

Synthesis, structure and magnetic properties of four unexpected di- and tetranuclear Robson-type macrocyclic complexes



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HIGHLIGHTS

- We obtained two dinuclear macrocyclic complex dimers and two dinuclear macrocyclic complexes.
- We report the structures and the magnetic properties of the complexes.
- The complex polymer can be obtained only by using $M(\text{ClO}_4)_2$ because of the weak coordination capacity of ClO_4^- .
- The strongly electron-withdrawing fluorine substituent in benzene ring weakens the antiferromagnetic exchange.

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ABSTRACT

Four symmetrical macrocyclic complexes, $[\text{Ni}_2\text{L}^1(\text{C}_6\text{H}_4\text{NO}_2)](\text{H}_2\text{O})_4$ (**1**), $[\text{Cu}_4\text{L}^1\text{N}_3(\text{ClO}_4)_2(\text{H}_2\text{O})_2]\cdot[\text{Cu}_2\text{L}^1(\text{ClO}_4)_2(\text{H}_2\text{O})_2]\text{N}_3$ (**2**), $[\text{Zn}_4\text{L}^2(\text{H}_2\text{O})_2]\cdot(\text{ClO}_4)_4$ (**3**) and $[\text{Zn}_2\text{L}^2(\text{N}_3)_2]\text{CH}_3\text{CN}$ (**4**) (where H_2L^1 and H_2L^2 are the [2 + 2] condensation products of 2,6-diformyl-4-fluorophenol with 1,3-diaminopropane and 1,4-diaminobutane, respectively), have been synthesized and characterized. The variable-temperature magnetisms of complexes **1** and **2** show that there are antiferromagnetic couplings between the two metal centers in both complexes, and the strongly electron-withdrawing fluorine groups in H_2L weaken the antiferromagnetic exchange.

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Introduction

The construction of inorganic coordination polymers or metal-organic frameworks (MOFs) with novel structures and topologies has received considerable attention over the past decade for their potential applications in many fields, such as separation [1], gas storage [2], magnetism [3], catalysis [4], anion/guest exchange [5] and luminescent materials [6]. However, structural uncertainty is an intrinsic characteristic of a self-assembled system, because we cannot ensure a particular counter anion or solvent molecule present in the solution will or will not participate in the resulting coordination polymer or the crystal. In other words, composition control is still a challenge for the designed assembly of coordination polymers. The final structures of coordination polymers are dependent mainly upon the geometrical and electronic properties of ligands and metal ions, and also strongly influenced by other factors such as counter-ion, solvent, pH value, temperature, and metal-to-ligand ratio [7,8].

Robson-type macrocyclic complexes have also been extensively studied because of their special electronic, magnetic and biological properties, which arise from the short distance between the metal centers in the macrocyclic units. Different substituents on the phenyl groups in Robson-type macrocyclic complexes can lead to varieties of structures and properties [9–15]. Although much work has been done on the Robson-type complexes with Me, Cl and Br substituents, only five complexes with fluoro substituents have been studied by our group, and the results showed that the substituent electronic effects associated with fluorine influenced the first and second one-electron reductions of the metal centers [16–19]. To date, many coordination polymers of Robson-type macrocyclic complexes have been reported, and three coordination dimers of Robson-type macrocyclic complexes have been reported by our group, however, studies on coordination behavior of Robson-type macrocyclic complexes are rare. On the other hand, fluoro atom is a good hydrogen bonding donor, and multi-dimensional supramolecular assembly can be obtained via hydrogen bonding interactions. With this in mind, one crucial aim of this work was to explore the supramolecular assembly behavior of Robson-type macrocyclic complex, but we obtained four complexes

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unexpectedly. Herein, we report four Robson-type macrocyclic complexes. The structure of the ligand is shown in Scheme 1.

Experimental

Materials and measurements

Unless otherwise stated, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. 2,6-Diformyl-4-fluorophenol was prepared with high yields using active MnO_2 as oxidant [20].

