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Polyhedron

Synthesis, crystal structure and magnetic properties of one-dimensional coordination polymers

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ABSTRACT

Three new coordination polymers of Robson-type macrocycles, $\{[Cu_2L^1(bipy)]\cdot(ClO_4)_2\cdot CH_3CN\}_\infty$ (1), $\{[Cu_2L^2(bipy)]\cdot(ClO_4)_2\cdot H_2O\}_\infty$ (2) and $\{[Cu_2L^1(C_8H_4O_4)]\cdot(H_2O)_3\}_\infty$ (3) (where H_2L^1 and H_2L^2 are the [2+2] condensation products of 1,3-diaminopropane with 2,6-diformyl-4-flurophenol and 2,6-diformyl-4-chlorophenol, respectively), have been synthesized and characterized. The magnetic susceptibility was measured for 1, 2 and 3 over the temperature range 2–300 K. The optimized magnetic data were $J = -317.6\ cm^{-1}$, $j' = 4.01\ cm^{-1}$, $\rho = 0.00031$ with $R = 8.5 \times 10^{-39}$ for 1, $J = -320.91\ cm^{-1}$, $j' = 4.39\ cm^{-1}$, $\rho = 0.0013$ with $R = 1.8 \times 10^{-39}$ for 2 and $J = -221.01\ cm^{-1}$, $TIP = 0.00225$, with $R = 6 \times 10^{-5}$ for 3.

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1. Introduction

The design and construction of metal-organic frameworks (MOFs) is one of the most active areas of materials research in recent years [1–6]. The intense interest in these materials is driven by their potential applications as functional materials (catalysis, magnetism, gas separation and non-linear optics) [7–11] as well as by their structural diversity and intriguing topologies [12–19]. Many Robson-type Schiff base macrocyclic complexes have been synthesized and their properties, such as magnetism and electrochemistry, have been studied [20–30]. Our group synthesized a series of Robson-type Schiff base macrocyclic complexes and studied their magnetic and electrochemical properties, along with their DNA cleavage and SOD activities [31–39]. We have recently reported some dimers in which the macrocycles were connected by 4,4′-bipyridine [40,41]. Huang et al. reported the coordination self-assembly of dinuclear Robson-type macrocyclic complexes, but the properties of the coordination polymers have not been studied [42–44].

Recently our attention has been drawn to the study of the interactions between paramagnetic metal ions in coupled systems, including polymeric and linear chains, and especially the study of strong interactions between metal ions relatively far away from each other through extended bridging ligands. Here, we report the interesting crystal structures and magnetic properties of three polymers of Robson-type macrocyclic dinuclear Cu(II) complexes. We have also made an attempt to compare the magnetic

susceptibilities of these polymeric binuclear copper(II) complexes with the magnetic susceptibilities observed in other octahedrally coordinated binuclear copper(II) systems to determine the influence of some structural parameters on the strength of the exchange coupling. Moreover, the influence of substituents and diamine types in the macrocycle rings, anions and metal ions on the final supramolecular assembly are also investigated.

2. Experimental

2.1. Materials and measurements

Unless otherwise stated, all commercial reagents and solvents were obtained from commercial providers and used without further purification. 2,6-Diformyl-4-fluorophenol was prepared in high yields using active MnO_2 as an oxidant [45].

IR spectra were recorded on a Vector 22 FIR spectrophotometer using KBr discs. 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 2.0–300 K, and the diamagnetic corrections were made according to Pascal's constants.

2.2. X-ray data collection and refinement

The crystals were measured on a Bruker AXS SMART diffractometer (Mo Kα radiation monochromator). Data reduction and cell refinement were performed by SMART and SAINT programs [46]. The structures were solved by direct methods (Bruker SHELXTL) and

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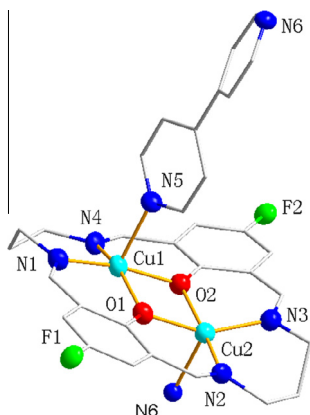E-mail address: zhiqpan@163.com (Z.Q. Pan).

Fig. 1. Perspective view of the complex cation of **1**. Hydrogen atoms have been omitted for clarity.

refined on F^2 by full-matrix least squares (Bruker SHELXTL) using all unique data [47]. The non-H atoms in the structure were treated as anisotropic. Hydrogen atoms were located geometrically and refined in the riding mode.

2.3. Synthesis of the complexes

2.3.1. Preparation of the complex {[Cu₂L¹(bipy)]·(ClO₄)₂·CH₃CN} (1)

To a mixture of acetonitrile–ethanol (1:1, 20 mL) containing 2, 6-diformyl-4-fluorophenol (0. 084 g, 0.5 mmol) and Cu(ClO₄)₂·6H₂O (0.186 g, 0.5 mmol), after adding three drops of triethylamine, 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 4,4′-bipy (0.156 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. Green crystals of complex **1** were obtained by vapor diffusion of diethyl ether into the solution of the complex in acetonitrile–ethanol. Yield: 0.136 g, 29%. *Anal.* Calc. for C₃₄H₃₁Cu₂F₂N₇O₁₀Cl₂: C, 43.74; H, 3.35; N, 10.50. Found: C, 44.19; H, 3.85; N, 10.22%. IR (KBr, cm⁻¹): 1638($v_{C=N}$), 1104(v_{ClO4}^-), 642(δ_{ClO4}^-).

