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Syntheses and structural characterization of nine coordination compounds assembled from copper acetate, 3,5-dimethylpyrazole and carboxylates

Shou-Wen Jin [a,*], Xiang-Hang Ye [a], Li Jin [a], Lu Zheng [a], Jing-Wen Li [a], Bin-Peng Jin [a], Da-Qi Wang [b]

[a] Tianmu College ZheJiang A & F University, ZhuJi 311800, PR China
[b] Department of Chemistry, Liaocheng University, Liaocheng 252059, PR China

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ABSTRACT

Nine coordination compounds, namely, $Cu(Hdmpz)_2(L1)_2$ (**1**) (Hdmpz = 3,5-dimethylpyrazole, L1 = 4-methylbenzoate), $Cu(Hdmpz)_2(L2)_2$ (**2**) (L2 = 3-methylbenzoate), $Cu(Hdmpz)_2(L3)_2$ (**3**) (L3 = 2-chlorobenzoate), $Cu(Hdmpz)_2(L4)_2$ (**4**) (L4 = 2-chloronicotinate), $Cu(Hdmpz)_2(L5)_2$ (**5**) (L5 = 4-methoxybenzoate), $Cu(Hdmpz)_2(L6)_2$ (**6**) (L6 = 1-naphthylacetate), $Cu_2(Hdmpz)_4(L7)_2$ (**7**) (L7 = 1,4-cyclohexanedicarboxylate), $Cu(Hdmpz)_2(L8)$ (**8**) (L8 = terephthalate) and $Cu_3(Hdmpz)_9(L9)_2{\cdot}Hdmpz$ (**9**) (L9 = trimesate) have been synthesized by the self-assembly of copper acetate, 3,5-dimethylpyrazole and carboxylate ligands at room temperature. All the compounds were structurally characterized by different techniques, including elemental analysis, IR spectra, TG and single crystal X-ray diffraction analysis. The X-ray studies suggested that these complexes display mononuclear to trinuclear structures with tetrahedral (for compounds **1**–**8**) or distorted square pyramidal (for compound **9**) geometries around the copper ion. The pyrazole and carboxylate groups in all the compounds are only coordinated in the monodentate fashion. The uncoordinated oxygen atom of the carboxylate groups in all of the compounds forms intramolecular/intermolecular hydrogen bonding with the N–H group of the coordinated 3,5-dimethylpyrazole. On the basis of the X-ray crystallographic study, the rich intra- and intermolecular N–H···O hydrogen bonds, and other weak interactions, including CH_3–C_π, Cl···O, C–H···O, CH_3···O, C–H···π, CH_3–π, and π–π associations, are analyzed. The various non-bonding interactions in these compounds are responsible for different structures such as sheet, 3D network and 3D layer structures. The thermal stabilities for **1**–**9** were examined and the results show that the complexes seem to be good candidates for novel inorganic–organic hybrid materials with good thermal stability.

1. Introduction

Investigations on the synthesis, structures and properties of coordination compounds including metal–organic frameworks or inorganic–organic hybrid compounds are an important field in chemical research. These compounds attract significant interest due to their intriguing architectures and wide range of possible applications. Owing to a vast amount of available nodes and connectors, it is possible to get new materials with diverse practical applications, such as adsorption science, gas storage, luminescent materials, catalysis, probes, sensors as well as magnetic materials [1–3].

However, it is still a great challenge to predict the exact structures and composition of the assembly products built by coordination bonds and/or hydrogen bonds in crystal engineering. The framework structure of coordination polymers is primarily dependent upon the coordination preferences of the central metal ions and the functionality of the ligands. Aside from the coordination bonding interactions, the hydrogen bonding, π–π stacking interactions, solvent molecules, counterions and ratio of metal salt to organic ligand also influence the formation of the ultimate architectures. Therefore, systematic research on this topic is still important for understanding the roles of these factors in the formation of the metal coordination frameworks.

Research on metal carboxylates has always been intriguing in that they play important roles not only in synthetic chemistry, with the essence of the labile coordination modes of the carboxylate group, with architectures of open and porous frameworks [4,5], but also with regard to biologic activities [6,7] and physiological effects [8,9]. The carboxylate groups can adopt a wide range of

* Corresponding author. Tel./fax: +86 575 8776 0141.
E-mail address: jinsw@zafu.edu.cn (S.-W. Jin).

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bonding modes, including monodentate, symmetric and asymmetric chelating, and bidentate and monodentate bridging [10].

Pyrazole ligands have been studied for over 40 years, both as neutral (Hpz) and as anionic ligands (pz). In the neutral case, hydrogen bonding is usually observed together with metal coordination; the interplay of both phenomenons is well known for many ligands, and certainly so for pyrazole compounds; this combination often can explain the formation and/or stability of the final structure of the coordination compounds [11–12].

