

Susanta Hazra and Anirban Karmakar*

Synthesis, molecular and supramolecular structure of a new dinuclear aluminium(III) complex derived from 3-aminopyrazine-2-carboxylic acid

Abstract: Solvothermal reaction of aluminum(III) nitrate nonahydrate with 3-aminopyrazine-2-carboxylic acid (HL) gave rise to a bis(μ_2 -hydroxo)-tetrakis(3-aminopyrazine-2-carboxylato)-dialuminium(III) complex $[\text{Al}(\text{L})_2(\text{OH})_2]$ (**1**) ($\text{L} = 3\text{-aminopyrazine-2-carboxylate}$). Crystal structure analysis reveals that each hexacoordinated Al(III) centre adopts a distorted octahedral geometry occupied by two $\text{O}_{\text{carboxylate}}$, two $\text{N}_{\text{pyrazine}}$ and two $\text{O}_{\text{hydroxo}}$ atoms. The L^- ligand binds the metal cation by means of one pyrazine N-atom and carboxylate O-atoms *via* chelating fashion. Two hydroxo groups bridge between two aluminium(III) centres, assisting to construct a dinuclear structure. In the crystal lattice of **1** two symmetry non-equivalent dinuclear complexes are present. A 3D supramolecular associate in the crystal lattice of **1** has been stabilized by a number of non-covalent H-bonding interactions. Topology of the hydrogen bonded network has been also analyzed.

Keywords: 3-aminopyrazine-2-carboxylic acid; crystal structure analysis; dinuclear aluminium(III) complex; topological analysis.

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*Corresponding author: Anirban Karmakar, Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal, E-mail: anirbanchem@gmail.com

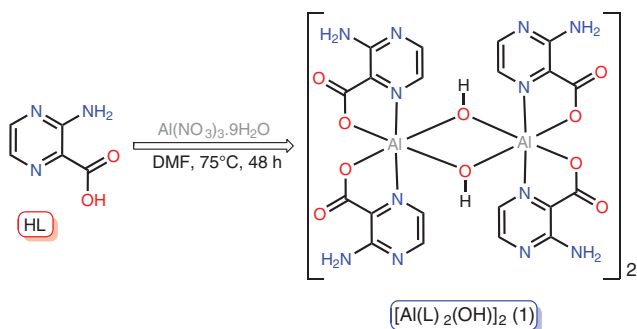
Susanta Hazra: Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal; and Department of Chemistry, University of Calcutta, 92 Acharya Prafulla Chandra Road, Kolkata 700 009, India

Introduction

The *N,O*-donor organic pyrazinecarboxylate ligands have been widely studied owing to their potential applications in constructing a variety of complexes and coordination polymers in recent years [1, 2]. These complexes not only show interesting molecular topologies, but also have potential applications in various areas such as functional materials [3, 4], catalysis [5], nonlinear optics [6–8], molecular magnetic materials [9, 10], and gas storage [11–13]. These *N,O*-atoms can act as either bonding atoms to central metals to form coordination complexes or construct supramolecular architectures by hydrogen bonding interactions [14–16].

Aluminium(III) usually forms very stable complexes with *O*-donor ligands, e.g., carboxylate and alcoholic hydroxyl which can be coordinated to Al(III) via deprotonation of the hydroxyl-group even in the acidic pH-range [17–19]. A remarkable progress has been made in recent years in the development of metal–organic networks by using aluminium(III) ions and carboxylic acid ligands as building blocks [20–23]. Few Al(III)-based metal organic frameworks with carboxylate linkers, such as those derived from terephthalic acid [24, 25], 2-aminoterephthalic acid [26], benzene tricarboxylic acid [27, 28] and benzene tetracarboxylic acid [29, 30], have been reported. Hydroxo [31, 32] and methoxy [33] bridged dinuclear aluminium(III) complexes of Schiff base ligands are also known.

