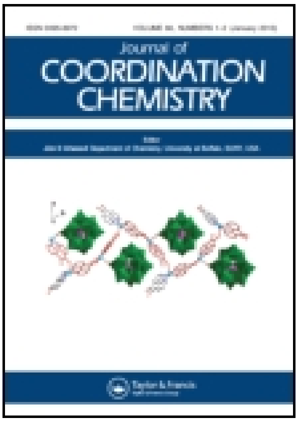

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Two new zinc(II) metal-organic frameworks based on 1,4-bis (2-methyl-imidazol-1-yl)butane: synthesis, structures, and properties

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Two new zinc(II) metal-organic compounds, $\{[Zn(ADC)(bib)]\cdot CH_3OH\cdot H_2O\}_n$ (**1**) and $[Zn(ADA)(bib)]_n$ (**2**) (H_2ADC = 1,3-adamantanedicarboxylic acid, H_2ADA = 1,3-adamantanediacetic acid, bib = 1,4-bis(2-methyl-imidazol-1-yl)butane), have been synthesized and characterized. In **1**, zinc(II) ions are bridged by ADC to form a 1-D chain. The chains are further connected by bib to form a 2-D wave structure. In **2**, zinc(II) ions are bridged by two ADA to form a 1-D looped chain, and then the 1-D looped chain is connected through bib resulting in a 2-D network. Fluorescent properties, TG analysis, and XRPD for **1** and **2** are also measured and discussed.

Keywords: Crystal engineering; Zinc compound; Luminescent properties

1. Introduction

The design and synthesis of inorganic–organic coordination polymers with flexible N-bridging ligands, especially bis(imidazole) ligands, have attracted attention for intriguing structures and potential applications, such as biological activity, nonlinear optics, molecular recognition, catalysis, magnetism, and sensors [1]. The bis(imidazole) ligand with flexible $–CH_2–$ spacers is a good representative of nitrogen-donor ligands. The ligand is able to rotate and bend freely when coordinating to metals [2]. Recently, a few metal–organic networks have been carried out by using different metal ions assembled with flexible bis(imidazole) ligands, examples of which are $(N\text{-im})_2(CH_2)_n$ (n = 1–6) [3–5].

Adamantane is one of the most stable hydrocarbons. This high degree of stability is due to four hexamethylene rings fused in the favorable chair conformation. As a consequence of this stability, it can be produced catalytically from a wide variety of precursors [6].

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Adamantane acid ligands, such as 1,3-adamantanedicarboxylic acid (H_2ADC) and 1,3-adamantanediacetic acid (H_2ADA), which possess two carboxylic groups may coordinate to metal ions and can act as light collectors and transfer absorbed energy to the metal ion resulting in luminescent hybrid inorganic–organic devices [7]. Despite the variety of coordination possibilities, only a few metal–organic framework structures based on adamantane acid ligands have been reported [8–10]. Therefore, more efforts are required to extend our knowledge on coordination behavior and corresponding properties of adamantane acid.

Upon careful inspection of the reported cases, we found that when $n = 4$, metal–bis(imidazole) is less developed [11]. In our previous work, we reported a silver(I) cluster framework with microporous structure based on 1,4-bis(2-methyl-imidazol-1-yl)butane [12]. In this contribution, we chose 1,3-adamantanedicarboxylic acid (H_2ADC) and 1,3-adamantanediacetic acid (H_2ADA) to react with zinc(II), and two new zinc(II) coordination polymers with bib, $\{[Zn(ADC)(bib)]\cdot CH_3OH\cdot H_2O\}_n$ (**1**) and $[Zn(ADA)(bib)]_n$ (**2**). Additionally, thermal stability, X-ray powder diffraction, and luminescent properties for **1** and **2** are also measured and discussed.

2. Experimental

2.1. *Materials and measurements*

All commercially available chemicals were of reagent grade and used without purification. The bib was prepared according to the description in the literature [13]. X-ray powder diffraction patterns were recorded with a Rigaku D/Max 3III diffractometer. Infrared spectra on KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer from 4000 to 400 cm^{-1}. Elemental analyzes were recorded on a Perkin-Elmer model 240C instrument. Thermal analysis was performed on a NETZSCH STA449C with a heating rate of 10 °C min^{-1} under N_2. Luminescence spectra for the solid samples were recorded on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. The luminescent lifetime was measured with an Edinburgh FLS920 fluorescence spectrometer at room temperature.

