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# Synthesis and structural studies of (2E,3E)-3-[(6-{[(1E,2E)-2-(hydroxyimino)-1-methylpropylidene]amino}pyridin-2-yl)imino]butan-2-one oxime, ligand and its mono-, di- and trinuclear copper(II) complexes

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## Abstract

A new dioxime ligand, (2*E*,3*E*)-3-[(6-{[(1*E*,2*E*)-2-(hydroxyimino)-1-methylpropylidene]amino}-pyridin-2-yl)imino]butan-2-one oxime, ($H_2$Pymdo) *(3)* has been synthesized in $H_2O$ by reacting 2,3-butenedione monoxime *(2)* with 2,6-diaminopyridine. Mono-, di- and tri-nuclear copper(II) complexes of the dioxime ligand ($H_2$Pymdo) and/or 1,10-phenanthroline have been prepared. The dioxime ligand ($H_2$Pymdo) and its copper(II) complexes were characterized by $^1$H-n.m.r., $^{13}$C-n.m.r. and elemental analyses, magnetic moments, i.r. and mass spectral studies. The mononuclear copper(II) complex of $H_2$Pymdo was found to have a 1:1 metal:ligand ratio. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that the metal ions are coordinated to the oxime and imine nitrogen atoms (C=N). In the dinuclear complexes, in which the first Cu(II) ion was complexed with nitrogen atoms of the oxime and imine groups, the second Cu(II) ion is ligated with dianionic oxygen atoms of the oxime groups and are linked to the 1,10-phenanthroline nitrogen atoms. The trinuclear copper(II) complex *(6)* was formed by coordination of the third Cu(II) ion with dianionic oxygen atoms of each of two molecules of the mononuclear copper(II) complexes. The data support the proposed structure of $H_2$Pymdo and its Cu(II) complexes.

## Introduction

Many reports are available for the preparation and properties of model copper complexes which mimic copper-containing metalloproteins such as hemocyanine and tyrosinase. Two noticeable properties of copper proteins are an intense absorption band [1–3] near 600 nm and relatively high copper(II)/copper(I) reduction potentials [2–4]. Particular attention was focused on their correlation with the active site of metalloenzymes and metalloproteins containing dinuclear metallocenters in order to elucidate the factors that determine the reversible binding and activation of $O_2$ in various natural oxygen transport systems and mono- and di-oxygenases and to mimic their activity [1–3].

In an attempt to design low-molecular weight complexes for mimicking active sites and functions of metalloproteins, paramagnetic copper or manganese complexes with ligands including salicylates, amino acids, porphyrins or Schiff-base derivatives have been prepared [5–9]. These complexes undergo redox reactions smilar to superoxide dismutases (SOD) and therefore, are efficient catalyst for scavenging superoxide radicals. Moreover, such mimics of SOD have been reported to show beneficial effects in protecting tissue against oxidative damage since these complexes catalyze dismutation of superoxide [10–13]; however, most of them lose their activity *in vivo* [14].

In the present paper novel complexes derived from (2*E*,3*E*)-3-[(2-{[(1*E*,2*E*)-2-(hydroxyimino)-1-methylpropylidene]amino}phenyl)imino]butan-2-one oxime ($H_2$P ymdo) are reported. Copper(II) complexes were prepared and characterized by elemental analyses, magnetic susceptibilities, i.r., u.v.–vis. and mass spectral studies.

## Experimental

$^1$H-n.m.r. and $^{13}$C-n.m.r. spectra were recorded on a Varian Gemini 200 spectrometer. DMSO-$d_6$ was used as solvent. Chemical shifts ($\delta$) are reported in ppm relative to tetramethylsilane, using the solvent signal as internal reference. C, H and N contents were determined microanalytically on a Hewlett Packard 85 CHN analyzer, and metal contents were estimated spectrophotometrically. I.r. spectra were recorded on an ATI Unicam Matson 1000 Model FTIR spectrophotometer and u.v.–vis spectra on an ATI Unicam UV2 Model UV/Vis spectrophotometer. Mass spectra (ESI) were recorded on Micromass Quattroo LC-MS/MS spectrophotometer. Room temperature magnetic susceptibility measurements were done on a PAR

