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### Synthesis, structural, and thermal analyses of copper(II) and oxido-vanadium(IV) complexes of 4-bromo-2-(((5-chloro-2-hydroxyphenyl)imino)methyl)phenol

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## Synthesis, structural, and thermal analyses of copper(II) and oxido-vanadium(IV) complexes of 4-bromo-2-(((5-chloro-2-hydroxyphenyl)imino)methyl)phenol

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Reaction of 4-bromo-2-(((5-chloro-2-hydroxyphenyl)imino)methyl)phenol ( $H_2L$ ) with  $Cu(OAc)_2 \cdot 4H_2O$  or  $VOSO_4 \cdot 3H_2O$  and 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) in a 1 : 1 : 1 mol ratio led to  $[CuL(phen)]$  and  $[VOL(bipy)]$  which have distorted square pyramidal and octahedral geometries, respectively. The compounds were characterized by elemental analyses, FT-IR, UV-Vis, TGA, and X-ray diffraction. Their thermolyses have three stages: phen or bipy removal, separation of  $H_2L$  minus chloride and bromide of  $H_2L$ , and complete thermal decomposition to the metal oxide.

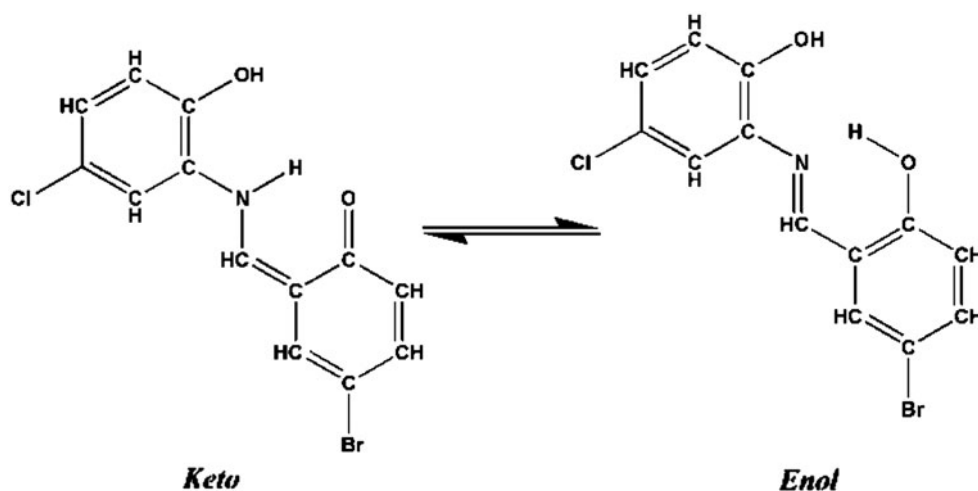
*Keywords:* Oxido-vanadium(IV) complex; Copper(II) complex; TGA; Spectroscopy; Crystal structures

### 1. Introduction

Salicylidene compounds containing ONO donors have special potential in biochemistry [1, 2]. The biological effects of metal complexes of these compounds are more pronounced than those of their ligands [3, 4]. One of the main reasons for attention to these types of ligands is that in many metalloproteins, the central element is surrounded by asymmetric ligands and the targeted synthesis of these complexes can help us design appropriate mimics for the study of enzymes [5, 6]. As the salicylidene used in this work showed antimicrobial properties, it is expected that its metal complexes demonstrate significant biological properties too [1]. In particular, complexes of vanadium and copper are interesting because they play significant roles in many biological processes [7].

Several reports have shown the bioactivities of copper complexes with  $CuL_1L_2$  formulas where  $L_1$  and  $L_2$  are the ONO Schiff base and the NN donor, respectively [8, 9]. These compounds are mimics for copper(II) protein species. The biological activity of these

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Scheme 1. General structures of the free ligand tautomers ( $H_2L$ ).

compounds depends on non-covalent interactions between the aromatic units [10]. Many complexes show antitumor and antimicrobial properties [11, 12]. Heterocyclic copper(II) complexes are associated with, or intercalated through, the DNA surface and assist in hydrolytic or oxidative cleavage of DNA [13, 14]. The oxido-vanadium(IV) complexes with ONO donors and heterocycles have significant impact on the biochemistry processes such as DNA cleavage [15]. Oxido-vanadium(IV) complexes are good candidates for insulin mimics [16]. Based on the physico-chemical investigations on oxido-vanadium(IV) complexes, these compounds are good models for protein studies [17, 18]. High absorption and low toxicity of these compounds make them suitable materials for bio-applications [19].

Herein, we report synthesis, spectroscopy, TGA, and X-ray structural studies of two new complexes of the Schiff base 4-bromo-2-(((5-chloro-2-hydroxyphenyl)imino)methyl)phenol ( $H_2L$ ) (scheme 1) with Cu(II) and V(IV),  $[CuL(phen)]$  and  $[VOL(bipy)]$ .

## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals and solvents were of analytical reagent grade and were used as received. 5-Bromo-2-hydroxybenzaldehyde and 2-amino-4-chlorophenol were purchased from Merck Company.  $H_2L$  was prepared according to our previous work [20]. Microanalyses for C, H, and N were performed on a Thermo Finnigan Flash Elemental Analyzer 1112EA. IR spectra were measured using KBr pellets on a FT-IR 8400-SHIMADZU spectrophotometer ( $400\text{--}4000\text{ cm}^{-1}$ ). Molar conductivities of  $10^{-3}\text{ M}$  solutions of the complexes in DMSO were determined by a Metrohm 712 Conductometer at  $25^\circ\text{C}$ . Electronic spectra of the compounds in DMSO (*ca.*  $25^\circ\text{C}$ ) were run on a SHIMADZU model 2550 UV-Vis spectrophotometer (260–800 nm). Thermogravimetric analyses (TGA and DTG) were carried out in an oxygen atmosphere (10 mL/min) with a heating rate of  $10^\circ\text{C}/\text{min}$  using a TGA-50 SHIMADZU thermal analyzer from 20–1000  $^\circ\text{C}$ . X-ray diffraction data were measured by a Bruker Smart APEX CCD diffractometer.

## 2.2. Preparation of 4-bromo-2-((5-chloro-2-hydroxyphenyl)imino)methylphenol (**H<sub>2</sub>L**)

A solution of 2-amino-4-chlorophenol (0.2 mmol, 0.03 g) in 5 mL of ethanol was added to an equimolar quantity of 2-hydroxy-5-bromobenzaldehyde in 5 mL of ethanol with vigorous stirring. After 30 min of refluxing and cooling, the solution resulted in the formation of a red precipitate, which was separated by filtration, washed with cold ethanol, and dried in a desiccator over anhydrous CaCl<sub>2</sub>. Red. Yield: 0.54 g, 82%. m.p.: 199 °C. Anal. Calcd for C<sub>13</sub>H<sub>9</sub>BrClNO<sub>2</sub> (326.57 g mol<sup>-1</sup>): C, 47.81; H, 2.87; N, 4.29. Found: C, 47.78; H, 2.80; N, 3.62%. FT-IR (KBr) cm<sup>-1</sup>: ν(OH) 3448wb, ν(N-H) 3130sb, ν(C=N) 1627s, ν(C=C<sub>ring</sub>) 1581s, ν(C-O) 1319 m, ν(C-Cl) 678s, ν(C-Br) 585s. UV/Vis (DMSO) λ<sub>max</sub>, nm (log(ε), L mol<sup>-1</sup> cm<sup>-1</sup>): 286(4.03), 368(4.14), 438(3.67).

## 2.3. Preparation of (1,10-phenanthroline)[4-bromo-2-((5-chloro-2-hydroxyphenyl)imino)methylphenol]copper(II) [CuL(phen)] (**1**)

Cu(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol, 0.02 g) was added to a solution of H<sub>2</sub>L (0.1 mmol, 0.03 g) and NaOH (0.2 mmol, 0.01 g) in 6 mL of boiling methanol and the mixture was refluxed in a water bath for 30 min. 1,10-Phenanthroline (0.1 mmol, 0.02 g) was added to the resulting dark green solution which was further refluxed for ca. 3 h. After cooling, the solution was filtered and left to stand overnight. Black crystals suitable for crystallography were separated after four days and were dried in a vacuum desiccator over CaCl<sub>2</sub>. Yield: 0.045 g, 78%. m.p.: >300 °C. Molar conductivity (1.0 × 10<sup>-3</sup> M, DMSO): 2.90 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd for C<sub>25</sub>H<sub>15</sub>BrClCuN<sub>3</sub>O<sub>2</sub>·0.50H<sub>2</sub>O (577.31 g mol<sup>-1</sup>): C, 52.01; H, 2.79; N, 7.28. Found: C, 52.17; H, 2.80; N, 7.24%. FT-IR (KBr) cm<sup>-1</sup>: ν(C=N) 1612s, ν(C=C<sub>ring</sub>) 1520s, ν(C-O) 1296 m, ρ(py<sub>ring</sub>) 1018 m, ν(C-Cl) 709 m, ν(C-Br) 656w. UV/Vis (DMSO) λ<sub>max</sub>, nm (log(ε), L mol<sup>-1</sup> cm<sup>-1</sup>): 272(4.5), 448(4.37), 474(4.32), 654(2.28).

