

Structural studies of complex compounds of 6,6'-diacetyl-2,2'-bipyridine dioxime with copper(I/II), platinum(II), and palladium(II) metal ions

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The tetradentate ligand 6,6'-diacetyl-2,2'-bipyridine dioxime (**L**) was obtained in high yield by the condensation reaction of 6,6'-diacetyl-2,2'-bipyridine with hydroxyl amine in alkaline solution. Density functional calculations and 3D modeling of the structure at the B3LYP/6-31G(d) level of theory for **L** revealed that the energy difference between the global *trans* conformer (*trans-L*), which possesses the C_{2h} point group, and the distorted *cis* conformer (*cis-L*) was 5.214 kcal/mol. Synthesis and characterization of the metal complexes with Cu(I), Cu(II), Pt(II), and Pd(II) metal ions were reported. **L** acted as a N₄-donor ligand to coordinate to the metal centers via N atoms of the 2,2'-bipyridine and the imine moieties to afford tetrahedral complex [Cu^I**L**]PF₆ (**1**), distorted octahedral complex [Cu^{II}**L**(OH₂)₂](NO₃)₂ (**2**), and square-planar complexes [Pt^{II}**L**]Cl₂ (**3**) and [Pd^{II}**L**]Cl (**4**), respectively. The CHN analysis for **1** implies that **L** coordinated to 2 copper(I) ions as a bridging ligand to form a dinuclear metal complex, [Cu₂**L**₂]²⁺, due to the twisting of the coordinated bonds exposed by the tetrahedral geometry preference for the metal ion. The ligand formed intramolecular hydrogen bonds between the oxime groups in **4**, as revealed by the spectroscopic studies. The most stable conformations of the compounds were obtained by using the molecular mechanics optimization feature in CAChe software with an augmented MM2 force field.¹

Key Words: Oxime, N-donor ligands, bipyridine, copper, platinum, palladium

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Introduction

The coordination chemistry of oximes has been widely explored, though their use in supramolecular coordination chemistry remains largely unexplored.²⁻⁴ The oxime moiety is potentially an ambidentate and can coordinate either through the N or O atoms.² The vast literature on structural studies of oxime complexes reveals some interesting features of its coordination behavior. It may coordinate to one metal ion through the N atom and another metal ion through the O atom. In the majority of complexes, only the nitrogen atoms coordinate to the metal center, and the oxygen atoms remain uncoordinated.⁴ The hydrogen atom of the oxime =N-OH group can form potentially strong intramolecular or intermolecular hydrogen bonds with other donor atoms or groups.⁵ Thus, metal complexes bearing nondeprotonated oximes may be considered as supramolecular synthons, capable of forming extended supramolecular networks via intermolecular hydrogen bonds. The orientation of the oxime group in these molecules plays a major role in determining the dimensionality of the extended network.⁶

Despite earlier studies establishing its capability to form hydrogen bonds,⁷⁻⁸ the oxime group has received far less attention in supramolecular chemistry and crystal engineering⁹ than have other groups such as carboxyl,¹⁰ amide,¹¹ and alcohol.¹² More specifically, molecular building blocks can be designed to carry particular functional groups that are capable of recognition of other groups or self-recognition through the formation of one or more hydrogen bonds. By such a synthetic approach, even quite complex molecular aggregates (supermolecules) can be prepared in a designed manner.¹³

In the solid state, 6,6'-dimethyl-2,2'-bipyridine is a planar centrosymmetric molecule in which the pyridine N atoms have a transoid arrangement by virtue of the symmetry.¹⁴ In general, 2,2'-bipyridines substituted at the 6,6'-positions form double-stranded helical metal complexes with metal ions having preference for tetrahedral geometry, i.e. Ag(I) and Cu(I), and mononuclear complexes with dicationic metal ions such as Cu(II).¹⁵ This was exemplified by the tetradentate ligand, 6,6'-bis(3-pyrazolyl)-2,2'-bipyridine ligand, which can behave either as a tetradentate chelate in a mononuclear Cu(II) complex, or as a bridging ligand in a dinuclear complex with Ag(I), by adopting to the stereoelectronic requirements of both metal centers.¹⁶ Herein we present a structurally similar N₄-donor ligand, 6,6'-diacetyl-2,2'-bipyridine dioxime, and its complex compounds with d¹⁰ copper(I), d⁹ copper(II), d⁸ platinum(II), and palladium(II) metal ions.