In this context, we have chosen 3-aminopyrazine-2-carboxylic acid (HL) which can be readily deprotonated to produce a multidentate ligand L^- (*O*- or *N*-donor) with versatile metal coordination and hydrogen bonding capabilities [34–38]. Recently, we have studied the complex-forming features of this ligand with different metal ions, such as Zn(II) and Pb(II) [39, 40]. It has also drawn extensive attention for the construction of coordination polymers with attractive architectures [38, 41, 42]. However,



Scheme 1: Chemical diagram of the synthesis of $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**) from HL.

most of the reported works has focused on s-block [34, 35], d-block [36, 37] and f-block [38] metal ions, whereas the corresponding chemistry of the p-block metal ions is still unexplored. Only few Pb(II) and Sn(IV) complexes are known so far [40, 43]. Therefore, synthesizing a new p-block metal complex from 3-aminopyrazine-2-carboxylic acid (HL) is important.

Hence, we reacted 3-aminopyrazine-2-carboxylic acid (HL) with a p-block metal salt aluminum(III) nitrate nonahydrate in solvothermal condition which lead to a new bis(μ_2 -hydroxo)-tetrakis(3-aminopyrazine-2-carboxylato)-dialuminium(III) $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**) (L = 3-aminopyrazine-2-carboxylate, Scheme 1). The crystal structure was established by single crystal X-ray diffraction analysis while the hydrogen bonded network of **1** was subjected to topological analysis. To our knowledge, this is the only example of Al(III) complex with 3-aminopyrazine-2-carboxylic acid (HL) after Pb(II) and Sn(IV) complexes.

Experimental

Materials and physical methods

All the reagents and solvents were purchased from Sigma-Aldrich and Fisher Scientific, respectively and used as received. Elemental (C, H and N) analysis was performed on a Perkin-Elmer 2400 II analyzer. IR spectrum was recorded in the region 400–4000 cm^{-1} on a Perkin-Elmer RXIFT spectrometer with sample as KBr disk.

Synthesis of $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**)

The mixture of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (94 mg, 0.25 mmol) and 3-aminopyrazine-2-carboxylic acid (69.5 mg, 0.5 mmol) was dissolved in 4 mL of DMF. The resulting colorless solution was sealed in an 8 mL glass vessel and heated at 75 °C for 48 h. Subsequent gradual cooling to room temperature (0.2 °C min^{-1}) afforded block-like colorless crystals.

Yield: 61% (based on Al). Anal. Calcd. for $\text{C}_{23}\text{H}_{27}\text{Al}_2\text{N}_5\text{O}_{12}$ ($M = 731.50$): C, 37.76; H, 3.72; N, 24.89; Found: C, 37.35; H, 3.66; N, 25.02. FT-IR (KBr, cm^{-1}): 3396 (bs), 3288 (bs), 1632 (s), 1596 (s), 1541 (s), 1440 (s), 1384 (s), 1361 (m), 1320 (s), 1233 (s), 1191 (m), 1151 (s), 920 (s), 821 (s), 686 (m), 599 (w), 543 (w).

Crystal structure determination

Diffraction data was collected on a Bruker-APEX II SMART CCD diffractometer at 296 K. For data processing and absorption correction the packages SAINT [44] and SADABS [45] were used. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXTL [46] and SHELXL-2014 [47] packages. The hydrogen atoms attached to carbon atoms and to the nitrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation; Uiso(H) were defined as 1.2 Ueq of the parent nitrogen atoms or the carbon atoms for phenyl and methylene residues. Compound **1** contained disordered noncoordinated molecules which could not be modeled reliably. PLATON/SQUEEZE was used to correct the data and potential volumes of 835 \AA^3 was found with 404 electrons per unit cell worth of scattering. The electron counts suggest the presence of ca. one DMF and one H_2O molecules per dinuclear complex. The elemental analysis data also supports that each dinuclear unit contains one of each disordered DMF and H_2O molecules. These disordered solvents were not included in the empirical formula of CIF file. The strategy improved the R1 factor by 41.38%. Using anisotropic treatment for the non-hydrogen atoms and isotropic treatment for the hydrogen atoms, the final refinement converged at the R_1 value ($I > 2\sigma(I)$) 0.0592 after SQUEEZE. The crystallographic data are summarized in Table 1. CCDC 1042324 contains the supplementary crystallographic data of **1** in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Results and discussion