## 2.4. Preparation of (2,2'-bipyridine)[4-bromo-2-((5-chloro-2-hydroxyphenyl)imino)methylphenol] oxido-vanadium(IV) [VOL(bipy)] (**2**)

VOSO<sub>4</sub>·3H<sub>2</sub>O (0.1 mmol, 0.02 g) was added to a solution of H<sub>2</sub>L (0.1 mmol, 0.03 g) in 6 mL of hot methanol and the solution was refluxed for 1 h on a water bath. 2,2'-Bipyridine (0.1 mmol, 0.02 g) was added to the resulting brown solution and the reflux was continued for 3 h. After one day, suitable single crystals appeared upon slow evaporation of the solvent. The product was isolated, washed with cold ethanol, and dried in a vacuum desiccator over CaCl<sub>2</sub>. Parallelepiped. Red. Yield: 0.039 g, 67%. m.p.: 236 °C. Molar conductivity (1.0 × 10<sup>-3</sup> M, DMSO): 21.5 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>19</sub>BrClN<sub>3</sub>O<sub>4</sub>V (579.72 g mol<sup>-1</sup>): C, 49.72; H, 3.30; N, 7.25. Found: C, 49.68; H, 3.22; N, 7.31%. FT-IR (KBr) cm<sup>-1</sup>: ν(C=N) 1597s, ν(C=C<sub>ring</sub>) 1512s, ν(C-O) 1288 m, ν(V=O) 948s, ρ(py<sub>ring</sub>) 905 m, ν(C-Cl) 702 m, ν(C-Br) 648w. UV/Vis (DMSO) λ<sub>max</sub>, nm (logε, L mol<sup>-1</sup> cm<sup>-1</sup>): 276(4.5), 444(4.1), 658(2.1).

## 2.5. X-ray crystal structure determination

Crystals of **1** and **2** were mounted on a Cryoloop™ with Paratone™ oil and placed in the cold nitrogen stream provided by the low temperature attachment to the diffractometer. Full spheres of the intensity data were collected using three sets of 400 frames, each of

Table 1. Crystal data for **1** and **2**.

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>25</sub> H <sub>15</sub> BrClCuN <sub>3</sub> O <sub>2</sub> ·0.50H <sub>2</sub> O	C <sub>24</sub> H <sub>16</sub> BrClN <sub>3</sub> O <sub>4</sub> V
Formula weight	577.31	579.72
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	12.6593(13)	9.562(4)
<i>b</i> (Å)	14.8471(16)	15.221(7)
<i>c</i> (Å)	15.306(3)	15.925(7)
$\alpha$ (°)	114.423(2)	
$\beta$ (°)	92.575(2)	99.612(6)
$\gamma$ (°)	114.961(1)	
Volume (Å <sup>3</sup> )	2289.3(5)	2285.4(18)
<i>Z</i>	4	4
Density (calculated, Mg/m <sup>3</sup> )	1.675	1.685
Absorption coefficient (mm <sup>-1</sup> )	2.847	2.337
<i>F</i> (000)	1152	1164
Crystal size (mm <sup>3</sup> )	0.23 × 0.16 × 0.16	0.20 × 0.07 × 0.03
$\theta$ range for data collection (°)	2.05 to 28.28	1.86 to 28.50
Reflns. total	40,081	19,511
Independent reflections	11,139	5370
<i>R</i> <sub>int</sub>	0.0794	0.0515
Completeness (%) ( $\theta_{\max}$ )	99.2 (27.50°)	99.5 (27.00°)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.6587 and 0.5277	0.9332 and 0.7143
Refinement	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	11,139/20/639	5370/0/308
Goodness of fit on <i>F</i> <sup>2</sup>	1.029	1.062
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0714, <i>wR</i> 2 = 0.1974	<i>R</i> 1 = 0.0510, <i>wR</i> 2 = 0.1230
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0931, <i>wR</i> 2 = 0.2084	<i>R</i> 1 = 0.0642, <i>wR</i> 2 = 0.1309
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.470 and -1.608	1.820 and -0.837

width 0.5° in  $\omega$ , collected at  $\varphi = 0.00, 90.00,$  and  $180.00^\circ$  and two sets of 800 frames, each of width 0.45° in  $\varphi$ , collected at  $\omega = -30.00$  and  $210.00^\circ$  (**1**) or three sets of 606 frames each of width 0.3° in  $\omega$  collected at  $\varphi = 0, 120,$  and  $240^\circ$  (**2**). The raw intensity data were converted to *F*<sup>2</sup> values with SAINT [21] with the same software executing a global refinement of unit cell parameters. Absorption corrections and the merging of symmetry equivalent reflections were carried out with SADABS [22] and the structures were solved by Patterson (**1**) and direct methods (**2**) using SHELXS [23]. The structures were refined by full-matrix least-squares procedures (SHELXS [23]) and all other calculations were carried out with SHELXTL [24]. Crystal data are provided in table 1.

### 3. Results and discussion

#### 3.1. General aspects

Reactions of the ligand and metal salts in an equimolar ratio resulted the metal complexes in good yield. The complexes were stable at room temperature and also soluble in DMSO and DMF, but are only partially soluble in other organic solvents such as methanol, acetone, acetonitrile, and chloroform. The C, H, and N elemental analysis data and the low

molar solution ( $1.0 \times 10^{-3}$  M) conductances of the complexes in DMSO are in conformity with the proposed formulas. Our attempts to prepare crystals of [CuL(bipy)] and [VOL(phen)] compounds were unsuccessful.

