Hydrogen-bonded sodium–organic frameworks from imidazole-4,5-dicarboxylic acid

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Coordination polymers $[Na(Hidc)(H_2idc)(H_2O)_2]$ (**1**) and $[Na(Hidc)(H_2O)]$ (**2**) ($H_2idc =$ imidazole-4,5-dicarboxylic acid) have been synthesized hydrothermally and analyzed by single-crystal X-ray diffraction analysis, TGA, and IR. Compound **1** displays a 1-D coordination network and **2** exhibits a layered coordination structure. Both compounds form 3-D frameworks through hydrogen bonds.

1. Introduction

The development and synthesis of new metal organic-coordination polymer materials have been extensively investigated due to their potential applications in separations and gas storage [1]. In comparison with traditional zeolites or activated carbons, these materials can be designed with desired pore sizes and functionalities by changing metal ions or the structures of organic linkers. In the process of assembling metal–organic frameworks (MOFs), strong covalent and coordinative bonding between the basic building blocks has played a predominant role and is considered the main factor in designing new MOF materials. However, the impact of weak intermolecular interactions, such as hydrogen-bonding, π-stacking, and hydrophobic interaction on the functionalities, in particular the flexibilities of MOFs have received increasing attention [2]. Light main group metal ions have been used as basic building units to replace heavier transition metal ions to make light materials with high absorption capacity [3]. Also, main group elements such as alkali cations show flexible coordination modes due to their mainly electrostatic interactions with diverse organic linkers [4]. Alkali ions are guest recognition sites in biological systems and catalytic sites for hydrocarbon transformation in zeolites [5]. Organic molecules containing carboxylates and nitrogen donating groups are excellent ligands in the synthesis of MOFs. For example, imidazole-4,5-dicarboxylic acid (H_3idc), a rigid planar ligand with multiple

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coordination sites, has been used for assembling many MOFs by incorporating appropriate metal ions in different ways [6]. The ligand H_3idc not only can be partially or fully deprotonated to $[H_2idc]^-$, $[Hidc]^{2-}$, and $[idc]^{3-}$, but also exhibits flexible coordination. Surprisingly, very few studies have been reported so far on sodium organic–inorganic materials with nitrogen-donor multicarboxylate ligands [7, 8]. In this contribution, we report the synthesis and structures of two sodium–idc frameworks: $[Na(Hidc)(H_2idc)(H_2O)_2]$ (**1**) and $[Na(Hidc)(H_2O)]$ (**2**).

2. Experimental

2.1. *Materials and equipment*

All chemicals purchased were of reagent grade and used without purification. Water used in the reactions was deionized. IR spectra were recorded from 400 to 4000 cm^{-1} on a Perkin Elmer Spectrum One FTIR spectrometer using KBr pellets. Thermogravimetric data were collected on a TA Q5000 TGA instrument at a heating rate of 10°C min^{-1} from room temperature to 800°C in air. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. The reaction vessels were filled to 30% volume capacity. Powder X-ray diffraction (PXRD) analysis was performed on an ARL Thermo X-ray Diffractometer using Cu-Kα radiation (1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA. Experimental PXRD data for both compounds match well with simulated powder patterns (figures S1 and S2).

2.2. *Syntheses*

2.2.1. Synthesis of [Na(Hidc)(H₂idc)(H₂O)₂] (1). Compound **1** was hydrothermally synthesized from a mixture of sodium hydroxide, calcium nitrate, imidazole-4,5-dicarboxylic acid, and water with pH = 4.8 at 150°C for 48 h. The products contain long plate colorless crystals of **1** and colorless crystals of $[Ca(Hidc)_2(H_2O)_3] \cdot H_2O$ [9]. Attempts to synthesize **1** without calcium nitrate were not successful. The crystals of **1** were manually separated for analysis. IR (KBr), 3552(s), 3268(m), 3184(m), 1627(s), 1587(s), 1516(s), 1474(s), 1383(s), 1236(m), 1177(w), 1087(m), 983(m), 951(m), 835(w), 793(m), 637(m), 519(m) (figure S3).