Synthesis and characterization

The reaction of HL with aluminum(III) nitrate nonahydrate under solvothermal reaction condition in dimethylformamide leads to the formation of the bis(μ_2 -hydroxo)-tetrakis(3-aminopyrazine-2-carboxylato)-dialuminium(III) $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**) (L = 3-aminopyrazine-2-carboxylate, scheme 1). The FT-IR spectra of compound **1** shows the expected band, revealing the characteristic asymmetric (1596 cm^{-1}) and symmetric (1384 cm^{-1}) stretching of carboxylic groups. A strong band at 1632 cm^{-1} is due to $\delta(\text{N-H})$ of amine group, whereas the asymmetrical and symmetrical $\nu(\text{N-H})$ of the amine groups appear in the 3396 cm^{-1}

Tab. 1: Crystallographic data for $[\text{Al}(\text{L})_2(\text{OH})_2]$ (**1**).

Formula	$\text{C}_{20}\text{H}_{18}\text{O}_{10}\text{N}_{12}\text{Al}_2$
Formula weight	638.41
Crystal color	Colorless
Crystal system	Tetragonal
Space group	$I\bar{4}c2$
$a=b/\text{\AA}$	18.142(5)
$c/\text{\AA}$	23.840(7)
$\alpha=\beta=\gamma/^\circ$	90
$V/\text{\AA}^3$	7846(5)
Z	8
T/K	296(2)
$2\theta/^\circ$	4.664–52.742
μ (Mo $K\alpha$)/ mm^{-1}	0.128
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.081
$F(000)$	2068
Absorption-correction	multi-scan
Index ranges	$-22 < h < 22$ $-22 < k < 22$ $-29 < l < 29$
Reflections collected	47398
Independent reflections	4023
R_{int}	0.0703
R_1^a/wR_2^b [$I > 2\sigma(I)$]	0.0592/0.1411
R_1^a/wR_2^b [for all F_o^2]	0.1016/0.1611
GOF on F^2	1.025

[48]. This complex was also characterized by X-ray diffraction analysis and elemental analysis.

Crystal structure description

An idealized ball and stick presentation of the bis(μ_2 -hydroxo)-tetrakis(3-aminopyrazine-2-carboxylato)-dialuminium(III) $[\text{Al}(\text{L})_2(\text{OH})_2]$ (**1**) is depicted in Figure 1, while the selected bond lengths and angles are listed in Table 2. Crystal structure of the compound contains two symmetry non-equivalent dihydroxo bridged dinuclear aluminium(III) complexes. Al(III) ions of each dimeric unit are connected by bis- μ_2 -hydroxo bridges and coordinated by two 3-aminopyrazine-2-carboxylate (L^-) ligands. Two dimeric units are stabilized by intra and intermolecular non-covalent H-bonding interactions through carboxylate amine (Figure 1 and Figure S1, Table 3).

The metal centre (Al1 or Al1' and Al2 or Al2'') in **1** adopts a slightly distorted octahedral coordination environment (Figure S2). As shown in Figure S2, two $\text{O}_{\text{carboxylate}}$ atoms (O1 and O1''' for Al1 and O4 and O4'''' for Al2) of two ligands (L^-) and two $\text{O}_{\text{hydroxo}}$ atoms (O3 and O3' for Al1 and O6 and O6'' for Al2) define the O_4 square plane of the aluminium(III) centers.

In the O_4 square plane of the octahedral geometry, Al– $\text{O}_{\text{hydroxo}}$ and Al– $\text{O}_{\text{carboxylate}}$ bond distances (1.852(3)–1.872(3) Å, Table 2) are almost identical within the experimental error while the axial Al– $\text{N}_{\text{pyrazine}}$ bond distances (2.049(3)/2.049(4) Å) are the longest ones.

