

Non-covalent O···O interactions among isopolyanions using a *cis*-{MoO₂} moiety by the assistance of N–H···O hydrogen bonds

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Abstract. An inorganic–organic hybrid material, [2-AmpH]₄[Mo₈O₂₆] (**1**) has been isolated by the reaction of Na₂MoO₄·2H₂O with 2-aminopyrimidine (2-Amp) from an acidic aqueous medium. In this low pH synthesis, the organic molecule (2-Amp) gets mono-protonated (2-AmpH⁺) and acts as the cation in stabilizing the octamolybdate anion in **1**. Compound **1** crystallizes in the triclinic space group *P*–*1* with *a* = 9.925(3), *b* = 10.020(3), *c* = 10.414(3) Å, *α* = 88.811(4), *β* = 64.907(4), *γ* = 89.506(4)°, *Z* = 1. An interesting three-dimensional supramolecular structure, having well-defined channels, is formed through N–H···O and C–H···O hydrogen bonds, in which the protonated organic cation plays a significant role. The crystal structure also reveals an unusual cluster–cluster (non-covalent O···O) interaction using *cis*-{MoO₂} moieties of the isopolyanion. N–H···O hydrogen bonds, originated from pyridimidinium cation and isopolyanion, are found to influence to attain such non-covalent O···O interactions among polyoxometalate anions. An interesting helical arrangement, formed from isopolyanion and organic cation, is observed.

Keywords. Octamolybdate anion; low pH synthesis; pyrimidinium cation; three-dimensional supramolecular structure; non-covalent O···O interactions; N–H···O and C–H···O hydrogen bonds; helical feature.

1. Introduction

The rational design of novel polyoxometalate (POM)-based solid state materials fascinates synthetic chemists because of their potential applications in diverse research areas, such as catalysis, medicinal chemistry, and materials science.¹ Since the POM clusters are anionic in nature, simply by changing the counter cation, novel materials can be achieved from an aqueous medium. For example, an isolated derivative of ammonium heptamolybdate [NH₃Pr⁺]₆[Mo₇O₂₄]·3H₂O has been found to have potent anti-tumor activity, and synthesized Keggin derivative K₃[Cr₃O(OOCH)₆(H₂O)₃][SiW₁₂O₄₀]·16H₂O shows applications in adsorption of small alcohols.² One of the applicable strategies to obtain the POM-based hybrid materials is to exploit the organic molecules as cations that can act as structure-directing components.³ POM-based organic–inorganic hybrid solids have been constructed either by electrostatic inter-

actions between inorganic and organic components or by the formation of covalent bonds between organic and inorganic moieties.⁴ The introduced structure-directing organic components are mostly organic amines that can easily act as cations (by protonation of the amine groups) for charge compensation and hence stabilize the POM cluster through supramolecular interactions.⁵ Previously reported pyridine ‘N’ ligands based POMs were mostly synthesized by hydrothermal techniques.⁶ In the present study, we have introduced 2-aminopyrimidine as an organic component which not only acts as the cation (on protonation) to stabilize an isopolyanion but also plays a significant role in assembling the isopolyanions (POM) leading to a three-dimensional supramolecular arrangement offering N–H···O and C–H···O hydrogen bonds. We have also observed non-covalent O···O interactions among the POM anions using a *cis*-{MoO₂} moiety. The non-covalent O···O interactions are well-established in the literature including their theoretical aspects. There are reports on O···O contacts that are a consequence of the N···O contacts in aromatic nitro derivatives.⁷ O···O

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non-covalent interactions are also known to be responsible for the sulfate anion helices.⁸ However, inter-POM cluster O...O contacts were not surveyed prior to this work.⁹ We describe here a new type of three-dimensional supramolecular structure of an organic–inorganic hybrid compound [2-AmpH]₄[Mo₈O₂₆] (**1**) emphasizing the O...O interactions among POM anions and stress the role of N–H...O hydrogen bonds. We have also demonstrated the helical features, observed in the relevant crystal structure.