2.2. *Preparation of $\{[Zn(ADC)(bib)]\cdot CH_3OH\cdot H_2O\}_n$ (1)*

A mixture of H_2ADC (0.10 mM, 22.4 mg) and bib (0.10 mM, 21.8 mg) in 5 mL CH_3OH was layered onto a solution of $Zn(NO_3)_2$ (0.10 mM, 18.9 mg) in 5 mL H_2O, and then was kept at room temperature resulting in colorless block crystals after one week. Yield: 60%. Anal. Calcd for $C_{25}H_{38}ZnN_4O_6$: C, 54.01; H, 6.89; N, 10.08. Found: C, 55.02; H, 6.62; N, 10.47. IR (KBr, cm^{-1}): 3442(m), 3069(w), 2885(s), 1939(w), 1612(s), 1578(m), 1507(s), 1425(w), 1400(m), 1384(w), 1303(s), 1123(w), 1071(w), 1032(w), 1003(w), 882(w), 847 (w), 820(s), 778(w), 708(w), 680(w), 655(w), 622(w), 578(w).

2.3. *Preparation of $[Zn(ADA)(bib)_{0.5}]_n$ (2)*

A mixture of H_2ADA (0.10 mM, 25.2 mg) and bib (0.10 mM, 21.8 mg) in 5 mL CH_3OH was layered onto a solution of $Zn(NO_3)_2$ (0.10 mM, 18.9 mg) in 5 mL H_2O, and then was kept at room temperature resulting in colorless block crystals after one week. Anal. Calcd for $C_{20}H_{27}ZnN_2O_4$: C, 56.54; H, 6.41; N, 6.59. Found: C, 56.51; H, 6.23; N, 6.71. IR

(KBr, cm^{-1}): 3442(m), 3307(w), 3082(w), 2986(m), 1612(s), 1557(w), 1440(w), 1348(s), 1300(m), 1242(w), 1072(m), 1026(w), 987(w), 835(m), 815(m), 767(m), 702(w), 674(w), 623(w), 579(m).

2.4. *Crystallographic data collection and structure determination*

Single-crystal X-ray diffraction analyzes of **1** and **2** were carried out on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo*K*α radiation (λ = 0.71073 Å) by using φ/ω scan technique at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97) [14], and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [14, 15]. The crystallographic data and selected bond lengths and angles for **1** and **2** are listed in table 1 and table S1.

3. Results and discussion

3.1. *Crystal structure*

3.1.1. {[Zn(ADC)(bib)]·CH_3OH·H_2O}$_n$ (1). Single crystal X-ray diffraction analysis shows that **1** crystallizes in the centrosymmetric *P21/c* space group. The 2-D layer structure has only one independent Zn(II). All the bond lengths are in agreement with those reported in other Zn(II) complexes of N, O-mixed ligands [16]. The coordination geometry around Zn(II) is shown in figure 1. There is one independent Zn(II), one ADC, and one bib in the fundamental building unit (the uncoordinated CH_3OH and H_2O molecules are omitted for clarity). Each Zn(II) is located in a five-coordinate quasi-square pyramidal geometry, surrounded by three oxygens from two ADC ligands and two nitrogens from two bib ligands. In **1**, the completely deprotonated ADC coordinates to two Zn(II) with one carboxylic

Table 1. Selected crystallographic data for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{25}H_{38}ZnN_4O_6$	$C_{20}H_{27}ZnN_2O_4$
Formula mass	555.96	424.81
Crystal system	Monoclinic	Monoclinic
Space group	*P21/c*	*P21/c*
a [Å]	12.0042(15)	10.4902(19)
b [Å]	15.906(2)	12.535(2)
c [Å]	17.2162(16)	15.912(3)
α [°]	90	90
β [°]	127.984(6)	108.746(3)
γ [°]	90	90
V [$Å^3$]	2590.9(5)	1981.3(6)
Z	4	4
μ (mm^{-1})	0.995	1.267
Reflections collected	4570	4021
Final R^a indices [I>2σ(I)]	R_1 = 0.0581 wR_2 = 0.2038	R_1 = 0.0596 wR_2 = 0.2222

