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A Heterobimetallic 2-D Coordination Polymer $[Na_2(Cu_2I_2(2pyCOO)_4)(H_2O)_4]_n$ ($2pyCOO^-$=picolinate) within a 3-D Supramolecular Architecture

Anis A. Kamari, Rosenani A. Haque and Mohd R. Razali *

School of Chemical Sciences, Universiti Sains Malaysia, Penang 11800, Malaysia;
anis.asila@gmail.com (A.A.K.); rose@usm.my (R.A.H.)
* Correspondence: mohd.rizal@usm.my

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Abstract: A heterobimetallic 2-D coordination polymer, $[Na_2(Cu_2I_2(2pyCOO)_4)(H_2O)_4]_n$ (**1**) (2pyCOO=picolinate) was synthesized and characterized. The complex was also structurally characterized using single X-ray diffraction studies that revealed the complex **1** having a vertex symbol of 4.8^2 which corresponds to *fes* topology. Together with hydrogen bonds and interdigitating π···π interactions, these thus facilitate the formation of 3-D supramolecular network. The nitrogen gas absorption amount of **1** at 77 K shows a small volume of N_2 sorption isotherm with a small Langmuir and a Brunauer-Emmett-Teller (BET) surface area indicating that the heterobimetallic 3-D supramolecular of **1** exhibits a very weak ability of adsorbing gas.

Keywords: 2-D coordination polymer; interdigitating stacking; *fes* topology; gas sorption

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1. Introduction

Coordination polymers have attracted wide interest owing to their potential application in numerous areas, especially in sensors [1], magnetism [2], and gas storage [3,4]. Other than that, the interest lies on the structural studies of the coordination polymers which reveal the formation of fascinating interpenetration networks and topologies [5,6]. Reaction conditions and selectivity of the ligands are crucial to obtain desired complexes. Carboxylic acid ligands are widely used in the formation of coordination polymers, owing to their tendency as bridging ligands [7].

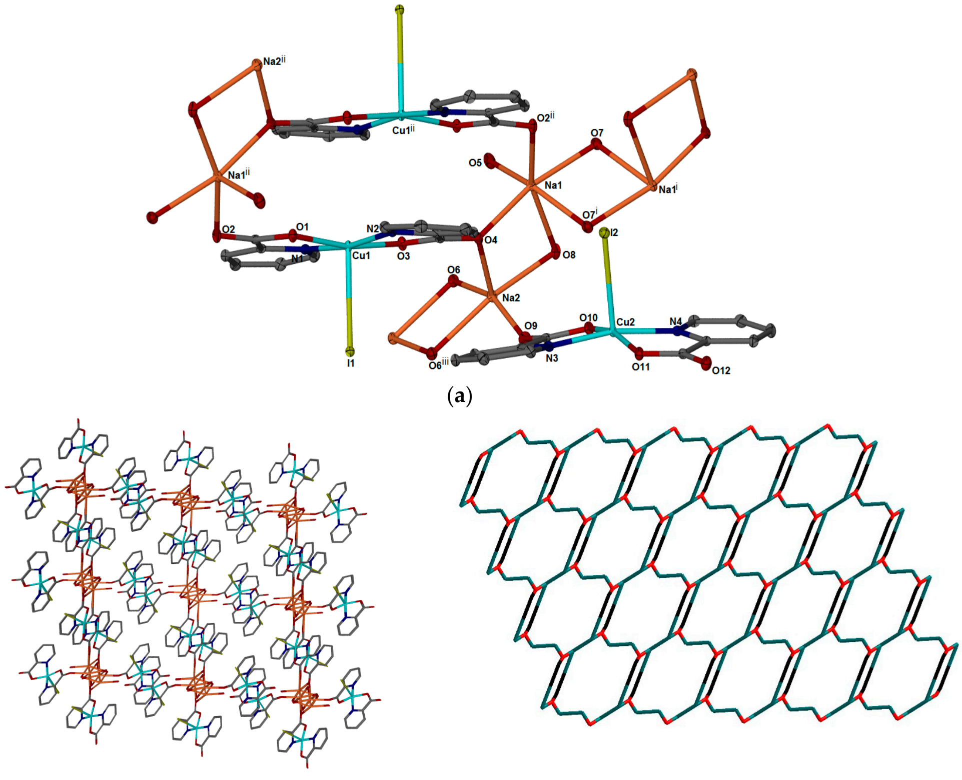
By utilizing the coordination and hydrogen bonds as driving forces, a large number of supramolecular crystalline frameworks, including hydrogen bonding-stabilized 3-D supramolecular frameworks, have been constructed [8]. The formation and stability of these supramolecular compounds however largely depend on the type of interactions, magnitude, and directions of intra/intermolecular forces during self-assembly. Single crystal X-ray analysis gives information about the interactions in packing of the molecules in the solid state, which is crucial for us to understand the formation and stability of 3-D supramolecular network. Although supramolecular hydrogen bonding interactions are frequently used in the creation of frameworks and host guest assemblies [9], examples of systems that exploit aromatics interactions are relatively limited [10]. These supramolecular framework structures are a pretty system due to their flexible conformations as a promising material for molecular recognition and sensors [11–13].

