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Synthesis, structure and properties of three 1D d^{10} metal–organic coordination polymers with 5-amino-2,4,6-triiodoisophthalic acid

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ABSTRACT

The work presents an further investigation on the coordination chemistry of 5-amino-2,4,6-triiodoisophthalic acid (H_2ATIBDC) and reveals the significant function of weak interactions in constructing the resultant supramolecular networks. Reactions of H_2ATIBDC with the d^{10} metal ions [Zn(II) and Cd(II)] in the presence of varied N-donor auxiliary imidazole ligands at ambient condition yield three new 1D metal–organic coordination polymers (CPs): $\{[Cd(ATIBDC)(biim)]\cdot 2H_2O\}_n$ (**1**), $\{[Zn(ATIBDC)(biim)]\cdot 3H_2O\}_n$ (**2**) and $[Cd(ATIBDC)(bbi)]_n$ (**3**) [biim = 2,2′-biimidazole, bbi = 1,1′-(1,4-butanediyl)bis(imidazole)], which are characterized by elemental analysis, IR spectroscopy, thermogravimetry and single crystal X-ray diffraction measurements. Generally, these three complexes display 1D $ATIBDC^{2-}$-bridged coordination arrays. Extended 3D supramolecular network architectures are further constructed through the weak secondary interactions: aromatic stacking, halogen bonding and hydrogen bonding. It should be interesting to emphasize that the C–I···π halogen bonding plays significant role in the supramolecular assembly of **3**. An acyclic trimeric water cluster (D3 chain) was observed and discussed in **2**. Thermal stabilities of **1**, **2** and **3** have been studied. The fluorescent properties of **1**, **2** and **3** have been investigated in the solid state. Compounds **1** and **2** show completely reversible dehydration–rehydration behaviors, which reveal that **1** and **2** may possibly be used as water adsorbents.

1. Introduction

Recently, the synthesis and investigation of new coordination polymers (CPs) have been of particular interest in coordination chemistry, supramolecular chemistry and materials chemistry due to not only their intriguing variety of topologies but also their potential applications, such as adsorption, magnetism, nonlinear optics, sensing, heterogeneous catalysis, and photoactive materials, etc. [1–11]. The construction of CPs depends on the combination of several factors, such as the coordination geometry of metal nodes, the nature of organic ligands, the use of noncovalent interactions, the ratio between metal ion and ligand, and sometimes the reaction temperature [12–19]. So, understanding how these considerations affect metal coordination and influence crystal packing is at the forefront of controlling coordination supramolecular arrays. It has been documented that the geometries of organic ligands play important roles in determining the resulted polymeric structures. Thus, much effort has been made to modify the building blocks and to control the assembled motifs for required products *via* selecting different organic ligands. In this context, the rational design of organic ligands has great effect on the construction of desirable supramolecular networks [20].

Currently, we are paying our special attention on using 5-amino-2,4,6-triiodoisophthalic acid (H_2ATIBDC) as the organic moiety to react with d^{10} metal ions in the presence of varied *N*-donor auxiliary imidazole ligands, which is based mostly on the following considerations: (1) The I atoms in H_2ATIBDC are potential interaction sites for forming halogen bonds (C–I···N/O, C–I···I or C–I···π, etc.) which may help to extend the linkage into high dimensional supramolecular network due to their specific directional nature and relatively high halogen bonding energy [21–23]. (2) The anion $ATIBDC^{2-}$ is a rigid aromatic dicarboxylate ligand and can play the role of a bridging rod. Therefore, a structural prediction of the resulting polymeric complexes may be

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Table 1
Crystallographic data and structure refinement details for **1**–**3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{14}H_{12}CdI_3N_5O_6$	$C_{14}H_{14}I_3N_5O_7Zn$	$C_{18}H_{16}CdI_3N_5O_4$
Formula weight	761.10	810.37	859.46
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$Pna2_1$	$Pna2_1$	$Pbcm$
a (Å)	17.4395(13)	16.7386(11)	7.1926(6)
b (Å)	18.9231(7)	9.3648(6)	17.4147(16)
c (Å)	14.2725(11)	13.7816(9)	18.9060(17)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	221.0(11)	2160.3(2)	2368.1(4)
Z	4	4	4
D_{calc} (Mg m^{-3})	2.510	2.492	2.411
Absorption coefficient (mm^{-1})	5.193	5.471	4.867
$F(000)$	1544	1512	1592
Θ range for data collection (°)	2.34–27.48	2.43–27.50°	2.34–25.00
Index ranges	$-22 \leqslant h \leqslant 20$ $-11 \leqslant k \leqslant 11$ $-10 \leqslant l \leqslant 18$	$-17 \leqslant h \leqslant 21$, $-12 \leqslant k \leqslant 7$, $-17 \leqslant l \leqslant 17$	$-8 \leqslant h \leqslant 8$ $-20 \leqslant k \leqslant 20$ $-21 \leqslant l \leqslant 22$
Reflections collected	13264	12978	15557
Unique (R_{int})	4084 (0.0415)	4631 (0.0335)	2147 (0.0481)
Completeness to θ = 27.48	100%	99.9%	99.4%
Maximum and minimum transmission	0.771 and 0.653	0.440 and 0.262	0.378 and 0.241
Goodness-of-fit on F^2	1.032	1.003	1.160
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0454 wR_2 = 0.1157	R_1 = 0.0307 wR_2 = 0.0659	R_1 = 0.1008 wR_2 = 0.1944
R indices (all data)	R_1 = 0.0722 wR_2 = 0.1326	R_1 = 0.0369 wR_2 = 0.0689	R_1 = 0.1128 wR_2 = 0.2026
Largest difference in peak and hole (e Å^{-3})	1.304 and −0.711	0.634 and −0.735	2.099 and −2.484