2. Experimental

2.1 Synthesis of [2-AmpH]₄[Mo₈O₂₆] (**1**)

Sodium molybdate dihydrate (1 g, 4.13 mmol) was dissolved in 20 mL of water, in which 10 mL of acetic acid was added. To this, a mixture of 0.5 g zinc(II)nitrate hexahydrate (1.68 mmol) and 0.22 g of 2-aminopyrimidine (2.31 mmol) in 20 mL of acetonitrile was added slowly and its pH was adjusted to 2 by conc. HCl. The final reaction mixture was stirred for 6 h at room temperature. During this time, little turbidity appeared in the reaction mixture, which on heating at around 50–60°C was dissolved and stirring was continued for another 15 h. The clear solution was kept open in beaker at room temperature for 2–3 days, whereby colourless crystals appeared were collected by filtration and washed with cold water and finally dried at room temperature. Yield 0.25 g (31% based on Mo). Anal. Calc. for C₁₆H₂₄Mo₈N₁₂O₂₆: C, 12.25; H, 1.54; N, 10.72%. Found: C, 12.22; H, 1.52; N, 10.85%.

IR (KBr pellet): 3327(s), 3229(s), 3163(s), 3107(m), 1865(s), 1662(m), 1622(s), 1539(s), 1456(s), 1342(s), 1203(s), 1068(s), 945(m), 902(m), 688(m), 501(s) cm⁻¹.

2.2 Physical measurements

All the chemicals were received as reagent grade and used without any further purification. IR spectra were recorded by using KBr pellet on a Jasco-5300 FT-IR spectrophotometer. The elemental analysis data were obtained with Flash 1112 SERIES EA analyzer. Thermogravimetric analysis was carried out on a STA 409 PC analyzer, under the flow of nitrogen gas.

2.3 X-ray crystal structure determination

The crystallographic data for compound **1** has been collected at 293 K on Bruker SMART APEX CCD, area detector system [$\lambda(\text{Mo K}\alpha) = 0.7103 \text{ \AA}$], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 10 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction by SAINTPLUS,¹⁰ absorption correction using an empirical method SADABS,¹¹ structure solution using SHELXS-97,¹² and refined using SHELXL-97.¹³ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the protonated nitrogen were located in the differential Fourier maps and were refined using isotropic thermal parameters. Complete crystallographic data and structural refinement parameter of compound **1** is given in the table 1. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-648194.

3. Results and discussion

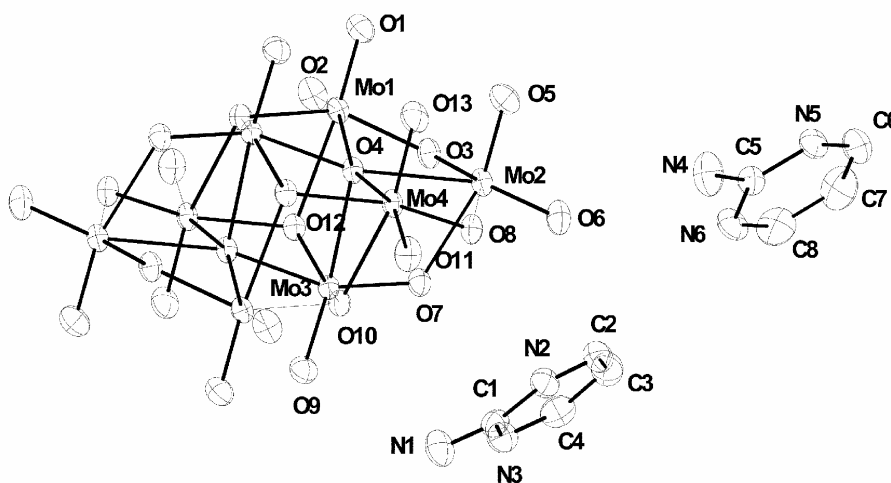
3.1 Synthesis and IR spectroscopy

Generally, inorganic–organic hybrid compounds are obtained through the hydrothermal synthesis route. But we have synthesized the title compound [2-AmpH]₄[Mo₈O₂₆] (**1**) from a simple wet synthesis that includes a low pH aqueous solution of sodium molybdate, acetic acid, zinc nitrate and the organic molecule, 2-aminopyrimidine. The formation of the cluster anion [Mo₈O₂₆]⁴⁻ in the acidic aqueous molybdate solution is not surprising but surprisingly, the isolated compound **1** does not contain zinc ion; instead the cluster anion is stabilized by the 2-aminopyrimidinium cation. The protonation on pyrimidine molecule is expected in this low pH. We could not isolate compound **1**, without using Zn²⁺ ion in the relevant synthesis. In this synthesis, the role of zinc ion is not clear. However, we speculate that, first the cluster anion is stabilized by Zn²⁺ ions in solution state and then during isolation/crystallization the Zn²⁺ ions are replaced by 2-amino-pyrimidinium cations.