Herein, a new 2-D polymeric structure of heterobimetallic compound, $[Na_2(Cu_2I_2(2pyCOO)_4)(H_2O)_4]_n$ (**1**) (2pyCOO = picolinate) is reported. Adjacent 2-D sheets are further assembled via intermolecular hydrogen bonding and interdigitating π-π interactions to facilitate a 3-D supramolecular architecture.

2. Results and Discussion

As continuation to our previous work [14,15], an attempt to synthesize copper(I) complexes containing picolinate, $2pyCOO^-$ was unsuccessful, instead the formation of copper(II) species in a heterobimetallic 2-D coordination polymer namely, $[Na_2(Cu_2I_2(2pyCOO)_4)(H_2O)_4]_n$ (**1**) was observed. The oxidation of copper(I) to copper(II) is due to the exposure to air during experimental work. A similar reaction conducted in an inert atmosphere resulting neither crystal nor precipitate after two months indicated that the copper(I) complex containing of 2pyCOOH is not favored.

Complex **1** crystallises in triclinic space group *P*-1 with two copper(II) ions, two sodium(I) ions, four $2pyCOO^-$anions, two iodide anions, and four water molecules contained in the asymmetric unit (Figure 1(a)). Each of copper(II) ions is five coordinated forming a square pyramidal geometry with the apical axis is occupied by iodide ion with the length of 2.9588(3) Å and 2.9288(3) Å, respectively (Table 1). One of the sodium(I) ions, Na2 is also in square pyramidal geometry surrounded by three bridging water molecules and two oxygen atoms of two $2pyCOO^-$. The other sodium(I) ion, Na1 displaying an octahedral geometry with the coordination sphere is occupied by three bridging water molecules, one terminal water molecule and two oxygen atoms of two $2pyCOO^-$. Overall, three of the four $2pyCOO^-$ anions display a μ_2-k^2(N,O)Cu:k^1(O')Na bridging mode while the remaining displays a k^2(N,O)Cu chelating mode. An extended structure of this complex can be viewed as a 2D structure (Figure 1(b)). If each of the sodium(I) and Cu1 are treated as connecting nodes along with three μ_2-$2pyCOO^-$and three bridging water molecules treated as linkers, the coordination polymer of **1** can be described as a 2-D network with the vertex symbol of 4.8^2 which corresponds to *fes* topology (Figure 1(c)) [16].



(**a**)

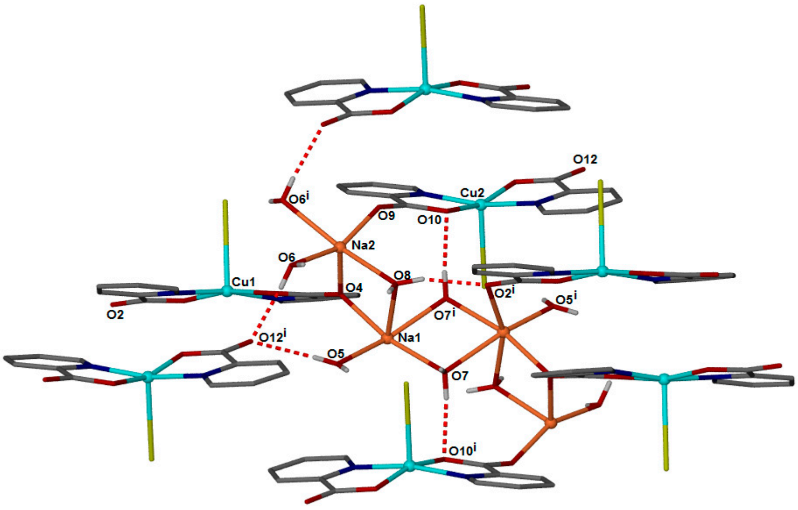
(**b**) (**c**)

