A gas–liquid interface synthesis in polyoxometalate chemistry: potential bag filter for volatile organic amines

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Abstract. Diffusion of piperidine and pyridine into an acidified aqueous solution of Na_2MoO_4 , yield compounds $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (pip = piperidine = $\text{C}_5\text{H}_{11}\text{N}$) (**1**) and $[(\text{pyH})_4][\text{Mo}_8\text{O}_{26}]$ (py = pyridine = $\text{C}_5\text{H}_5\text{N}$) (**2**), respectively. Compound **1** possesses supramolecular 3-D network and the relevant connectivity pattern generates channels of approximate dimensions of $10.76 \times 11.57 \text{ \AA}^2$, in which the piperidinium cations are located as guests. Multidimensional supramolecular frameworks (3-D in compound **1** and 2-D layer type of network in compound **2**) have been made possible, as the organic cations and polyoxometalate (POM) anions are glued together by significant hydrogen bonding interactions. The synthesis of compounds **1** and **2** provides a unique ‘gas–liquid’ synthetic route in POM chemistry that result in organic–inorganic hybrid materials with structural diversities. This synthetic approach, first time in POM chemistry, can be described as a potential bag filter for volatile organic amines.

Keywords. Volatile organic amines; hydrogen bonding; Lindqvist-type isopolyanions; gas–liquid diffusion.

1. Introduction

Polyoxometalates (POMs) were reported over 200 years ago. However, even today POMs have attracted augmented attention because of their potential applications in interdisciplinary research areas like catalysis, materials science, medicine, biochemical analysis, *etc.*¹ One of the recent advances in POM chemistry is the synthesis of organic-inorganic hybrid materials that are important in the context of their material properties as well as framework-like stable construction having well-defined channels and cavities.^{2,3} An assortment of reviews presented in the recent years give a comprehensive account of a range of aspects including synthetic strategies, types and applications of these polyoxometalate based frameworks.⁴ A review by Ya-Qian Lan *et al.*, presents an important and emerging field in the polyoxometalate based framework materials, that is, polyoxometalates based metal-organic frameworks (MOFs).⁵ These materials have got the advantage of both POMs and the MOFs and hence have got a wide range of applications.⁵ The POM-based hybrid materials are generally synthesized by hydrothermal techniques, that normally use high

temperature.⁶ Simple wet syntheses are also known to generate such framework type hybrid POM compounds⁷ but are very rare. There are reports on photochemical reactions, which result in the isolation of POM-based compounds.^{8a} Conventional synthesis also provides some POM-based organic-inorganic compounds that can be used as photoactive systems.^{8b–g} We introduce a new synthetic strategy/route here, namely, a ‘gas-liquid-interface’ reaction that can simply be described as the diffusion of volatile organic amines (*e.g.*, pyridine and piperidine in the present work) into an acidified aqueous molybdate solution (Schemes 1 and 2). The above said volatile organic amines are released into the environment from various sources including some industrial processes, like, steel manufacture processing of oil shale, coal gasification and incinerators.⁹ These amines have less reports of being carcinogenic to humans, but are highly documented as harmful to various animals. They are proven to be neurotoxic, genotoxic and clastogenic in nature.¹⁰ Volatile organic amines are extreme pollutants and they are the source of dreadful health and environmental problems due to their odorous and toxic characteristics owing to their existence in stored meat, food, dustbins, and sewers.^{11,12} High doses of amines can promote uncontrolled reactions in the human body

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and can initiate acute or delayed toxicities to nervous systems, hematopoietic systems, human skin, urinary systems, respiratory systems thus causing cancer, strokes or other diseases.^{13–16} Volatile amines can form nitrosamines, which are cancer-causing substances,^{17,18} and thus, trapping of volatile organic amines is a critical need in order to monitor the real environment.¹⁹