2.2.2. Synthesis of [Na(Hidc)(H₂O)] (2). Compound **2** was hydrothermally synthesized using H_3idc (0.103 g), sodium hydroxide (2 mol L^{-1} NaOH, 0.35 mL), and water (2.0 mL) at 130°C for 48 h. The pH of the initial mixture was 7.8. Colorless needles were filtered, washed with water, and dried in air overnight. IR (KBr): 3473(s), 3405(s), 3135(s), 2975(m), 2853(w), 1697(m), 1584(s), 1555(s), 1507(s), 1430(s), 1391(s), 1391(s), 1245(m), 1109(m), 1086(m), 1030(m), 1191(w), 944(m), 867(m), 829(m), 777(m), 655(m), 562(m), 520(m) (figure S4).

Table 1. Crystal data of **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{10}H_{11}N_4NaO_{10}$	$C_5H_5N_2NaO_5$
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$
Unit cell dimensions (Å, °)		
a	3.5886(1)	3.5926(1)
b	6.7093(1)	13.7451(3)
c	15.2392(2)	14.8042(3)
α	100.270(1)	
β	95.821(1)	95.429(2)
γ	99.877(1)	
Volume (Å^3), Z	352.37(1), 1	727.76(3), 4
θ range for data collection (°)	34.99	37.67
Reflections collected	11,568	25,896
Independent reflections	3078 [R(int) = 0.0173]	3858 [R(int) = 0.0444]
Completeness (%)	99.4	99.7
Goodness-of-fit on F^2	1.036	1.048
Final R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0392$, $wR_2 = 0.1157$	$R_1 = 0.0495$, $wR_2 = 0.1276$
R indices (all data)	$R_1 = 0.0458$, $wR_2 = 0.1234$	$R_1 = 0.0894$, $wR_2 = 0.1453$

$w = 1/[\backslash s^2(F_o^2) + (0.0661P)^2 + 0.0897P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **1**.
$w = 1/[\backslash s^2(F_o^2) + (0.0542P)^2 + 0.2872P]$, where $P = (F_o^2 + 2F_c^{2^2})/3$ for **2**.

2.3. *X-ray crystallographic study*

Single-crystal X-ray diffraction data for **1** and **2** were collected on an Apex II CCD diffractometer. Data were integrated with a Bruker SAINT package and corrected for absorption using SADABS. The structures were solved by direct methods and refined against F^2 by weighted full-matrix least-squares calculations. Hydrogen atoms were found by successive Fourier syntheses and refined using a riding mode. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography [10]. Crystal data and relevant details of the structure determinations are summarized in table 1 and selected geometrical parameters are given in table 2.

3. Results and discussion

3.1. *Descriptions of the structures*

3.1.1. [Na(Hidc)(H$_2$idc)(H$_2$O)$_2$] (1). Single-crystal structure analysis revealed that **1** is a 1-D network composed of sodium ions, idc, and coordinated water. As shown in figure 1, the asymmetric unit of **1** consists of a half crystallographic independent Na$^+$ ion, one idc ligand, and one water molecule. The water is a μ_2-ligand bridging two sodium ions and idc is a monodentate ligand binding to only one sodium ion.

Each sodium ion binds to four oxygen atoms of water and two oxygen atoms from two idc ligands, exhibiting a distorted octahedral coordination geometry (as shown in figure S5) with bond lengths of 2.3797(7) Å, 2.3943(8) Å, and 2.4355(9) Å. Neighboring [NaO$_6$] octahedra edge-share two water molecules to form the 1-D inorganic chain

Table 2. Selected interatomic distances (Å).

Compound 1		Compound 2	
Na(1)–O(3)	2.3796(7)	Na(1)–O(1W)	2.3389(12)
Na(1)–O(3)#1	2.3796(7)	Na(1)–O(3)#2	2.3540(12)
Na(1)–O(1W)#2	2.3940(9)	Na(1)–O(1W)#3	2.3648(15)
Na(1)–O(1W)#3	2.3940(9)	Na(1)–O(1)	2.3828(12)
Na(1)–O(1W)	2.4352(10)	Na(1)–N(2)	2.5051(12)
Na(1)–O(1W)#1	2.4352(10)		
O(3)–C(5)	1.2782(12)	C(3)–N(1)	1.3669(16)
N(1)–C(1)	1.3380(12)	C(3)–C(2)	1.3821(16)
N(1)–C(3)	1.3698(11)	C(3)–C(5)	1.4816(17)
O(4)–C(5)	1.2330(12)	C(4)–O(1)	1.2265(15)
C(3)–C(2)	1.3770(11)	C(4)–O(2)	1.2976(16)
C(3)–C(5)	1.4835(12)	C(4)–C(2)	1.4773(17)
N(2)–C(1)	1.3239(12)	O(4)–C(5)	1.2394(15)
N(2)–C(2)	1.3743(11)	N(2)–C(1)	1.3194(17)
C(2)–C(4)	1.4826(12)	N(2)–C(2)	1.3795(17)
C(4)–O(2)	1.2127(12)	C(1)–N(1)	1.3447(17)
C(4)–O(1)	1.3043(12)		

