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# An unusual Cu(II) complex of a Schiff-base ligand of 3-aminoquinoline with a hydronated pyridine unit: Synthesis, characterizations, and computational studies

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ABSTRACT

A very unusual Cu(II) compound of formula $[Cu(mqmp)_2(ClO_4)_2]$ was synthesized *in situ* from a one-pot reaction between copper(II) perchlorate and a Schiff base ligand, 2-methoxy-6-((quinolin-3-ylimino)methyl)phenol, abbreviated mqmp. The resulting compound, bearing positively charged side groups was characterized using single-crystal X-ray diffraction, elemental analysis, electrospray-ionization mass spectrometry (ESI-MS), infrared spectroscopy (IR), ligand-field (LF) spectroscopy, and powder electron paramagnetic resonance (EPR) spectroscopy. The coordination chromophore consists of tetragonal $[CuN_2O_2O'_2]$ units. The compound shows a step-like molecular assembly assisted by hydrogen-bond interactions from $–NH^+$ to $ClO_4^-$ between the neighbouring molecules. The presence of pyridinic nitrogens bearing a $H^+$ (“hydron”) on the quinoline unit is quite unusual, and was validated with computational studies which clearly suggested that this hydronated nitrogen stabilizes the structure by 164 kJ mol$^{-1}$ compared to the hydronated phenolic version of the structure.

## 1. Introduction

Schiff base complexes have been widely popular due to their versatile coordination chemistry. Besides structural diversity, different types of mononuclear and polynuclear Schiff base complexes have been studied for their catalytic [1], magnetic [2–9], optical [10,11], antibacterial [12–14] and cytotoxic properties [14–16]. Due to their rational design and predictable coordination geometry, Schiff base ligands have been used to mimic active sites of different enzymes, like PS-II and hydrogenases [17–19].

Aminoquinolines are potential precursors in the synthesis of Schiff base ligands with versatile coordination behaviour. For example, recently the impact of different co-ligands on coordination chemistry of Cu(II) with 8-aminoquinoline has been studied together with the catecholase activity of one of the resulting complex by Saha and co-workers [20]. In another study mononuclear complexes and a one-dimensional chain derived from a Schiff base based on 8-aminoquinoline and Cu(II) were reported by Chattopadhyay and co-workers [21].

In the recent past we have reported a series of complexes from planar tridentate Schiff base ligand derived from 8-aminoquinoline, including catalytic oxidation of cyclohexane using the Fe(III) complex of the ligand [2]. Schiff base complexes of 3-aminoquinoline are relatively less studied, however [22–24]

Here we report a new Schiff base compound of Cu(II) using the ligand 2-methoxy-6-((quinolin-3-ylimino)methyl)phenol (mqmp, see Scheme 1) prepared from 3-aminoquinoline and 3-methoxysalicylaldehyde (*o*-vanillin) *in situ*. Notably, the synthesized complex, $[Cu(mqmp)_2(ClO_4)_2]$ (Fig. 1) contains two hydronated (i.e. a $H^+$ on the nitrogen) pyridine units in the structure which to the best of our knowledge has been seen extremely rarely for the related aminoquinoline complexes [25].

## 2. Experimental

### 2.1. General

3-Aminoquinoline was purchased from Tokyo Chemical Industries (TCI-UK), 3-methoxysalicylaldehyde and copper(II) perchlorate were purchased from Sigma–Aldrich, and all the solvents

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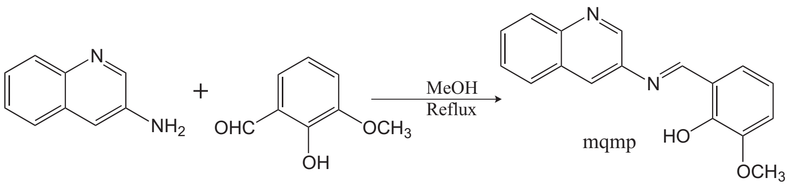

**Scheme 1.** The Schiff base ligand 2-methoxy-6-((quinolin-3-ylimino)methyl)phenol (mqmp) synthesized *in situ* from 3-aminoquinoline and 3-methoxysalicylaldehyde.

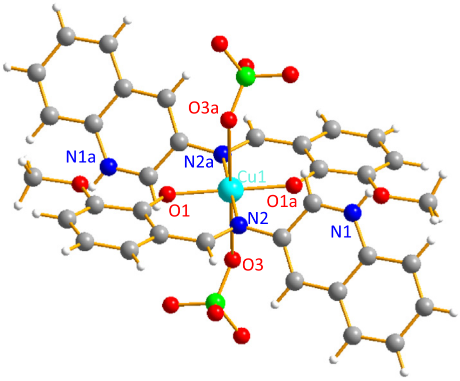

**Fig. 1.** Crystallographic view of the molecule $[Cu(mqmp)_2(ClO_4)_2]$ with elongated axial bond (Cu–O3). Colour codes for the atoms: blue (N), cyan (Cu), grey (C), green (Cl), white (H). Symmetry operation: a, 2-*x*, -*y*, 2-*z*. (Colour online.)

were purchased from Fischer Scientific. All the chemicals were used as received.