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

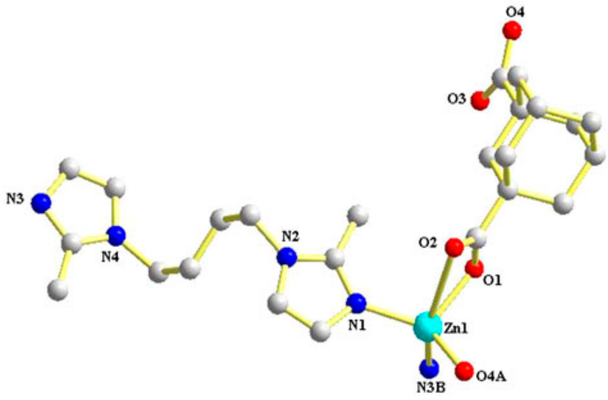

Figure 1. The coordination environment of the Zn(II) in **1**.

group bidentate chelating and another monodentate, resulting in a 1-D chain. The chains are further connected by bib ligands to form the 2-D structure (figure 2), and the 2-D grid layers have parallel stacking with the grid of each layer occupied by groups from adjacent ones, as shown in figure 3.

3.1.2. $[Zn(ADA)(bib)_{0.5}]_n$ (2).

The single-crystal X-ray diffraction analysis reveals that **2** has a 2-D structure. The structure of **2** contains one Zn(II), coordinated to three oxygens from three different ADA ligands and one nitrogen from bib. The view of the coordination geometry around Zn(II) is shown in figure 4.

Different from **1**, the ADA is a tridentate with one carboxylic group bidentate chelating, while another is bridging bidentate. Two ADA molecules form a closed loop by

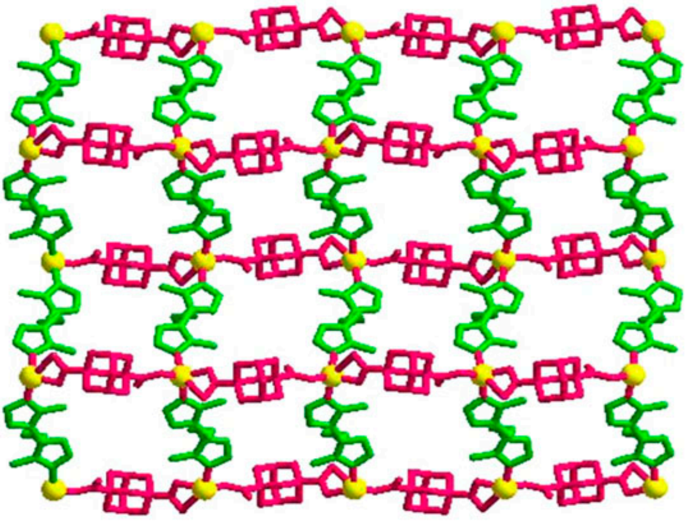

Figure 2. 2-D network grid in **1**.

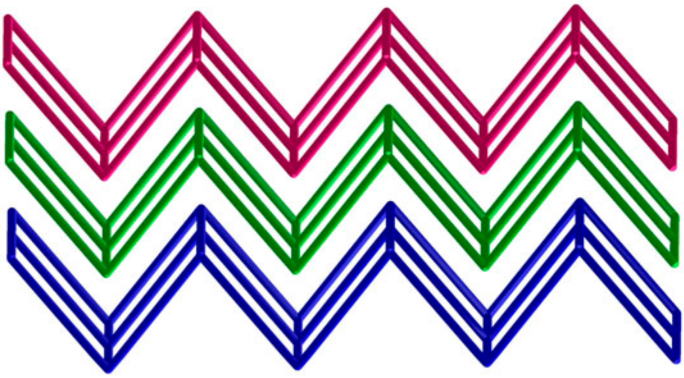

Figure 3. Schematic representation of the parallel stacking with the grid of each layer.

coordinating to zinc, resulting in a 1-D looped chain with M_2L_2-metallocyclic motif (M = Zn, L = ADA, see figure S1 in the Supplementary material). The 1-D looped chain is connected through bib resulting in a 2-D network, as shown in figure 5. Adjacent 2-D gird layers have parallel stacking and arrange in an offset fashion as viewed along the *a* axis (figure 6).