Symmetry codes: for **1**: #1: $-x+2, -y+2, -z+1$; #2: $x-1, y, z$; #3: $-x+3, -y+2, -z+1$; #4: $x+1, y, z$.
For **2**: #2: $-x+1, y+1/2, -z+1/2$; #3: $x+1, y, z$.
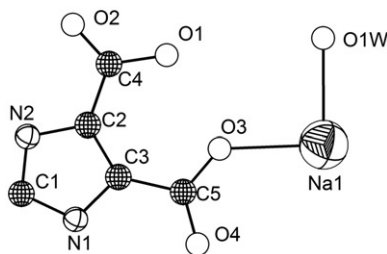
Figure 1.   The asymmetric unit and atom-numbering scheme for **1**.

$[Na(H_2O)_2]^+$ running along the *a*-axis (figure S6). Only one of the two carboxylates on each idc shows close interaction with sodium (Na–O 2.38 Å). The other carboxylate shows no Na–O interactions within 2.50 Å. This indicates that H_2idc in **1** loses one proton to form $[Hidc]^-$. Since there are two idc molecules per sodium in the formula, one of the two ligands must be neutral according to the charge balance in $[Na(Hidc)(H_2idc)(H_2O)_2]$. With only one unique idc ligand in the asymmetric unit of **1**, we will use idc to represent the two forms (H_2idc and $[Hidc]^-$) in **1** in the description below. Each sodium ion of the inorganic chain $[Na(H_2O)_2]^+$ coordinates to two idc ligands through carboxylate (figure S5). The two idc ligands of the $[NaO_6]$ octahedron are *trans*. The imidazole rings of idc from adjacent sodium ions within the chain are parallel with a distance of 3.264 Å, indicating strong π–π interactions. Intrachain hydrogen bonds (O(1w)$\cdots$O(4) = 2.862 Å) tilt the imidazole plane of idc away from the perpendicular position of the chain.

Interchain interactions are hydrogen bonds between the imidazole nitrogen and the carboxylate (N(1)$\cdots$O(1): 2.946 Å, $\angle$N(1)–H$\cdots$O(1) = 160.8°) and also between
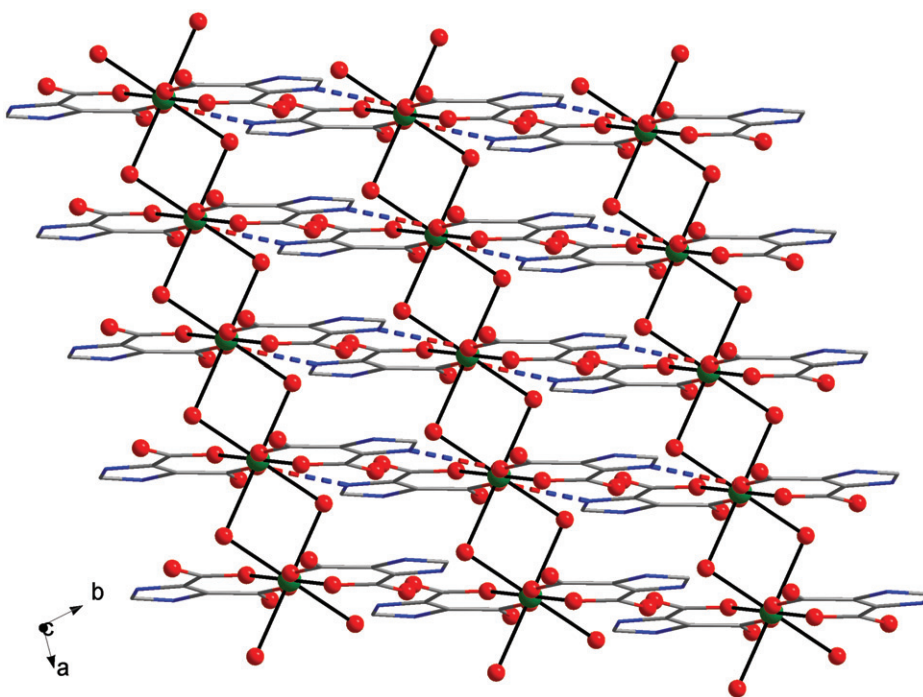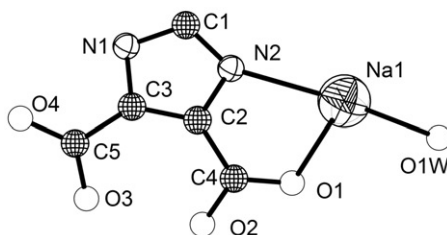
Figure 2. The layered structure parallel to the *ab*-plane in **1**.

