

Three Co complexes based on 1-(imidazol-1-yl)-4-(imidazol-4-yl)benzene: Syntheses, structures and stability property



Jing Xu*, Ming-dao Zhang, Min-dong Chen

Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environment Science and Technology, Nanjing University of Information Science and Technology, Nanjing 210044, China

ARTICLE INFO

Article history:

Received 9 December 2014

Accepted 31 January 2015

Available online 7 February 2015

Keywords:

Cobalt(II) complex

Preparation methods

H-bonding interaction

Stability

Gas sorption

ABSTRACT

Three cobalt(II) complexes with the formulas: $\{H[CoL_3] \cdot 4.17MeOH \cdot 13.3H_2O\}_n$ (**1**), $\{[Co(HL)_3(H_2O)_2](ClO_4)_2 \cdot 2H_2O\}_n$ (**2**), and $\{[Co(HL)_2(H_2O)_2]Cl_2\}_n$ (**3**), were obtained by self-assembly of the cobalt(II) salt with HL (HL = 1-(imidazol-1-yl)-4-(imidazol-4-yl)benzene) under different conditions. X-ray diffraction analysis reveals that complex **1** is a 2-fold interpenetrated porous **crs** framework filled with water molecules and methanol molecules, in which the metal atom has distorted octahedral coordination geometry and the ligand was deprotonated. In **2**, the HL without deprotonation links two different Co(II) atoms to form an infinite 1D chain. While complex **3** with octahedral Co(II) atom is a 4-fold interpenetrated **dia** framework with chloride as counteranions and no deprotonation of the ligand occurred under room temperature condition. In addition, the stability properties of the complexes **1–3** were studied.

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1. Introduction

Much research in coordination chemistry has been influenced by the development of supramolecular chemistry, which involves the design and assembly of porous coordination polymers with specific structures or functions in recent years, such as gas adsorption, catalysis, separation, ion exchange and so on [1–3]. The recent results based on the investigation of adsorption properties of interpenetrated porous metal–organic frameworks (MOFs) proved that the increased adsorption capacity of such MOFs makes them as a new candidate for adsorption materials [4–7]. It is known that the origin of interpenetration can be ascribed to the presence of large free voids in a single framework and it has been demonstrated that the interpenetration does not prevent the possibility for obtaining open porous frameworks [8–10]. However, the factors that control the resulted degree of interpenetration remain largely unknown and/or unproven [11,12].

Furthermore, it is known that self-assembly process is greatly affected by factors such as the nature of the ligand and metal center, reaction medium, template, metal-to-ligand ratio, pH value, and the counterions [13–17]. Therefore, further investigation is required for understanding the assembly process. In addition, suitable guests/templates can not only transform a higher interpenetrated coordination polymer to lower interpenetrated ones but also affect the dynamic of the framework [18,19].

Compared to the well-developed coordination chemistry of transition and rare earth metal complexes with 1H-imidazol-1-yl-containing organic ligands [20–24], for example 1,4-bis(1-imidazolyl)benzene (bib), 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (iimb), 1,3,5-tris(1-imidazolyl)benzene (tib), 1,3,5-tris(imidazol-1-yl)methylbenzene (timb), the ones with 1H-imidazol-4-yl substituted ligands are not well studied until now (Scheme 1) [25–27]. Obviously, there will be great difference between the coordination chemistry of 1H-imidazol-1-yl- and 1H-imidazol-4-yl-containing ligands, since the former ones can only act as neutral ligands and their metal complexes must have anionic part to balance the positive charge of the metal ions and the counteranions may have great influence on the structures as well as properties of the complexes, however, the later ones can serve not only as neutral ligands but also as anionic ones in the case of the 1H-imidazol-4-yl groups deprotonated to generate imidazolate anion. Therefore, the coordination mode of the 1H-imidazol-4-yl-containing ligand is feasible affected by the reaction pH, and as a result MOFs with varied structure and topology can be expected.