2.3.2. Preparation of the complex {[Cu₂L²(bipy)]·(ClO₄)₂·H₂O} (2)

Complex **2** was obtained in a manner similar to that used for complex **1**, except that 2,6-diformyl-4-chlorophenol was used instead of 2,6-diformyl-4-fluorophenol. Yield: 0.095 g, 21%. *Anal.*

Calc. for C₃₂H₃₀Cu₂N₆O₁₁Cl₄: C, 40.73; H, 3.20; N, 8.91. Found: C, 41.02; H, 3.56; N, 8.53%. IR (KBr, cm⁻¹): 1638($v_{C=N}$), 1102(v_{ClO4}^-), 645(δ_{ClO4}^-).

2.3.3. Preparation of the complex {[Cu₂L¹(C₈H₄O₄)]·(H₂O)₃} (3)

Complex **3** was obtained in a manner similar to that used for complex **1**, except that terephthalic acid was used instead of 4,4′-bipy. Yield: 0.087 g, 19%. *Anal.* Calc. for C₃₀H₃₀Cu₂F₂ N₄O₉: C, 47.68; H, 4.00; N, 7.41. Found: C, 47.31; H, 3.86; N, 7.69%. IR (KBr, cm⁻¹): 1639($v_{C=N}$), 1100(v_{ClO4}^-), 647 (δ_{ClO4}^-).

3. Results and discussion

3.1. Synthesis and characterization

The complexes were obtained by the reaction of 1,3-diaminopropane with 2,6-diformyl-4-fluoro-phenol and 2,6-diformyl-4-chlorophenol in the presence of 4,4′-bipy/terephthalic acid and Cu(ClO₄)₂·6H₂O in acetonitrile/ethanol (V₁/V₂, 1:1) solution. In the process of the experiment, three kinds of metal salts, M(OAc)₂, MCl₂ and M(ClO₄)₂, were used to investigate the possibility for the formation of polymers, and we found that the title polymers can be obtained only by using M(ClO₄)₂ because of the weak coordination capacity of ClO₄⁻ compared with those of OAc⁻ and Cl⁻. X-ray structure determinations show that the three complexes are coordination polymers connected by 4,4′-bipy/terephthalic acid. In the IR spectra of the complexes, the sharp C=N stretching vibration bands, corresponding to imine groups of the ligand framework, are observed at 1638 cm⁻¹ for **1** and **2** and 1639 cm⁻¹ for **3**, indicating that macrocyclic complexes have been synthesized.

3.2. Electrospray mass spectra

The ES-MS spectra of complexes **1** and **3** in acetonitrile solution are shown in the Supplementary material, S1 and S2, respectively. In S1, the peak at m/z 636.92, corresponding to [Cu₂L¹(ClO₄)]⁺, is dominant and can be ascribed to the molecule ionic peak of complex **1**, confirming the formation of the macrocyclic complex and indicating that [Cu₂L¹(ClO₄)]⁺ is very stable in CH₃CN solution. In S2, the peak at m/z 610.58, corresponding to [CuHL¹(HClO₄)(H₂O)₂]⁺, is dominant and can be ascribed to the molecule ionic peak of complex **3**, confirming the formation of the macrocyclic complex. The peak at m/z 595.00 attributed to [CuHL¹(HClO₄) (H₂O)]⁺, and the peak at m/z 573.00 is attributed to [CuHL¹(HClO₄)]⁺. The

Table 1
Crystallographic data for complexes **1**, **2** and **3**.

	1	2	3
Empirical formula	C₃₄H₃₁Cl₂Cu₂F₂N₇O₁₀	C₃₂H₃₀Cu₂N₆O₁₁Cl₄	C₃₄H₃₄Cu₂Cl₂N₆O₁₃
Formula weight	933.64	943.50	538.43
Crystal system, Space group	orthorhombic, P2₁2₁2₁	orthorhombic, P2₁2₁2₁	monoclinic, C2/c
a, b, c (Å)	12.097(2), 16.9507(13), 18.6656(15)	12.0908(12), 16.9971(17), 18.8379(18)	20.835(4), 11.531(2), 20.278(4)
Volume (Å³)	3827.4(8)	3871.4(7)	4573.2(15)
Z, D_calc (g cm⁻³)	4, 1.620	4, 1.619	8, 1.564
μ (Mo Kα) [mm], F(000)	1.326, 1896	1.440, 1912	1.119, 2216
Crystal size (mm)	0.20 × 0.22 × 0.26	0.22 × 0.24 × 0.28	0.20 × 0.22 × 0.26
Temperature (K)	291	291	291
Mo Kα radiation (Å)	0.71073	0.71073	0.71073
θ range (°)	2.0, 26.0	2.2, 26.0	2.1, 26.0
Dataset	−14: 14; −18: 20; −15: 22	−14: 14; −20: 18; −22: 23	−25: 24; −14: 14; −12: 24
Total unique data R_int	22 190, 7516, 0.034	22 397, 7595, 0.062	12 656, 4462, 0.036
Observed data [I > 2.0σ(I)]	7064	5706	3388
Nref, Npar	7516, 515	7595, 514	4462, 323
R, wR₂, S	0.0437, 0.1176, 1.09	0.0575, 0.1285, 1.01	0.0563, 0.1405, 1.06
Maximum and average shift/error	0.00, 0.00	0.00, 0.00	0.00, 0.00
Minimum and maximum residual density (e Å⁻³)	−0.41, 0.26	−0.49, 0.27	−0.41, 0.26