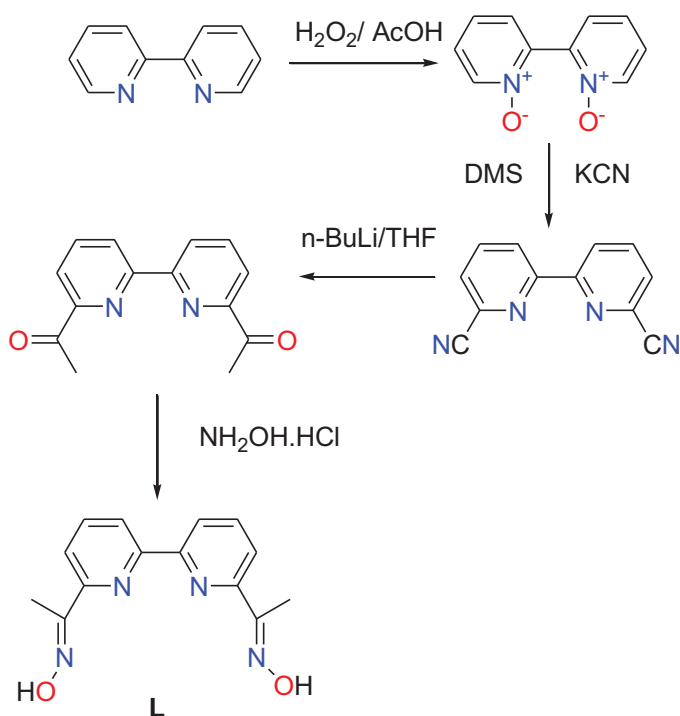
Experimental

Physical measurements

Melting points were determined with a Büchi Melting Point B-540 Model digital melting point instrument. Elemental analysis data were obtained with a LECO 932 CHNS analyzer. ¹H NMR spectra were recorded on a Bruker DPX 400 spectrometer, using DMSO-d₆ as a solvent and TMS as an internal standard. Infrared spectra, as KBr pellets, were recorded using a JASCO FT-IR-300 E spectrophotometer. API-ESI mass spectra were obtained with an LC/MS Agilent 1100 MSD mass spectrometer.

Synthesis of 6,6'-diacetyl-2,2'-bipyridine dioxime (**L**)

The syntheses of *N,N'*-dioxide-2,2'-bipyridine,¹⁷ 6,6'-dicyano-2,2'-bipyridine,¹⁸ and 6,6'-diacetyl-2,2'-bipyridine^{19,20} were previously reported. The 6,6'-diacetyl-2,2'-bipyridine dioxime (**L**) was synthesized according to the literature,^{19,20} as depicted in Scheme 1. The reaction was carried out under a dry N₂ atmosphere. An excess amount of hydroxylamine hydrochloride (1.10 g, 15.6 mmol) was dissolved in ethanol (10 mL) and mixed with an excess amount of sodium hydroxide (0.62 g, 15.6 mmol) in water (5 mL). To this solution, 6,6'-diacetyl-2,2'-bipyridine (1.50 g, 7.1 mmol) dissolved in ethanol (5 mL) was added slowly. The solution was set to reflux for 2 h. The solution was filtered and washed with water and ethanol, and dried under a vacuum. The white precipitate was recrystallized from DMF to give 1.62 g (85%). Mp: 301 °C. Anal. Calc. for C₁₄H₁₄N₄O₂: C, 62.21; H, 5.22; N, 20.73. Found: C, 62.0; H, 5.2; N, 20.7 (%). IR (ν cm⁻¹): 3382 (O-H), 3143 (C-H_{ar}), 2838 (C-H_{al}), 1627 (C=N), 1560 (C=N), 1419 (C-C), 955 (N-O).



Scheme 1.

Synthesis of copper(I) complex (1) [CuL]PF₆ or [Cu₂L₂](PF₆)₂

Since the geometrical isomers of the dioxime ligand could not be separated by column chromatography, **L** was obtained as a mixture of (*E*) and (*Z*) isomers, and was used without separation. The establishment of the conformational and configurational features of the ligand will be a future study, including X-ray analysis and molecular mechanics investigations.