3.2. *Luminescent properties*

The solid-state luminescence of pure bib and **1** and **2** is depicted in figure 7. Complex **1** shows a main peak at 401 nm upon excitation at 280 nm. Whereas, the pure bib ligand exhibits a fluorescent emission at 465 nm (λ_{ex} = 280 nm, the solid H_2ADC ligand does not possess any luminescence at room temperature), the emission peak of **1** is blue shifted by about 64 nm compared to bib. The emission spectrum for **2** shows a main peak at 422 nm upon excitation at 280 nm. The emission peaks are blue shifted about 43 nm relative to that of bib (the solid H_2ADA ligand does not possess any luminescence at room temperature). The emissions of **1** and **2** probably are assigned to ligand to metal charge-transfer (LMCT)

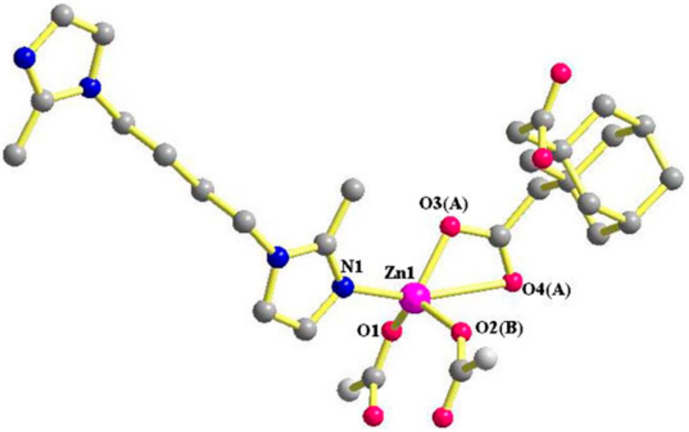

Figure 4. Coordination environment of Zn(II).

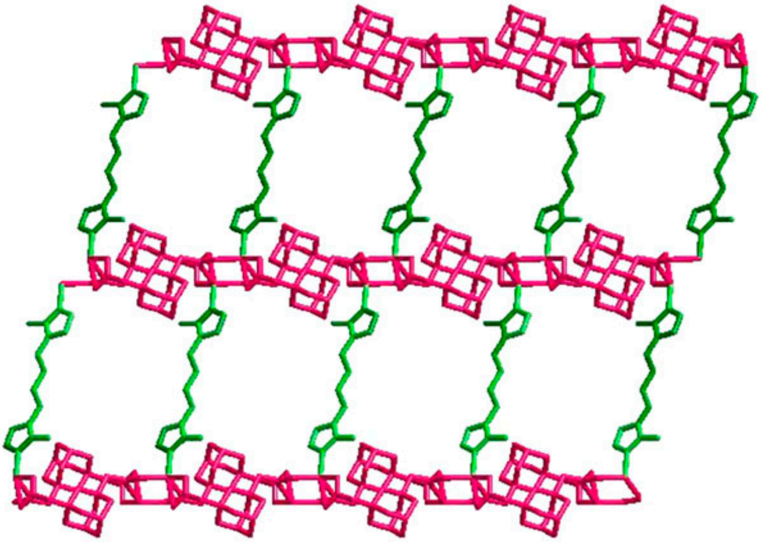

Figure 5. The 1-D looped chains are connected through bib resulting in a 2-D network.

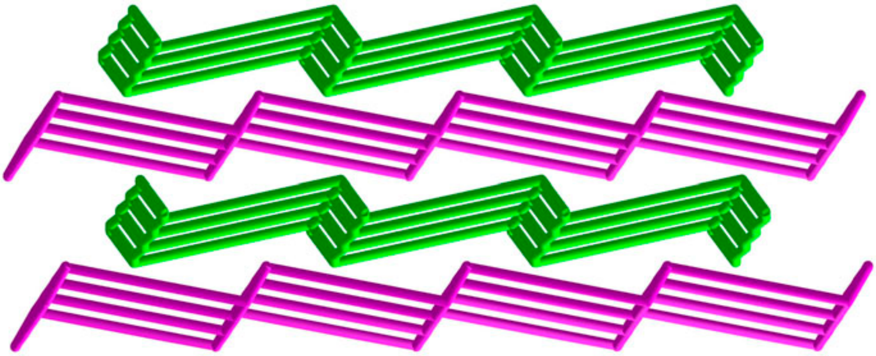

Figure 6. Adjacent 2-D grid layers with parallel stacking and arranged offset.