The infrared spectrum of compound **1** exhibited characteristic broad feature of $\nu(\text{Mo–O–Mo})$ in the region of 650–700 cm⁻¹. The strong peaks at 902 and 945 cm⁻¹ are attributed to the vibrations of Mo=O bonds. Comparison of the IR spectra of 2-

Table 1. Crystal data and structure refinement for compound **1**.

Compound	1
Empirical formula	C ₁₆ H ₂₄ Mo ₈ N ₁₂ O ₂₆
Formula weight	1567.99
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.925(3)
<i>b</i> (Å)	10.020(3)
<i>c</i> (Å)	10.414(3)
α (degrees)	88.811(4)
β (degrees)	64.907(4)
γ (degrees)	89.506(4)
Volume (Å ³)	937.7(5)
<i>Z</i>	1
ρ (g cm ⁻³)	2.777
μ (mm ⁻¹)	2.696
<i>F</i> (000)	748
Crystal size (mm)	0.44 × 0.32 × 0.22
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0231, <i>wR</i> 2 = 0.0590
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0251, <i>wR</i> 2 = 0.0601

**Figure 1.** Thermal ellipsoid plot of the asymmetric unit of compound [2-AmpH]₄[Mo₈O₂₆] (**1**) with 50% probability. Full molecule of octamolybdate (half of this is in the asymmetric unit) is shown.

aminopyrimidine and compound [2-AmpH]₄[Mo₈O₂₆] (**1**) clearly shows the presence of 2-aminopyrimidinium cation in compound **1** (see figures S7 and S8 in Supplementary materials for the IR spectra of compound [2-AmpH]₄[Mo₈O₂₆] (**1**) and 2-aminopyrimidine respectively).

3.2 Description of the crystal structure

Single-crystal X-ray diffraction analysis of **1** revealed the presence of half of the octamolybdate isopolyan-

ion and two mono-protonated 2-aminopyrimidinium cations in its asymmetric unit. Thus the formula unit contains one full cluster anion and four mono-protonated 2-aminopyrimidinium cations and accordingly it is formulated as [(2-AmpH)₄][Mo₈O₂₆] (**1**). The thermal ellipsoidal representation of compound **1** is shown in figure 1. In the crystal structure, the octamolybdate cluster anion [Mo₈O₂₆]⁴⁻ is composed of eight edge-sharing {MoO₆} octahedra, in which a {Mo₆O₆} ring is capped on opposite faces by two MoO₆ octahedra. Generally in such POM cluster, the

Table 2. The selected bond lengths (Å) and bond angles (degrees) for compound 1.

Mo(1)–O(1)	1.6982(19)	Mo(1)–O(2)	1.7044(17)
Mo(1)–O(3)	1.8945(16)	Mo(1)–O(4)	2.2876(16)
Mo(2)–O(6)	1.6992(17)	Mo(2)–O(5)	1.7047(19)
Mo(2)–O(7)	2.2627(17)	Mo(2)–O(4)	2.5010(16)
Mo(3)–O(9)	1.6867(18)	Mo(3)–O(7)	1.7466(16)
Mo(3)–O(4)	2.3684(17)	Mo(4)–O(11)	1.6976(18)
Mo(4)–O(8)	1.8863(16)	Mo(4)–O(12)	1.9958(16)
C(1)–N(1)	1.307(4)	C(1)–N(2)	1.350(3)
C(1)–N(3)	1.356(3)	C(2)–C(3)	1.391(4)
C(4)–N(3)	1.344(4)	C(5)–N(4)	1.312(3)
C(5)–N(6)	1.338(3)	C(6)–N(5)	1.338(4)
O(1)–Mo(1)–O(2)	105.55(9)	O(1)–Mo(1)–O(4)	94.35(8)
O(3)–Mo(1)–O(4)	78.38(6)	O(6)–Mo(2)–O(5)	105.62(9)
O(6)–Mo(2)–O(8)	104.12(8)	O(5)–Mo(2)–O(8)	98.08(8)
O(8)–Mo(2)–O(4)	73.08(6)	O(3)–Mo(2)–O(4)	72.63(6)
O(9)–Mo(3)–O(10)	101.82(8)	O(7)–Mo(3)–O(10)	97.76(8)
O(11)–Mo(4)–O(8)	101.03(8)	O(13)–Mo(4)–O(8)	101.19(8)
O(11)–Mo(4)–O(12)	99.73(8)	O(13)–Mo(4)–O(12)	97.59(8)
Mo(1)–O(3)–Mo(2)	117.96(8)	Mo(1)–O(4)–Mo(4)	162.95(8)
Mo(1)–O(4)–Mo(3)	97.92(6)	Mo(4)–O(4)–Mo(3)	96.71(6)
N(1)–C(1)–N(2)	119.6(2)	N(1)–C(1)–N(3)	120.3(2)
C(4)–C(3)–C(2)	116.9(3)	N(3)–C(4)–C(3)	119.2(3)
N(4)–C(5)–N(6)	119.6(2)	N(4)–C(5)–N(5)	119.5(2)
N(6)–C(5)–N(5)	120.8(2)	N(5)–C(6)–C(7)	119.3(3)
C(6)–C(7)–C(8)	116.9(3)	N(6)–C(8)–C(7)	124.4(3)
C(2)–N(2)–C(1)	117.4(2)	C(4)–N(3)–C(1)	122.0(2)