L (0.27 g, 1.0 mmol) was dissolved in acetonitrile (40 mL) under an inert nitrogen atmosphere. A few drops of trifluoroacetic acid were added to this solution with vigorous stirring to assure the dissolution

of the ligand. $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.372 g, 1.0 mmol) was added to the homogenous solution and it was stirred for an additional 15 min. In order to prevent the oxidation of the metal center, as indicated by the occurrence of a yellowish-green solution, hydrazine dihydrochloride ($\text{H}_2\text{NNH}_2 \cdot 2\text{HCl}$) was added with stirring. The solution was concentrated under a vacuum and filtered, washed with hexane, and dried in a desiccator over silica gel, 0.25g (75%). The complex was soluble in acetonitrile, ethanol, methanol, and DMF. Anal. Calc. for $[\text{Cu}_2\text{L}_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$: C, 33.85; H, 3.25; N, 11.28. Found: C, 33.2; H, 3.1; N, 11.4 (%). API-ES (m/z): 307.0 $[\text{L} \cdot 2\text{H}_2\text{O}]$; 334.0 $[\text{CuL}]$ or $[\text{Cu}_2\text{L}_2]^{2+}$. IR ($\nu \text{ cm}^{-1}$): 3535 (H_2O), 3414 (O-H), 3125 (C-H_{ar.}), 1621 (C=N), 1500 (C=C), 960 (N-O).

Synthesis of copper(II) complex (2) $[\text{CuL}](\text{NO}_3)_2$

L (0.27 g, 1.0 mmol) was dissolved in aqueous methanol (35 mL). The pH of the solution was adjusted to approximately 2 with 1 M HCl (10 mL) and set to reflux to obtain a clear solution. To this homogenous solution, $\text{Cu}(\text{NO}_3)_2$ (0.187 g, 1.0 mmol) was added and the reaction was kept at 50 °C with continuous stirring for 1 h. The pH of the yellowish-green solution was adjusted to approximately 4 with a 1 M NaOH solution. The solution was then concentrated on a rotary evaporator, filtered, and allowed to cool to room temperature. An excess of a concentrated aqueous solution of NaNO_3 was added. The precipitate was filtered off, washed with methanol and water, and dried in a desiccator over silica gel, 0.22 g (59%). API-ES (m/z): 307.0 $[\text{L}] \cdot 2\text{H}_2\text{O}$; 334.0 $[\text{CuL}]^{2+}$; 372.0 $[\text{CuL}(\text{H}_2\text{O})_2]^{2+}$; 369.1 $[\text{Cu}(\text{L})]^{2+}$. IR ($\nu \text{ cm}^{-1}$): 3500 (H_2O), 3400 (O-H), 3150 (C-H), 2800 (C-H), 1610 (C=N), 1500 (C-C), 1450 (C=C), 965 (N-O).

Synthesis of platinum(II) complex (3) $[\text{PtL}]\text{Cl}_2$

L (0.15 g, 0.5 mmol) was dissolved in 2 M HCl (10 mL), and K_2PtCl_4 (0.21 g, 0.5 mmol) in water (10 mL) was added with vigorous stirring. The solution was refluxed for 2 h. The dark solid was filtered and dried in a desiccator, 0.11 g (60%). The crude product was slightly soluble in common polar organic solvents such as MeCN, MeOH, CHCl_3 , THF, and DMF. Anal. Calc. for $[\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_4\text{Pt}]$: C, 29.38; H, 3.17; N, 9.79. Found; C, 29.1; H, 3.3; N, 7.4 (%). ^1H NMR (DMSO- d_6 , δ ppm): 11.60 (s, 2H, N-OH), 8.60 (t, $J_{4,3} = 8.5$ Hz, 2H, H_{4,4'}), 8.53 (d, $J_{3,4} = 8,5$ Hz, 2H, H_{3,3'}), 8.39 (d, $J_{5,4} = 8,4$ Hz, 2H, H_{5,5'}). IR ($\nu \text{ cm}^{-1}$): 3382 (N-H), 3143 (O-H), 2838 (C-H), 1627 (C=N), 1450 (C=C), 1419 (C-C), 966 (N-O).