Figure 1. (**a**) Extended asymmetric unit of $[Na_2(Cu_2I_2(2pyCOO)_4)(H_2O)_4]_n$ (**1**) with the ellipsoids shown at 50% probability. Hydrogen atoms omitted for clarity. Symmetry elements used: *i* = 2 − *x*, 2 − *y*, −*z*; *ii* = 3 − *x*, 1 − *y*, −*z*; *iii* = 2 − *x*, 1 − *y*, −*z*. (**b**) A 2D sheet of **1**, viewed along the *b* axis, which can be simplified as (**c**) *fes* topology based on three connected nodes.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

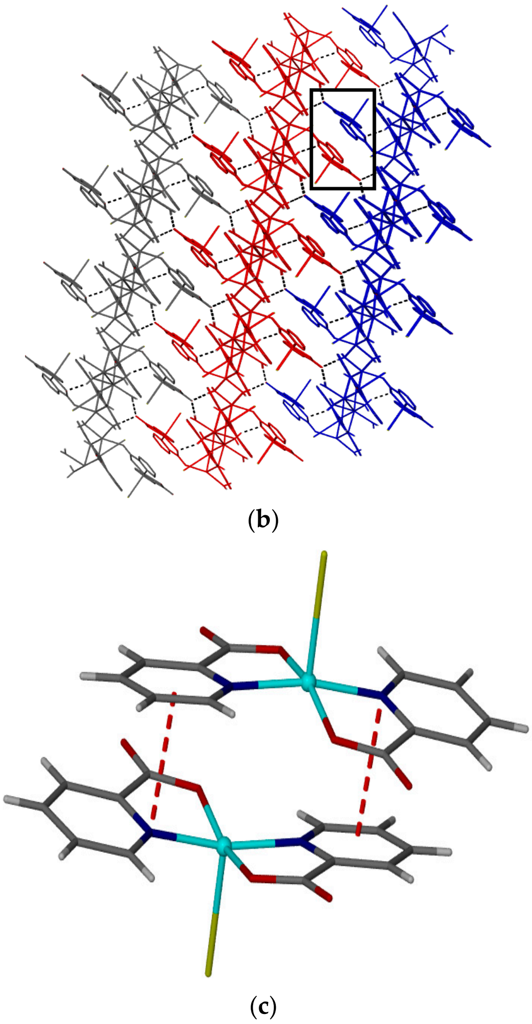
Cu1-I1	2.9588(3)	Cu1-N2	1.9844(15)
Cu1-I2	2.9288(3)	Cu2-O10	1.9636(12)
Cu1-O1	1.9500(13)	Cu2-O11	1.9564(12)
Cu1-O3	1.9453(13)	Cu2-N3	1.9741(15)
Cu1-N1	1.9704(15)	Cu2-N4	1.9693(15)
Na1···Na2	3.4098(10)	Na1-O8	2.5508(16)
Na1···Na1^{i}	3.5958(14)	Na2-O4	2.2881(15)
Na1-O2^{ii}	2.4111(15)	Na2-O6	2.3186(15)
Na1-O4	2.2958(14)	Na2-O6^{i}	2.4114(16)
Na1-O5	2.3347(16)	Na2-O9^{iii}	2.2638(15)
Na1-O7	2.3656(15)	Na2-O8	2.3921(16)
Na1-O7^{i}	2.4351(15)		