{Mo–O} groups can be classified into four categories: 14Mo–Ot (Ot = terminal oxygen) with the bond lengths in the range of 1.687–1.715 Å; six μ_2 -type bridged Mo–Ob (Ob = bridging oxygen) with bond distances in the range of 1.747–2.263 Å; four μ_3 -type Mo–Ob bonds that are in the range of 1.940–2.342 Å and two μ_5 -type of Mo–Ob with the bond lengths in the range of 2.158–2.501 Å. Selected bond lengths and angles for compound 1 are listed in table 2.

Interestingly, in the crystal structure, the *cis*-dioxo group (O1 and O2) of Mo1 (there are two Mo1, because it is a centro-symmetric cluster) of one $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster anion directly interacts to its two adjacent neighbouring $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster anion using same *cis*-{MoO₂} leading to a chain-like arrangement (see figure S1 in Supplementary materials). In the linking region, O1 faces O2 and O2 faces O1 and so on as shown in figure 2. This O---O interaction is characterized by the O/O separation of 3.012 Å, which is in the range of hydrogen bonding distance. The careful examination of packing of the molecules in the crystal structure of compound 1 demonstrates that 2-aminopyrimidinium cation [2-AmpH]⁺ plays a significant role in bringing the isopolyanions closer (in the range of hydrogen bonding

distance) to accomplish O---O non-covalent interaction involving the above mentioned *cis*-{MoO₂} moieties of the adjacent isopolyanions. The role of the 2-aminopyrimidinium cation on isopolyanion --- isopolyanion O---O interaction is schematically presented in scheme 1. This clearly shows how a pyrimidinium cation, using its two arms (X⁺–H and Y–H) separated by two C–N bonds, fetches two POM anions nearer by forming strong hydrogen bonds with the oxo groups that are involved in O---O contact (scheme 1). Figure 2 shows the real situation of the chain-like arrangement that is formed by the assistance of the 2-aminopyrimidinium cation, [2-AmpH]⁺. The linking region involves two [2-AmpH]⁺ cations (from two sides of the chain). It is interesting to note that O1 is hydrogen bonded to the ring nitrogen and O2 is linked to –NH₂ hydrogen by N–H...O hydrogen bonds. The ring nitrogen atom is more basic in nature than the amine group nitrogens, hence it is not surprising that protonation occurs on the ring nitrogen atom only. It is worth mentioning that $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster anion rarely gets protonated and less competes for hydrogen bonding. Bond valence calculation confirmed that, all the molybdenum atoms are in fully oxidized state (+6). In the