Synthesis of palladium(II) complex (4) $[\text{PdL}]\text{Cl}$

L (0.15 g, 0.5 mmol) was dissolved in DCM/ CH_3CN (15/10 v/v), and dichloro(1,5-cyclooctadine)palladium(II), $\text{Pd}(\text{COD})\text{Cl}_2$ (0.5 mmol, 10 ml), in CH_2Cl_2 (15 mL) was added with vigorous stirring. The solution was kept at 70 °C for 2 h. The resulting dark solid was filtered and dried in a desiccator, 0.12 g (66%). ESI-MS (m/z): 375.3 $[\text{Pd}(\text{L})]^+$. ^1H NMR (DMSO- d_6 , δ ppm): 7.38 (t, 2H, H_{4,4'}), 7.23 (2H, H_{3,3'}), 7.06 (d, 2H, H_{5,5'}), 2.50 (s, 6H, CH_3). IR ($\nu \text{ cm}^{-1}$): 3400 (O-H), 3200 (C-H_{ar.}), 2900 (C-H), 1580 (C=N), 1500 (C-C), 1460 (C=C), 1419 (C-C), 967 (N-O).

Results and discussion

Synthesis and characterization of 6,6'-diacetyl-2,2'-bipyridine dioxime (L)

The synthesis of **L** is depicted in Scheme 1. The spectroscopic and physical data were identical to the reported data in the literature^{19–21} and in good agreement with the molecular structure optimized by DFT as shown in Figure 1. The intense OH-stretching vibrational band of the oximes lay in the expected region of 3450-3030 cm^{-1} .²¹ The band of the C=N- group appeared at between 1615-1585 and 1625-1620 cm^{-1} .^{21,22} Since the aromatic ring vibrations occurred in the same region, the C=N band was usually not clearly recognizable. The N-O stretching vibrational band lay in the region of 1055 and 870 cm^{-1} and often split into several maxima.²¹ In the IR spectrum, **L** showed major absorption bands at 2838 cm^{-1} , which were attributed to the C-H vibrations of the methyl groups. The characteristic band at 3382 cm^{-1} was attributed to the O-H vibrations. The aromatic stretching mode of the aromatic C-H groups appeared at 3143 cm^{-1} . The strong absorption band at 1560 and 1419 cm^{-1} was the combination stretching of the C=N and C-C vibrations. The stretching mode of the N-O bond was attributed to 955 cm^{-1} . The stretching mode of the oxime C=N bond was attributed to 1627 cm^{-1} .

Molecular structure of L

Calculations and 3D modeling for **L** were performed using the Gaussian 03 quantum chemistry package.²³ To save computational time, initial geometry optimizations were carried out with the molecular mechanics (MM) method, using the MM+ force fields. The lowest energy confirmations of the molecules obtained by the MM method were further optimized by the DFT method,²⁴ by employing Becke's 3-parameter hybrid functional (B3LYP)²⁵ and the 6-31G (d) basis set. Fundamental vibrations of **L** were also calculated using the same method to check whether there were true minima. The possible stable conformers of **L** were determined by potential energy scan calculations over the single rotatable bond between the 2 rings. In order to find the final geometric parameters of the obtained stable conformers, each structure was optimized at the same theory level. Via subsequent single point energy calculations by varying the dihedral angle of 18N-1C-6C-17N atoms, 2 stable low-energy conformers of **L** were obtained. The energy difference between the global *trans* conformer (*trans-L*), which possesses the C_{2h} point group, and the distorted *cis* conformer (*cis-L*) was 5.21 kcal/mol. The pyridine rings in the *cis-L* had a dihedral angle of 40°. The optimized geometries of these conformers and the numeration of the atoms of **L** are presented in Figure 1. The comparison of the geometric parameters of the *trans* and the *cis* conformers of **L** are presented in Table 1.

Synthesis and characterization of copper(I) complex (1)

Copper(I) complex **1** was synthesized by the reaction of **L** with the $[\text{Cu}(\text{CH}_3\text{CN})_4]\cdot\text{PF}_6$ salt in CH_3CN and a minimum amount of trifluoroacetic acid mixture, as illustrated in Scheme 2. The infrared spectra of the transition metal oxime complexes were diagnostic of binding.^{26–30} All of the complexes displayed a strong stretch near 3400-3480 cm^{-1} , indicating that the complexes were protonated in the solid state and that the oxime protons were not hydrogen-bonded. While these $\nu(\text{O-H})$ absorptions did occur in the typically broad O-H stretching region, 3000-3500 cm^{-1} ,²⁵ they were observed at higher energies than those that are observed

for most *cis*-configured bis(*vic*-dioximato) complexes (3180-3300 cm^{-1}) or uncoordinated oxime ligands.²⁶ Generally, values at approximately 3650 cm^{-1} are assigned to nonhydrogen-bonded $\nu(\text{OH})$, while $\nu(\text{NO}\cdots\text{H})$ is assigned to values of approximately 3255 cm^{-1} .^{29,30}