Figure 3. The asymmetric unit and atom-numbering scheme for **2**.

coordinated water and carboxylate $\angle O(1w)–H \cdots O(4) = 165°$, $O(1w) \cdots O(4) = 2.867$ Å. These hydrogen bonds connect the chain into a 2-D network parallel to the *ab*-plane (figure 2).

A 3-D porous structure is formed through weak $C–H \cdots O$ ($C(1) \cdots O(2)$, 3.006 Å, $\angle C(1)–H \cdots O(2)$ 127.2°) hydrogen-bonding between layers. Rectangular channels are formed along the [110] directions (figure S7). The size of the channels are 3.6×15 Å (distance Na–Na). Channels are also formed along the *a*-direction (4.2×4.4 Å). These channels are connected to form 3-D channels.

3.1.2. [Na(Hidc)(H₂O)] (2).

3.1.2. [Na(Hidc)(H$_2$O)] (2). The structure of **2** is composed of layered networks constructed from sodium ions, water molecules, and idc ligands. As shown in figure 3, the asymmetric unit of **2** contains one unique Na ion, one water molecule, and
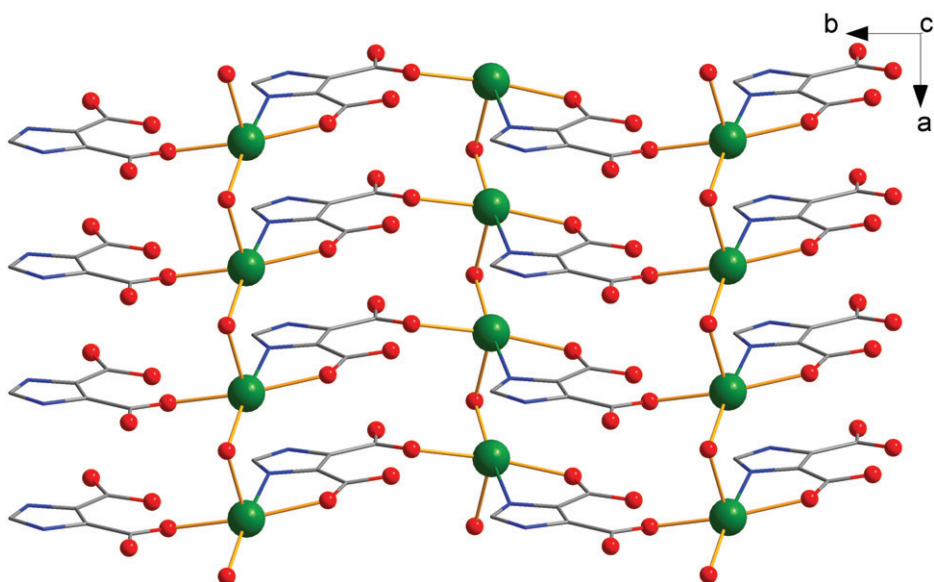
Figure 4.   The 2-D network structure of **2**.

one [Hidc]$^-$. The sodium ion adopts a square-pyramidal coordination geometry, coordinated to two water molecules, two oxygen atoms, and one nitrogen atom from [Hidc]$^-$ (Na–O 2.339(1) Å, 2.354(1) Å, 2.365(2) Å, 2.383(1) Å; Na–N: 2.505(1) Å). The bond length and angle values are comparable to those observed for other sodium carboxylate complexes [7, 11, 12]. The idc ligands are tridentate connecting with two sodium ions.

