

Structure modulation of metal–organic frameworks via reaction pH: Self-assembly of a new carboxylate containing ligand *N*-(3-carboxyphenyl)iminodiacetic acid with cadmium(II) and cobalt(II) salts

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Abstract

Self-assembly of a new carboxylate containing ligand, *N*-(3-carboxyphenyl)iminodiacetic acid (H_3L), with Cd(II) and Co(II) salts under different reaction pH results in the formation of four new coordination polymers, namely $[Cd(HL)(H_2O)]$ (**1**), $[Co(HL)(H_2O)]$ (**2**), $[Cd(HL)(H_2O)_4]$ (**3**) and $[Cd_3(L)_2(H_2O)_9] \cdot 7H_2O$ (**4**). Single crystal X-ray diffraction analysis indicates that **1** and **2** are isomorphous and isostructural with a 2D wave-like network structure, while **3** has a 1D zigzag chain structure. The complexes **1–3** were obtained at low pH (<7) which makes the ligands only partly deprotonated. However, complex **4**, obtained at pH 7 with all the carboxylate groups deprotonated, exhibits a 2D network structure. The results suggest that the reaction pH is one of the key factors in the formation of the coordination architectures. In addition, the photoluminescence properties of the free ligand (H_3L) and complexes **1**, **3** and **4** were studied in the solid state at room temperature. Moreover, the magnetic property of complex **2** was investigated.

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1. Introduction

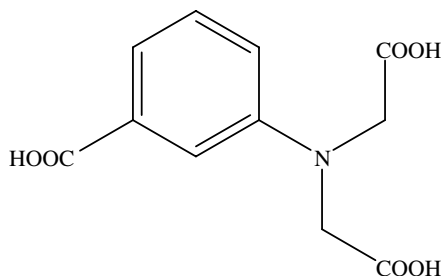
In recent years, much attention has been focused on metal–organic frameworks (MOFs) due to their fascinating structures such as zero-dimensional (0D) cages, one-dimensional (1D) helical chains, two-dimensional (2D) grids and three-dimensional (3D) frameworks [1], as well as their attractive properties which can be further utilized in the fields of magnetism, catalysis, absorption, optics, etc. [2]. Among them, MOFs with carboxylate containing ligands are especially of great interest in recent years because the carboxylate groups can adopt varied coordination modes

such as monodentate, bis-monodentate, chelating, and as a result diverse structures can be obtained [3]. However, it is still a labyrinth because not all of the structures could be generated as predicted, which might be attributed to the factors that influence the formation of the architectures [4]. Particularly, the pH value of the reaction solution and crystallization conditions are crucial parameters, for example, Stock and co-workers have demonstrated the role of the acid/base ratio, temperature, etc., in determining the structure of the complexes [5].

Taking in account of the factors mentioned above, we have focused our attention on the reactions of various metal salts with multi-carboxylate ligands and the influence of reaction pH on the structure of the resultant complexes was investigated. Recently, a new carboxylate containing

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Scheme 1. Schematic drawing structure of the H₃L ligand.

ligand, *N*-(3-carboxyphenyl)iminodiacetic acid (H₃L) (Scheme 1), was obtained, which has remarkable features as follows: (a) it contains three carboxylate groups, therefore quite a lot of bridging modes could be adopted in the formation of MOFs; (b) the three carboxylate groups would be partially or completely deprotonated by tuning the reaction pH; (c) it is a semi-rigid ligand with a carboxyphenyl group fixed and an iminodiacetic moiety which is somewhat flexible, whereby different conformations of the ligand could be achieved which would further generate various architectures; (d) the introduced aromatic and the carboxylate groups could offer additional π – π and hydrogen bonding interactions, respectively, to further consolidate the structure [6].

Herein, we report the synthesis, crystal structure and properties of four new coordination polymers, namely [Cd(HL)(H₂O)] (1), [Co(HL)(H₂O)] (2), [Cd(HL)(H₂O)₄] (3) and [Cd₃(L)₂(H₂O)₉] · 7H₂O (4), obtained by the reactions of H₃L with Cd(NO₃)₂ · 4H₂O or CoCl₂ · 4H₂O under different reaction pH.