The *transoid* angles ($\text{O}_{\text{hydroxo}}-\text{Al}-\text{O}_{\text{carboxylate}}$ or $\text{N}_{\text{pyrazine}}-\text{Al}-\text{N}_{\text{pyrazine}}$) are in the range of 164.2(2)–168.83(16)° for Al1 and 164.5(2)–168.40(15)° for Al2 while the *cisoid* angles are in between 77.5(2)–102.5(2)° for Al1 and 76.5(2)–103.5(2)° for Al2, indicating the octahedral coordination environments (Figure S2) around Al1 and Al2 centres are similarly distorted. Distance (Al...Al) and angle ($\angle \text{Al}-\text{O}-\text{Al}$) between metal centres in Al1 unit are somewhat less than those in Al2 unit (Table 2). An idealized ball and stick presentation of a single dinuclear unit of **1** is shown in Figure S3.

As shown in Figures 1 and 2, the crystal lattice of the compound contains a number (three) of intra and intermolecular H-bonding interactions involving carboxylate oxygens (O2, O4 and O5) and amine groups (N3 and N6). Overall a H-bonded 3D network (Figure 2) has been formed due to these H-bonding interactions (Table 3). The three dimensional packing view of **1** is characterized by 1D hexagonal channels along the crystallographic c axis (Figure 2) with approximate dimension of $7 \times 9 \text{ \AA}^2$.

In addition to the intramolecular H-bonding interactions ($\text{N3}-\text{H3A}\cdots\text{O2}$ and $\text{N6}-\text{H6B}\cdots\text{O5}$ in Al1 and Al2 units, respectively, Figures 1 and S1), there is an intermolecular H-bonding interaction where amine moiety act as donors to the carboxylate moiety of vicinal molecules ($\text{N3}-\text{H3B}\cdots\text{O4}$, Figure S1).

These interactions are of variable strength as evidenced by their corresponding H-bond geometric values [$d(\text{D}\cdots\text{A}) = 2.79\text{--}2.93 \text{ \AA}$ and $\angle \text{D}-\text{H}\cdots\text{A} = 128.3\text{--}130.3^\circ$, Table 3] but intramolecular ones ($\text{N3}-\text{H3A}\cdots\text{O2}$ and $\text{N6}-\text{H6B}\cdots\text{O5}$) are slightly stronger (Table 3) than the only intermolecular interaction ($\text{N3}-\text{H3B}\cdots\text{O4}$).

Topological analysis

Topological analysis [49] of the three dimensional hydrogen bonded network of $[\text{Al}(\text{L})_2(\text{OH})_2]$ (**1**) has been carried out. The 3D hydrogen bonded network in **1** can be represented as a 4-connected uninodal net with **dia** topology (Figure 3a) and the point symbol for this net is $\{6^6\}$. In compound **1**, one dinuclear unit being connected with four another dinuclear unit via hydrogen bonding, represents a 4-connected node. This hydrogen bonded network has twofold interpenetration which is shown in Figure 3b.