The stabilization of a title compound is supported by the supramolecular interactions defined as hydrogen bonds and π-π interactions [17,18]. The intermolecular and intramolecular hydrogen bonds are observed as all water molecules in compound **1** behaving as hydrogen bond donors to the nearest oxygen atoms. However, the most significant hydrogen bond interaction is the intermolecular hydrogen bonds between 2D-sheets that observed between O5···H with O12^{i} and O6···H with O12^{i} (and their symmetry equivalent elements), that facilitate the formation of 3-D net. The separation between O5···O12^{i} and O6···O12^{i} was determined to be 2.817(2) Å and 2.852(2) Å, respectively (Table 2). It is worth noting that the O12 is carboxylate oxygen contained in one of the 2pyCOO^{-} that uncoordinated with any metal ions. In this case, the O12 behaving as bifurcated hydrogen bonds acceptor (Figure 2(a)). The adjacent 2-D sheet are stacked parallel to each other along the *c* axis through the aforementioned hydrogen bonds as well as the π-π interactions between the [CuI(2pyCOO)$_2$]$^{-}$ moieties. The separation between the two centroids of these moieties being 3.543(5) Å (Figure 2(b),(c)), thus enhance the stability of the 3-D net.



(**a**)

Figure 2. *Cont.*



(**b**)

(**c**)

Figure 2. (**a**) Intramolecualr and intermolecular hydrogen bonding interactions in **1**. Symmetry element used: $i = x, y - 1, 1 + z$. (**b**) Interdigitating π-π interactions between adjacent 2-D sheets along the *c* axis, facilitate the formation of 3-D supramolecular network. The three independent 2-D sheets are represented in three different colors for clarity. Image in the square has been enlarge to (**c**) that shows the π-π interactions between the $[CuI(2pyCOO)_2]^-$ moieties.

Table 2. Details of The Hydrogen Bonding Lengths [Å] and Angles [°] In **1**.

D-H···A	D-H	H···A	D···A	D-H···A
O5-HW···O12^{i}	0.865(10)	1.986(10)	2.8504(19)	177(3)
O6-HW···O12^{i}	0.871(10)	1.952(11)	2.8169(19)	172(3)
O7-HW···O10^{i}	0.875(10)	2.112(17)	2.9317(18)	156(3)
O8-HW···O2^{i}	0.873(10)	0.873(10)	2.8286(18)	161(3)

The pore aperture defined by four dimeric sodium(I) centre units in one self-assembled macrocycle a square-like conformation, is calculated to be ca. 15.486 Å (L_1) X 14.751 Å (L_2) (Figure 3). The dimensionality of each square grid is identical. Some examples of the 3-D supramolecular networks having gas storage property are also known before [19]. The nitrogen gas absorption amount of crystals **1** at 77 K shows a small amount of N_2 sorption isotherm with a Langmuir surface area of 9.9945 $m^2 \cdot g^{-1}$ and a Brunauer-Emmett-Teller (BET) surface area of 7.8557 $m^2 \cdot g^{-1}$. These results thus show that the heterobimetallic 3-D supramolecular network of **1** exhibits a very weak ability of adsorbing gas.

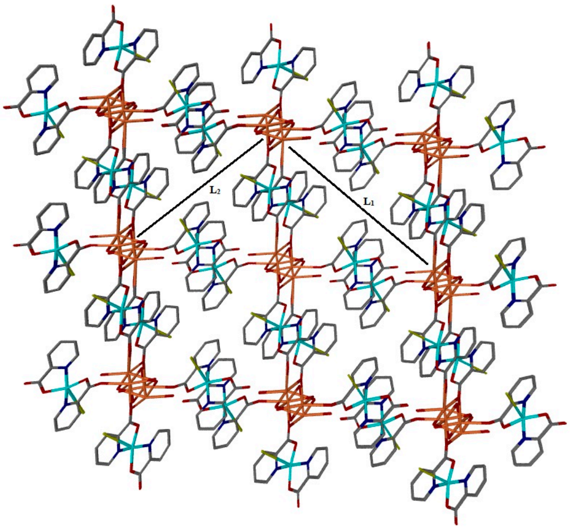


Figure 3. Extended structure of **1** showing a square-grid macrocycle along the *b* axis.