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model 155 vibrating sample magnetometer. All chemicals were of the highest quality available, obtained from local suppliers, and used as received

### *Preparation of ligand (3)*

2,6-Diaminopyridine (1.09 g, 10 mmol) and 2,3-butenedione monoxime (2.19 g 20 mmol) were mixed and dissolved in $H_2O$ (15 $cm^3$). This solution was heated and stirred for 1 h at 80 °C. Then the ligand was crystallized from water at room temperature. The deep green crystalline product was isolated by vacuum filtration, then the product was dried *in vacuo*., Yield: 2.34 g (80%), m.p. 104 °C. Ms: (ESI) $m/z$ = 293.32 (15), 273.36 (17), 269.36 (40), 230.25 (30), 213.23 (100), 160.17 (27), 122.19 (30).

### *[Cu(H$_2$Pymdo)(ClO$_4$)$_2$, (4)*

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.85 g, 5 mmol) in $H_2O$ (20 $cm^3$) was added to the ligand solution (1.375 g, 5 mmol) in $H_2O$ (20 $cm^3$), and this mixture was heated with stirring for 2 h at 80 °C. The resulting brown solution was filtered while hot. As the solution cooled, a pale brown product precipitated. The brown product was filtered off, washed with $H_2O$, EtOH and $Et_2O$ respectively. Then the brown solid product was dried *in vacuo*. Yield: 1.57 g (65 %). Ms: (ESI) $m/z$ = 541.25 (20), 525.11 (50), 371.18 (80), 353 (75), 217.12 (100).

### *[Cu$_2$[(Pymdo)phen](ClO$_4$)$_2$, (5)*

The mononuclear copper complex *(4)* (962 mg, 2 mmol) was added to $Et_3N$ (2 mmol) in dry MeOH (25 $cm^3$) and this mixture was stirred for 1 h. The separated solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (640 mg, 2 mmol) in MeOH (10 $cm^3$) and 1,10-phenanthroline monohydrate (400 mg 2 mmol,) in MeOH (10 $cm^3$) was added to the resulting mixture, which was boiled under reflux for 2 h. The dark-brown product was filtered off, washed with EtOH and $Et_2O$ and dried *in vacuo*. Yield: 1.60 g (60%). Ms: (ESI) $m/z$ = 781.45 (10), 663.07 (10), 601.12 (55), 271 (100), 158.99 (60), 129.96 (65).

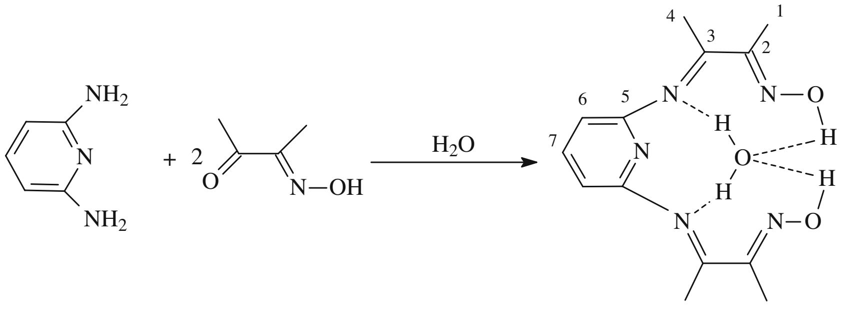
### *[Cu$_3$(Pymdo)$_2$(ClO$_4$)$_2$, (6)*

The mononuclear copper complex *(4)* (962 mg, 2 mmol) was added to $Et_3N$ (2 mmol) in dry MeOH (25 $cm^3$) and this mixture was stirred for 1 h. The separated solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (370 mg, 1 mmol) in EtOH (10 $cm^3$) was added to a solution of the copper complex which was heated under reflux for 2 h. The light-brown product was filtered off, washed with EtOH and $Et_2O$ and dried *in vacuo*. Yield: 0.539 g (55 %). Ms: (ESI) $m/z$ = 935.48 (5), 835.48 (10), 662.33 (55), 660.38 (100), 578.39 (70), 564.39 (35), 482.34 (25), 310.13 (65).