Following this approach and also as an extension of our work, we are carrying out the research on the coordination chemistry of 1H-imidazol-4-yl-containing ligand. A compound with two different substituted imidazole groups, 1-(imidazol-1-yl)-4-(imidazol-4-yl)benzene (HL), was designed and prepared. Herein, we report three novel Co(II) complexes with the HL ligand, namely, $\{H[CoL_3] \cdot 4.17MeOH \cdot 13.3H_2O\}_n$ (**1**), $\{[Co(HL)_3(H_2O)_2](ClO_4)_2 \cdot 2H_2O\}_n$ (**2**) and $\{[Co(HL)_2(H_2O)_2]Cl_2\}_n$ (**3**) based on the different preparation methods. The stabilities properties of the complexes are also investigated.

* Corresponding author.

E-mail address: xjnuist@gmail.com (J. Xu).

2. Experimental

2.1. Materials and methods

All commercially available solvents and starting materials were used as received without further purification. The ligand HL was synthesized by reaction of imidazole and 1-(1H-imidazol-4-yl)-4-bromobenzene following the procedures reported for preparation of tib [21]. FT-IR spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr disks. Elemental analyses for C, H and N were taken on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analyses (TGA) were performed using a TGA V5.1A Dupont 2100 instrument heating from room temperature to 700 °C under N₂ with a heating rate of 20 °C/min.

2.2. Synthesis of complexes

2.2.1. $\{[CoL_3] \cdot 4.17MeOH \cdot 13.3H_2O\}_n$ (**1**)

Solid Co(ClO₄)₂·6H₂O (0.018 g, 0.05 mmol) placed at the bottom of a glass vial was covered with CH₂Cl₂ (6 mL), then a mixed solution of HL (0.011 g, 0.05 mmol) and NaOH (0.002 g, 0.05 mmol) in MeOH (6 mL) was layered over. Over a period of approximately two weeks, the solid metal salts gradually dissolved in the solvent mixture with concomitant formation of octahedron violet crystals of the product on the wall of the vial with a yield of 49%. *Anal. Calc.* for C_{40.17}H_{71.30}N₁₂O_{17.48}Co (**1**): C, 45.71; H, 6.81; N, 15.99. Found: C, 45.80; H, 6.85; N, 15.95%. IR (KBr pellet, cm⁻¹): 3374 (m), 3136 (s), 1619 (ms), 1562 (m), 1521 (s), 1334 (m), 1309 (s), 1251 (s), 1121 (s), 1071 (s), 965 (ms), 949 (ms), 838 (s), 736 (s), 656 (s), 623 (s).

2.2.2. $\{[Co(HL)_3(H_2O)_2](ClO_4)_2 \cdot 2H_2O\}_n$ (**2**)

A mixture of HL (0.021 g, 0.10 mmol), Co(ClO₄)₂·6H₂O (0.036 g, 0.10 mmol), NaOH (0.004 g, 0.10 mmol), and H₂O (10 mL) was kept in a 15 mL Teflon liner autoclave at 80 °C for 3 days. After the mixture was cooled to the room temperature, pink block crystals of complex **2** were collected with a yield of 33%. *Anal. Calc.* for C₃₆H₃₈N₁₂O₁₂Cl₂Co (**2**): C, 45.01; H, 3.99; N, 17.50. Found: C, 45.08; H, 4.05; N, 17.48%. IR (KBr pellet, cm⁻¹): 3362 (m), 3132 (ms), 1627 (ms), 1524 (s), 1449 (m), 1358 (m), 1312 (s), 1262 (s), 1162 (m), 1130 (s), 1074 (s), 962 (ms), 946 (ms), 826 (s), 752 (s), 646 (s). *Caution:* Perchlorate metal salts as explosive items should be used carefully under hydrothermal condition.

2.2.3. $\{[Co(HL)_2(H_2O)_2]Cl_2\}_n$ (**3**)

A buffer layer of 5 mL of a methanol/water (1/4, v/v) mixed solvent was carefully layered over 4 mL of an aqueous solution of CoCl₂·6H₂O (0.018 g, 0.05 mmol), then 4 mL of a methanol solution of HL (0.011 g, 0.05 mmol) and NaOH (0.002 g, 0.05 mmol) was layered over the buffer layer. After four weeks, pink block crystals of **3** were obtained with a yield of 29%. *Anal. Calc.* for C₂₄H₂₄Cl₂N₈O₂Co (**3**): C, 48.78; H, 4.09; N, 18.96. Found: C, 48.80; H, 4.05; N, 18.95%. IR (KBr pellet, cm⁻¹): 3453 (s), 3134 (ms), 1620 (ms), 1522 (s), 1454 (m), 1383 (m), 1310 (s), 1259 (s), 1162 (m), 1133 (s), 1073 (s), 964 (ms), 947 (ms), 835 (s), 746 (s), 645 (s).