possible to some extent. Furthermore, due to the presence of aromatic rings of ATIBDC^{2-} and the hetero conjugate imidazole rings in *N*-donor auxiliary imidazole ligand in the assembled system, the delicate π...π stacking interactions are available to play a significant role in regulating the resulting supramolecular networks, which are also important in constructing and stabilizing the biological systems [24,25]. So far, several novel CPs with the ATIBDC^{2-} ligand have been reported [26–28].

On the basis of the above considerations, as a continual study of the previous work focusing on the main group *p* block metal ion lead(II) with the ATIBDC^{2-} ligand [29], in this contribution we will describe the preparation, crystallography and properties of a series of 1D d^{10} metal–organic coordination polymers with H_2ATIBDC in order to further understand the coordination chemistry of H_2ATIBDC. With the introduction of different kinds of auxiliary imidazole ligands: the chelating ligand 2,2′-biimidazole (biim) and the flexible bridging spacer 1,1′-(1,4-butanediyl)bis(imidazole) (bbi) (Scheme S1), three new 1D coordination polymers: $\{[Cd(ATIBDC)(biim)]\cdot 2H_2O\}_n$ (**1**), $\{[Zn(ATIBDC)(biim)]\cdot 3H_2O\}_n$ (**2**) and $[Cd(ATIBDC)(bbi)]_n$ (**3**), have been obtained. Based on this work, we attempt to demonstrate the role of weak interactions such as π...π stacking, hydrogen bonding and halogen bonding in engineering the resultant supramolecular network architectures. The acyclic water trimer $(H_2O)_3$ is found in **2**. Dehydration–rehydration behaviors of **1** and **2** have been studied in detail. The solid state fluorescent properties for **1**, **2** and **3** have been investigated.

2. Experimental

2.1. Materials and characterization

The nitrogenous auxiliary imidazole ligands: 2,2′-biimidazole (biim) and 1,1′-(1,4-butanediyl)bis(imidazole) (bbi), were synthesized according to the literature method [30,31]. The other reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were carried out on a 240 C Elemental analyzer. FT-IR spectra (400–4000 cm^{-1}) were recorded from KBr pellet in Magna 750 FT-IR spectrophotometer. The solid state fluorescence emission spectra were recorded using an F-4500 Fluorescence spectrophotometer (Hitachi). Both the excitation and emission pass width are 5.0 nm. Thermogravimetric analysis (TG) was taken on NETZSCH STA 409 PG/PC instrument from room temperature to 800 °C at a heating rate of 10 °C/min in N_2. X-ray powder diffraction data were collected on a computer controlled Bruker D8 Advanced XRD diffractometer equipped with Cu Kα monochromator (λ = 1.5418 Å) at a scanning rate 0.02°/s from 5° to 50°.

2.2. Synthesis of complexes

2.2.1. Synthesis of $\{[Cd(ATIBDC)(biim)]\cdot 2H_2O\}_n$ (*1*)

A mixture of H_2ATIBDC (0.084 g, 0.150 mmol) and NaOH (0.3 ml, 0.5 mol/l) was dissolved in water (5 ml) and then an aqueous solution of $CdCl_2\cdot 2.5H_2O$ (0.034 g, 0.150 mmol) in water (5 ml) was added whilst stirring. To this solution biim (0.008 g, 0.050 mmol) in methanol (5 ml) was added and then filtered. The compound was obtained from the filtrate with a 68% yield based on H_2ATIBDC. *Anal.* Calc. for $C_{14}H_{12}CdI_3N_5O_6$: C, 22.09; H, 1.59; N, 9.20. Found: C, 22.20; H, 1.50; N, 9.28%.

2.2.2. Synthesis of $\{[Zn(ATIBDC)(biim)]\cdot 3H_2O\}_n$ (*2*)

Complex **2** can be obtained following the same synthetic procedure but different reactant molar ratio as that for **1**: $Zn(NO_3)_2\cdot 6H_2O$ (0.034 g, 0.150 mmol), biim (0.008 g, 0.150 mmol), H_2ATIBDC (0.084 g, 0.150 mmol), and NaOH (0.6 ml, 0.5 mol/l). Pale yellow block crystals were formed from the filtrate with a 62% yield based on H_2ATIBDC. *Anal.* Calc. for $C_{14}H_{14}I_3N_5O_7Zn$: C, 20.73; H, 1.73; N, 8.63. Found: C, 20.61; H, 1.82; N, 8.49%.