### 3.2. Characterization

The  $\nu(\text{OH})$  due to the presence of water (for **1**) or methanol (for **2**) in the lattice occurs at 3417 and 3232  $\text{cm}^{-1}$ , respectively. The band at 3070  $\text{cm}^{-1}$  is attributed to the  $\text{NH}\dots\text{O}$  stretch (for  $\text{H}_2\text{L}$ ), confirming the presence of the *keto* form in the solid (scheme 1) [25]. In solution, the ligand exists in the *enol* tautomeric form and by loss of its *enolic* proton in complexation forms a dianionic ligand. The band at 1627  $\text{cm}^{-1}$  is assigned to the azomethine of  $\text{H}_2\text{L}$  and shifts to 1612  $\text{cm}^{-1}$  and 1597  $\text{cm}^{-1}$  in [CuL(phen)] and [VOL(bipy)], respectively [26]. This variation in frequency supports the coordination of the azomethine nitrogen. By coordination, the C–O vibration of the ligand at 1319  $\text{cm}^{-1}$  shifts to 1296 and 1288  $\text{cm}^{-1}$ , respectively, for **1** and **2** [27]. This reduction supports the coordination of the ligand oxygen to the metal. Bands at 1018  $\text{cm}^{-1}$  in **1** and 905  $\text{cm}^{-1}$  in **2** are attributed to the breathing vibration of pyridine [28]. The  $\nu(\text{V}=\text{O})$  of the vanadyl is at 948  $\text{cm}^{-1}$  [29].

The high energy portion of the electronic spectrum of **1** consists of bands at 272, 448, and 474 nm while that of **2** shows bands at 276 and 444 nm. The bands at *ca.* 270 nm are attributed to a  $\pi \rightarrow \pi^*$  transition of the azomethine in the complexes while those at 444 nm and 448 nm for **1** and **2**, respectively, are attributed to the LMCT charge transfer band which is evidence for the coordination of pyridyl nitrogen to copper(II) and oxido-vanadium(IV) [30]. Finally, the peaks at 654 nm in **1** and 658 nm in **2** are attributed to d–d transitions.

### 3.3. Crystallographic description of complexes

The asymmetric unit of **1** consists of two crystallographically independent molecules of the complex plus two lattice waters while that of **2** is a single molecule. In **1**, there are two asymmetric units per unit cell, while in **2** there are four. Perspective views of one isomer each (*vide infra*) of the two independent molecules of **1** are presented in figures 1 and 2, while the unique molecule of **2** is presented in figure 3. Pertinent bond distances and the angles are shown in tables 2 and 3, respectively.

The metal ion in both the independent molecules of **1** adopts a slightly distorted square pyramidal coordination in which the Schiff base occupies basal positions and phen spans basal and axial positions with the axial Cu–N distance significantly longer than the basal Cu–N3 and Cu–N2 distances as expected. With this geometry, an unsymmetrical ligand coordinating in the basal plane can do so in two different ways, as shown figure 4. Since the peripheries of these two isomers are quite similar, they could easily co-crystallize in the same sites in the unit cell. Were this to occur, the majority of the atoms of both the isomers would occupy essentially the same positions with the only ones not doing so being the halides and the  $-\text{CH}=\text{N}-$ . The result would be an apparent disorder in Cl and Br substituents as well as in the azomethine portion and this is clearly seen in the difference Fourier maps. This phenomenon has been observed in very similar tetradentate Schiff-base ligands and it is also found in Mn(III) and Fe(III) complexes [31]. However, there are some cases with a single isomer [32]. This may be caused by the size of the substituents on phenyl

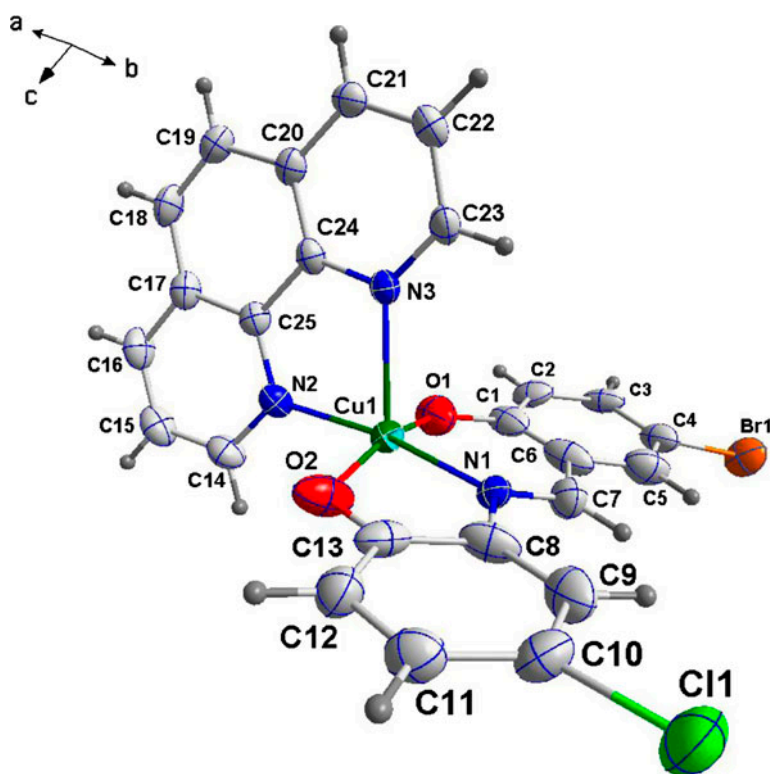


Figure 1. Perspective view of molecule **1** for **1**. Displacement ellipsoids are drawn at the 50% level and hydrogens are shown as spheres of arbitrary radius. Only one component of the disorder is shown.