In the crystal structure of **2**, the sodium ions are connected into chains [Na(OH$_2$)]$^+$ along the *a*-axis by sharing a water molecule between neighboring cations. The tridentate [Hidc]$^-$ bridge [Na(OH$_2$)]$^+$ chains into a 2-D network (figure 4). Thus, each Na ion bonds to four Na ions through two water molecules and two [Hidc]$^-$. These layers are held together by hydrogen-bonding interactions involving water, imidazole, and carboxylate (O(1w)···O(1) = 2.818 Å; N(1)···O(4) = 2.757 Å) in the structure to yield a tightly held 3-D framework solid. An extended 1-D channel system with an elliptically-shaped pore of 10-membered or 6-membered rings can be discerned as shown in figure S8.

3.1.3. Related structures.   Although there are a number of sodium coordination polymers reported in the literature [7, 8, 12], only a few consist of aza-aromatic carboxylate ligands (table 3). Because of their flexible coordination, the ligands can bind to sodium ions to form coordination polymers of different dimensionalities and framework structures. Main group elements such as alkali cations have flexible coordination modes because of electrostatic interactions with organic linkers [4]. However, sodium ions demonstrate rather rigid coordination modes with these aza-aromatic carboxylates as the common coordination number of sodium in these compounds is six, even though sodium ions in **2** have coordination number five.

Table 3.   List of sodium coordination polymers based aza-aromatic carboxylate ligands.

Formula	Dimensional	CN	COO group	Ref.
[Na(3-pdc)]	1-D	6	Tetradentate	[7c]
[Na(Hidc)(H$_2$idc)(H$_2$O)$_2$] (**1**)	1-D	6	Monodentate	[1]
[Na(Hidc)(H$_2$O)] (**2**)	2-D	5	Tridentate	[2]
[Na$_2$(apzc)$_2$(H$_2$O)$_3$]	2-D	6	Bidentate	[7d]
[Na$_2$(3,5-pdc)(H$_2$O)$_4$]	3-D	6	Bidentate	[7e]
[Na(H$_2$pimdc)(H$_2$O)] · 0.5H$_2$O	3-D	6	Tridentate	[8]

Most six-coordinate sodium polyhedra are distorted octahedral. However, the {NaO$_6$}/ {NaO$_5$N} polyhedra in [Na(3-pdc)] are highly distorted and irregular [7c]. The idc in **1** and **2** shows flexible coordination. In **1**, idc is monodentate binding to only one sodium ion, while in **2** idc is tridentate binding to three sodium ions. This can be attributed to the different pH of the reaction mixtures. At lower pH, the −COO$^-$ tends to be protonated, limiting its interaction with metal ions, while at higher pH, carboxylate is not protonated and forms bonds with metal ions. Thus, a change of the reaction pH can lead to the formation of different MOFs.

3.2. *Thermogravimetric analyses*

To study the thermal stability, thermogravimetric analysis was performed on **1** and **2** (figure S9). A crystalline sample of **1** was heated from 30°C to 800°C in air at 10°C min^{-1}. An initial weight loss of 9.3% at 120–200°C was observed for **1**, attributed to loss of two water molecules (Calcd 9.74%). Weight loss of 77.3% (250–800°C, Calcd 81.6%) is attributed to decomposition of idc. Compound **2** shows similar behavior with a weight loss of approximately 9.2% at 90–150°C from loss of one water molecule (Calcd 9.18%) and a weight loss of 62.7% (250–800°C, Calcd 63.8%) corresponding to decomposition of idc.

4. Conclusion

Using idc as ligand, we have synthesized two new sodium coordination polymers with 3-D framework structures formed through hydrogen bonds and coordination bonds. Channel systems with small pores are formed in the 3-D structures of the hydrogen-bonded frameworks. Compound **1** shows a 1-D coordination network while **2** is a 2-D coordination network. The idc shows different coordination modes in these two compounds. Both compounds contain inorganic chains formed by sodium ions and coordinated water.

Supplementary material

Further details on the crystal structure investigations of **1** and **2** can be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2

1EZ, UK [Telephone: 44 -(0)1223-762-910, Fax: 44-(0)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit], on quoting the depository number CCDC: 865293 and 865294.

Acknowledgments

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