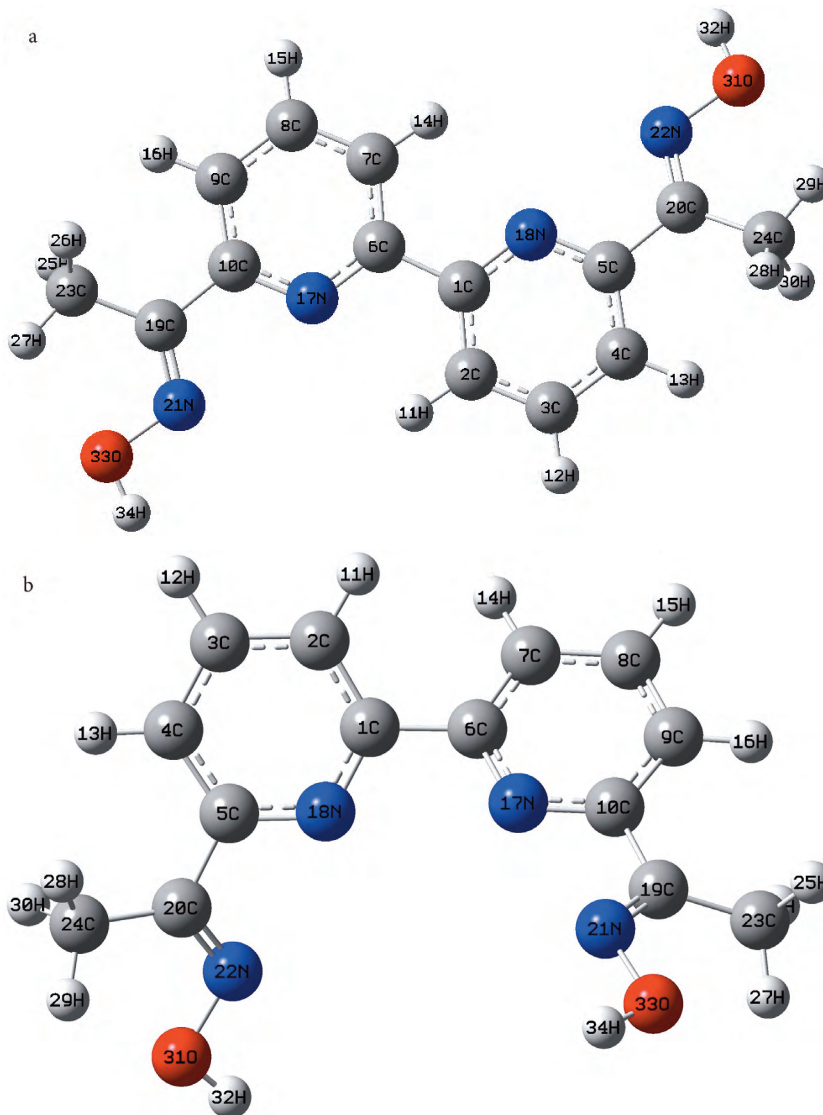
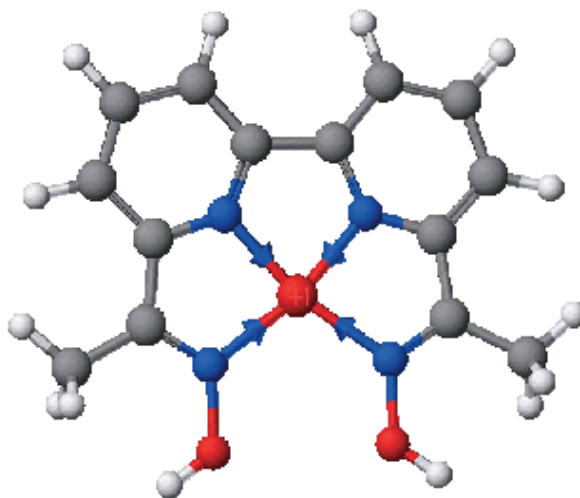


Figure 1. The 2 low-energy stable conformers of free ligand 6,6'-diacetyl-2,2'-bipyridine dioxime (**L**): **a**) *trans* global conformer, **b**) distorted *cis* conformer.