The basic idea of this synthetic route lies in the fact that an aqueous molybdate solution, on acidification, gives rise to a range of isopolyanions, *e.g.*, $[\text{Mo}_6\text{O}_{19}]^{2-}$, $[\text{Mo}_8\text{O}_{26}]^{4-}$, $[\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{18}]^{8-}$, *etc.*, depending on various parameters such as pH, concentration of the relevant POM solution and temperature.^{1c, 20} Since these polyanions (formed in POM solution) are anionic in nature, they need obligatory cations for their successful isolation. Volatile organic amines having “N” donors can be diffused to such aqueous acidic POM solution, in which organic cations are formed by protonation of respective “N” donor atoms and the relevant POM cluster can be isolated as ion pair compounds, that can be described as inorganic-organic hybrid materials (Schemes 1 and 2). Previously reported organic amine-based POMs were synthesized by hydrothermal techniques.²¹ There are various reports on the compounds containing $[\text{Mo}_8\text{O}_{26}]^{4-}$ and organic cations.²² The compound **1** is also known earlier,²³ but in that report, it is synthesized by using the conventional method. Similarly, various other inorganic-organic hybrids

including diverse polyoxometalates with piperidines²⁴ and pyridines²⁵ have been reported. To the best of our knowledge, this is the first report, where the volatile amines are made to interact with *in situ* formed polyoxometalates, through the vapour-diffusion method, which makes them being used as a potential bag to isolate volatile amines from a mixture of organic amine systems.

Herein, we report two hybrid inorganic-organic compounds $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (**1**) and $[(\text{pyH})_4][\text{Mo}_8\text{O}_{26}]$ (**2**) that are isolated by above-described gas-liquid interface method (see Schemes 1 and 2). More specifically, compounds **1** and **2** were prepared by dissolving Na_2MoO_4 in distilled water in a small beaker, acidified to pH range of 2 - 2.2 with concentrated HCl. This small beaker was then kept in another large sized beaker containing amines (piperidine or pyridine) as shown in Scheme 1, resulting in crystals of **1** and **2** of respective systems. Compounds **1** and **2** were characterized by FT-IR, elemental analysis and unambiguously by single crystal X-ray diffraction techniques. We have described a detailed supramolecular analyses of compounds **1** and **2** in the perspective of relevant hydrogen bonding interactions.

2. Experimental

2.1 Materials and Physical Methods

All the chemicals were received (from Fisher Scientific) as reagent grade and used without any further purification. Elemental analyses were determined by FLASH EA series 1112 CHNS analyzer. Infrared spectra of solid samples were obtained as KBr pellets on a JASCO-5300 FT-IR spectrophotometer.

2.2 Synthesis

2.2a Synthesis of $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (1**)** (*pip* = *piperidine*): Sodium molybdate (5.0 g, 20.67 mmol) was dissolved in 50 mL of water followed by the addition of 10 mL of glacial acetic acid with stirring at room temperature. This reaction mixture was then acidified to pH 2 by the drop-wise addition of conc. HCl, which results in a clear solution. The resultant reaction mixture was filtered into a 100 mL beaker. This 100 mL beaker was kept in a 250 mL beaker containing piperidine. Then the experimental setup was closed by aluminium foil and kept at room temperature. The crystal growth started within two hour duration time. After two days, the crystals were filtered, washed with cold distilled water and dried at room temperature. Yield: 2 g (48.23% based on Mo). IR (KBr pellet) (ν/cm^{-1}): 3533(b), 3136(w), 1606(s), 1454(s), 1377(m), 1267(w), 1174(m), 1024(w), 918(vs), 843(s), 715(s), 524(w), 421(w). Elemental analysis: Calcd. (%). C, 15.01; H, 3.52; N, 3.50. Found (%): C, 14.54; H, 2.95; N 3.32.

Scheme 1. The general schematic synthetic ‘gas-solid-in-interface’ procedure for the compounds **1** and **2**.

Scheme 2. Reaction route for the synthesis of the compounds **1** and **2**.