rings or also by the reaction conditions, but there are insufficient systematic studies to suggest a pattern of causative factors. The data in tables 2 and 3 indicate that the only notable difference between the coordination spheres of copper in the two independent molecules is in the N–Cu–O angle in the 6-membered chelate ring. However, because of the disorder, significance should not be placed on this difference and detailed discussions of the full geometry of the coordination sphere of copper are inappropriate. The Schiff base in **1** is twisted such that the dihedral angles between the phenoxy rings are, respectively,  $7.1(1)^\circ$  and  $13.5(4)^\circ$  for molecule 1 and molecule 2. There is a  $\pi$ -stacking interaction between the pyridine ring containing N3 in molecule 1 with that containing N6 in molecule 2 (distance between ring centroids =  $3.498(3)$  Å, interplanar spacing =  $3.356(2)$  Å, and interplanar angle =  $4.42^\circ$ ). Additionally, the pyridine ring containing N3 in the molecule 1 participates in a  $\pi$ -stacking interaction with its centrosymmetrically-related counterpart at  $-x, 1-y, -z$  (distance between ring centroids =  $3.521(2)$  Å and interplanar spacing =  $3.311(2)$  Å), while that containing N5 shows  $\pi$ -stacking with its centrosymmetrically-related counterpart at  $-x, 2-y, 1-z$  (distance between ring centroids =  $3.803(4)$  Å and interplanar spacing =  $3.350(2)$  Å). These interactions are depicted by the dotted lines in figure 5.

As is evident from table 3, the vanadium in **2** adopts a distorted octahedral geometry with the distortions mainly resulting from the geometrical constraints of the ligands. Unlike **1** and its related compounds [20], **2** has one molecule in the asymmetric unit and



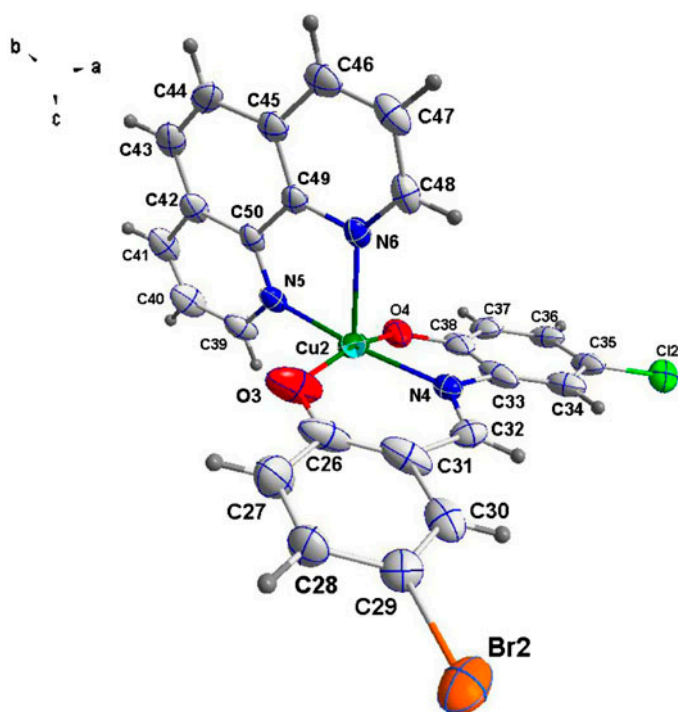


Figure 2. Perspective view of molecule 2 for 1. Displacement ellipsoids are drawn at the 50% level and hydrogens are shown as spheres of arbitrary radius. Only one component of the disorder is shown.

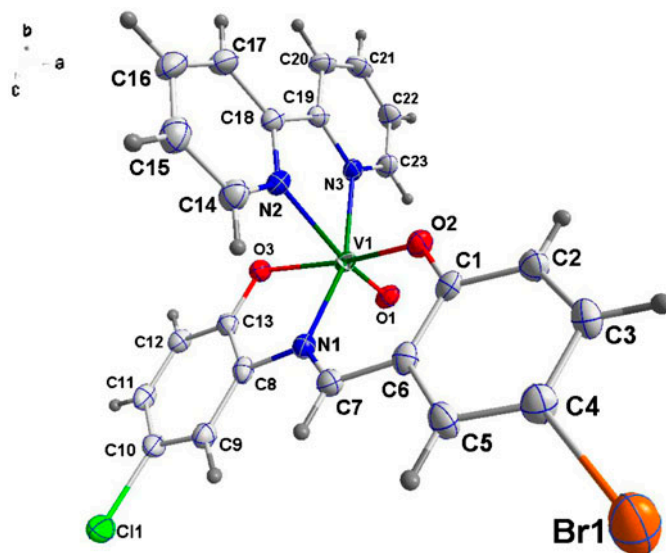


Figure 3. Perspective view of 2. Displacement ellipsoids are drawn at the 50% level and hydrogens are shown as spheres of arbitrary radius.

