



Synthesis, crystal structure and properties of a new 3D supramolecular unsymmetrical tetradentate Schiff bases copper (II) framework with stable tunnels

Mousa Al-Noaimi ^{a,*}, Firas F. Awwadi ^b, Raiid Al-Razagg ^c, Fatima T. Esmadi ^{c,**}

^a Department of Chemistry, Hashemite University, P.O.Box 150459, Zarqa, 13115, Jordan

^b Department of Chemistry, The University of Jordan, Amman, 11942, Jordan

^c Department of Chemistry, Yarmouk University, Irbid, Jordan

ARTICLE INFO

Article history:

Received 31 May 2016

Received in revised form

1 July 2016

Accepted 8 July 2016

Available online 10 July 2016

Keywords:

Copper

Electrochemistry

Supramolecular MOF

Polymorphs

ABSTRACT

Flexible unsymmetrical Schiff base ligand (L) which is derived from the half unit $Y = C_6H_5COCH_2C(N=CH_2C_6H_4NH_2)CH_3$ (obtained from the reaction of benzoylacetone and 2-aminobenzylamine) and 2-quinolinecarboxaldehyde have been successfully co-assembled with $Cu(ClO_4)_2$ to give out the $[Cu(L)]ClO_4$ complex. The complex crystallizes in two different space groups; $P2_1/n$ and $P-1$. The crystal structure of the $P-1$ phase indicates the presence of tunnels; the volume of these tunnels is 157 \AA^3 which is big enough to accommodate solvent molecules. The X-ray data indicates that these tunnels are most probably filled by highly disordered solvent molecules or solvent molecules with partial occupancy. The tunneled structure is stabilized via $\pi-\pi$ stacking interactions to give a supramolecular MOF with 1D rhomboidal tunnels array. The copper(II) atom assumes a distorted-square pyramidal coordination geometry where the perchlorate is located on the apex of the pyramid. In addition, this work presents and discusses the spectroscopic (IR, UV/vis), electro-chemical (cyclic voltammetry) behavior of the Cu(II) complexes. The Cu(II) oxidation state is stabilized by the novel tetradentate ligands, showing Cu(I/II) couple around 0.1 vs. Cp_2Fe/Cp_2Fe^+ .

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Metal-complexes containing Schiff-base ligands have been extensively investigated due to their novel structures and potential applications in many fields [1,2]. These Schiff-base ligands may act as a bidentate [3], multidentate ligands [4] to form homo- and heterometallic complexes with varied stereochemistry [5]. Also, these complexes can be used as single-molecule magnets [6], a luminescent material [7] and as catalysts for DNA cleavage reactions [8,9]. Crystal engineering of metal complexes, especially coordination polymers with open-framework structures have received more attention in the past decades [10,11]. In contrast, the research about flexible ligands is still few due to the difficulty of crystallization [12–14]. In this paper, Cu (II) complex of unsymmetrical flexible tetradentate Schiff bases was prepared by the reaction of 1-half unit (Y) prepared from (benzoylacetone and 2-aminobenzylamine) and 2-quinolinecarboxaldehyde with

$Cu(ClO_4)_2$. The redox (cyclic voltametry) and spectroscopic behavior for this complex was investigated. The complex was characterized on the basis of their molar conductance, magnetic susceptibility, IR, UV–Vis, cyclic voltametry and single crystal X-ray structure determination.

2. Experimental

2.1. Materials

Benzoylacetone, 2-aminobenzylamine, benzoylacetone and 2-quinolinecarboxaldehyde, $Cu(ClO_4)_2 \cdot 6H_2O$ were purchased from Aldrich. Perchlorate salts are potentially explosive. They should be handled with caution and small quantities only. The half unit ($Y = C_6H_5COCH_2C(N=CH_2C_6H_4NH_2)CH_3$) was prepared by a method similar to that reported in the literature [15].

2.2. Preparation of $[Cu(L)]ClO_4$

(370.50 g, 1 mmol) of the $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol (10 ml) was

* Corresponding author.