In the IR spectrum of **1**, the bands in the mid-IR range were mostly due to the stretching vibrations of the oxime moieties and in-plane vibrations of the pyridine rings. Generally, after coordination, the position of some vibrations would change. Thus, in the case of **1**, the strong and broad absorption band at 3535 cm^{-1} was attributable to intramolecular hydrogen-bonded $\text{O-H}\cdots\text{O}$ groups. The aromatic C-H vibration appeared at 3125 cm^{-1} . The C=N vibration of oxime moved to a lower frequency at 1621 cm^{-1} with a lower intensity. The C=C vibrations appeared at 1500 cm^{-1} . The N-O vibration appeared at 960 cm^{-1} .

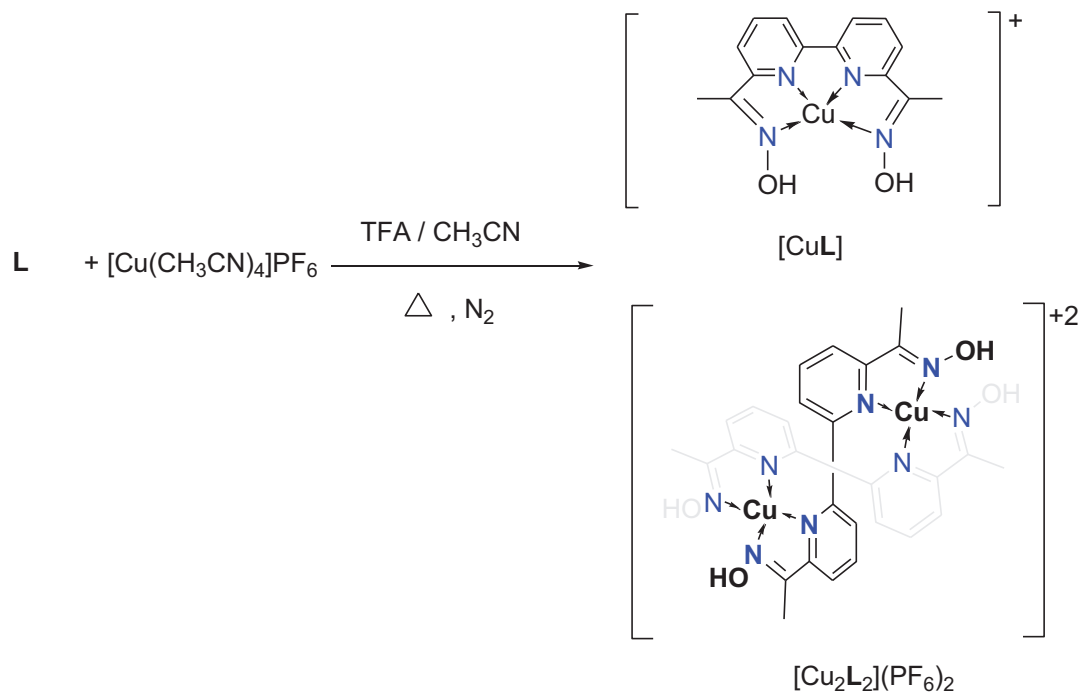
Table. Selected structural parameters from the DFT/B3LTP method using the 6-31G(d) basis set.

Bond lengths (Å)	<i>Trans</i> -L	<i>Cis</i> -L	Bond angles (°)	<i>Trans</i> -L	<i>Cis</i> -L
O31-N22	1.402	1.403	C19-C10-C9	120.60	120.07
N22-C20	1.287	1.286	C19-C10-N17	117.76	117.70
C20-C24	1.508	1.509	N17-C10-C9	121.63	122.21
C20-C5	1.492	1.491	C10-N17-C6	119.26	118.83
C5-C4	1.403	1.405	C10-C9-C8	118.85	118.75
C4-C3	1.395	1.392	N17-C6-C7	122.85	122.68
C3-C2	1.388	1.404	N17-C6-C1	116.57	116.93
C1-N18	1.336	1.337	Dihedral Angles (°)		
N18-C5	1.342	1.342	O33-N21-C19-C10	-179.30	-178.74
C1-C6	1.492	1.496	O33-N21-C19-C23	-0.04	-0.05
Bond angles (°)			C23-C19-C10-C9	-11.18	-23.91
H34-O33-N21	101.60	101.59	N21-C19-C10-N17	-11.56	-24.41
O33-N21-C19	112.42	111.831	C10-N17-C6-C7	0.17	0.37
N21-C19-C23	124.30	123.87	C10-N17-C6-C1	-179.89	179.91
C23-C19-C10	119.57	120.18	N17-C6-C1-N18	-189.80	-39.14
N21-C19-C10	116.11	115.93	C7-C6-C1-C2	-178.94	-40.05