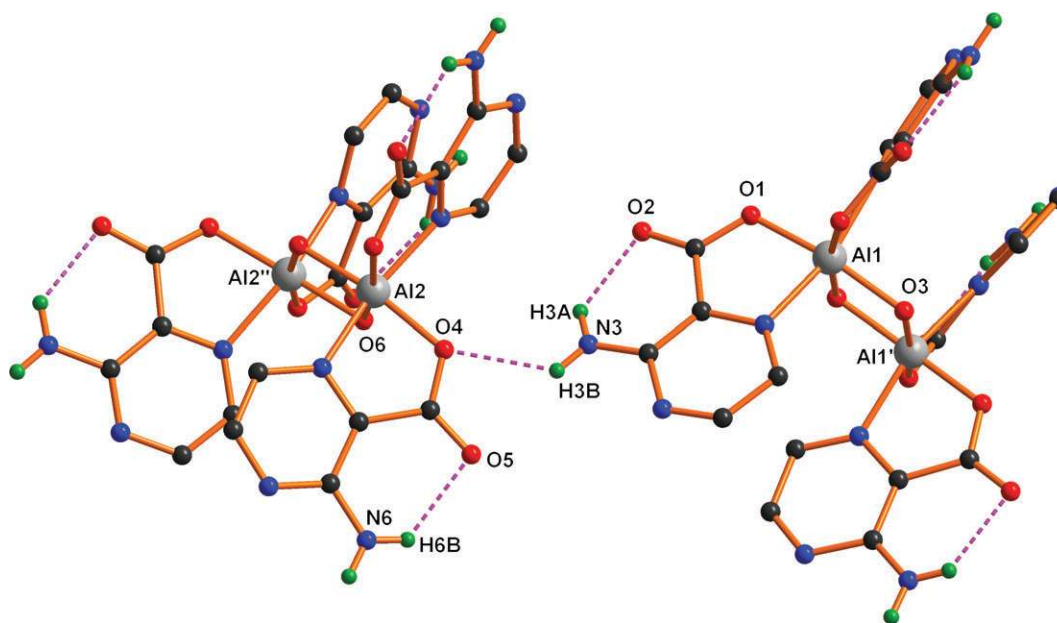


Fig. 1: Ball and stick presentation of the crystal structure of $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**). All H-atoms except those of amine groups are omitted for clarity. Symmetry: i) $1-x, 2-y, z$; ii) $-x, 2-y, z$; iii) $0.5+x, -0.5+y, 2-z$; iv) $1-x, 1-y, 1.5-z$; v) $x, 2-y, -0.5+z$.

Conclusion

We have synthesized a new bis(μ_2 -hydroxo)-tetrakis(3-aminopyrazine-2-carboxylato)-dialuminium(III)

$[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**) by reacting 3-aminopyrazine-2-carboxylic acid (HL) with Al(III) nitrate in *N,N'*-dimethylformamide. To our knowledge, this is the only Al(III) complex and only the second p-block metal complex with 3-aminopyrazine-2-carboxylic acid (HL). Structural analyses indicate that the L⁻ ligand coordinate to the Al(III) centres *via* O-carboxylate and N-pyrazine atoms in a chelating fashion and construct a dihydroxo bridged dinuclear Al(III) complex. In the crystal structure two symmetry non-equivalent dinuclear complexes are present. The dimeric units are stabilized by a number of H-bonding interactions (intra- and intermolecular) which work together to result in a beautiful 3D network. Topological analysis of this 3D hydrogen bonded network has been also carried out, which shows a twofold interpenetrated net with **dia** topology. Further explorations into the uses of this type of linker for the synthesis of the similar type of coordination polymers are ongoing.

Tab. 2: Selected bond lengths (Å) and angles (°) for $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**). Symmetry as in the Figure 1.

Al1–O1	1.859(3)	O1–Al1–O3	168.83(16)
Al1–O3	1.852(3)	N1–Al1–N1'''	164.2(2)
Al1–N1	2.049(4)	N1–Al1–O1	81.65(15)
Al1...Al1'	2.887(4)	N1–Al1–O3	95.37(11)
		N1–Al1–O1'''	88.08(15)
		N1–Al1–O3'	96.89(11)
		O1–Al1–O1'''	98.6(2)
		O1–Al1–O3'	92.06(13)
		O3–Al1–O3'	77.5(2)
		Al1–O3–Al1'	102.5(2)
Al2–O4	1.872(3)	O4–Al2–O6''	168.40(15)
Al2–O6	1.854(3)	N4–Al2–N4'''	164.5(2)
Al2–N4	2.049(3)	N4–Al2–O4	80.76(15)
Al2...Al2''	2.907(4)	N4–Al2–O6	96.48(11)
		N4–Al2–O4'''	89.13(14)
		N4–Al2–O6''	95.60(11)
		O4–Al2–O4'''	98.1(2)
		O4–Al2–O6	92.84(14)
		O6–Al2–O6''	76.5(2)
		Al2–O6–Al2''	103.5(2)

Tab. 3: Geometries [distances in (Å) and angles in (°)] of the H-bonds in the crystal lattice of $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**). Symmetry as in the Figure 1.

