



Dimeric complexes of transition metal based on azole nucleating ligands involving hydrogen bonding interactions



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ABSTRACT

Self-assembly through tuning the *N*-donor azole ligands and coordinative preferences of transition metal Cu(II), Cd(II) and Co(II) ions, three dimeric complexes, namely $[\text{Cu}_2(\text{Hmpz})_4(\mu_2\text{-Cl})_2\text{Cl}_2]$ (**1**), $[\text{Cd}_2(\text{pmtz})_2\text{Cl}_2(\text{H}_2\text{O})_4]$ (**2**) and $[\text{Co}_2(\text{Hmpztz})_2\text{Cl}_2(\text{H}_2\text{O})_4]\text{Cl}_2\cdot\text{H}_2\text{O}$ (**3**) have been synthesized at solvent method and hydrothermal conditions and characterized by single crystal X-ray diffraction analyses and fluorescent property were investigated, where Hmpz = 3-methyl-1*H*-pyrazole, Hpmtz = 5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid, and H_2mpta = 5-methyl-1-(1*H*-pyrazol-3-yl)-1*H*-1,2,3-triazole-4-carboxylic acid, respectively. In order to investigate the intermolecular contacts, Hirshfeld surface was studied in this work. The Hirshfeld surface analysis was successfully deployed here to visualize and elaborate the similarities and differences in the molecular environments of the three complexes.

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1. Introduction

In recent years, the design and growth of metal-organic frameworks (MOFs) have been developed rapidly [1], as they have displayed not only charming architectures in topology but also potential applications in areas of catalysis, adsorption, electric, magnetism, and so on [2]. In this field, how to design reasonably and predict complex structures is still a great challenge since various factors could impose effects on the construction, such as ligands, metal centers, solvents, anions, pH values and temperatures [3–7]. Among these factors, ligands have attracted great attention as they are the easily tuning. They usually cause marked varieties on both structures and properties by slight changes on steric structures [8], bulks [9], and lengths [10]. As a special category, homologous ligands, azoles have been attracted scientists' attention in recent years. Xiong [11] and his coworkers have reported the many triazole and tetrazole complexes and investigated ferroelectric properties. R. G. Raptis's group devotes themselves to pyrazolate complexes and do researches in electrochemistry [12]. Other azole ligands such as bis(pyrazol-1-yl)-alkanes [13], bis(triazol-1-yl)alkanes [14], and bis(tetrazol-1-yl)-alkanes [15], are also greatly focused on recently. Azole ligands have special virtues on several aspects. Firstly, a family of azole ligands could be synthesized easily, in which the reaction condition almost similar. Secondly is that *N*-donor azole groups have

shown strong ability to coordinate the transition metal constructing polynuclear or multi dimensional compounds. The last is that azole ligands have a variety of coordination modes. Our group has also devoted great effort to explore the unique characters of pyrazole and triazole ligands [16]. What's more, as our further planning assumption, the ligands containing both pyrazole and triazole have been researched, and it is possible to generate significant variations, if a full set of homologous ligands are employed. Pyrazole based triazole ligand does not only possess the feature of pyrazoles, but also has the characteristics of triazoles.

In general, as our ongoing research, how to bound pyrazole to triazole indissolubly is our more urgent task. Fortunately, through constant efforts and attempts, we succeeded in achieving a wholly new compound 5-methyl-1-(1*H*-pyrazol-3-yl)-1*H*-1,2,3-triazole-4-carboxylic acid (H_2mpta) which combining pyrazole with triazole [17]. Under these circumstances, herein we carried out series of azole based ligands 3-methyl-1*H*-pyrazole (Hmpz) and 5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carboxylic acid (Hpmtz) to synthesize coordination compounds. In order to observe the differences, we also take the ligand H_2mpta for comparison. As a result, three novel dimeric complexes $[\text{Cu}_2(\text{Hmpz})_4(\mu_2\text{-Cl})_2\text{Cl}_2]$ (**1**), $[\text{Cd}_2(\text{pmtz})_2\text{Cl}_2(\text{H}_2\text{O})_4]$ (**2**) and $[\text{Co}_2(\text{Hmpztz})_2\text{Cl}_2(\text{H}_2\text{O})_4]\text{Cl}_2\cdot\text{H}_2\text{O}$ (**3**) were obtained. All complexes were studied by means of Hirshfeld surfaces analysis, which serves as a powerful tool for elucidating intermolecular contacts in crystals by using precise crystallographic data [18]. Hirshfeld surface can further reduced to a two dimensional (2D) fingerprint plot, which summarize the complex information on intermolecular interactions present in molecular