**Figure 2.** Optimized structure of (1) $[\text{CuL}]^+$ generated from the CAChe software package with augmented MM3 parameters.

In the API-ES mass spectrum, the molecular ion peak corresponding to **1** was observed at m/z 334.0, which supports the formulation of $[\text{CuL}]^{+1}$ as shown by the optimized molecular structure in Figure 2. This value also corresponds to dinuclear complex $[\text{Cu}_2\text{L}_2]^{+2}$, as illustrated in Scheme 2. These 2 species could not be differentiated due to the low resolution of the mass spectrometer. However, the CHN analysis for **1** implies that the ligand acted as a bridging ligand to coordinate to 2 copper(I) ions to form a dinuclear metal complex

$[\text{Cu}_2\text{L}_2]^{2+}$, due to the twisting of the coordinated bonds exposed by the tetrahedral geometry preference of the metal center, as revealed by the very similar ligand.¹⁶



Scheme 2.

Synthesis and characterization of copper(II) complex (2)

Copper(II) is a 6-coordinate elongated octahedral complex with CuN_4O_2 , where the equatorial position is defined by the N atoms of the ligand and the axial position by the water molecules, as shown in Figure 3.

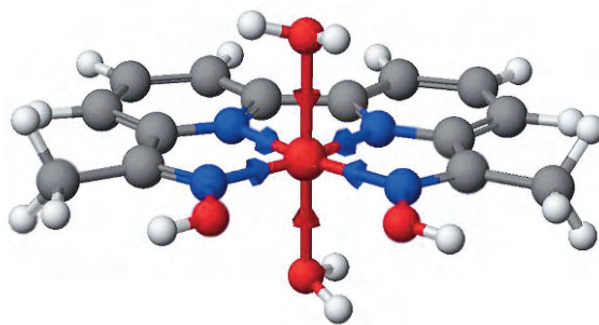


Figure 3. Optimized structure of (2) $[\text{CuL}(\text{H}_2\text{O})_2]^{2+}$ generated from the CAChe software package with augmented MM3 parameters.

In the IR spectrum of complex 2, the coordinated H_2O molecules were identified by a broad O–H absorption band at around 3400 cm^{-1} . The broad band at 3500 cm^{-1} was attributed to the N–H vibration.

The aromatic C–H vibration appeared at 3150 cm^{-1} and the aliphatic C–H vibration appeared at 2800 cm^{-1} . The intensity of characteristic stretching and bending vibrations of the free ligand were shifted and lowered on the complex formation, and new vibrational bands characteristic for complex **2** were observed. The N–O vibration moved to a higher frequency at 965 cm^{-1} . The oxime C=N stretch decreased from 1627 cm^{-1} in the free ligand to 1610 cm^{-1} in complex **2**. The characteristic band due to (C–C) and (C=C) vibrations appeared at 1500 and 1450 cm^{-1} .^{2,30} In the API-ES mass spectrum, the molecular ion peak at m/z 334.0 corresponded to the cationic fragment of $[\text{CuL}]^{2+}$. The simulated isotopic pattern was in good agreement with the measured spectrum. The secondary peak at m/z 372.0 could be attributed to $[\text{CuL}(\text{H}_2\text{O})_2]^{2+}$ in the solution, and was identical to the calculated value at m/z 370.0. The tertiary peak at m/z 307.0 could be attributed to $[\text{L}](\text{H}_2\text{O})_2$ in the solution, showing that the complex underwent demetallation under the mass condition.

Synthesis and characterization of platinum(II) complex (**3**)

The optimized molecular structure of **3** is shown in Figure 4. In the IR spectrum of complex **3**, a broad O–H absorption peak appeared at 3382 cm^{-1} . The aromatic C–H vibration appeared at 3143 cm^{-1} and the aliphatic C–H vibration appeared at 2838 cm^{-1} . The N–O vibration appeared at 966 cm^{-1} . The C=N stretching vibrations of the oxime and the pyridine rings appeared at 1627 and 1582 cm^{-1} . The characteristic band due to C–C and C=C vibrations appeared at 1500 and 1450 cm^{-1} .