Up until now, a variety of complexes containing pyrazole (pz) ligands have been synthesized and employed in coordination chemistry and organometallic chemistry [13–15]. Many complexes with simple pyrazole ligands, both in terminal as well as bridging modes, are also available [16–18]. However, complexes in the presence of carboxylic acids and pyrazole derivatives are not very common, except for some recently reported examples in the literature [19]. We have been working on coordination compounds with mixed ligands of carboxylate and pyrazole derivatives [20]. The pyrazole and carboxylate ligands appear to possess similar steric requirements and, to a certain extent, also similar bonding capabilities. In order to know the influence of the carboxylate residue on the formation of new complexes and the role that weak non-covalent interactions play in forming the final supramolecular frameworks, we selected carboxylic acids bearing CH_2, CH_3, CH_3O, N, Cl and aromatic units which are good groups to form hydrogen bonds and other non-bonding interactions [21]. Thus, in the following, we report the synthesis, structural characterization and thermal behavior of nine Cu complexes via combination of 3,5-dimethylpyrazole (Hdmpz) and different carboxylate ligands (Scheme 1), namely $Cu(Hdmpz)_2(L1)_2$ (**1**) (Hdmpz = 3,5-dimethylpyrazole, L1 = 4-methylbenzoate), $Cu(Hdmpz)_2(L2)_2$ (**2**) (L2 = 3-methylbenzoate), $Cu(Hdmpz)_2(L3)_2$ (**3**) (L3 = 2-chlorobenzoate), $Cu(Hdmpz)_2(L4)_2$ (**4**) (L4 = 2-chloronicotinate), $Cu(Hdmpz)_2(L5)_2$ (**5**) (L5 = 4-methoxybenzoate), $Cu(Hdmpz)_2(L6)_2$ (**6**) (L6 = 1-naphthylacetate), $Cu_2(Hdmpz)_4(L7)_2$ (**7**) (L7 = 1,4-cyclohexanedicarboxylate), $Cu(Hdmpz)_2(L8)$ (**8**) (L8 = terephthalate) and $Cu_3(Hdmpz)_9(L9)_2{\cdot}Hdmpz$ (**9**) (L9 = trimesate).

2. Experimental

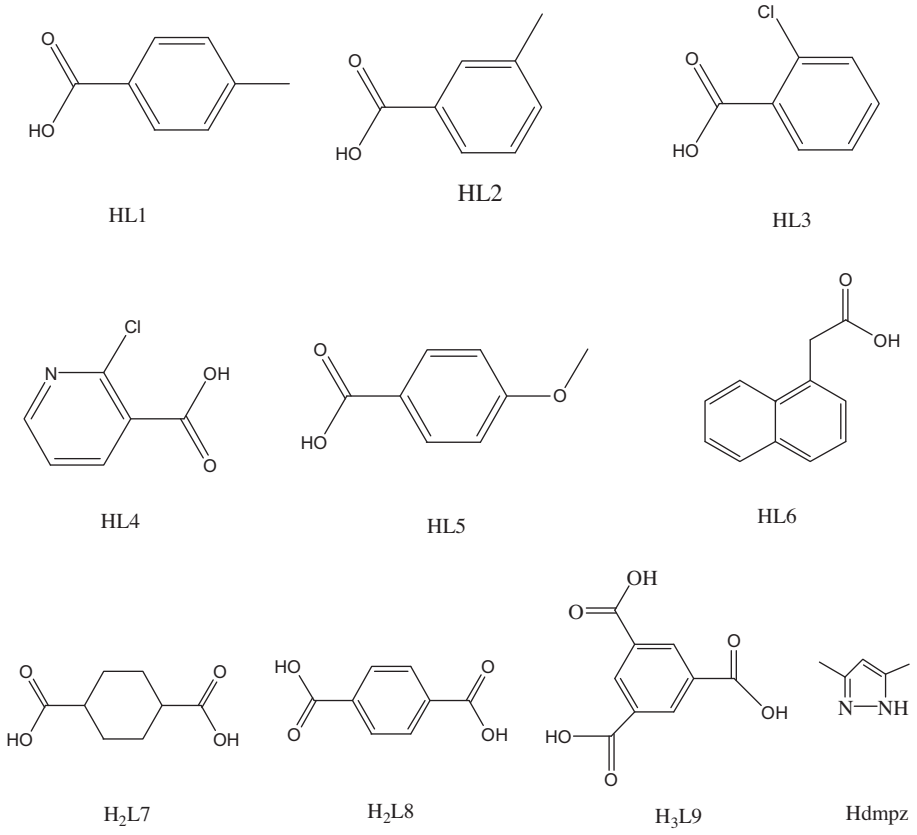
2.1. Materials and physical measurements

The chemicals and solvents used in this work were of analytical grade and available commercially and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H and N) data were obtained with a Perkin-Elmer Model 2400II elemental analyzer. Thermogravimetric analyses (TGA) were studied with a Delta Series TA-SDT Q600 in a N_2 atmosphere between room temperature and 800 °C (heating rate 10 °C min^{-1}).

2.2. Typical preparation procedure

2.2.1. Synthesis of $Cu(Hdmpz)_2(L1)_2$ (*1*)

A solution of $Cu(CH_3COO)_2{\cdot}H_2O$ (0.0199 g, 0.1 mmol) in 6 mL of MeOH was added to a MeOH solution (12 mL) containing Hdmpz (0.0192 g, 0.2 mmol) and 4-methylbenzoic acid (HL1) (0.0272 g, 0.2 mmol), under continuous stirring. The solution was stirred for about 2 h at room temperature, the solution became turbid, then a few drops of conc. ammonia was added until the solution became completely clear. The clear solution was filtered into a test tube and after several days blue crystals formed, which were filtered off, washed with MeOH and dried under vacuum to afford



Scheme 1. The ligands used in this paper.