Table 2. Bond distances (Å) and angles (°) for **1**.

Molecule 1		Molecule 2	
Cu(1)–O(1)	1.934(5)	Cu(2)–O(3)	1.917(5)
Cu(1)–O(2)	1.946(4)	Cu(2)–O(4)	1.933(5)
Cu(1)–N(1)	1.972(6)	Cu(2)–N(4)	1.985(7)
Cu(1)–N(2)	2.005(4)	Cu(2)–N(5)	2.013(4)
Cu(1)–N(3)	2.297(4)	Cu(2)–N(6)	2.308(4)
O(1)–Cu(1)–O(2)	165.61(19)	O(3)–Cu(2)–O(4)	164.5(2)
O(1)–Cu(1)–N(1)	99.6(2)	O(3)–Cu(2)–N(4)	104.1(2)
O(2)–Cu(1)–N(1)	78.4(2)	O(4)–Cu(2)–N(4)	74.7(2)
O(1)–Cu(1)–N(2)	91.69(19)	O(3)–Cu(2)–N(5)	90.42(19)
O(2)–Cu(1)–N(2)	89.29(17)	O(4)–Cu(2)–N(5)	90.4(2)
N(1)–Cu(1)–N(2)	167.4(2)	N(4)–Cu(2)–N(5)	165.1(2)
O(1)–Cu(1)–N(3)	92.90(16)	O(3)–Cu(2)–N(6)	91.04(18)
O(2)–Cu(1)–N(3)	101.35(16)	O(4)–Cu(2)–N(6)	104.27(16)
N(1)–Cu(1)–N(3)	106.7(2)	N(4)–Cu(2)–N(6)	105.6(2)
N(2)–Cu(1)–N(3)	78.12(15)	N(5)–Cu(2)–N(6)	76.90(15)

Table 3. Bond distances (Å) and angles (°) for **2**.

V(1)–O(1)	1.611(3)	V(1)–N(1)	2.080(3)
V(1)–O(2)	1.947(3)	V(1)–N(3)	2.135(3)
V(1)–O(3)	1.994(3)	V(1)–N(2)	2.314(3)
O(1)–V(1)–O(2)	100.18(13)	O(3)–V(1)–N(3)	89.68(11)
O(1)–V(1)–O(3)	100.73(13)	N(1)–V(1)–N(3)	158.70(12)
O(2)–V(1)–O(3)	158.03(11)	O(1)–V(1)–N(2)	169.28(12)
O(1)–V(1)–N(1)	103.57(12)	O(2)–V(1)–N(2)	81.07(11)
O(2)–V(1)–N(1)	88.65(11)	O(3)–V(1)–N(2)	79.64(11)
O(3)–V(1)–N(1)	80.00(11)	N(1)–V(1)–N(2)	87.07(11)
O(1)–V(1)–N(3)	96.60(12)	N(3)–V(1)–N(2)	72.68(11)
O(2)–V(1)–N(3)	94.52(11)		

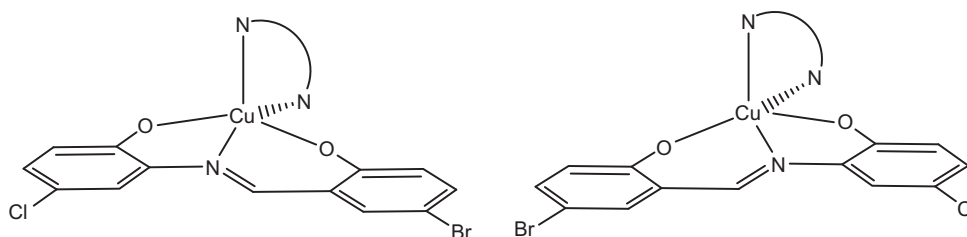


Figure 4. Two different ways of coordination of the unsymmetrical ligand in the basal plane to copper(II).

appears to be a single isomer. The twist of the Schiff base in **2**, measured as for **1**, is  $5.2(2)^\circ$ , while bipy shows a slight twist of  $4.9(2)^\circ$  between the pyridine rings. The vanadium is  $0.359(2) \text{ \AA}$  out of the plane defined by O2, N3, O3, and N2 towards O1, while this plane makes an angle of  $87.20(7)^\circ$  with that defined by V1, N2, C18, C19 and N3.