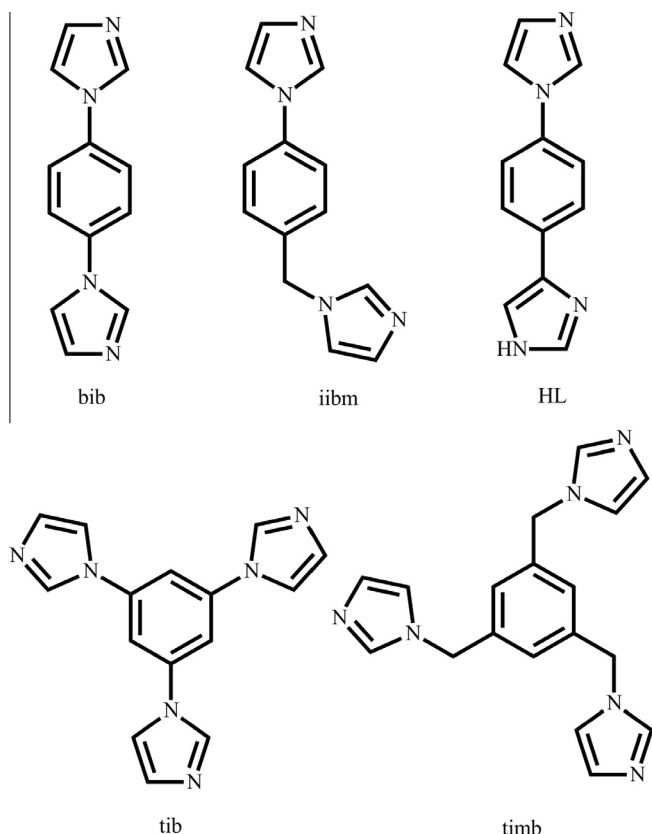
2.3. X-ray structure determination

Crystallographic data of **1–3** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K using graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å). The structures of **1–3** were solved by direct methods with SIR92 [28] and expanded using Fourier techniques [29,30]. All the non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares methods, and the hydrogen atoms except those of water molecules were generated geometrically and refined isotropically using the riding model. The C and N atoms of imidazole ring on 3- and 4-positions in **1–3** are disordered and treated by performing half-occupancies of 50%:50%. The O atoms of solvent water molecule and methanol molecules in **1** are disordered. The high R-factor of complex **1** may be attributed to the lower crystal stability and the disorder atoms such as C14/N13, N13/C13, and the other solvents in the accessible void spaces. The details of the crystal parameters, data collection and refinements for **1–3** are summarized in Table 1. Selected bond lengths and angles for **1–3** are listed in Table 2. Further details are provided in Supporting information.

3. Results and discussion

3.1. Description of the crystal structure of **1**

The result of X-ray diffraction analysis revealed that complex **1** crystallizes in high symmetry of cubic form with space group of $Pn\bar{3}$ and the asymmetric unit has a one-sixth Co(II) atom sitting on a special position with a one-sixth occupancy, half of the deprotonated L⁻ ligand, solvent water molecules and methanol molecules. Every Co(II) center in the framework is octahedral coordinated. Considering the balance of the charge, the anionic charge of framework is balanced by a proton H⁺, which could not be located by X-ray diffraction, but are probably bound to the nucleophilic N atoms of imidazole rings, or one of the solvent water molecules was protonated. As shown in Fig. 1a, each Co(II) atom is coordinated by six nitrogen atoms from six individual L⁻ ligands with distorted octahedral coordination geometry. The Co–N distance of 2.141(4) Å and N–Co–N bond angles of 91.77(1)°, 88.23(1)° and 180° are typical for the octahedral Co–N₆im



Scheme 1. Different kinds of imidazole-containing ligands bib, iibm, tib, timb and HL.

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