IR spectra were recorded on a vector 22 FIR spectrophotometer using KBr disc. Elemental analyses were performed on a Perkin–Elmer 240 analyzer. Magnetic susceptibility of a crystalline-powdered sample was measured on a SQUID-based sample magnetic meter in the temperature range of 2.0–300 K, and the diamagnetic corrections were made according to Pascal's constants.

X-ray data collection and refinement

The crystals were measured on a Bruker AXS SMART diffractometer (Mo K α radiation monochromator). Data reduction and cell refinement were performed by SMART and SAINT Programs [21]. The structures were solved by direct methods (Bruker SHELXTL) and refined on F^2 by full-matrix least squares (Bruker SHELXTL) using all unique data [22]. The non-H atoms in the structure were treated as anisotropic. Hydrogen atoms were located geometrically and refined in riding mode.

Synthesis of complexes

Preparation of complex 1

$[\text{Ni}_2\text{L}^1(\text{C}_6\text{H}_4\text{NO}_2)_3](\text{H}_2\text{O})_4$. To the mixture of acetonitrile–ethanol (1:1, 40 mL) containing 2,6-diformyl-4-fluorophenol (0.084 g, 0.5 mmol) and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.124 g, 0.5 mmol), 1,3-diaminopropane (0.037 g, 0.5 mmol) in acetonitrile–ethanol (1:1, 10 mL) was slowly added. The mixture was stirred for 4 h, then 4-pyridine carboxylic acid (0.124 g, 1 mmol) in acetonitrile–ethanol (1:1, 10 mL) was introduced. The mixture was refluxed for 1 h, then cooled to room temperature and filtered. Yellow crystals of complex 1 were obtained by vapor diffusion of diethyl ether into the solution of the complex in acetonitrile–ethanol. Yield: 0.18 g, 51%. Anal. Calc. for $\text{C}_{40}\text{H}_{40}\text{F}_2\text{N}_7\text{Ni}_2\text{O}_{12}$: C, 49.72, H, 4.17, N,

10.15; Found: C, 49.68, H, 4.35, N, 10.41; IR (KBr, v/cm^{-1}): 1526, 1421(COO^-), 1639 ($\text{v}_{\text{C}=\text{N}}$), 1103(v_{ClO_4}), 637 (δ_{ClO_4}).

Preparation of complex 2

$[(\text{Cu}_2\text{L}^1)_2\text{N}_3(\text{ClO}_4)_2(\text{H}_2\text{O})_2] \cdot [\text{Cu}_2\text{L}^1(\text{ClO}_4)_2(\text{H}_2\text{O})_2] \cdot \text{N}_3$. To the mixture of methanol (20 mL) containing 2,6-diformyl-4-fluorophenol (0.084 g, 0.5 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.186 g, 0.5 mmol), 1,3-diaminopropane (0.037 g, 0.5 mmol) in methanol (10 mL) was slowly added. The mixture was stirred for 4 h, then NaN_3 (0.0324 g, 1 mmol) in methanol (10 mL) was introduced. The mixture was refluxed for 1 h, then cooled to room temperature and filtered. Green crystals of complex 2 were obtained by vapor diffusion of diethyl ether into the solution of the complex in acetonitrile. Yield: 0.145 g, 39%. Anal. Calc. for $\text{C}_{66}\text{H}_{68}\text{Cl}_4\text{Cu}_6\text{F}_6\text{N}_{18}\text{O}_{26}$: C, 49.72, H, 4.17, N, 10.15; Found: C, 49.59, H, 4.36, N, 10.54; IR (KBr, v/cm^{-1}): 3045, 2918 (C–H), 1641(C=N), 1070($\text{v}_{\text{ClO}_4^-}$), 641 ($\delta_{\text{ClO}_4^-}$).

