



# Structural features and electronic properties of a cupric complex with redox active 1-(2-pyridylazo)-2-phenanthrol (pap1)



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## ABSTRACT

We report the structural properties and electronic structure of a neutral homoleptic copper(II) complex bearing the anion of 1-(2-pyridylazo)-2-phenanthrol (pap1). In the solid state the complex is disordered and this presents itself as a nearly equal mixture of five and six coordinate copper ions with the ligand bound in two different configurations, with one of the terminal pyridine rings uncoordinated in the case of the five coordinate ion, which also features a very short Cu–N<sub>azo</sub> coordinate bond. The six coordinate complex features a Jahn–Teller elongated octahedron with one of the ligands coordinated in a typical fashion with coordinate bond distances typical of other divalent ion–pap1 complexes while the distances to the other donor atoms are much longer.

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## 1. Introduction

The coordination chemistry of copper is a storied history with countless examples in all areas of inorganic chemistry: From the intriguing magnetic properties of copper(II) acetate [1], which in part ushered in the era of molecular magnetism to the fascinating structures and electron transport properties of copper blue proteins in the bioinorganic realm [2]. The range of coordination geometries, paramagnetism, and redox activity offered by the copper ion make it a terrific platform to coordinate ligands to generate new materials with interesting magnetic, electronic or optical properties. We have been interested in the coordination chemistry of redox-active ligands, such as 1-(2-pyridylazo)-2-phenanthrol (Fig. 1, pap1), and have reported a number of complexes containing this ligand bound to relatively redox-inactive metals, such as Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, or Co<sup>3+</sup> [3,4]. These complexes feature intense visible absorption bands and in some cases reversible cathodic electrochemical behavior. We are also interested in the coordination of redox-active metals to **1**, including Cu<sup>2+</sup>. A handful of copper complexes containing the anion of **1** have been reported by Chiswell and Lions [5], as well as Pandeya et al. [6], using a range of different cupric salts as reagents. In all cases the complexes are assumed to

be four or five coordinate, containing one equivalent of the anion of **1** with copper in the +2 oxidation state. There is no structural data from X-ray diffraction for any of the reported copper–pap1 complexes. Our objective was to react **1** with a source of cuprous ion, such as [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, in an attempt to produce a cupric complex of pap1 via electron transfer from the Cu(I) ion to the ligand. This would produce a complex containing Cu(II) and **1** in a reduced, open-shell, dianion–radical oxidation state, of which there are no examples. Herein we report the structure and properties of an unusual neutral copper complex containing two equivalents of the anion of **1**; two complexes are found disordered in the same crystal, one featuring a five-coordinate cupric ion, the other complex is six-coordinate.

## 2. Materials and methods

### 2.1. General procedures

All reagents were commercially available and used as received unless otherwise stated. FT-IR data was recorded on a Shimadzu IR-Affinity spectrometer as KBr discs. UV–Vis data was recorded in CH<sub>2</sub>Cl<sub>2</sub> solution on a Shimadzu 3600 UV–Vis–NIR spectrophotometer using quartz cuvette cells. Cyclic voltammetry (CV) or differential pulse voltammogram (DPV) experiments were performed with a Bioanalytical Systems Inc. (BASi) Epsilon electrochemical workstation. Compound **2** was dissolved in anhydrous solvent

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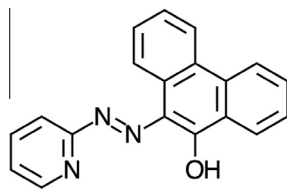


Fig. 1. Structure of **1** (pap1).

(CH<sub>2</sub>Cl<sub>2</sub>), and then deaerated by sparging with N<sub>2</sub> gas for 10–15 min. Solution concentrations were approximately 10<sup>−3</sup> M in analyte containing approximately 0.1 M supporting electrolyte (Bu<sub>4</sub>NPF<sub>6</sub>). A typical three-electrode set-up was used including a glassy carbon working electrode, Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The scan rates for all CV experiments were 100 or 200 mV/s and 25 mV/s for DPV experiments. EPR spectra were recorded using a Bruker Elexsys E580 pulse spectrometer operating in CW mode. EPR sample was prepared by dissolving **2** in dichloromethane. The solution was placed in Suprasil EPR sample tube (4 mm o.d.) and was degassed by several freeze–pump–thaw cycles and then sealed under vacuum. Spectra were recorded at 100 K.

## 2.2. Variable temperature magnetic susceptibility measurements

Solid-state variable temperature magnetic susceptibility measurements were recorded on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) with a 5.5 T magnet (temperature range 1.8–400 K) in an external field of 2000 Oe. A sample of **2** was carefully weighed into a gelatin capsule, loaded into a plastic straw and attached to the sample transport rod. The magnetization of the sample was scanned over a 2–300 K temperature range. Diamagnetic corrections to the paramagnetic susceptibilities were accomplished using Pascal's constants.