2.2b Synthesis of $[(pyH)_4][Mo_8O_{26}](2)$ (py = pyridine): Sodium molybdate (3.5 g, 14.46 mmol) was dissolved in 50 mL of water followed by the addition of 10 mL of glacial acetic acid with stirring at room temperature. This reaction mixture was acidified to pH 2.2 by the drop-wise addition of conc. HCl, which results almost in the clear solution. This mixture was filtered into a 100 mL beaker. This beaker was then kept in 250 mL beaker containing pyridine and it was then closed by aluminum foil and kept at room temperature. The crystal growth started within the two hours duration of time. After 24 h, these crystals were filtered, washed with cold distilled water and dried at room temperature. Yield: 2.1 g (77.22% based on Mo). IR (KBr pellet) (ν / cm^{-1}): 3105(b), 1604(s), 1529(s), 1485(s), 1332(m), 1240(m), 1201(s), 1167(s), 1049(m), 947(vs), 682(w). Elemental analysis: Calcd. (%). C, 15.97; H, 1.60; N, 3.73. Found (%): C, 15.38; H, 1.95; N 3.10.

2.3 Crystallography

Single crystals of compounds $[(pipH)_4][Mo_8O_{26}] \cdot 4H_2O$ (**1**) and $[(pyH)_4][Mo_8O_{26}]$ (**2**) were measured at room

temperature on a Bruker SMART APEX CCD area detector system [λ (Mo K α) = 0.7103 Å] graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 8s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was done by SAINTPLUS,²⁶ absorption correction was performed using an empirical method (SADABS) structure solution using SHELXS-97²⁷ and refined using SHELXL-97.²⁸ All non-hydrogen atoms were refined anisotropically. The crystallographic data and structure refinement parameters for compounds **1** and **2** are presented in Table 1.

3. Results and Discussion

3.1 Synthesis

In this work, we have provided a unique synthetic route to generate a polyoxometalate (POM) cluster $[Mo_8O_{26}]^{4-}$. We have called it a ‘gas-liquid-interface’ approach in POM chemistry (Scheme 1). In contrast to normal wet synthesis, the present route is much more

Table 1. Crystal data and structure refinement for compounds **1** and **2**.

	Compound 1	Compound 2
Empirical formula	C ₂₀ H ₅₆ N ₄ O ₃₀ Mo ₈	C ₂₀ H ₂₄ Mo ₈ N ₄ O ₂₆
Formula weight	1600.21	1503.95
Temperature	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n	Triclinic, P -1
Unit cell dimensions		
a	12.8945(6) Å	9.5680(19) Å
b	9.2935(5) Å	9.949(2) Å
c	19.1953(9) Å	10.659(2) Å
α	90°	83.70(3)°
β	92.4670(1)°	76.36(3)°
γ	90°	69.01(3)°
Volume	2298.1(2) Å ³	1014.6(3) Å ³
Z, Calculated density	2, 2.312 Mg/m ³	1, 2.714 Mg/m ³
Absorption coefficient	2.203 mm ⁻¹	2.735 mm ⁻¹
F(000)	1560	716
Crystal size	0.42 x 0.35 x 0.21 mm ³	0.50 x 0.50 x 0.45 mm ³
Theta range for data collection	1.87 to 28.27°	1.97 to 28.69°
Limiting indices	-17 ≤ h ≤ 17, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected/unique	26037 / 5496 [R(int) = 0.0695]	10538 / 4332 [R(int) = 0.0275]
Completeness to theta	28.27 96.4%	28.69 91.1%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	5496 / 0 / 281	4332 / 0 / 264
Goodness-of-fit on F ²	1.107	1.137
Final R indices [I > 2sigma(I)]	R1 = 0.0281, wR2 = 0.0756	R1 = 0.0251, wR2 = 0.0631
R indices (all data)	R1 = 0.0296, wR2 = 0.0767	R1 = 0.0267, wR2 = 0.0642
Largest diff. peak and hole	1.097 and -0.894 e.Å ⁻³	0.556 and -1.127 e.Å ⁻³

easy and clean. Compound $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (**1**), synthesized in the present work in a gas-liquid interface reaction (Schemes 1 and 2), was synthesized earlier in a wet synthesis, by the reaction of sodium molybdate and piperidine in an aqueous solution and concerned single crystals were obtained from CH_3NO_2 solution by recrystallization.^{23a} We feel that this gas-liquid-interface approach is not only simple and clean but also it does not need a recrystallization step. Moreover, we got much more well-resolved structure of compound **1** in the present study compared to that reported earlier.^{23a} We maintained the pH of sodium molybdate solution 2.0 and obtained octamolybdate type POM cluster anion as shown in equation 1. The *in situ* formed octamolybdate $[\text{Mo}_8\text{O}_{26}]^{4-}$ can be isolated as piperidinium salt, $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (**1**), when piperidine was diffused to the concerned solution (Scheme 1).