## Results and discussion

(2*E*,3*E*)-3-[(6-{[(1*E*,2*E*)-2-(hydroxyimino)-1-methylpropylidene]amino}pyridin-2-yl)imino]butan-2-one oxi me, ($H_2$Pymdo) (**3**) was prepared as a surprise in $H_2O$ by reacting butane-2,3-dione mono-{*O*-[4-(1-methyl-2-oxo-propylideneaminooxy)-2, 3-bis-(1-methyl-2-oxo-propylideneaminooxy-methyl)-but-2-enyl]-oxime} *(2)* with 1,2-phenylenediamine (Figure 1), but the ligand wasn't synthesized in a common organic solvent. The structural formula of (2*E*,3*E*)-3-[(6-{[(1*E*,2*E*)-2-(hydroxyimino)-1-methylpropylidene]amino}pyridin-2-yl)-imino]butan-2-one oxime, $H_2$Pymdo *(3)*, which is a precursor of the $H_2$Pymdo, was verified by elemental analysis and its magnetic moment (Table 1), $^1$H-n.m.r. and $^{13}$C-n.m.r. (Table 2) and i.r. data (Table 3). In the proposed structure of ($H_2$Pymdo) *(3)*, $N_4$ units are available for the complexation of metal ions in square-planar coordination geometry. The corresponding copper complex *(4)* have been prepared by reaction of the dioxime ligand mixture in $H_2O$ with copper(II) salts.

The $^1$H-n.m.r. spectra of a $CDCl_3$ solution of the dioxime ligand *(3)* show well resolved signals as expected (Table 2). The spectrum of the oxime ligand shows singlets at 2.05 (6H), singlets at 2.38 (6H), the triplet at 7.94 (1H) and the doublet at 5.89 (2H) p.p.m., corresponding to the $CH_3$-1, $CH_3$-4, aromatics (pyridine) C-6, C-7 proton resonances, respectively. The $^1$H-n.m.r. spectral data of a $CDCl_3$ solution of $H_2$Pymdo support the proposed structure and indicate the forma-



**(1)** **(2)** **(3)**

*Fig. 1.* Preparation of ligand, (2E,3E)-3-[(6-{[(1E,2E)-2-(hydroxyimino)-1-methylpropylidene]amino}-pyridin-2-yl)imino]butan-2-one oxime, ($H_2$Pymdo).

*Table 1.* Elemental analyses, magnetic moment and u.v.–vis. spectral data of ligand and its complexes

| Complex | Color | Yield (%) | Found (Calcd.) (%) | | | | $\mu_{eff}$(B.M.) | Sol.$\lambda_{max}$$^a$ |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | Cu | | |
| *(3)* | Deep green | 80 | 56.8(56.7) | 6.1(6.2) | 25.5(25.4) | | – | 296, 350, 400 |
| *(4)* | Brown-green | 65 | 34.3(34.4) | 4.3(4.1) | 14.4(14.3) | 13.2(13.0) | 1.80 | 266, 320, 335, 550 |
| *(5)* | Brown-green | 60 | 38.7(38.5) | 2.9(3.0) | 12.7(12.6) | 16.5(16.3) | 1.65 | 275, 296, 356, 540 |
| *(6)* | Brown-green | 55 | 37.4(33.3) | 3.4(3.2) | 15.1(15.0) | 20.2(20.4)Cu | 1.55 | 317, 341, 533 |

$^a$ The spectra were taken in DMF.

*Table 2.* $^1$H-, $^{13}$C-n.m.r. data for H2Pymdo

| | $CH_3$-1 | C-3 | $CH_3$-4 | C-5 | C-6 | C-7 | C=N–OH (C-2) | $H_2O$ |
|---|---|---|---|---|---|---|---|---|
| $^1$H- | 2.05(s. 6H) | – | 2.38(s. 6H) | – | 5.89 (d, 2H) | 7.94 (t, 1H) | 11.8 | 4.57 |
| $^{13}$C- | 8.27 | 157.1 | 25.15 | 156.3 | 140.5 | 97.75 | 197.36 | – |

