



# Coordination compounds from the planar tridentate Schiff-base ligand 2-methoxy-6-((quinolin-8-ylimino)methyl)phenol (mqmpH) with several transition metal ions: Use of $[\text{Fe}^{\text{III}}(\text{mqmp})(\text{CH}_3\text{OH})\text{Cl}_2]$ in the catalytic oxidation of alkanes and alkenes

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## ABSTRACT

Four coordination compounds were synthesized in high yields from different transition metal ions ( $\text{Fe}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$ ) and an *in situ* generated Schiff-base ligand, *i.e.* 2-methoxy-6-((quinolin-8-ylimino)methyl)phenol (mqmpH). The compounds were characterized by single-crystal X-ray diffraction, ESI-MS, IR spectroscopy, and ligand-field spectroscopy. The iron(III) complex is an efficient catalyst for the oxidation of alkanes and alkenes, under relatively mild conditions and with dihydrogen peroxide as terminal oxidant.

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## 1. Introduction

Schiff-base ligands are ubiquitous in coordination chemistry where they are used in synthesis of a large variety of transition-metal complexes with a range of structural architectures. These ligands are often obtained in good yields and high purity, through straightforward synthetic pathways. Moreover, in many cases, this type of ligands can be produced *in situ* during coordination reactions. All these reasons justify their high popularity in coordination chemistry [1]. Many (Schiff-base)-containing coordination compounds have shown attractive properties. For example, salen-based complexes have found interesting applications in catalysis [2–8]. Many Schiff-base coordination compounds also exhibit interesting magnetic properties [9–14], a DNA-hydrolytic character [15–17], an antibacterial behaviour [18,19], nonlinear optical [20–26] and fluorescence properties [27]. In addition, Schiff-base coordination compounds have also been used as building blocks to generate higher order transition-metal complexes [28].

In the present study, a new Schiff-base ligand, namely 2-methoxy-6-((quinolin-8-ylimino)methyl)phenol (mqmpH), was synthe-

sized *in situ*, prior to its reactions with different transition metals, generating four new coordination compounds, *i.e.*  $[\text{Fe}(\text{mqmp})(\text{CH}_3\text{OH})\text{Cl}_2]$  (**1**),  $[\text{Co}^{\text{II}}(\text{mqmp})_2]$  (**2**),  $[\text{Cu}^{\text{II}}(\text{mqmp})(\text{H}_2\text{O})_2]\text{ClO}_4$  (**3**), and  $[\text{Cu}^{\text{II}}_2(\text{mqmp})_2\text{Cl}_2]$  (**4**), in high yields. All these compounds were characterized by elemental analysis, IR spectroscopy, ESI-MS spectroscopy, and single-crystal X-ray crystallography. Compound **1** was successfully used as an effective catalyst for the catalytic oxidation of alkanes and alkenes, using dihydrogen peroxide as terminal oxidant.

## 2. Experimental

### 2.1. General

All chemicals and solvents used in this study were purchased from Sigma–Aldrich, and Biosolve, respectively. All the experiments were carried out under air, unless otherwise mentioned.

### 2.2. Physical methods

Elemental analyses (C, H, and N) were carried out on a Perkin–Elmer 2400 series II analyzer. Infrared spectra were recorded using the reflectance technique over the range of  $4000\text{--}300\text{ cm}^{-1}$  on a

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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 Finnigan AQA mass spectrometer equipped with an electrospray ionization (ESI) source.

### 2.3. Synthesis

#### 2.3.1. Synthesis of **1**

*o*-Vanillin (0.25 mmol) was added to a solution of 8-aminoquinoline (0.25 mmol) in 30 mL of methanol, and the resulting reaction mixture was stirred at room temperature for 20 min. To this red solution, 0.5 mmol of iron(III) chloride was added and the resulting mixture was filtered. Dark-red crystals started to form immediately. Yield = 87%. Elemental analysis (%): *Anal. Calc.* for  $C_{18}H_{17}Cl_2FeN_2O_3$ : C, 49.58; H, 3.93; N, 6.42. Found: C, 49.35; H, 3.67; N, 6.56%. IR data (neat,  $\nu/cm^{-1}$ ): 1597 (s), 1585 (s), 1544 (s), 1507 (m), 1427 (s), 1403 (s), 1259 (s), 1217 (m), 1085 (m), 1007 (s), 833 (s), 735 (s), 575 (m), 329 (m).