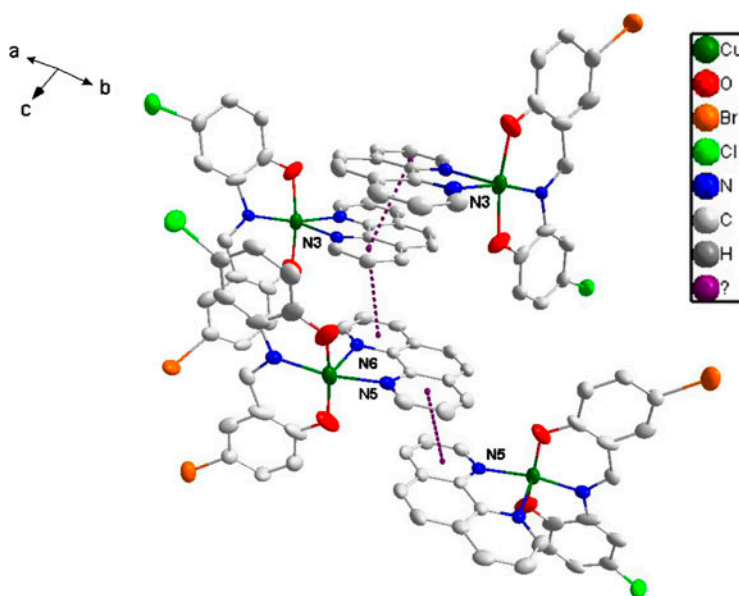


Figure 5. Illustration of the  $\pi$ - $\pi$  stacking interactions in **1** with hydrogens omitted for clarity.

### 3.4. Thermogravimetric analysis

TGA and DTG curves of **1** and **2** are shown in Supplementary material, from which **1** is seen to undergo three thermal decomposition stages and **2** shows only two.

The first combined mass loss for **1** is attributed to the removal of 1,10-phenanthroline at 334–405 °C with a mass loss of 35.23% (Calcd mass loss = 35.21%). The second DTG peak, having a maximum at 428 °C, corresponds to a weight decrease of about 29.93% (Calcd mass loss = 30.08%), which is consistent with the removal of the chloride and bromide of the Schiff base. In the last step at 437–632 °C (maximum at 534 °C), it loses 23.46% (Calcd mass loss = 22.08%) of its mass by the decomposition of the remaining ligand leaving CuO as the final residue. In **2**, the TGA curve shows a mass loss of 28.52% (Calcd mass loss = 28.47%) at 271 °C, which is in agreement with the loss of bipy. In the other step, the Schiff base is removed at 327 °C with a 53.95% (Calcd mass loss = 53.60%) decrease in mass. The 28.75% mass of the remaining residue indicates it to be V<sub>2</sub>O<sub>5</sub> (Calcd value for V<sub>2</sub>O<sub>5</sub> = 29.0%).

## 4. Conclusion

Preparation and characterization of (1,10-phenanthroline)(4-bromo-2-((5-chloro-2-hydroxyphenylimino)methyl)phenol) copper(II) [CuL(phen)] and (2,2'-bipyridine)(4-bromo-2-((5-chloro-2-hydroxyphenylimino)methyl)phenol) oxido-vanadium(IV) [VOL(bipy)] involving a dinegative tridentate ONO donor in the form of H<sub>2</sub>L are reported. The [CuL(phen)] and [VOL(bipy)] complexes are structurally characterized as five- and six-coordinate species with distorted square pyramidal and octahedral geometries, respectively. On the basis of the spectral and X-ray structure analysis, H<sub>2</sub>L is doubly deprotonated and coordinated to

Cu and V as a dianionic tridentate ligand via the ONO donors. The coordination spheres of the complexes are completed by phen in [CuL(phen)] and an oxygen atom and a bipy in [VOL(bipy)]. The TGA results, showing a stepwise removal of the ligands to finally yield metal oxide, are fully consistent with the structural results.

### Supplementary data

CCDC 880833 and CCDC 880832 contain the supplementary crystallographic data for [CuL(phen)] and [VOL(bipy)], respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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### References