D–H...A	D...A	H...A	D–H...A
N3–H3A...O2	2.79	2.15	130.3
N3–H3B...O4	2.93	2.32	128.3
N6–H6B...O5	2.81	2.19	129.1

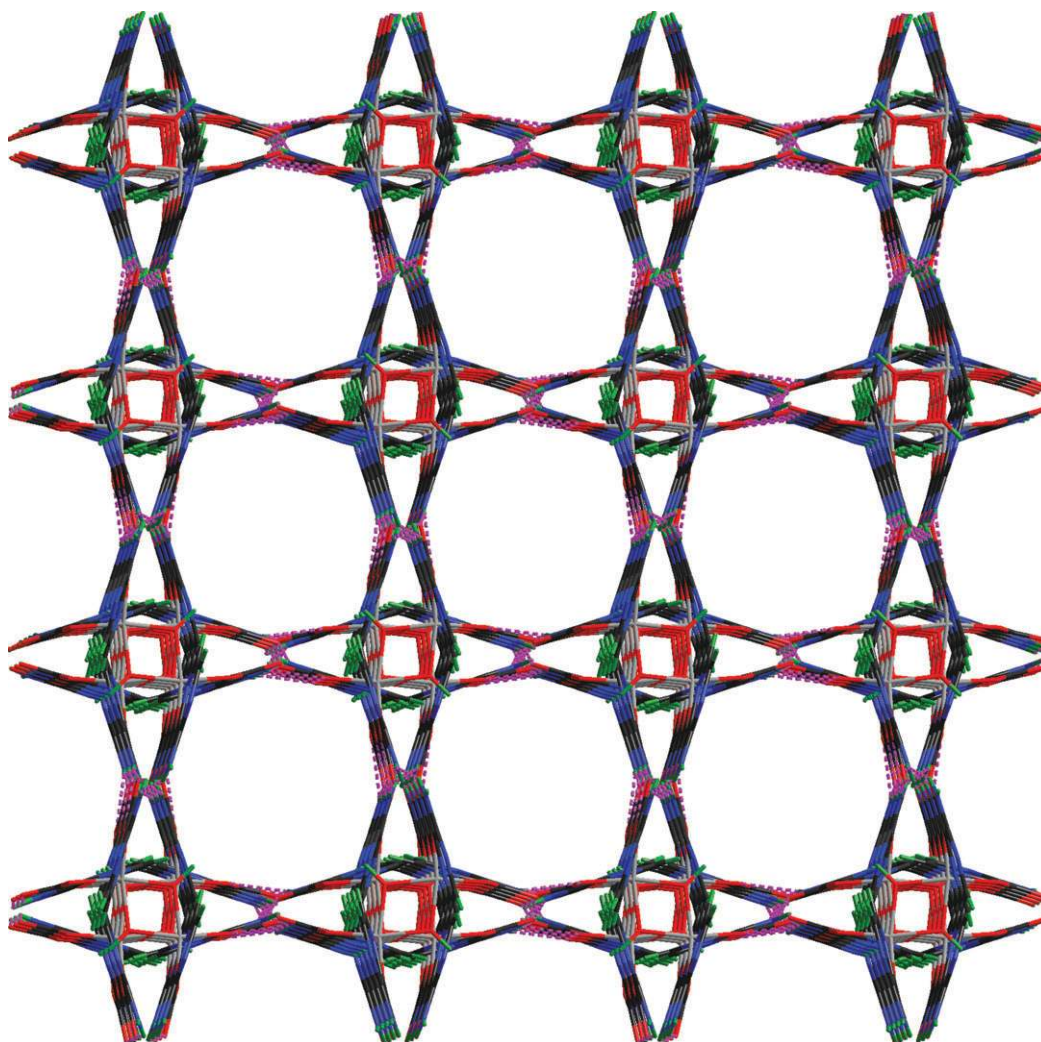


Fig. 2: Idealized wire and stick presentation of the hydrogen bonded 3D network in the crystal lattice of $[\text{Al}(\text{L})_2(\text{OH})]_2$ (**1**).