#### 2.3.2. Synthesis of **2**

*o*-Vanillin (0.25 mmol) was added to a solution of 8-aminoquinoline (0.25 mmol) in 20 mL of methanol, and the resulting reaction mixture was stirred at 80 °C for 20 min. To the resulting red solution, a 10 mL methanolic solution of  $CoCl_2 \cdot 6H_2O$  (0.125 mmol) was added and the mixture was stirred for 5 min. After filtration, the slow evaporation of the filtrate produced dark pink, needle-shaped crystals after two days with a yield of 77%. Elemental analysis (%): *Anal. Calc.* for  $C_{34}CoH_{28}N_4O_4Cl$ : C, 62.73; H, 4.34; N, 8.61. Found: C, 62.55; H, 4.01; N, 8.72%. IR data (neat,  $\nu/cm^{-1}$ ): 3098 (w), 2930 (w), 1581 (s), 1417 (m), 1304 (s), 1148 (m), 1048 (s), 1023 (s), 808 (s), 746 (s), 667 (m), 373 (m).

#### 2.3.3. Synthesis of **3**

*o*-Vanillin (0.25 mmol) was added to a solution of 8-aminoquinoline (0.25 mmol) in 10 mL of methanol, and the resulting reaction mixture was stirred at 80 °C for 20 min. To the red solution, a 10 mL aqueous solution of  $CuClO_4 \cdot 6H_2O$  (0.125 mmol) was added and the mixture was stirred for 30 min. After filtration, the slow evaporation of the filtrate produced dark-red, needle-shaped crystals after two days with a yield of 70%. Elemental analysis (%): *Anal. Calc.* for  $C_{17}H_{17}ClCuN_2O_8$ : C, 42.87; H, 3.60; N, 5.88. Found: C, 42.95; H, 3.57; N, 5.78%. IR data (neat,  $\nu/cm^{-1}$ ): 3391 (w), 1603 (s), 1541 (s), 1508 (m), 1435 (s), 1247 (s), 1221 (s), 1179 (m), 1041 (b), 1007 (s), 833 (s), 730 (s), 434 (m), 336 (m).

#### 2.3.4. Synthesis of **4**

*o*-Vanillin (0.25 mmol) was added to a solution of 8-aminoquinoline (0.25 mmol) in 10 mL of methanol, and the resulting reaction mixture was stirred at 80 °C for 20 min. To the red solution, 0.5 mmol of  $CuCl_2 \cdot 6H_2O$  was added which resulted into green precipitation. To this suspension, 15 mL of water were added and the mixture was refluxed for 30 min and filtered. Slow evaporation of the filtrate produced small needle-shaped red crystals after two days with a yield of 65%. Elemental analysis (%): *Anal. Calc.* for  $C_{34}H_{26}Cl_2Cu_2N_4O_4$ : C, 54.26; H, 3.48; N, 7.44. Found: C, 54.32; H, 3.66; N, 7.42%. IR data (neat,  $\nu/cm^{-1}$ ): 1602 (s), 1582 (s), 1538 (s), 1506 (s), 1457 (m), 1423 (s), 1385 (m), 1243 (m), 1213 (s); 1093 (m), 977 (m), 856 (m), 823 (s), 749 (s), 653 (m), 431 (m).