** Corresponding author.

E-mail address: manoaimi@hu.edu.jo (M. Al-Noaimi).

added to a solution of the 2-Quinolinecarboxaldehyde (0.16 g, 1 mmol) and a half unit(Y) (0.57 g, 1 mmol) in 20 ml solution of (1:1 ml dichloromethane:ethanol). The mixture was refluxed for 3 h and then stirred overnight at room temperature. The products was filtered and recrystallized from ethanol. Yield. (0.3 g, 42%). Anal. Calc. for $\text{CuC}_{27}\text{H}_{22}\text{ClN}_3\text{O}_5$: C, 57.14; H, 3.91; N, 7.41%. Found: C, 57.30; H, 3.96; N, 7.55%. UV–Vis in dichloromethane: $\lambda_{\text{max}}(\text{nm})$ ($\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$): 243 (4.7×10^4), 290 (2.9×10^4), 364 (1.3×10^4), 420 (1.1×10^4). IR: $\nu(\text{N}=\text{N})$ 1470, $\nu(\text{C}=\text{N})$ 1615, $\nu(\text{C}=\text{O})$ 1701 cm^{-1} .

2.3. Instrumentation

^1H NMR spectra were recorded using NMR–spectrometer, Bruker advanced III 400MZ. IR spectra were measured by Bruker Vertex 70. Elemental analyses were carried out on a Eurovector E.A.3000 instrument using copper sample-tubes. UV–Vis SHIMADZU UV-spectrophotometer for 3.3×10^{-4} M solutions in DMF. Melting points were measured on an electrothermal melting point apparatus (Staffordshire, UK). Magnetic susceptibility measurements were done using an instrument obtained from Sherwood Scientific Ltd (Cambridge, UK). Cyclic voltammograms were recorded using a PGSTAT 204 apparatus. The electrochemical cell consisted of a double-jacketed glass container, which was charged with approximately 15 ml of solvent. The cell temperature was set at 25 °C by means of a Haake D8-G refrigerated bath and circulator (accuracy 0.02 °C). The cell was fitted with a Teflon cap that had four holes to permit insertion of electrodes and an argon gas bubbler into the cell. Three electrodes were utilized in this system, two platinum-disk working and counter (auxiliary) electrodes (1.6-mm diameter), and a silver wire pseudo-reference electrode with ferrocene as an internal reference. The potential was controlled by the BAS CV-27. Tetrabutylammonium hexafluorophosphate (TBAHF, 0.1 M) was used as supporting electrolyte. TBAHF was recrystallized twice from ethanol:water (1:1) and vacuum-dried at 110 °C overnight. Referencing was done with an addition of one crystal of ferrocene (Cp_2Fe) as an internal standard to the analyte solution after all data of interest had been acquired. The platinum working-electrode was manually cleaned with 1 mM diamond polish before each scan. Solvents used in all cyclic voltammetry experiment was deoxygenated by bubbling with argon for 15 min. Conductivity measurement was obtained using a CyberScan 540 conductivity meter for 1×10^{-3} M solutions in DMF at 25 °C.

2.4. Crystallography

$[\text{Cu}(\text{L})]\text{ClO}_4$ complex crystallizes into two types of crystals; parallelepiped and sword shaped crystals with roughly 50:50% (by inspection). Suitable crystals of the two polymorphs were mounted on a glass fiber and the data collected at room temperature employing enhanced Mo radiation, $\lambda = 0.71073$ Å, using Xcalibur/Oxford Diffractometer equipped with Eos CCD detector. The space group of parallelepiped shaped crystals is *P*-1 while it is *P*21/*n* for the sword shaped crystals. CrysAlis Pro software was used for data collection, absorption correction and data reduction to give SHELX-format-*hkl* files, [16]. ‘Multi-scan’ absorption corrections were applied with Min and Max transmission factors of 0.80809 and 1.000 for the *P*21/*n* phase and 0.73172 and 1.000 for the *P*-1 phase, respectively [16]. Cell parameters were retrieved using 6419 for *P*21/*n* phase and 2230 for the *P*-1 phase reflections. The structure was solved using SHELXTL program package [17]. All nonhydrogen atoms were refined anisotropically except hydrogen atoms which were placed in calculated positions and refined using a riding model. CheckCif program of the cif file of the *P*-1 phase gave alert B which indicates the presence void volume (157 Å³) (~12% of the total volume), this volume is big enough to accommodate a solvent