### 2.2. Physical methods

Elemental analyses (for C, H and N) were performed on a Perkin-Elmer 2400 series II analyzer. Infrared spectra were recorded using the reflectance technique over the range of 4000–300 $cm^{-1}$ on a Perkin-Elmer 15 Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device. Ligand field spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer, using the diffuse reflectance technique with MgO as a reference. ESI Mass Spectra were recorded using a Micromass Quattro Ultima Mass Spectrometer equipped with an electrospray ionization (ESI) source, with a sample dissolved in methanol and injected at 10 μL/min. EPR spectra were recorded at X band frequencies on the solid powder at room temperature using a Bruker EMXplus electron spin resonance spectrometer (field calibrated with DPPH ($g = 2.0036$).

### 2.3. Synthesis

A mixture of 3-aminoquinoline (36 mg, 0.25 mmol) and 3-methoxysalicylaldehyde (38 mg, 0.25 mmol) was refluxed in 25 mL of methanol for 25 min. To the resulting yellow solution, 185 mg (0.5 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ were added, which resulted in a dark solution. The reaction mixture was refluxed for another 30 min and allowed to cool down to room temperature before filtration. Slow evaporation of the filtrate resulted in very small dark-red crystals suitable for single-crystal X-ray analysis. Yield: 45 mg (44%, based on 3-aminoquinoline), Elemental analysis (%): *Anal.* Calc. for: $C_{34}H_{28}Cl_2CuN_4O_{12}$: C, 49.86; H, 3.45; N, 6.84. Found: C, 49.30; H, 3.10; N, 6.92. IR (ATR-FTIR): presented in Fig. S1.

### 2.4. Crystallography

A single crystal of the title compound, $[Cu(mqmp)_2(ClO_4)_2]$, was measured at room temperature, by using a Nonius Kappa CCD area-detector diffractometer. A graphite monochromated Mo Kα radiation source ($\lambda = 0.71073$) was employed. The structure was solved by direct methods using SIR-92 [26] and refined with a full-matrix least-squares procedure based on $F^2$ using SHELXL-97 [27].

All of the non-hydrogen atoms were refined anisotropically. All the C–H hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The hydrogen atom bonded to nitrogen N1 was visible in the last stages of the refinement and was refined freely (distance N1–H1N = 0.80 (4) Å). Details of the crystal data are given in Table 1.

## 3. Results and discussion

### 3.1. General observations

The Schiff base ligand was synthesized *in situ* by reaction of 3-aminoquinoline and 3-methoxysalicylaldehyde in 1:1 ratio in methanol under reflux. The formation of the Schiff base can be clearly observed from rapid colour change of the solution. In the following step, two equivalents of copper(II) perchlorate hexahydrate were added to the methanolic solution of the ligand and the colour turned to dark brown instantly. Upon cooling and slow evaporation of the resulting solution, small block-shaped dark red crystals were obtained and characterized by spectroscopic techniques and single crystal X-ray diffraction.

### 3.2. Structural description

Single crystal X-ray diffraction revealed a six-coordinate copper (II) coordination entity with formula of $[Cu(mqmp)_2(ClO_4)_2]$ in which the copper(II) ion is coordinated to an alkoxy oxygen and

**Table 1**
Crystallographic data for $[Cu(mqmp)_2(ClO_4)_2]$.

| | |
|---|---|
| Empirical formula | $C_{34}H_{28}Cl_2CuN_4O_{12}$ |
| Formula weight | 819.04 |
| Temperature (K) | 293(2) |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| *a* (Å) | 9.2075(4) |
| *b* (Å) | 9.6627(5) |
| *c* (Å) | 10.2358(5) |
| α (°) | 73.554(3) |
| β (°) | 73.238(3) |
| γ (°) | 89.142(3) |
| Volume ($Å^3$) | 834.09(7) |
| *Z* | 1 |
| $\rho_{calc}$ ($g/cm^3$) | 1.631 |
| μ ($mm^{-1}$) | 0.889 |
| *F*(000) | 419 |
| Crystal size (mm) | 0.10 × 0.10 × 0.05 |
| Reflections collected | 6580 |
| Independent reflections | 3748 |
| $R_{int}$ | 0.0304 |
| Reflections observed | 2952 |
| Parameters | 246 |
| Goodness-of-fit (GOF) on $F^2$ | 1.059 |
| Final *R* indexes [$I \geqslant 2\sigma(I)$] | $R_1 = 0.0474$, $wR_2 = 0.1136$ |
| Final *R* indexes [all data] | $R_1 = 0.0686$, $wR_2 = 0.1269$ |
| Largest difference peak/hole (e $Å^{-3}$) | 0.54/−0.44 |