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crystals quantitatively [19]. The principles of Hirshfeld surface and fingerprint plot are reported in other literature [20].

2. Experimental

2.1. Materials and instrumentation

All chemicals were commercially available and used as received without further purification. Elemental analyses (CHN) were performed using an Elemental Vario-EL CHN elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. The X-ray crystal structures were determined by single-crystal X-ray diffraction using the SHELXL crystallographic software for molecular structures. Hirshfeld surface calculations were carried out on CrystalExplorer 3.1.

2.2. Syntheses

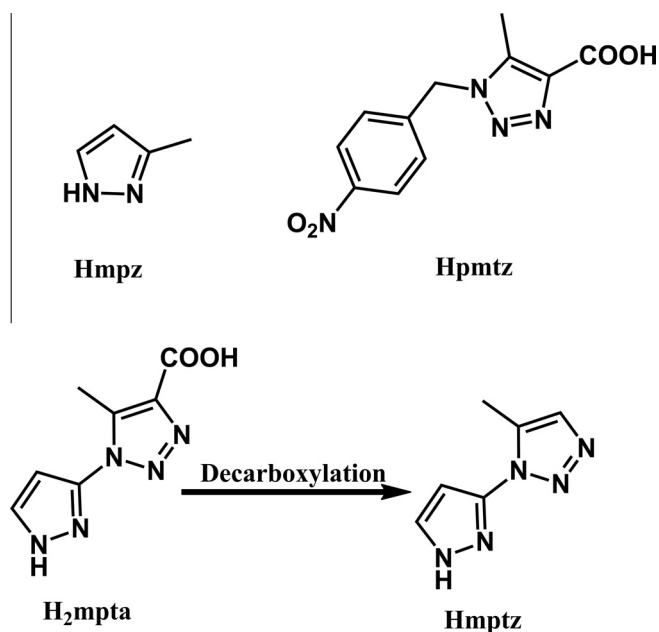
The ligand Hmpz is commercial, the Hpmtz and H₂mpta were synthesized according related literatures [17,21]. Azole ligands used in this work were shown in Scheme 1.

2.2.1. The synthesis of $[\text{Cu}_2(\text{Hmpz})_4(\mu_2\text{-Cl})_2\text{Cl}_2]$ (**1**)

A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0340 g, 0.2 mmol), Hmpz (0.082 g, 0.1 mmol), methanol (15 mL) with a pH adjusted to 8.5 by addition of triethylamine was stirred for 15 min at room temperature. The resulting solution was left at room temperature and blue crystals of **1** were obtained after 2 days. The blue crystals of **1** were collected by filtration, washed with methanol and dried in air. Phase pure crystals of **1** were obtained by manual separation (yield: 42.70% based on Hmpz ligand). *Anal. Calc.* for **1**: $\text{C}_{16}\text{H}_{24}\text{Cl}_4\text{Cu}_2\text{N}_8$ ($M_r = 597.31$), calc.: C, 32.14; H, 4.02; N, 18.76. Found: C, 32.02; H, 4.18; N, 18.65%. IR (KBr, cm^{-1}): 3254 (m), 2921 (m), 1767 (w), 1568 (s), 1446 (s), 1238 (s), 1232 (s), 1105 (s), 978 (s), 952 (s), 896 (s), 788 (w), 711 (w).

2.2.2. The synthesis of $[\text{Cd}_2(\text{pmtz})_2\text{Cl}_2(\text{H}_2\text{O})_4]$ (**2**)

Complex **2** was prepared in a similar way to **1**, except that $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was replaced by $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.1 mmol 0.0225 g).