- [1] A. Cinarli, D. Gürbüz, A. Tavman, A.S. Birteksöz. *Chin. J. Chem.*, **30**, 449 (2012).
- [2] P. Melnyk, V. Leroux, C. Sergheraert, P. Grellier. *Bioorg. Med. Chem. Lett.*, **16**, 31 (2006).
- [3] H. Guo, J. Lu, Z. Ruan, Y. Zhang, Y. Liu, L. Zang, J. Jiang, J. Huang. *J. Coord. Chem.*, **65**, 191 (2011).
- [4] K. Pothiraj, T. Baskaran, N. Raman. *J. Coord. Chem.*, **65**, 2110 (2012).
- [5] R. Lontie. *Copper Proteins and Copper Enzymes*, CRC Press, Boca Raton, FL (1984).
- [6] N. Ito, S.E.V. Phillips, C. Stevens, Z.B. Ogel, M.J. McPherson, J.N. Keen, K.D.S. Yadav, P.F. Knowles. *Nature*, **350**, 87 (1991).
- [7] (a) H. Keypour, M. Shayesteh, R. Golbedaghi, A. Chehregani, A.G. Blackman. *J. Coord. Chem.*, **65**, 1004 (2012); (b) N. Sharma, M. Kumari, V. Kumar, S.C. Chaudhry, S.S. Kanwar. *J. Coord. Chem.*, **63**, 1940 (2010).
- [8] R.N. Patel, S.P. Rawat, M. Choudhary, V.P. Sondhiya, D.K. Patel, K.K. Shukla, D.K. Patel, Y. Singh, R. Pandey. *Inorg. Chim. Acta*, **392**, 283 (2012).
- [9] P.A.N. Reddy, M. Nethaji, A.R. Chakravarty. *Inorg. Chim. Acta*, **337**, 450 (2002).
- [10] O. Yamauchi, A. Odani, M. Takani. *J. Chem. Soc., Dalton Trans.*, 3411 (2002).
- [11] C.A. Bolos, A.T. Chaviara, D. Mourelatos, Z. Iakovidou, E. Mioglou, E. Chrysogelou, A. Papageorgiou. *Bioorg. Med. Chem.*, **17**, 3142 (2009).
- [12] X. Qiao, Z.-Y. Ma, C.-Z. Xie, F. Xue, Y.-W. Zhang, J.-Y. Xu, Z.-Y. Qiang, J.-S. Lou, G.-J. Chen, S.-P. Yan. *J. Inorg. Biochem.*, **105**, 728 (2011).
- [13] A.K. Patra, S. Roy, A.R. Chakravarty. *Inorg. Chim. Acta*, **362**, 1591 (2009).
- [14] A.T. Chaviara, P.J. Cox, K.H. Repana, R.M. Papi, K.T. Papazisis, D. Zambouli, A.H. Kortsaris, D.A. Kyriakidis, C.A. Bolos. *J. Inorg. Biochem.*, **98**, 1271 (2004).
- [15] P.K. Sasmal, A.K. Patra, M. Nethaji, A.R. Chakravarty. *Inorg. Chem.*, **46**, 11112 (2007).
- [16] A. Sigel, H. Sigel, *Metal Ions in Biological Systems: Vanadium and its Role for Life*, Taylor & Francis, 31 (1995).
- [17] C. Yuan, L. Lu, X. Gao, Y. Wu, M. Guo, Y. Li, X. Fu, M. Zhu. *J. Biol. Inorg. Chem.*, **14**, 841 (2009).
- [18] H. Han, L. Lu, Q. Wang, M. Zhu, C. Yuan, S. Xing, X. Fu. *Dalton Trans.*, 11116 (2012).
- [19] H. Michibata. *Vanadium: Biochemical and Molecular Biological Approaches*, Springer, Netherlands (2011).
- [20] S.Y. Ebrahimipour, J.T. Mague, A. Akbari, R. Takjoo. *J. Mol. Struct.*, **1028**, 148 (2012).
- [21] Bruker-AXS, *SAINT, Ver. 7.68A*, Madison, Wisconsin, USA (2009).
- [22] G.M. Sheldrick, *SADABS, Ver. 2009/1*, University of Göttingen, Germany (2009).

- [23] G.M. Sheldrick. *SHELXS, Acta Crystallogr., Sect. A: Found. Crystallogr.*, **64**, 112 (2008).
- [24] Bruker-AXS, *SHELXTL, Ver. 2008/4*. Madison, Wisconsin, USA (2008).
- [25] P. Mayer, K.C. Potgieter, T.I.A. Gerber. *Polyhedron*, **29**, 1423 (2010).
- [26] M. Ebel, D. Rehder. *Inorg. Chem.*, **45**, 7083 (2006).
- [27] R. Takjoo, M. Ahmadi, A. Akbari, H.A. Rudbari, F. Nicolò. *J. Coord. Chem.*, **65**, 3403 (2012).
- [28] T. Kar, M.S. Liao, S. Biswas, S. Sarkar, K. Dey, G.P.A. Yap, K. Kreisel. *Spectrochim. Acta. Part A*, **65**, 882 (2006).
- [29] L.R. Guilherme, A.C. Massabni, A. Cuin, L.A.A. Oliveira, E.E. Castellano, T.A. Heinrich, C.M. Costa-Neto. *J. Coord. Chem.*, **62**, 1561 (2009).
- [30] V. Philip, V. Suni, M.R. Prathapachandra Kurup, M. Nethaji. *Polyhedron*, **25**, 1931 (2006).
- [31] (a) M.A. Yampolskaya, S.G. Shova, N. V. Gerbeleu, Yu. A. Simonov, V.K. Belskii, A.A. Dvorkin. *Russ. J. Inorg. Chem.*, **28**, 984 (1983); (b) M.D. Revenko, N.V. Gerbeleu, V.G. Rusu, S.G. Shova, Yu. A. Simonov. *Russ. J. Inorg. Chem.*, **31**, 994 (1986).
- [32] (a) M.A. Yampolskaya, S.G. Shova, N.V. Gerbeleu, V.K. Belskii, Yu. A. Simonov. *Russ. J. Inorg. Chem.*, **27**, 1443 (1982); (b) V.M. Leovac, E.V. Ivegeš, N. Galešić, D. Horvatić. *Inorg. Chim. Acta*, **162**, 277 (1989); (c) N. Özdemir, M. Şahin, T. Bal-Demirci, B. Ülküseven. *Polyhedron*, **30**, 515 (2011).