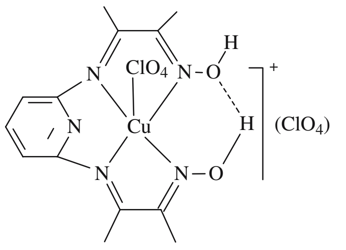
*Table 3.* Observed i.r. frequencies and proposed mode of assignments for the ligand (H2Pymdo) and its complexes

| Complex | (O–H or $H_2O$) | (C=N) | (N–O) | ($ClO_4$) | O–H···O |
|---|---|---|---|---|---|
| *(3)* | 3434 (sh. s.)<br>3368 (sh. s.)<br>3338 (sh. s.) | 1677 | 1461 | – | – |
| *(4)* | 3335 (br. s.) | 1634 | 1430 | 1144<br>1113<br>1089<br>627 | 1680 |
| *(5)* | – | 1618 | 1428 | 1140<br>1110<br>1087<br>626 | – |
| *(6)* | – | 1648 | 1384 | 1138<br>1110<br>1088<br>627 | – |

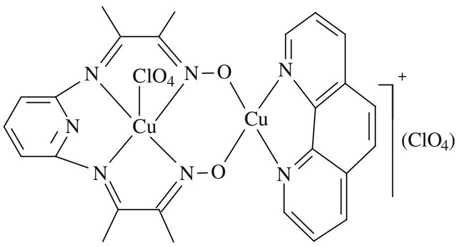
tion of $H_2$Pymdo. The $^1$H-n.m.r. resonances with expected integrated intensities were observed at 1.95 (6H), 2.38 (6H), 7.74 (2H), 7.94 (2H) and 11.8 (2H) p.p.m. corresponding to the $CH_3$-1, $CH_3$-4, aromatic and oxime –OH proton resonances, respectively. The oxime proton signals at 11.8 p.p.m. disappear on deuterium exchange. The seven resonances observed in the $^{13}$C-n.m.r. spectra of $H_2$Pymdo *(3)* are also consistent with the proposed formula. In addition to shows a broad singlet is shown at 4.57 ppm belonging to $H_2O$.

The mass (ESI) of $H_2$Pymdo exhibited the molecular ion at *m/z* 293 $[M + H_2O]^+$, and 273 $[M - 2]^+$, which indicates formation of the $H_2$Pymdo *(3)*. The molecular ion peak appeared at *m/z*, ESI) 541 $[M+2]^+$ for the mononuclear copper(II) *(4)*, at 781 $[M + 1]^+$ for the dinuclear copper(II) *(5)*, at 935 $[M - 1]^+$ for the trinuclear copper(II) *(6)* indicating the formation of the complexes. The molecular ion peak of the copper(II) complex *(4)* was attributed to the fact that this molecule has one ligand molecule, one copper and two perchlorate ions. The molecular ion peak of the homodinuclear copper complex *(5)* was attributed to the fact that this molecule has one ligand molecule, two coppers, two perchlorate ions and one 1,10-phenanthroline molecule. The molecular ion peak of the homotrinuclear copper(II) *(6)* was attributed to the fact that this molecule has two ligand molecules, three coppers are two perchlorate ions.

In general, the complexes exhibited very comparable i.r. features, suggesting that they are of similar structure. The presence or absence of certain bands in the generally complicated i.r. spectra has been used to establish the nature of the complexes. Relevant bands are given in Table 3. In the i.r. spectrum of ligand *(3)*, the –O–H band was observed at *ca.* 3338 cm$^{-1}$. Complex *(4)* has three bands at 1144, 1113, 1089 featuring typical characteristics of coordinated perchlorates and a band at 627 cm$^{-1}$ featuring typical characteristics of uncoordinated perchlorates [8, 15–17]. In the i.r. spectrum of mono nuclear copper(II) complex was observed at 1680 cm$^{-1}$ for mononuclear copper(II) complex due to H–O···H intramolecular hydrogen bond[18]. I.r. data confirm the binding of the copper(II) by $N_4$ donor groups of the present ligand and support the tentative structure of the complex (Figure 2). The significant shifts in *v*(C–N) and *v*(O–H) upon complexation are consistent with complex formation and support the concept of coordination of the ligand through the nitrogen atoms. NO stretching vibrations for $H_2$Pymdo were seen as medium-strong bands at 1360 cm$^{-1}$ [18]. The sharp band at 1630 cm$^{-1}$for the imine and 1461 cm$^{-1}$ for the oxime groups of $H_2$Pymdo were assigned to *v*(N–O) stretching vibrations for metal complexes *(4)* shift to lower frequency suggesting that the oxime groups are nitrogen coordinated. The i.r. data confirm the binding or copper(II) ions to $N_4$ donor groups of the ligand and support the tentative structure of the complexes (Figure 2) [19]. The results are all in good agreement with the proposed structures for the compounds obtained. Complex *(5)* has tri band at 1140, 1112, 1087, a weak band at 784 cm$^{-1}$ featuring typical characteristics of coordinated perchlorates and a band at 626 cm$^{-1}$ featuring typical characteristics of uncoordinated