Preparation of complex 3

$[(\text{Zn}_2\text{L}^2)_2(\text{OH})_2] \cdot (\text{H}_2\text{O})_2 \cdot (\text{ClO}_4)_2$. To the mixture of acetonitrile–ethanol (1:1, 40 mL) containing 2,6-diformyl-4-fluorophenol (0.084 g, 0.5 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.182 g, 0.5 mmol), 1,4-diaminobutane (0.044 g, 0.5 mmol) in acetonitrile–ethanol (1:1, 10 mL) was slowly added. The mixture was stirred for 4 h, then 4-aminopyridine (0.108 g, 1 mmol) in acetonitrile–ethanol (1:1, 10 mL) was introduced. The mixture was refluxed for 1 h, then cooled to room temperature and filtered. Yellow crystals of complex 3 were obtained by vapor diffusion of diethyl ether into the solution of the complex in acetonitrile–ethanol. Yield: 0.067 g, 16%. Anal. Calc. for $\text{C}_{48}\text{H}_{54}\text{Cl}_2\text{F}_4\text{N}_8\text{O}_{16}\text{Zn}_4$: C, 40.95, H, 3.87, N, 7.96; Found: C, 40.56, H, 3.57, N, 8.16; IR (KBr, v/cm^{-1}): 3045, 2911 (C–H), 1639(C=N), 1073(v_{ClO_4}), 638 (δ_{ClO_4}).

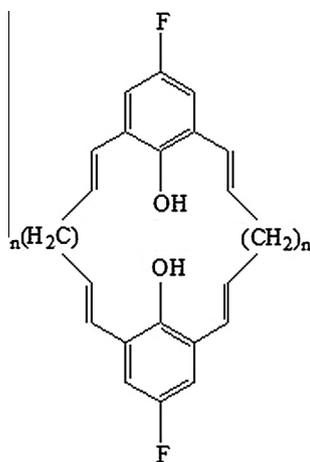
Preparation of complex 4

$[\text{Zn}_2\text{L}^2(\text{N}_3)_2] \cdot \text{CH}_3\text{CN}$. To the mixture of acetonitrile (20 mL) containing 2,6-diformyl-4-fluorophenol (0.084 g, 0.5 mmol) and $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.182 g, 0.5 mmol), 1,4-diaminobutane (0.044 g, 0.5 mmol) in acetonitrile (10 mL) was slowly added. The mixture was stirred for 4 h, then NaN_3 (0.0162 g, 0.5 mmol) in acetonitrile (10 mL) was introduced. The mixture was refluxed for 1 h, then cooled to room temperature and filtered. Yellow crystals of complex 4 were obtained by vapor diffusion of diethyl ether into the solution of the complex in acetonitrile. Yield: 0.29 g, 66.2%. Anal. Calc. for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{N}_{11}\text{O}_2\text{Zn}_2$: C, 44.97, H, 3.92, N, 22.19; Found: C, 44.91, H, 3.82, N, 22.53; IR (KBr, v/cm^{-1}): 3050, 2911 (C–H), 1638($\text{v}_{\text{C}=\text{N}}$), 1101(v_{ClO_4}), 639 (δ_{ClO_4}).

Results and discussion

Synthesis and characterization

The complexes were obtained by the reaction of 2,6-diformyl-4-fluorophenol with 1,4-diamino-butane/1,3-diaminopropane in the presence of $\text{M}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in solution. In the process of the experiment, three kinds of metal salts, $\text{M}(\text{OAc})_2$, MCl_2 and $\text{M}(\text{ClO}_4)_2$, were used to investigate the possibility for the formation of tetranuclear complexes, and we found that the title complexes can be obtained only by using $\text{M}(\text{ClO}_4)_2$ because of the weak coordination capacity of ClO_4^- compared with those of OAc^- or Cl^- . On the other hand, no coordination polymer was formed because of the highly twisted macrocycles. In the IR spectra of the complexes, the sharp C=N stretching vibration bands corresponding to imine groups of the ligand framework are observed, indicating that the macrocyclic complexes have been synthesized. The similarity of the relative vibration bands of IR in the complexes are in agreement with the comparability of their crystal structures.



Scheme 1. Chemical structure of the macrocyclic ligand H_2L , L^1 , $n = 3$; L^2 , $n = 4$.

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