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Trinuclear and mononuclear copper(II) complexes incorporating tetradentate 2,2′-[1,1′-(ethylenedioxydinitrilo)diethylidyne]diphenol ligand: Syntheses, crystal structures, spectral and thermal behaviors

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ABSTRACT

Mononuclear and trinuclear Cu(II) complexes with chemical formula $[CuL]\cdot CH_3OH$ (1) and $[\{(Cu(\mu\text{-}L))_2(OAc)_2\}Cu]$ (2), where H_2L = 2,2′-[1,1′-(ethylenedioxydinitrilo)diethylidyne]diphenol, have been synthesized and characterized by elemental analyses, ^1H NMR, IR and UV–vis spectra et al. Crystallographic data of complex **1** reveal the formation of an asymmetric mononuclear structure and a slight distortion toward tetrahedral geometry from the square planar structure, in which the introduction of the non-coordinated methanol molecule lead to the assembly of the 1D chains by hydrogen bonding, $Cu\cdots\pi$ and $\pi\cdots\pi$ interactions. Complex **2** have the elongated square pyramidal geometries for the two terminal Cu(II) ions and an octahedral coordinated geometry for the central Cu(II) ion. In complex **2**, two acetate ions coordinate to three Cu(II) ions adopting a familiar *syn–syn* (μM-O-C-O-M) coordinated fashion. The central Cu(II) ion sits in a crystallographic inversion centre. Therefore, the whole molecule of complex **2** is rigorously centrosymmetric, and forms a 3D supramolecular networks through intermolecular $C–H\cdots O$ and $C–H\cdots\pi$ interactions.

1. Introduction

Schiff base ligands have played an integral and important role in the development of coordination chemistry since the late 19th century. Metal complexes of these ligands are ubiquitous due to their facile synthesis, wide applications and the accessibility of diverse structural modifications [1]. The chemistry of Schiff base ligands and their metal complexes has expanded enormously and encompasses a vast area of organometallic compounds and various aspects of bioinorganic chemistry [2]. Schiff base complexes have been reported to show a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, herbicidal, clinical, analytical, electrochemical, magnetic, catalytic and biological activities, especially in the study of the interaction with DNA [3–7]. The chemistry of metal complexes containing Salen-type Schiff base ligands derived from condensation of aldehydes and diamines is of enduring significance, since they have common features with metalloporphyrins with respect to their electronic structure and catalytic activities that mimic enzymatic oxidation [8].

There has also been substantial interest in the rational design of metal–organic framework structures of Salen-type complexes have received enormous attention in recent years. The framework structures of the complexes are primarily dependent upon the coordination performances of the central metal ions and the functionality of the ligands. Aside from the coordination bonding interactions, the hydrogen bonding and π–π stacking interactions, the solvent molecules, counterions and the ratio of metal salt to organic ligand also influence the formation of the ultimate architectures.

It is well known that acetate ions often play an important role in coordination chemistry which can adopt various binding modes such as terminal monodentate, chelating to one metal centre, bridging bidentate in a *syn–syn*, *syn–anti* and *anti–anti*, and bridging tridentate to two metal centres [9–11]. In this paper, mononuclear and linear trinuclear Cu(II) complexes, $[CuL]\cdot CH_3OH$ (1) and $[\{(Cu(\mu\text{-}L))_2(OAc)_2\}Cu]$ (2), have been synthesized and structurally characterized. In complex **1**, a methanol molecule is attached to one of the phenoxo oxygen atoms via intramolecular hydrogen bond, while in complex **2** each of the coordinated acetate ions adopts *syn–syn* configuration to two Cu(II) centres. This configuration of the coordinated acetate ions is usually observed in cobalt, nickel and zinc complexes [12–14] reported earlier, however, which rarely exists in the documented Salen-type copper(II) complexes to the best of our knowledge.

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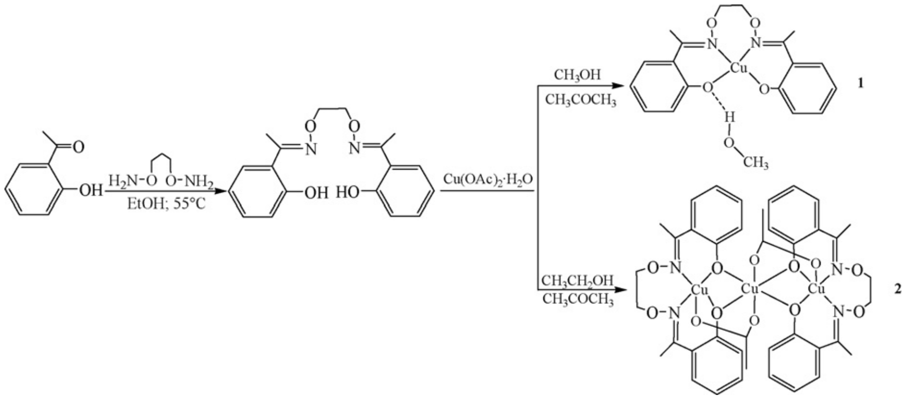

Scheme 1. Synthesis of ligand H_2L and solvent- or counterions-induced Cu(II) complexes **1** and **2**.

