

A new tetraaminodiphenol macrocyclic ligand and its two dicopper(II) complexes: Syntheses, crystal structures, electrochemistry and magnetochemistry

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ABSTRACT

This paper deals with the diprotonated salt, $[H_4L](ClO_4)_2$ (**1**), of the tetraaminodiphenolate macrocyclic ligand, H_2L which is the [2 + 2] condensation product of 4-ethyl-2,6-diformylphenol and 2,2'-dimethyl-1,3-diaminopropane, and two diphenoxo-bridged dicopper(II) complexes $[Cu_2L(ClO_4)_2]$ (**2**) and $[Cu_2L(ClO_4)](ClO_4)$ (**3**). The syntheses, characterization and crystal structures of **1–3** and the magnetic and electrochemical properties of the metal complexes **2** and **3** are presented. The cationic macrocycle $[H_4L]^{2+}$ is stabilized by four intramolecular and symmetric $N-H \cdots O \cdots H-N$ hydrogen bonds involving phenoxo oxygen and imino nitrogen atoms. One metal center in **3** is tetracoordinated and in a square planar geometry. The second metal ion of **3** and both the metal ions in **2** are pentacoordinated and in a square pyramidal geometry; one perchlorate oxygen atom occupies the apical position in each case. Both **2** and **3** exhibit quasireversible two-step one-electron couples in the reduction window. The $E_{1/2}$ (ΔE_p) values (in mV) for the $Cu^{II}Cu^{II}/Cu^{II}Cu^I$ couple is -0.466 V (0.067 V) for **2** and -0.490 V (0.076 V) for **3**, while the $E_{1/2}$ (ΔE_p) values (in mV) for the $Cu^{II}Cu^I/Cu^I Cu^I$ couple is -0.953 V (0.060 V) for **2** and -0.985 V (0.069 V) for **3**. Variable-temperature (2–300 K) magnetic susceptibility measurements of the two compounds reveal that the metal centers in both of the complexes are coupled by strong antiferromagnetic interactions with $2J$ values ($H = -J\mathbf{S}_1 \cdot \mathbf{S}_2$) of -780 and -820 cm^{-1} for **2** and **3**, respectively.

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1. Introduction

Interest in the investigation of new dinuclear complexes is still continuing, although a number of such complexes were reported earlier due to their relevance in bioinorganic chemistry [1–3], magnetochemistry [4–17], electrochemistry [13–19] and homogeneous catalysis [20–23]. Several works on dicopper(II) complexes have been reported due to their relevance to copper-containing enzymes such as hemocyanin, tyrosinase and catechol oxidases [24–26]. Again, being the simplest exchange-coupled systems, magnetic properties of dicopper(II) complexes have been studied [5–11,13–17] and a number of magneto-structural correlations have been determined [5]. However, new dicopper(II) systems derived from new preorganized ligands deserve study for the enlightenment they can shed on the structure–property correlations.

In 1970, Robson introduced 4-methyl-2,6-diformylphenol as the precursor for the synthesis of preorganized bi-/oligonucleating ligands and since then there has been a continuous growth of this area; several macrocyclic [27–36] and acyclic ligands [24–26] and

di-/oligonuclear metal complexes derived therefrom have been reported. By changing the 4-substituent from methyl [5–9,14,17–19,32–36] to chloro [12,29], Fluoro [15,30], bromo [11,31], butyl [14], tertiarybutyl [10], trifluoromethyl [16], etc., several ligands and their metal complexes have also become known. These complexes have occupied a dominating position in coordination chemistry research that explores the electrochemical, magnetic, biomimetic and catalytic phenomena. In these and other types of complexes, small changes in the ligand environment can result in tremendous change of the metal complexes with respect to topology/composition, structural parameters and magnetic or electrochemical properties. For example, change of magnetic and electrochemical properties in dicopper(II) complexes of tetraaminodiphenolate macrocyclic ligands are known on changing the 4-substituent of the 4-substituent-2,6-diformylphenol fragment of the ligand from methyl to butyl, *t*-butyl or trifluoromethyl. Similarly, the number of components, self-assembly and topology of the complexes of 3-ethoxysalicylaldehyde-diamine ligands [37,38] are dramatically different from the complexes of 3-methoxysalicylaldehyde-diamine ligands [39,40]. With the expectation of variation in their structure and properties, we have begun studies of systems derived from ligands having 4-ethyl-2,6-diformylphenol [41] as a precursor. In comparison to the 4-methyl