### 2.4. Crystallography

The single-crystal structures of compounds **1** and **3** were determined at 150 K, using a Nonius Kappa CCD area-detector diffractometer. The single-crystal X-ray structure of compound **2** was

determined at 100 K, using an IPDS2 diffractometer. Tiny single crystals of compound **4** were obtained; hence, they were measured using a synchrotron radiation source (ESRF BM16) with a single-axis HUBER diffractometer at 100 K. The crystal structure determinations and refinements were performed using the SHELXTL program suite [29]. Crystal data and structure refinement data for compounds **1–4** are listed in Table 2.

## 3. Results and discussion

### 3.1. Ligand

The Schiff-base ligand (Scheme 1) is formed easily *in situ* from the reaction of *o*-vanillin and 8-aminoquinoline. The formation of the Schiff-base ligand can be visualized by a change in color of the solution from yellow to red. The ligand exhibits a meridional tridentate coordination pocket with a NNO donor-set. Many coordination compounds with NNO-type Schiff-base ligands have been reported [30–39]; in contrast, coordination compounds with NNO-type Schiff-base ligands are relatively less studied [40–45].

### 3.2. Syntheses and single-crystal X-ray diffraction structures of the coordination compounds

Compound **1**,  $[Fe^{III}(mqmp)(CH_3OH)Cl_2]$ , is synthesized in a one-pot reaction by addition of anhydrous  $FeCl_3$  to a solution of  $mqmpH$  (M:L = 2:1), generated *in situ* through the reaction of *o*-vanillin with 8-aminoquinoline (in a one-to-one ratio). Compound **1** crystallizes in the orthorhombic space group  $P2_12_12_1$ . A representation of the molecular structure of **1** is shown in Fig. 1. The ligand  $mqmp^-$  coordinates the iron(III) center equatorially through its three donor atoms (O, N, N). The other three coordination sites of the octahedral environment are occupied by two  $Cl^-$  anions and one methanol molecule. Selected bond lengths and angles are given in Table S5 (supporting information). In the crystal lattice, the mononuclear coordination compounds are connected *via* hydrogen bonds ( $MeOH \cdots Cl$ ), with  $O \cdots Cl$  separation distances of 3.26(2) Å (see Figs. S5, S6, also for the packing diagram).

Compound **2**,  $[Co^{II}(mqmpH)_2]Cl$ , is synthesized by addition of  $CoCl_2 \cdot 6H_2O$  to a methanolic solution of the ligand in a M:L ratio of 1:2. The compound crystallizes in the monoclinic space group  $P2_1/c$ . The needle-shaped crystals are severely twinned and all efforts to obtain a reasonable refinement from the X-ray diffraction data have failed. However, it has been possible to get a basic crystallographic structure of compound **2** which is presented in Fig. S7 in the supporting information. From these crystallographic data and the elemental, IR and ESI-MS analyses, **2** can be formulated as  $[Co^{II}(mqmpH)_2]Cl$ . The cobalt cation is coordinated by two tridentate ligands, in an octahedral environment. The planar ligands are perpendicular to each other.

Compound **3**,  $[Cu^{II}(mqmp)(H_2O)_2]ClO_4$ , is synthesized by addition of an aqueous solution of  $CuClO_4 \cdot 6H_2O$  to a methanolic solution of  $mqmpH$  (M:L = 2:1). The compound crystallizes in monoclinic space group  $P2_1/n$ . The molecular structure of compound **3** is shown in Fig. 2. The  $Cu^{II}$  center is pentacoordinated, showing a square-pyramidal geometry. The tridentate ligand coordinates the  $Cu^{II}$  metal ion with its NNO donor atoms in meridional fashion, comparable to that observed for compound **1**. The other two coordination sites are satisfied by two water molecules which are *cis*-coordinated to the  $Cu^{II}$  ion. The monocationic charge of the complex is balanced by a perchlorate anion outside the coordination sphere. Intra- and intermolecular hydrogen-bonding interactions are present in the crystal packing of compound **3**. Thus, the coordination molecules are connected by hydrogen bonds, involving the perchlorate anion, along the *a*-axis. The  $O \cdots OH$  contact

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