Scheme 1. Azole ligands used in this work.

Colorless crystals of **2** were collected by filtration, washed with methanol and dried in air. Phase pure crystals of **2** were obtained by manual separation (yield: 50.30% based on $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$). *Anal. Calc.* For **2**: $\text{C}_{22}\text{H}_{26}\text{Cd}_2\text{Cl}_2\text{N}_8\text{O}_{12}$ ($M_r = 890.21$), calc.: C, 29.66; H, 2.92; N, 12.58. Found: C, 29.58; H, 3.11; N, 12.41%. IR (KBr, cm^{-1}): 3370 (w), 1623 (s), 1615 (s), 1581 (s), 1556(m), 1496 (m), 1420 (m), 1391(s), 1374 (m), 1303 (w), 1292 (w), 1246 (w), 1135 (m), 1070 (m), 1026 (m), 835 (m), and 769 (m).

2.2.3. The synthesis of $[\text{Co}_2(\text{Hmptz})_2\text{Cl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**3**)

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0238 g, 0.1 mmol), H₂mpta (0.0290 g, 0.1 mmol), KOH (0.0112 g 0.2 mmol), and MeCN (15 mL) was stirred for 10 min at room temperature with the pH value of 8.0. The resulting solution was put into a Teflon-lined autoclave. The reaction mixture was heated at 130 °C for 5 days, followed by slow cooling to room temperature and phase pure red crystals of **3** were obtained by manual separation (yield: 0.0160 g, ca. 48.10 % based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). *Anal. Calc.* for $\text{C}_6\text{H}_{13}\text{Cl}_2\text{-CoN}_5\text{O}_3$ ($M_r = 333.04$): C, 21.62; H, 3.90; N, 21.02. Found: C, 21.51; H, 4.12; N, 20.53%. IR (KBr, cm^{-1}): 3414 (s), 1637 (s), 1617 (s), 1577 (w), 1266 (w), 1540 (m), 1384 (w), 1226 (m), 1127 (w), 1049 (w), 1017 (w), 972 (w), 772 (w).

2.3. Crystal structure determination

Single-crystal X-ray diffraction measurements for complexes **1–3** were carried out using a Rigaku SCX mini diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 with SHELXL-97 [22]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added theoretically and refined with riding model and fixed isotropic thermal parameters. The crystallographic parameters and structural determination of **1–3** are summarized in Table S1. Selected bond lengths, bond angles and hydrogen bonding geometry of **1–3** are listed in Tables S2 and S3.

2.4. Hirshfeld surface calculations

Molecular Hirshfeld surface calculations were performed by using the CrystalExplorer program. The principles of Hirshfeld surfaces were reported in the literature [23]. When the cif files of **1–3** were read into the CrystalExplorer 3.1 program for analysis, all bond lengths to hydrogen were automatically modified to typical standard neutron values (C–H = 1.083 Å and N–H = 1.009 Å). In this study, all the Hirshfeld surfaces were generated using a standard (high) surface resolution. The 2D fingerprint plots displayed by using the standard 0.6–2.6 Å view with the d_e and d_i distance scales displayed on the graph axes.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. $[\text{Cu}_2(\text{Hmpz})_4(\mu_2\text{-Cl})_2\text{Cl}_2]$ (**1**)

The complex of **1** crystallized in the monoclinic $P2_1/n$ space group, monoclinic system and crystallographic details are given in Table S1. The structure is a Cu(II) dimer (Fig. 1), in which the Hmpz ligand remains protonated. Each Cu(II) has two terminals, coordinated with one N atom from Hmpz and a terminal Cl atom. The coordination geometries of the copper atoms are slightly distorted square-pyramidal, and the axial Cu–Cl bond distance is above 2.7 Å, which is due to the Jahn–Teller effect. Equatorial bond lengths come in sets of two, the copper to pyrazole nitrogen, which fall in 1.995 (2)–2.001 (2) Å, and the copper to chloride, which

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