## 2.3. Computational details

All DFT calculations were performed using the Gaussian09 (Revision D.01) package [7] using the B3LYP hybrid functional [8,9] and the 6-31G(d,p) basis set for the geometry optimizations and frequency calculations or the def2-TZVP basis set for single point energy calculations. The converged wave functions were tested to confirm that they correspond to the ground state surface. Tight SCF convergence criteria were used for all calculations. The program Chemissian [10] was used for determining atomic orbital compositions employing Mulliken Population Analysis. The intensities of the 40 lowest-energy electronic transitions for the five- and six-coordinate complexes were calculated by TD-DFT [11,12] with the same functional/basis set combination employed for the single-point calculations using the PCM method to model solvation.

## 2.4. X-ray crystallography

Data were collected on a Bruker Kappa APEX-DUO diffractometer using monochromated Mo K $\alpha$  radiation (Bruker Triumph) and were measured using a combination of  $\varphi$  scans and  $\omega$  scans. The data were processed using APEX2 and SAINT [13]. Absorption corrections were carried out using SADABS [13]. The structure was solved and refined using SHELXTL [14] for full-matrix least-squares refinement that was based on  $F^2$ . H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U<sub>iso</sub> tied to the carrier atom.

## 2.5. Synthesis

### 2.5.1. Cu(pap1)<sub>2</sub> (**2**)

1-(2-Pyridylazo)-2-phenanthrolyl (0.10 g, 0.34 mmol) was dissolved in dichloromethane (30 mL) under N<sub>2</sub> in a Schlenk flask cooled in ice/water. Several drops of triethylamine were added followed by tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.067 g, 0.18 mmol). The ice bath was removed and the reaction mixture was stirred at room temperature for 3 h. The reaction solution was diluted with dichloromethane (15 mL) and diethyl ether (25 mL) was carefully layered on top of the solution, which was covered in foil (in air). Over a period of days dark green crystals suitable for X-ray diffraction formed out of the slowly evaporating solution. The crystals were collected by vacuum filtration, washed with methanol and dried. Yield (0.062 g, 51%). FT-IR (KBr, cm<sup>−1</sup>): 3063 (w), 1599 (w), 1521 (w), 1462 (w), 1437 (w), 1371 (m), 1344 (m), 1323 (m), 1273 (m), 1249 (s), 1223 (s), 1142 (m), 1028 (w), 1001 (w), 928 (m), 756 (m), 669 (m), 658 (w), 421 (w). Anal. Calc. for CuC<sub>38</sub>H<sub>24</sub>N<sub>6</sub>O<sub>2</sub>·0.3CH<sub>2</sub>Cl<sub>2</sub>: C, 67.09; H, 3.62; N, 12.26. Found: C, 67.23; H, 3.62; N, 12.30%. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon$  (M<sup>−1</sup> cm<sup>−1</sup>)): 311 nm (2.9 × 10<sup>4</sup>), 517 (4.1 × 10<sup>4</sup>), 546 (4.6 × 10<sup>4</sup>).

## 3. Results and discussion

### 3.1. Synthesis, structural and electronic properties

Complex **2** was prepared by reaction of pap1 with [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> in dichloromethane under an inert atmosphere. Typically, pap1 coordinates as a closed-shell monoanion [3–6,15–17], but our aim was to use the reducing power of the Cu(I) ion to generate a coordinated pap1 radical dianion. Instead, we obtained a neutral copper complex containing two equivalents of pap1 bound as a monoanion. All spectroscopic properties indicate a cupric ion and closed shell anionic pap1 ligands. Complex **2** represents the first structurally characterized copper complex with pap1 via single crystal X-ray diffraction. Other copper–pap1 complexes reported previously were assumed to contain only one pap1 ligand based on spectroscopic data [5,6]. Crystals of **2** suitable for single crystal X-ray diffraction were obtained by slow evaporation of the reaction solution layered with diethyl ether (Table 1). In the crystal there are two different complexes, which manifest as disorder in a nearly equal ratio of 53:47. One complex features a six-coordinate, pseudo-octahedral cupric ion, where two equivalents of the pap1 anion are binding as tridentate ligands in the typical fashion

Table 1  
Crystallographic data for **2**.

	<b>2</b>
Empirical formula	C <sub>38</sub> H <sub>24</sub> N <sub>6</sub> CuO <sub>2</sub>
$f_w$	660.17
Dimensions (mm)	0.330 × 0.200 × 0.080
$a$ (Å)	13.1831(12)
$b$ (Å)	22.225(2)
$c$ (Å)	12.9700(11)
Crystal system	monoclinic
$\alpha$ (°)	90
$\beta$ (°)	118.373(2)
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	3343.7(5)
Space group	P <sub>21/c</sub>
$Z$	4
$\mu$ (mm <sup>−1</sup> )	0.696
$T$ (K)	147(2)
Independent reflections	7715
Number of parameters	417
$R_1$ [ $I > 2\sigma(I)$ ]	0.0517
$wR_2$ (all data)	0.1423

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