**(4)**



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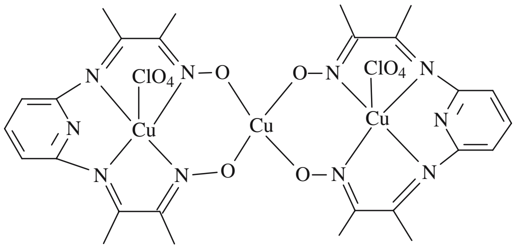

**(6)**

*Fig. 2.* Proposed structures for the copper(II) complexes.

perchlorates [8, 15–17]. In the i.r. spectrum the O–H vibration wasn't observed at 3434 $\text{cm}^{-1}$ for complex *(6)*. Complex *(6)* has a strong tri band centered at 1140, 1110, 1087 $\text{cm}^{-1}$ featuring typical characteristics of coordinated perchlorates and a band at 626 $\text{cm}^{-1}$ featuring typical characteristics of uncoordinated perchlorates [8, 15–17]. I.r. data confirms the binding of the copper(II) by O and N donor groups of the present ligand and supports the tentative structure of the complexes (Figure 2).

The room temperature magnetic moment of all the mono-, di- and tri-nuclear complexes showed a normal magnetic moment (Table 1). The magnetic moment data of the copper(II) complex *(4)* is *ca.* 1.80 B.M., corresponding to one unpaired electron. The observed magnetic moment of the dinuclear copper(II) *(5)* complex is 1.65 B.M. The magnetic moment of the trinuclear *(6)* complex is *ca.* 1.55 B.M. The copper(II) complexes may be considered to have tetragonal geometry [20, 21]. Mononuclear copper(II) complex showed normal magnetic moments. The di- and tri-nuclear copper(II) complex shows indicating an exchange coupled. The ligand and copper(II) complex were dissolved in DMF. In the U.v.–vis. spectra were observed characteristic bands of the oxime ligand. The absorption bands are given in Table 1. The absorbtion $\lambda_{\text{max}}$ of the free ligand $H_2$Pymdo was seen at *ca.* 300 nm and is attributable to the $\pi$–$\pi^*$ transition of the C=N group. The electronic spectra of the complexes showed intense absorption at *ca.* 400 nm which are assigned to charge-transfer (MLCT) transition from the p$\pi$ orbitals of the donor atoms to d orbitals of the metal. In the all complexes, d-d transitions were observed at *ca.* 550 nm. The energy of the d-d transition suggests distorted tetragonal geometry [20–24] for each.

As a conclusion, in the present study, we have demonstrated the preparation of a new dioxime ligand providing N4 donor array moiety, and its mono-, di- and tri-nuclear copper(II) complexes. In the dinuclear complexes, in which the first copper(II) ion was complexed with nitrogen atoms of the oxime imine nitrogen atoms in a square-planar coordination geometry, the second copper(II) ion is ligated with dianionic oxygen atoms of the oxime groups and are linked to the 1,10-phenanthroline nitrogen atoms. However, the trinuclear copper(II) complex *(6)* was formed by coordination of the third Cu(II) ion with dianionic oxygen atoms of each of two molecules of the mononuclear copper(II) complexes *(4)* . All the spectral, elemental analyses data support the formation of the copper(II) and a distorted tetragonal geometry for copper(II) ions.

## Acknowledgements

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TMCH 6578