3. Materials and Methods

Reagents and solvents were obtained from commercial sources and used without any further purification. The melting point was tested using a Stuart Scientific SMP-1 (Staffordshire, UK) instrument. Elemental analysis was carried out on a Perkin Elmer Series II, 2400 microanalyzer (Waltham, MA, USA). The FT-IR spectra were recorded in potassium bromide disks using a Perkin Elmer 2000 system spectrometer in the range of 4000 cm^{-1} to 400 cm^{-1}. The test of the adsorption property carried out on an ASAP 2020 Chemi equipment of Micromeritics. The BET surface area was measured by the Langmuir method.

Copper(I) iodide (0.20 g, 1.10 mmol) dissolved in acetonitrile (10 mL) was added to ascorbic acid (0.08 g, 0.40 mmol). The mixture was stirred until a clear solution was obtained. To the clear solution, NaI was added until it was saturated. The excess NaI was then removed by filtration. The reaction mixture was refluxed for 1 hour which was then picolinic acid (0.13 g, 1.00 mmol) dissolved in acetonitrile (5 mL) was slowly added into the reaction mixture. The solution mixture left to reflux for 15 minutes, filtered and the clear filtrate was left for slow evaporation. Brown crystals of **1** obtained within a week. Yield (0.11 g, 72%). M.P = 192 °C–196 °C. IR (cm^{-1}) = 3415 (s, v(O-H)), 1600 (m, v(C=O)), 1435 (m, v(C=N)), 1366 (m, v(C-O)), 1288 (m, v(C-N)), 996 (w, v(C-H)). Calculated for $C_{24}H_{24}Cu_2I_2N_4Na_2O_{12}$ (Mw = 997.35 $g\cdot mol^{-1}$): C 29.20, H 2.45, N 5.67; found: C 29.15, H 2.52, N 5.73.

Single Crystal X-Ray Structure

Single crystal X-ray diffraction data for **1** was collected on APEXII Duo CCD area-detector diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å) at 173 K. Data collection and reduction were performed using the APEX2 and SAINT software. The SADABS software was used for absorption correction. Solution was obtained by direct methods using SHELXS-97 [20] followed by successive refinements using full matrix least squares method against F^2 using SHELXL-2014/7 [21]. The program X-Seed was used as a graphical SHELXL interface [22]. Details of the X-ray crystal data structure determination and refinement are provided in Table 3. CCDC No. 1487739 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www/ccdc/cam/ac/uk/conts/retriving.html.

Table 3. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{24}H_{24}Cu_2I_2N_4Na_2O_{12}$
Formula weight	987.33
Crystal system	Triclinic
Space group	*P*-1
a/Å	11.5781(6)
b/Å	12.1044(7)
c/Å	13.4651(7)
α/deg	65.4000(10)
β/deg	71.7270(10)
γ/deg	68.1360(10)
V/Å^3	1564.03(15)
Z	2
Density calcd/(g/cm^3)	2.097
μ/mm^{-1}	3.428
F(000)	956
T/K	173(2)
Θ range (deg)	2.25–30.35
reflns collected	60617
reflns unique	9316
reflns obs [$I > 2\sigma(I)$]	8842
R_{int}	0.0417
R_1 (obs, all)	0.0211
wR_2 (obs, all)	0.0508
GooF	1.112

4. Conclusions

A new heterobimetallic 2-D coordination polymer, $[Na_2(Cu_2I_2(2pyCOO)_4)(H_2O)_4]_n$ (**1**) has been synthesized and fully characterized. Structural analysis has revealed that the complex is a 2-D coordination polymer that having a vertex symbol of 4.8^2 which corresponds to *fes* topology. Supramolecular interactions within the adjacent 2-D sheets have facilitates the formation of 3-D network with the large pore aperture. Complex **1** shows a small amount of N_2 sorption isotherm with a Langmuir surface area of 9.9945 m^2·g^{-1} and a Brunauer-Emmett-Teller (BET) surface area of 7.8557 m^2·g^{-1}.

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Author Contributions: Anis A. Kamari performed the experiments and analyzed the data. Rosenani A. Haque and Mohd. R. Razali conceived, designed the experiments and wrote the paper.

Conflicts of Interest: The authors declare no competing financial interests.

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