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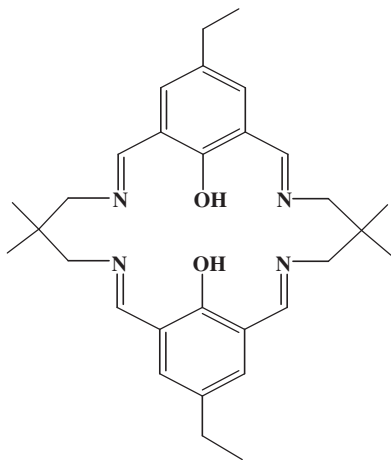


Chart 1. Chemical structure of H_2L .

analogue, new and interesting structures/topologies/properties have already been observed in the complexes derived from an acyclic ligand having 4-ethyl-2,6-diformylphenol as a fragment. To explore further the systems having 4-ethyl-2,6-diformylphenol as a fragment, we have synthesized the diprotonated salt, $[H_4L](ClO_4)_2$ (**1**) of the tetraiminodiphenolate macrocyclic ligand, H_2L (Chart 1) which is the [2 + 2] condensation product of 4-ethyl-2,6-diformylphenol and 2,2'-dimethyl-1,3-diaminopropane, and two diphenoxo-bridged dicopper(II) complexes $[Cu_2L(ClO_4)_2]$ (**2**) and $[Cu_2L(ClO_4)](ClO_4)$ (**3**). Herein, we report the syntheses, characterization and crystal structures of **1–3** and the magnetic and electrochemical properties of the metal complexes **2** and **3**.

2. Experimental

Caution! Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

2.1. Materials and physical methods

All reagents and solvents were purchased from commercial sources and used as received. 4-ethyl-2,6-diformylphenol was synthesized by a known procedure [42]. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region $400\text{--}4000\text{ cm}^{-1}$ on a Bruker-Optics Alpha-T spectrophotometer with samples as KBr disks. Electronic spectra were obtained by using a Hitachi U-3501 spectrophotometer. The electrospray ionization mass spectra were recorded on a Micromass Qtof YA 263 mass spectrometer. Variable-temperature (2–300 K) magnetic susceptibility measurements under a fixed field strength of 1 T were carried out with a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were estimated from Pascal constants. Cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were done using a Bio-analytical System EPSILON electrochemical analyzer. The concentration of the supporting electrolyte, tetrabutylammonium perchlorate (TBAP) was 0.1 M, while that of the complexes was 1 mM. Cyclic voltammetric measurements for **2** and **3** were carried out in dimethylsulphoxide solution, with a three-electrode assembly comprising a glassy carbon disk working electrode, a platinum auxiliary electrode and an aqueous Ag/AgCl reference electrode, the later of which was connected with the solution through a salt bridge (tetrabutylammonium perchlorate in acetonitrile). Under identical conditions, the $E_{1/2}$ value of the ferrocene/ferrocenium couple was 0.380 V ($\Delta E = 0.062$ V) in dimethylsulphoxide.