transitions [17], because the highest occupied molecular orbital (HOMO) is presumably the π-bonding orbital from the imidazole rings and the lowest unoccupied molecular orbital (LUMO) is associated mainly with the Zn–O (carboxylate) σ*-antibonding orbital, which is localized mostly on the metal centers [18].

The lifetimes in **1** and **2** are measured at room temperature upon excitation at 280 nm; the data are well fitted (see figure S2 in the Supplementary material). The lifetime at 401 nm emission of **1** shows 0.8372 ns (36.35%)/4.0994 ns (63.65%), $\chi^2 = 1.303$ and lifetime at 422 nm emission of **2** shows 1.7724 ns (59.69%)/5.3576 ns (40.31%), $\chi^2 = 1.254$. The observation indicates that **1** may be for potential photoactive materials.

3.3. *XRPD Pattern and thermal stability analysis*

To confirm the phase purity of **1** and **2**, the X-ray powder diffraction patterns were checked at room temperature; although minor differences can be seen in the intensities, positions

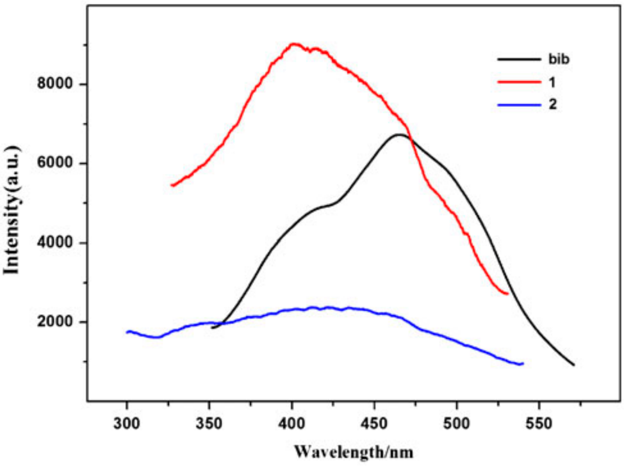

Figure 7. Photoluminescent spectra of complexes and the free ligand.

and widths of some peaks, the data indicate that **1** and **2** were obtained as a single phase (see figure S3 in the Supplementary material).

Thermal stabilities of **1** and **2** were also examined (see figure S4 in the Supplementary material). For **1**, the first major weight loss equals 8.8% corresponding to loss of lattice water and CH_3OH, which starts at 60 °C and is completed at 150 °C (Calcd: 9.0%). From 150 to 335 °C, the TGA curve of **1** passes through a flat area, and then decomposition of organic components occurs (obsd: 79.1%, Calcd: 79.2%). Finally, the residual percentage weight (obsd: 14.2%) at the end of the decomposition of the complex is consistent with the formation of ZnO (Calcd: 14.6%). For **2**, from 25 to 300 °C, the TGA curve of **2** passes through a flat area, and then decomposition of organic components occurs. Weight loss of 81.6% was observed (Calcd: 84.6%). Finally, the remaining weight of 18.4% is in accord with the percentage (Calcd: 19.2%) of ZnO.

4. Conclusion

Research focuses on the synthesis, structural characterization, and properties of two new zinc (II) metal-organic compounds based on 1,4-bis(2-methyl-imidazol-1-yl)butane (bib) and adamantane acid. Comparing **1** and **2**, the use of flexible ligands can make the complex more complicated than rigid ligands. In **1**, rigid H_2ADC results in parallel layers (see figure 3). In **2**, when flexible H_2ADA is employed, adjacent 2-D grid layers stack parallel and arrange in an offset fashion (see figure 6). Thermal stability, X-ray powder diffraction, and the luminescent properties for **1** and **2** are also measured and discussed.

Supplementary material

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC: 941235 and 941236). The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.)+44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk. Supplemental data for this article can be accessed [http://dx.doi.org/10.1080/00958972.2013.851381].

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