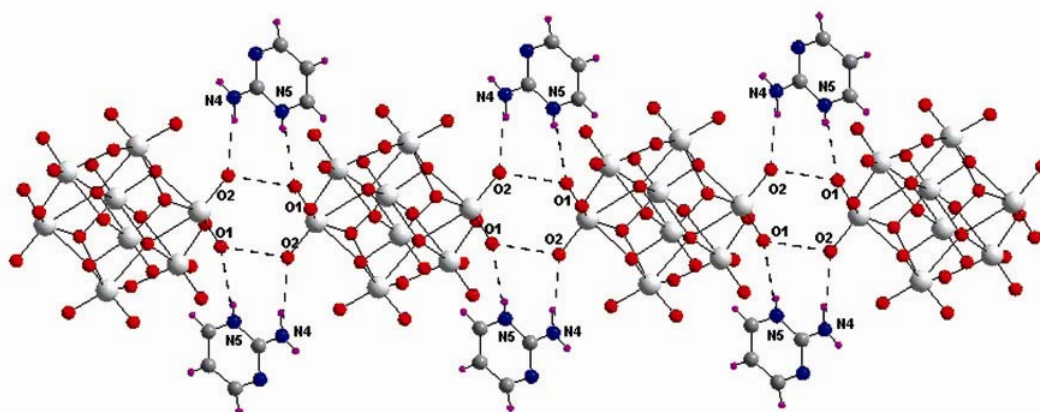
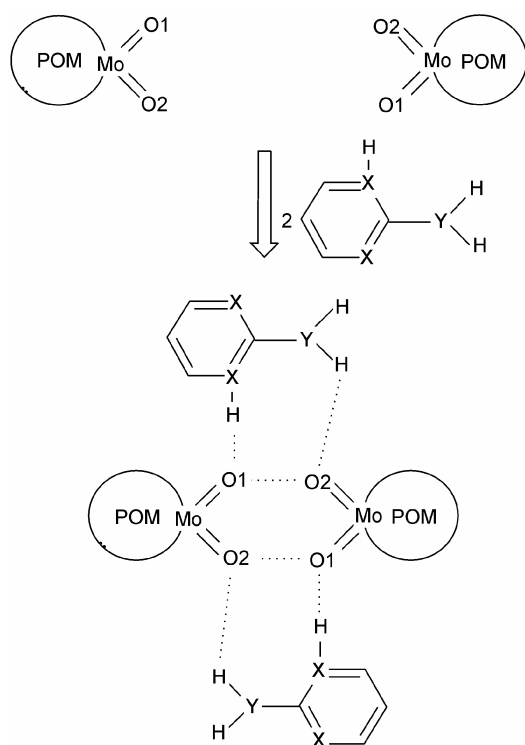


Figure 2. One type of the 2-aminopyrimidinium cations (named as ‘N4N5N6’) assists the formation of the chain by exerting N–H···O hydrogen bonds. Colour code: O, red; Mo, light gray; C, dark gray; H, purple; N, blue; dotted lines represent the hydrogen bonding interactions.



Scheme 1. Depiction of pyrimidinium cations that show the influence on the isopolyanions to come closer and achieve non-covalent O···O interactions among isopolyanions.

present study, the structure-directing role is mainly dominated by the organic cations. In the crystal structure, we have observed that there are two crystallographically independent $[2\text{-AmpyH}]^+$. One of these (can be named as ‘N4N5N6’) is involved in

forming hydrogen bonds (N–H···O) involving O1 and O2 that assist the chain formation through non-covalent O···O contacts (scheme 1 and figure 2). The other crystallographically independent organic cation (named as ‘N1N2N3’) is attached to the cluster anion in unique manner, i.e. both N3 (ring nitrogen) and N1 (from $-\text{NH}_2$ group) of the organic cation undergo hydrogen bonding interactions with O13 terminal oxygen atom of the isopoly anion in a bifurcated fashion (see figure S2a in Supplementary materials). This cation is not involved in forming extended hydrogen bonding structure. The immediate hydrogen bonding surrounding/environment of ‘N4N5N6’ cation is presented in figure S2b in Supplementary materials. Figure 3 shows an interesting hydrogen bonding environment around a $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster anion in the crystal structure. It is remarkable that an isopolyanion interacts with its ten surrounding organic cations (figure 3). Repeating of this motif (figure 3) and the pattern (figure S2b, Supplementary materials) or combination of both result in the formation of a new type of three-dimensional supramolecular structure having well-defined channels (see figure S3 in Supplementary materials). The relevant N–H···O and C–H···O interactions are presented in table 3.

Careful examination of crystal structure of the title compound shows an interesting helical pattern. Both left- and right-handed helices are observed, whereby both handed helices are formed by hydrogen bonding interactions between ‘N4N5N6’ cation and the isopolyanion involving N4–H4A···O2 and N5–H5A···O1 hydrogen bonds (see figure S4 in Supplementary materials). Interestingly, both handed heli-

Table 3. Hydrogen bonding parameters in compound **1**.