molecule. The R-indices are $R = 5.8\%$ and $wR2 = 0.1744$ and the largest diff. peak and hole 0.845 and -0.346 e.Å⁻³. Analysis of electron density map using Olex2 program package indicated the presence of unidentified electron density is accommodated inside the tunnels (Fig. 1). Therefore, the void space was squeezed using Platon program [18]. The refining parameters have improved significantly, R-indices after squeezing the void volume has been reduced to $R = 4.95\%$ and $wR2 = 0.1323$, the details of refining parameters are given in Table 1. Details of data collection and refinement for the two phases are given in Table 1.

3. Results and discussion

3.1. Synthesis

The half unit (Y) was prepared by refluxing benzoylacetone and 2-aminobenzylamine in ethanol (Scheme 1) [15]. The milky white powder half unit which melts at 170 °C has IR spectrum stretching frequencies at 1520, 1597 and 3462 cm^{-1} which are assigned to C=C, C=N and NH₂, respectively. The ^1H NMR spectrum of this compound shows a singlet at 2.12 ppm due to methyl group, a doublet in the 4.42–4.41 ppm range due to benzyl protons, and a singlet at 5.77 ppm due N=C–H proton. A multiplet in the 6.72–7.90 ppm range is due to aromatic protons. A broad peak at 3.78 ppm is assigned to NH₂ protons, and a broad peak at 11.53 ppm is attributed to O–H proton, indicating that the compound is present in the enol form [15].

Reaction of this half unit (Y) with 2-quinolinecarboxaldehyde produce unsymmetrical tetradentate Schiff base ligand (L). The ligand (L) has neither been isolated nor characterized spectroscopically due to its stability. Therefore, preparation of the Cu(II) complex was carried out by the reaction of the half-unit (Y) with the 2-quinolinecarboxaldehyde in the presence of the $\text{Cu}(\text{ClO}_4)_2$ (Scheme 1). The obtained complex was analyzed by infrared and UV–Visible spectroscopy. In the IR spectrum, the formation of the

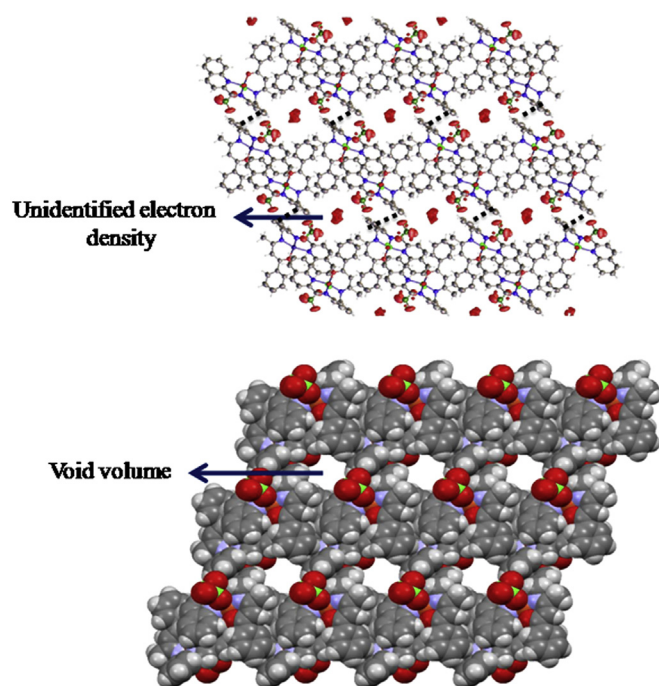


Fig. 1. Three dimensional structure of Polymorph 2 phase viewed along the a-axis showing the unidentified electron density in the tunnels (above) and in spacefill format (below), dash lines depict π - π bonds.

Download English Version:

<https://daneshyari.com/en/article/1400960>

Download Persian Version:

<https://daneshyari.com/article/1400960>

[Daneshyari.com](https://daneshyari.com)