We have rationalized this gas-liquid interface synthesis approach by using another volatile amine, pyridine and isolated compound $[(\text{pyH})_4][\text{Mo}_8\text{O}_{26}]$ (**2**).

The uniqueness of this gas-liquid synthesis is that, at the experimental condition (an aqueous molybdate solution at a low pH) that we used, formation of several polyoxometalate clusters is possible, such as, hexamolybdate ($[\text{Mo}_6\text{O}_{19}]^{2-}$), heptamolybdate ($[\text{Mo}_7\text{O}_{24}]^{6-}$), octamolybdate ($[\text{Mo}_8\text{O}_{26}]^{4-}$), etc. Even then, this synthetic strategy allows selective isolation of only octamolybdate. We have described below the basic mechanism of this gas-liquid synthesis leading to the formation of compounds **1** and **2**.

Diffusion of volatile organic amines into an aqueous acidic sodium molybdate solution occurs as mass transfer, favoured by chemical (acid-base) reaction. After diffusion occurs into the aqueous solution, the volatile organic amines react with the acidic aqueous sodium molybdate to form non-volatile ionic species consisting of protonated organic amines (for example, in the present case, pyridinium and piperidinium) as cations and octamolybdate as the common anion, which is selectively formed in the present experimental condition. The overall gas-liquid synthetic approach can be described as the mass transfer of volatile organic amine from a concentrated volatile liquid phase to the bulk liquid phase (sodium molybdate aqueous solution at a low pH value), in which the chemical reaction occurs. The following events are expected to occur during synthesis: (1) diffusion of volatile organic amine from a concentrated volatile liquid phase to the gas-liquid interface followed by absorption (dissolution) into the liquid (sodium molybdate aqueous solution), (2) diffusion of the reactants from the gas-liquid interface to the bulk

liquid phase, (3) reaction between the dissolved volatile amine and the liquid reactant in the liquid phase occurs simultaneously with mass transfer, and (4) diffusion of the reaction products into the bulk liquid phase due to concentration gradients created by the chemical reactions, resulting in the isolation of the ion-pair products, **1** and **2**.

3.2 Description of Crystal Structures

3.2a Crystal structure of $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (1**):** In the crystal structure of compound **1**, the asymmetric unit consists of half of the octamolybdate, two crystal/lattice water molecules and two piperidinium cations (Figure 1). Thus, the formula unit of **1** includes an octamolybdate cluster anion, four piperidinium cations and four lattice water molecules *i.e.*, $[(\text{pipH})_4][\text{Mo}_8\text{O}_{26}] \cdot 4\text{H}_2\text{O}$ (**1**). Crystallographically, an octamolybdate anion $[\text{Mo}_8\text{O}_{26}]^{4-}$ is composed of eight edge-sharing octahedral $\{\text{MoO}_6\}$ units. The $\{\text{Mo} - \text{O}\}$ groups can be classified into four categories: fourteen $\text{Mo} - \text{O}_t$ (O_t = terminal oxygen) with the bond lengths in the range of 1.686 – 1.709 Å; six μ_2 -type bridged $\text{Mo} - \text{O}_b$ (O_b = bridging oxygen) with bond distances in the range of 1.747–2.269 Å; four μ_3 -type bridged $\text{Mo} - \text{O}_b$ bonds that are in the range of 1.943–2.338 Å and two μ_5 -type $\text{Mo} - \text{O}_b$ bonds (2.141–2.458 Å). The structure can also be described as four $\{\text{Mo} - \text{O}_6\}$ octahedra lying above one another and joined by edge-sharing.