2.2. Syntheses of the complexes

2.2.1. $[H_4L](ClO_4)_2$ (**1**)

The diprotonated perchlorate salt, $[H_4L](ClO_4)_2$, of the macrocyclic Schiff base ligand H_2L was synthesized by condensation of 4-ethyl-2,6-diformylphenol with 2,2'-dimethyl-1,3-diaminopropane following a known procedure to prepare the related other macrocyclic ligands [27,28]. To a boiling methanol solution (30 mL) containing 2,6-diformyl-4-ethylphenol (0.356 g, 2 mmol), $NaClO_4$ (1 g, 8 mmol) and acetic acid (0.25 mL, 4 mmol) was added a methanol solution (5 mL) of 2,2'-dimethyl-1,3-propanediamine (0.208 g, 2 mmol). The solution was removed from the source of heating and kept at room temperature overnight. The product separated as orange crystals that were collected by filtration and washed with methanol and diethyl ether. (Yield: 0.63 g, 92%) Anal. Calcd. for $C_{30}H_{42}N_4Cl_2O_{10}$ (689.59): C, 52.25; H, 6.14; N, 8.12%. Found C, 52.40; H, 6.26; N, 8.24%. IR data, $\nu(\text{cm}^{-1})$: 1649 vs (C=N), 1088 vs, 625 w (ClO_4).

2.2.2. $[Cu_2L(ClO_4)_2]$ (**2**)

To a stirred acetonitrile solution (10 mL) of $H_4L(ClO_4)_2$ (0.689 g, 1 mmol), an acetonitrile solution (5 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.742 g, 2 mmol) was added. To the resulting reddish solution, was added dropwise an acetonitrile solution (5 mL) of triethylamine (0.404 g, 4 mmol) to produce a green solution. After 2 h stirring, the green solution was filtered to remove out any suspended particles. The filtrate was kept at room temperature for slow evaporation. After a few days, diffraction quality green crystals deposited were collected by filtration and air dried. (Yield: 0.568 g, 70%) Anal. Calcd. for $C_{30}H_{38}N_4O_{10}Cl_2Cu_2$ (812.65): C, 44.34; H, 4.71; N, 6.89%. Found C, 44.52; H, 4.84; N, 6.78%. IR data, $\nu(\text{cm}^{-1})$: 1641 vs (C=N), 1105 vs, 624 w (ClO_4). UV-vis (dmf, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/M^{-1}\text{ cm}^{-1}$)): 357(12,800), 604 (136).

2.2.3. $[Cu_2L(ClO_4)](ClO_4)$ (**3**)

To a boiling methanol solution (30 mL) of 4-ethyl-2,6-diformylphenol (0.356 g, 2 mmol), was added a methanol solution (10 mL) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) and $Cu(OAc)_2 \cdot 2H_2O$ (0.199 g, 1 mmol). A methanol solution (20 mL) of 2,2'-dimethyl-1,3-propanediamine (0.202 g, 2 mmol) was then added dropwise. The resulting green solution was refluxed for 1 h. On cooling this solution, green solid deposited which was collected by filtration and washed well with methanol. Recrystallization from acetonitrile/toluene mixture produced green crystals suitable for X-ray diffraction. (Yield: 0.650 g, 80%) Anal. Calcd. for $C_{30}H_{38}N_4O_{10}Cl_2Cu_2$ (812.65): C, 44.34; H, 4.71; N, 6.89%. Found C, 44.50; H, 4.60; N, 6.98%. IR data, $\nu(\text{cm}^{-1})$: 1640 vs (C=N), 1105 vs, 624 w (ClO_4). UV-vis (dmf, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/M^{-1}\text{ cm}^{-1}$)): 357(12,800), 604 (136).

2.3. Crystal structure determination of $[H_4L](ClO_4)_2$ (**1**), $[Cu_2L(ClO_4)_2]$ (**2**) and $[Cu_2L(ClO_4)](ClO_4)$ (**3**)

The crystallographic data of these three compounds **1–3** are summarized in Table 1. Diffraction data for **1** were collected on a Nonius Kappa diffractometer at 120 K whereas the data for **2** and **3** were collected on a Nonius APEX-II diffractometer with CCD-area detector at 293 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) with data collection and reduction performed using the NONIUS program suite DENZO-SMN package [43,44]. All data for the compound **1–3** were corrected for Lorentz, polarization, background and absorption effects. For all the compounds, crystal structures were determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 using SHELXL-97 [45]. The perchlorate oxygen atoms of **1** (O2, O3, O4 and O5) were disordered over two sites with 0.5 occupancy for each. The following hydrogen

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