2. Experimental

2.1. Materials

2′-Hydroxyacetophenone of 97% purity from Alfa Aesar was used without further purification. Copper acetate monohydrate of 99% purity was purchased from Tianjin Chemical Reagent Factory and used as received. 1,2-Dibromoethane and other commercially available chemicals and solvents were used and purified by standard procedures [15].

2.2. Methods

C, H and N contents were determined using a GmbH VariuoEL V3.00 automatic elemental analyzer. Elemental analyses for Cu were detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. FT-IR spectra in the range of 400–4000 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. UV–vis absorption spectra in the 200–800 nm range were recorded on a Hitachi UV-3010 spectrophotometer in DMF solution. TG–DTA analyses were carried out on a ZRY-1P thermoanalyzer at a heating rate of 3 °C/min. ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. Single crystal X-ray diffraction data were collected on a Bruker AXS single crystal X-ray diffractometer using Bruker Smart 1000 APEX CCD area detector. The X-ray generator was operated at 50 kV and 35 mA using Mo Kα radiation ($\lambda = 0.71073$ Å). Melting points were measured by the use of a microscopic melting point apparatus made by Beijing Taike Instrument Limited Company, and the thermometer was uncorrected. Molar conductance value measurements were carried out on a model DDS-11D type conductivity bridge using 1.0×10^{-3} mol dm^{-3} solution in DMF at 25 °C.

2.3. Synthesis and characterization of H_2L

1,2-Bis(phthalimidoxy)ethane was prepared according to the literature [16]. Yield, 95.6%. m.p., 250 °C.

1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier [16]. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.79(s, 4H), 5.52(s, 4H).

As shown in Scheme 1, the ligand H_2L was synthesized according to an analogous method reported earlier [17]. Reaction of 1,2-bis(aminooxy)ethane (92.1 mg, 1.00 mmol) with 2 equivalents of 2′-hydroxyacetophenone (283.0 mg, 2.00 mmol) in ethanol (7 ml) afforded the desired ligand as colorless microcrystal. Yield, 72.1%. m.p., 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.34 (s, 6H), 4.50 (*t*, *J* = 3.4 Hz, 4H), 6.90 (dd, *J* = 7.8, 1.4 Hz, 2H), 6.96 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.25 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.41 (dd, *J* = 8.0, 1.4 Hz, 2H), 11.10 (s, 2H). Anal. Calcd. for $C_{18}H_{20}N_2O_4$ (H_2L): C, 65.84; H, 6.14; N, 8.53. Found: C, 65.76; H, 6.24; N, 8.46%.

2.4. Synthesis of complexes **1** and **2**

Controlled design of solvent- or counterions-induced Cu(II) complexes **1** and **2** are obtained by the reaction of Salen-type bisoxime ligand H_2L with $Cu(OAc)_2 \cdot H_2O$ in a 1:1 molar ratio in methanol/acetone and ethanol/acetone mixed solutions, respectively (Scheme 1). The single crystals of complexes **1** and **2** suitable for X-ray diffraction analysis were grown up by means of gaseous diffusion method.

2.4.1. Synthesis of $[CuL]\cdot CH_3OH$ (**1**)

A solution of $Cu(OAc)_2 \cdot H_2O$ (5.7 mg, 0.03 mmol) in methanol (2 ml) was added dropwise to a solution of H_2L (9.3 mg, 0.03 mmol) in acetone (3 ml) at room temperature. The color of the mixed solution turned to dark-green immediately. The obtained transparent mixed solution was placed in *n*-hexane atmosphere and stored at room temperature for about three months, along with diffusion of *n*-hexane into the mixed solution of the complex, dark-green block-shaped single crystals suitable for X-ray crystallographic analysis were obtained. Yield, 23.1%. Anal. Calcd. for $C_{19}H_{22}CuN_2O_5$ ($[CuL]\cdot CH_3OH$): C, 54.09; H, 5.26; N, 6.64; Cu, 15.06. Found: C, 54.21; H, 5.18; N, 6.58; Cu, 15.01%.

2.4.2. Synthesis of $[\{(Cu(\mu\text{-}L))_2(OAc)_2\}Cu]$ (**2**)

The single crystal of complex **2** was grown up by a similar procedure aforementioned taking $Cu(OAc)_2 \cdot H_2O$ (7.6 mg, 0.04 mmol) and H_2L (12.4 mg, 0.04 mmol) in a mixed solution of 2 ml ethanol and 3 ml acetone. The obtained transparent mixed solution was placed in *n*-hexane atmosphere and stored at room temperature for about six months. Along with diffusion of *n*-hexane into the mixed solution of the complex, dark-green prismatic single crystals suitable for X-ray crystallographic analysis were obtained. Yield, 32.5%. Anal. Calcd. for $C_{40}H_{42}Cu_3N_4O_{12}$ ($[\{(Cu(\mu\text{-}L))_2(OAc)_2\}Cu]$): C, 49.97; H, 4.40; N, 5.83; Cu, 19.83. Found: C, 49.99; H, 4.46; N, 5.72; Cu, 19.80%.

2.5. X-ray crystallography

The single crystals of complexes **1** and **2** with approximate dimensions of 0.65 mm × 0.53 mm × 0.51 mm and 0.42 mm × 0.23 mm × 0.17 mm were determined. The raw intensities were corrected for Lorentz, polarization effects and a numerical absorption correction was applied for the two complexes. The data were reduced by SAINT-PLUS and an empirical absorption correction was applied using the package SADABS. The structures were