D–H	H...A	D...A	<(DHA)	
0.84(5)	2.10(5)	2.917(3)	166(4)	N4-H4B...O6
0.69(4)	2.21(4)	2.852(3)	155(4)	N1-H1B...O13 #1
0.77(3)	2.35(3)	3.021(3)	146(3)	N3-H3A...O13 #1
0.94(4)	2.34(4)	3.180(3)	148(3)	C7-H7...O12 #2
0.93(4)	2.47(4)	3.339(3)	155(3)	C8-H8...O3 #3
0.86(4)	2.07(4)	2.925(3)	170(4)	N4-H4A...O2 #4
0.70(3)	2.20(3)	2.823(3)	149(3)	N5-H5A...O1 #5
0.87(3)	2.20(4)	3.076(4)	176(3)	C6-H6...O9 #6

Symmetric transformations used to generate equivalent atoms: #1 $x, y, -1 + z$; #2 $1 + x, 1 + y, -1 + z$; #3 $1 - x, 1 - y, 1 - z$; #4 $1 + x, y, z$; #5 $1 - x, 1 - y, 2 - z$; #6 $1 + x, 1 + y, z$

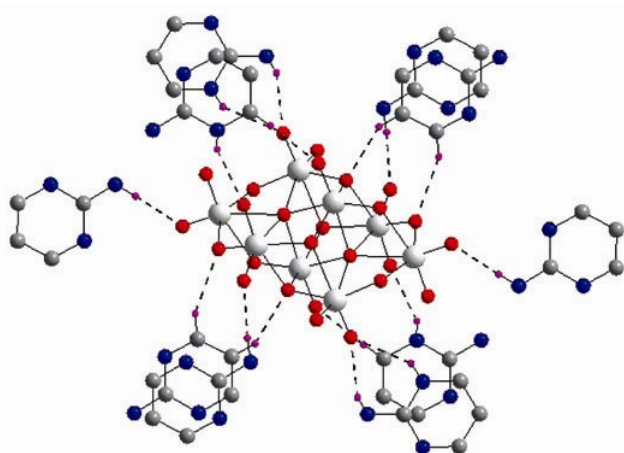


Figure 3. Hydrogen bonding environment around a $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster anion in the crystal structure of $[\text{2-AmpH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**).

ces cross through a common atom (Mo1) resulting in double helical feature (figure S5 in Supplementary materials). These helices run along the chain-like arrangement that is formed by $\text{O}\cdots\text{O}$ contacts (figure 2), thereby the $\text{O}\cdots\text{O}$ interactions are naturally observable in the double helical structure (figure S5 in Supplementary materials). Molecular and supramolecular helical arrangements based on inorganic complex/cluster fragments are well documented in literature.¹⁴

3.3 TGA analysis

The thermogravimetric analysis for compound **1** was performed in flowing nitrogen with a heating rate of 5° per minute in the temperature range from 30 to 1100°C . The TGA curve (see figure S6 in Supplementary materials) shows the first weight loss of

22.38% in the temperature range of $200\text{--}300^\circ\text{C}$. This corresponds to the loss of four 2-aminopyrimidine molecules (calculated 24.26%) per formula unit. Since the compound $[\text{2-AmpH}]_4[\text{Mo}_8\text{O}_{26}]$ (**1**) has four 2-aminopyrimidinium cations per formula unit, the remaining two stages of the TG curve, that occur between 350 and 1100°C , have been assigned due to the decomposition of the POM cluster anion, which we did not attempt to take into account.

4. Conclusion

We have isolated and structurally characterized an inorganic–organic hybrid material **1**. In its crystal structure, novel *cis*-dioxo $\text{O}\cdots\text{O}$ non-covalent interactions have been observed forming a chainlike arrangement. We have argued that one of the crystallographically independent organic cations assist to achieve such $\text{O}\cdots\text{O}$ non-covalent interactions resulting in a supramolecular chain. The combination of $\text{N}\text{--}\text{H}\cdots\text{O}$ and $\text{C}\text{--}\text{H}\cdots\text{O}$ hydrogen bonding interactions that involve both cationic and anionic components leads to a new type of supramolecular three-dimensional structure that has well-defined channels. The present work of supramolecular non-covalent interactions (namely, $\text{O}\cdots\text{O}$, $\text{N}\text{--}\text{H}\cdots\text{O}$ and $\text{C}\text{--}\text{H}\cdots\text{O}$) open a new route for the study of cluster–cluster interaction in polyoxometalate chemistry. Interesting helical arrangement, formed from isopoly-anion and organic cation, has been demonstrated.

Moreover, amino-pyrimidine derivatives are supposed to be biologically important compounds because they occur in nature as components of nucleic acids.¹⁵ Indeed, some amino-pyrimidine compounds have been shown to have potential to act as antifolate drugs.¹⁶ Compound **1** is the unique combination, in which both individual components are

potential candidates for drug activity. Compound **1** is a rare example in which a pyrimidine type molecule interacts with a cluster anion.

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