3.2b Hydrogen bonding situation among supramolecular entities in compound 1: The crystal water/lattice water molecules (O(14) and O(15)) are exclusively involved in hydrogen bonding interactions that result in a 3-D supramolecular network in the crystal structure of compound **1**. These two lattice water molecules (O(14) and O(15)) are strongly hydrogen bonded to each other within the bond limit of 2.710 Å to form a supramolecular water dimer (Figure 2). One of the crystal water O(14) of the water dimer is again hydrogen bonded to two adjacent octamolybdate cluster anion through a terminal (from one side) oxygen atom (O(7)) and bridging (from other side) oxygen atom (O(6)), respectively. This results in the formation of a one-dimensional chain-like arrangement as shown in the Figure 3. Interestingly, two O(14) oxygen atoms (head to tail fashion) are involved in linking two cluster anions along the chain. In the crystal lattice of **1**, these chains run parallel to crystallographic *a* axis (Figure 3).

Figure 1. Thermal ellipsoid plot of compound **1** (50% probability). Full molecule of octamolybdate is shown (in the asymmetric unit, only half of the cluster is present).

Figure 2. H-bonding environment in compound **1**. left: water dimer that connects three surrounding isopolyanions; right: the isopolyanion that communicates with six surrounding water dimers.

The lattice water O15 is further hydrogen bonded to terminal oxygen (O11) atoms of surrounding/neighbouring isopolyanions resulting in a three-dimensional supramolecular network having well-defined channels as shown in Figure 4. In other words, these hydrogen bonding interactions are responsible for the formation of the irregular square-grids with the inner dimensions of $10.76 \times 11.57 \text{ \AA}^2$. Interestingly, the piperidine cations are observed to reside in these channels/grids as guests (Figure 5).

The supramolecular interactions between host (formed exclusively by isopolyanions and crystal water molecules) and guests (piperidinium cations) are characterized by C–H...O and N–H...O hydrogen bonds, in which a piperidinium cation interacts with its surrounding isopolyanions of the host framework. Both

hydrogens on N(2) of the piperidinium cation, undergo bifurcating hydrogen bonding interactions by donating hydrogens to four terminal oxygens (O(1), O(4), O(8) and O(11)), (Figure 6) from the both faces of isopolyanion with the average bond length of $2.98 \text{ \AA}$ and bond angle of 132.2° . The relevant hydrogen bonding interactions are presented in Table S1 (Supplementary Information). The presence of the hydrogen bond donor groups like –NH₂– and –CH₂– in the piperidinium cations makes the hydrogen bonding interactions possible with both terminal and bridging oxygens of the anionic POM cluster. Interestingly, each isopolyanion, in the crystal structure interacts with 10 surrounding piperidinium cations as shown in Figure 7.

3.2c Crystal structure of compound [(pyH)₄][Mo₈O₂₆] (2): The compound **2** consists of two pyridine cations and half of the octamolybdate anion in its asymmetric unit as shown in Figure 8. Thus the formula unit of **2** includes an octamolybdate cluster anion and four pyridinium cations *i.e.*, [(pyH)₄][Mo₈O₂₆] (**2**).

C–H...O and N–H...O type hydrogen bonding interactions that involve both pyridinium cation and the isopolyanion, result in a chain-like structure in compound **2** as shown in Figure 9.

The C(3) and N(1) atoms of the pyridinium cation donate their hydrogens to two terminal oxygens O(2) and O(13), respectively, from two adjacent cluster anions. Along the chain, the linking region consists of two such hydrogen bonding patterns in a head-to-tail

Figure 3. View of the one-dimensional chain in compound **1** looking down to the crystallographic *c* axis. The octamolybdate (shown in polyhedra) anions are connected by the crystal water O(14).

Figure 4. The square grid-type channels formed in the crystal of compound **1**.