Figure 4. Optimized structure of (**3**) $[\text{PtL}]^{2+}$ generated from the CAChe software package with augmented MM3 parameters.

The CHN analysis showed the ratio of metal to ligand for complex **3** to be 1:1, which was consistent with the formulation of $[\text{Pt}(\text{L})]\text{Cl}_2$ for $[\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_4\text{Pt}]$.

The ^1H NMR of the ligand in DMSO showed OH proton resonance at 11.60 ppm as a broad singlet due to the exchange of protons with solvent. The aliphatic methyl group's resonance was at 2.33 ppm as a singlet. The aromatic protons of the ligand appeared in the expected region, at 8.60, 8.53, and 8.39 ppm, and were assigned accordingly, almost identical to the reported oxime derivatives.³¹

Synthesis and characterization of palladium(II) complex (4)

The optimized molecular structure of **4** is depicted Figure 5. In the IR spectrum of complex **4**, a broad O–H absorption peak appeared at 3400 cm^{-1} . The aromatic C–H vibration appeared at 3200 cm^{-1} and the aliphatic C–H vibration appeared at 2900 cm^{-1} . The N–O vibration appeared at 967 cm^{-1} . The characteristic bands for C–C and C=C vibrations appeared at 1500 and 1460 cm^{-1} . The C=N stretching vibration of the pyridine rings appeared at 1580 cm^{-1} . The coordination of the oxime groups to the metal center through the N atoms are expected to reduce the electron density and lower the C=N absorption frequency.

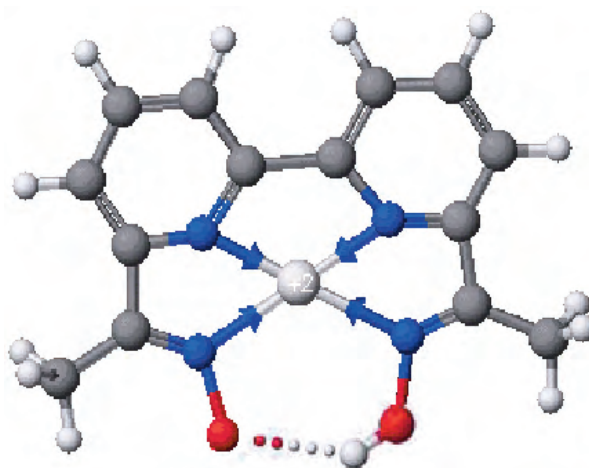


Figure 5. Optimized structure of (**4**) $[\text{PdL}]^{1+}$ generated from the CAChe software package with augmented MM3 parameters.

ESI-MS measurements have been widely used to identify the species in solution as a very soft technique that reduces demetallation in mass condition.³² The ESI-MS analysis was consistent with the formulation of $[\text{PdL}]^+$ for $[\text{C}_{14}\text{H}_{13}\text{N}_4\text{O}_2\text{Pd}]^+$. The molecular ion peak at m/z 375.3 corresponded to the cationic fragment. The simulated isotopic pattern was in good agreement with the measured spectrum and was identical to the calculated value at m/z 376.0. This result also supported the (O···H–O) bonding, where one of the oximes was deprotonated to act as a monoanionic ligand.

O–H···O stretching and bending vibrations are usually observed in the ranges of $2200\text{--}2400\text{ cm}^{-1}$ and $1600\text{--}1800\text{ cm}^{-1}$, respectively.² The stretching vibrations between $1550\text{--}1650\text{ cm}^{-1}$ and $2250\text{--}2300\text{ cm}^{-1}$ supported the intramolecular O–H···O hydrogen bond, as depicted in Figure 5.

The ^1H NMR spectrum of the **4** did not show any signal for the N–OH protons in $\text{DMSO-}d_6$, suggesting that the complex underwent rapid H–D exchange with the solvent. The aliphatic methyl group's resonance was as a singlet at 2.50 ppm. The aromatic protons appeared at 7.38, 7.23, and 7.06 ppm. These values were in accordance with the previously reported oxime derivatives and support the intramolecular hydrogen bonding.³⁰

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