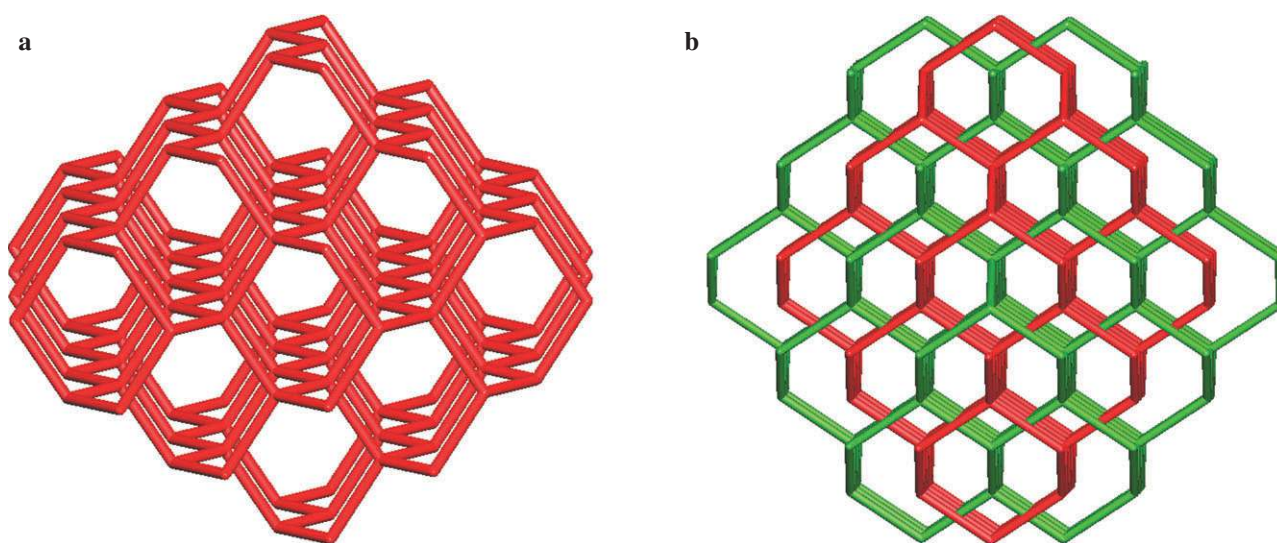


Fig. 3: (a) Node-and-linker-type description of the 3D hydrogen bonded network of **1**. (b) Two-fold interpenetrated network of **1** (one represented in red and the other in green color).

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Graphical Synopsis

Susanta Hazra and Anirban
Karmakar

**Synthesis, molecular and
supramolecular structure of a new
dinuclear aluminium(III) complex
derived from 3-aminopyrazine-
2-carboxylic acid**

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Synopsis: Solvothermal reaction of aluminum(III) nitrate nonahydrate with 3-aminopyrazine-2-carboxylic acid (HL) gave rise to a bis(μ_2 -hydroxo)-tetrakis(3-aminopyrazine-2-carboxylato)-dialuminium(III) complex $[\text{Al}(\text{L})_2(\text{OH})_2]$ (**1**). Crystal structure analysis reveals that each hexacoordinated Al(III) centre adopts a distorted octahedral geometry occupied by two $\text{O}_{\text{carboxylate}}$, two $\text{N}_{\text{pyrazine}}$ and two $\text{O}_{\text{hydroxo}}$ atoms. The hydrogen bonded network of **1** was subjected to topological analysis.

