared to that of the asymmetrically coordinated Cu(II) complexes also supports the symmetric structure of Cu(Me-IAI)₂.



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