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C Elemental Analyzer at the Analysis Center of Nanjing University. FT-IR spectra were recorded in the range 400–4000 cm⁻¹ on a Bruker Vector22 FT-IR spectrophotometer as KBr pellets. ¹H NMR spectra were measured on a Bruker DRX 500 MHz NMR spectrometer at room temperature. Magnetic measurements for complex 2 in the range 1.8–300 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on crystalline samples in the temperature settle mode. The diamagnetic contributions of the samples were corrected by using Pascal's constants. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a Xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5.0 nm. All the measurements were carried out under the same experimental conditions.

2.2. Synthesis of the ligand *N*-(3-carboxyphenyl)iminodiacetic acid (H₃L)

A solution of KOH (33.6 g, 0.6 mol) in water (100 ml) was added dropwise to a solution of monochloroacetic acid (28.4 g, 0.3 mol) in water (100 ml). To the resulting alkaline solution, 3-aminobenzoic acid (13.7 g, 0.1 mol) was added and the mixture was refluxed for 30 h. Then the reaction mixture was cooled to room temperature and a pale brown precipitate appeared, which was collected by filtration, washed by water and recrystallized from water (yield: 52% based on 3-aminobenzoic acid). ¹H NMR (500 MHz, in K₂CO₃, D₂O): δ 7.18 (t, 1H), 7.03 (d, 1H), 6.89 (s, 1H), 6.55 (d, 1H), 3.83 (s, 4H). IR (KBr pellet, cm⁻¹): 3446 (w), 2926 (w), 2552 (w), 1723 (m), 1682 (s), 1603 (m), 1580 (m), 1494 (w), 1465 (m), 1423 (w), 1376 (m), 1361 (m), 1299 (m), 1230 (w), 1183 (w), 1130 (w), 992 (w), 975 (w), 864 (w), 757 (m), 679 (w), 661 (w), 608 (w).

2.3. Synthesis of the complexes

2.3.1. Synthesis of [Cd(HL)(H₂O)] (1)

A mixture containing Cd(NO₃)₂ · 4H₂O (30.8 mg, 0.1 mmol), H₃L (25.3 mg, 0.1 mmol), KOH (2.8 mg, 0.05 mmol), 6 ml H₂O and 3 ml CH₃OH was sealed in a 16 ml Teflon lined stainless steel container and heated at 140 °C for 3 days. After cooling to room temperature for 12 h, colorless block crystals of 1 suitable for X-ray diffraction analysis were obtained in 68% yield. *Anal.* Calc. for C₁₁H₁₁CdNO₇: C, 34.62; H, 2.90; N, 3.67. Found: C, 34.65; H, 2.90; N, 3.70%. IR (KBr pellet, cm⁻¹): 3493 (m), 2917 (w), 1699 (m), 1583 (s), 1439 (m), 1416 (m), 1341 (w), 1313 (m), 1294 (m), 1197 (w), 1135 (w), 992 (w), 971 (w), 931 (w), 878 (w), 809 (w), 774 (w), 756 (w), 720 (w), 690 (w), 664 (w), 620 (w).

2.3.2. Synthesis of [Co(HL)(H₂O)] (2)

The preparation of 2 is similar to that of 1 except that CoCl₂ · 4H₂O (30.8 mg, 0.1 mmol) was used and that the Teflon container was heated at 120 °C for 3 days. After cooling to room temperature for 12 h, purple block crystals of 2 were collected in 63% yield. *Anal.* Calc. for C₁₁H₁₁CoNO₇: C, 40.26; H, 3.38; N, 4.27. Found: C, 40.16; H, 3.27; N, 4.38%. IR (KBr pellet, cm⁻¹): 3474 (m), 2921 (w), 1698 (m), 1586 (s), 1492 (w), 1445 (m), 1419 (m), 1340 (w), 1315 (m), 1295 (m), 1248 (w), 1193 (w), 1175 (w), 1123 (w), 1048 (w), 990 (w), 968 (w), 936 (w), 925 (w), 907 (w), 879 (w), 808 (w), 777 (w), 756 (w), 729 (w), 690 (w), 666 (w), 632 (w).

2.3.3. Synthesis of [Cd(HL)(H₂O)₄] (3)

Complex 3 was prepared by a layering method. An aqueous solution (5 ml) of H₃L (25.3 mg, 0.1 mmol) was carefully adjusted to pH 6 by tetrabutylammonium hydroxide (10%) solution and placed at the bottom of a test tube. Then a buffer layer of a solution (5 ml) of

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