Figure 5. View of the square-grid channels in the compound **1**, showing the guest piperidine molecules residing in the channels. Isopoly anion is shown in polyhedra; piperidinium cations are presented in space filling model and hydrogen bonding interactions are shown in dashed lines.

fashion making this chain a ladder type of structure (Figure 9).

These chains are then laterally linked by C–H $\cdots$ O hydrogen bonding interactions that involve O(12) (a bridging oxygen of the polyanion) and C(5) of the pyridinium cation leading to the layer-like structure (Figure 10). In the crystal structure of compound **2**, each cluster anion is surrounded by 12 pyridinium cations (Figure 11). The relevant packing diagram (compound **2**) shows two types of void spaces as shown in Figure 12.

3.3 Potential bag filter for volatile organic amines

Many industries release volatile organic amines, that are not only harmful to human beings (carcinogenic), but

Figure 6. The bifurcation hydrogen bonding situation in compound **1**. The supramolecular assembly consists of isopolyanion and piperidinium cations. Hydrogen bonding interactions are shown in dotted lines.

Figure 7. The hydrogen bonding interactions surrounding the isopolyanion in compound **1**. The relevant hydrogen bonding parameters are presented in Table S2.

are also harmful to various animals. Moreover, gaseous organic amines are among the dreadful pollutants, due to their presence in diverse stored foods, meat, drains, *etc.* Thus, trapping of volatile organic amines is very important to make our environment volatile organic

amine-free. The present work of ‘gas-liquid-interface’ synthesis can be described as potential bag filter for these volatile amines. Sodium molybdate and ammonium molybdate are inexpensive chemicals, present in any UG, PG and industrial laboratories, and are highly soluble in water. Adding HCl acid into this aqueous molybdate solution to pH around 2.0 can simply make this bag filter, which can capture volatile amines to form

respective organic ammonium cations. These cations can be associated with *in situ* formed POM cluster anion (in the present study, the POM cluster anions is octamolybdate anion, $[\text{Mo}_8\text{O}_{26}]^{4-}$) leading to the isolation of

Figure 8. Thermal ellipsoid plot of compound **2** (50% probability). Full molecule of octamolybdate is shown (in the asymmetric unit only half of the cluster is present).

Figure 11. The isopolyanion surrounded by twelve pyridine cations *via* C–H...O and N–H...O supramolecular interactions.

Figure 9. The hydrogen bonding interactions between the pyridinium cations and isopolyanions in compound **2**. These interactions make the one-dimensional ladder-type structure.

Figure 10. View illustrating hydrogen bonding situation around each pyridinium cation as well as around each POM anion in compound **2**.

Figure 12. The packing of the cluster anions and pyridinium cations in the crystal of compound **2**, exhibiting two types of void spaces.

organic-inorganic hybrid compounds. The isolated solid (ion pair compound) is not any more volatile organic amine and thereby non-toxic.

4. Conclusions

Inorganic-organic hybrid materials of diverse supramolecular topologies can simply be obtained using a gas-liquid-interface reaction system by diffusion of the volatile organic amines into an aqueous POM solution at an ambient condition. This system has the potential to filter the volatile organic amines from other volatile organic substances, in which the aqueous POM solution can pick up the volatile organic amines resulting in the formation of inorganic-organic hybrid materials, viz., compounds **1** and **2** in the present work. In general, organic amines (that are severely toxic to human beings and cause CNS depression, damage to liver and kidney, etc.) have been detected around hazardous waste sites and industrial areas. We believe that the present system can be used as a potential ‘bag filter’ for volatile organic amines by keeping an aqueous POM solution in an environment of volatile organic amines with other volatile organic substances. This new gas-liquid synthetic strategy triggered us to isolate different POM anions as organic ammonium salts and the technical part of using this system as a ‘bag filter’ is in progress in our laboratory.

Supplementary Information (SI)

CCDC-1571536 and CCDC 1571537 contain the supplementary crystallographic data for compounds **1** and **2**, respectively. Relevant crystal data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, 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. The crystallographic information for both compounds **1** and **2**, including their bond lengths and angles, are given in the Supplementary Information. Supplementary Information is available at www.ias.ac.in/chemsci.

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