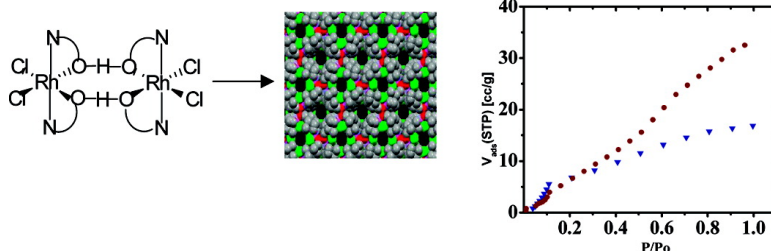


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Cryst. Growth Des., **2009**, 9 (4), 1643-1645 • DOI: 10.1021/cg800987f • Publication Date (Web): 16 March 2009Downloaded from <http://pubs.acs.org> on April 27, 2009

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Dimeric Rh(III) Complex Stabilized by Hydrogen Bonding: Building Block of a Nanoporous Supramolecular Assembly

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Received September 5, 2008; Revised Manuscript Received February 21, 2009

ABSTRACT: The dimeric units $[\text{RhCl}_2(\text{Hhmp})(\text{hmp})]_2$, where Hhmp and hmp are 2-(hydroxymethyl)pyridine and anionic deprotonated ligand, respectively, is formed by strong hydrogen bonding interactions between pairs of Hhmp and hmp ligands that act as building blocks and self-assemble remarkably through aromatic π - π and CH/π interactions to generate a nanoporous supramolecular structure exhibiting permanent porosity and selective adsorption properties.

Self-organization of metal complexes through noncovalent interactions including electrostatic interaction and hydrogen bonding has great potential for creating supramolecular architectures with well-defined shapes and functions.^{1–10} Aromatic π - π stacking interactions also play vital roles in highly efficient and specific biological reactions and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry.^{11,12} Ordered porous materials are widely used in many practical applications including size and shape selective catalysis and separations by exploiting their well-defined channels and cavities.¹³ However, the assembly of porous materials from organic ligands and metal-ion building blocks to generate new supramolecular architecture is challenging.^{14–17} Though the framework instability such as the collapse of the framework upon guest removal has been a serious shortcoming of these materials, the pioneering works of Yaghi and co-workers led to successful synthesis of metal organic frameworks with permanent porosity.¹⁸ In many cases, the metal dimers/carboxylate linkages have proven to be sufficiently strong to stabilize networks against collapse.^{19–21} As such, the porous metal–organic frameworks have attracted great interests for numerous applications including ion exchange,²² catalysis,²³ optoelectronics,²⁴ gas separations,²⁵ and gas storage, in particular H_2 storage.²⁶ The remarkable ability of some of these materials in the sorption of methane and hydrogen highlights their applications in the storage of these gases. Among the factors useful for attaining high uptake of hydrogen are small pores, open metal coordination sites, and low framework mass.²⁷ As a part of our continuing research activities,²⁸ we report here a new metal–organic material: the dimeric Rh(III) complex stabilized by strong intermolecular hydrogen bonding as a building block of a nanoporous supramolecular assembly that exhibits permanent porosity and selective gas adsorption properties.

Bridge splitting reaction of the dimer $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ²⁹ with 2-(hydroxymethyl)pyridine (Hhmp) in a 1:2 mole ratio affords the complex of the type $[\text{Rh}(\text{CO})_2\text{Cl}(\text{Hhmp})]$ (**1**), which on storing in 1:1 dichloromethane and hexane for about 10 days in the presence of the ligand generates the dimeric chelated species $[\text{RhCl}_2(\text{Hhmp})(\text{hmp})]_2$ (**2**), (where hmp is the anionic deprotonated ligand). The complexes **1** and **2** were characterized by elemental analysis and IR spectroscopy.

The molecular structure of complex **2** is shown in Figure 1, while attempts to develop suitable crystals of complex **1** for X-ray structural analysis were unsuccessful. The complex **2** crystallized in the space group $P4(2)/nbc$. The coordination geometry around the Rh atom is octahedral, surrounded by two cis chlorine atoms ($\text{Rh}-\text{Cl} = 2.33 \text{ \AA}$), a pair of trans N atoms ($\text{Rh}-\text{N} = 2.04 \text{ \AA}$), and cis oxygen atoms ($\text{Rh}-\text{O} = 2.03 \text{ \AA}$) of ligand molecules. The dimer

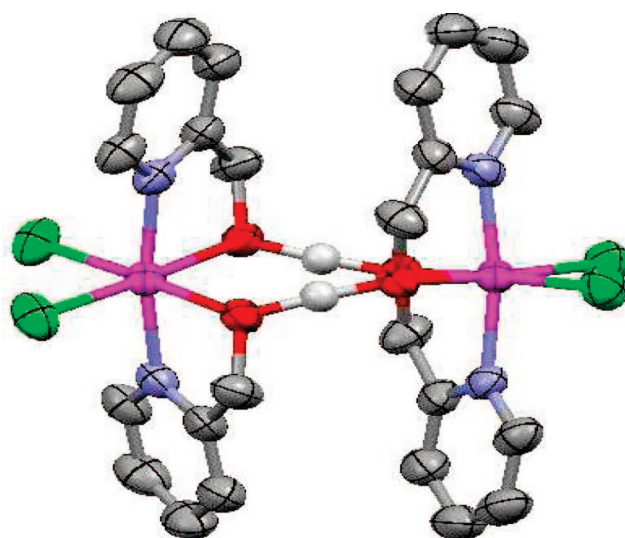


Figure 1. Molecular structure of the complex **2**.

is stabilized by strong hydrogen bonding with a $\text{O}\cdots\text{O}$ distance 2.42 \AA . A probable mechanism to account for the formation of **2** is shown in Scheme 1. The complex **1** underwent decarbonylation in the presence of Hhmp and leads to chelate formation (**1'**) and is substantiated by IR-spectral data, that is, the dicarbonyl stretching bands at 2086 and 2010 cm^{-1} gradually vanish. The chelate **1'** then adds CH_2Cl_2 oxidatively to form the chloromethyl species (**1''**).^{30–32} Subsequently, dehydrohalogenation occurred to form the bis chelate complex (**1'''**) followed by elimination of ethylene³³ to result in the $\text{O}-\text{H}-\text{O}$ bridged dimeric complex **2**.

In the crystal packing diagram (Figure 2a), the stacked orientation between the aromatic rings of the two neighboring molecules are caused by the intermolecular π - π and CH/π interaction. The centroid–centroid distance between the pyridine rings is 3.72 \AA , and the closest contact between them is 3.33 \AA , a typical distance for the system held by π - π stacking interactions. CH/π interactions between the ortho hydrogen atom of a pyridine moiety and an sp^2 carbon atom of a nearby ring are observed with a mean atomic distance of 2.86 \AA . The above characteristics and interactions are attributable to the dimeric form of **2** which is stabilized by two strong hydrogen bonding interactions.

Thus, complex **2** packed in the crystal by intermolecular π - π and CH/π interaction from the pyridine moiety. This gives rise to a three-dimensional open supramolecular architecture with channels along the c axis (Figure 2b). These channels possess approximate dimensions of $5.4 \times 5.4 \text{ \AA}$ and are occupied by disordered dichloromethane molecules as established by thermogravimetric

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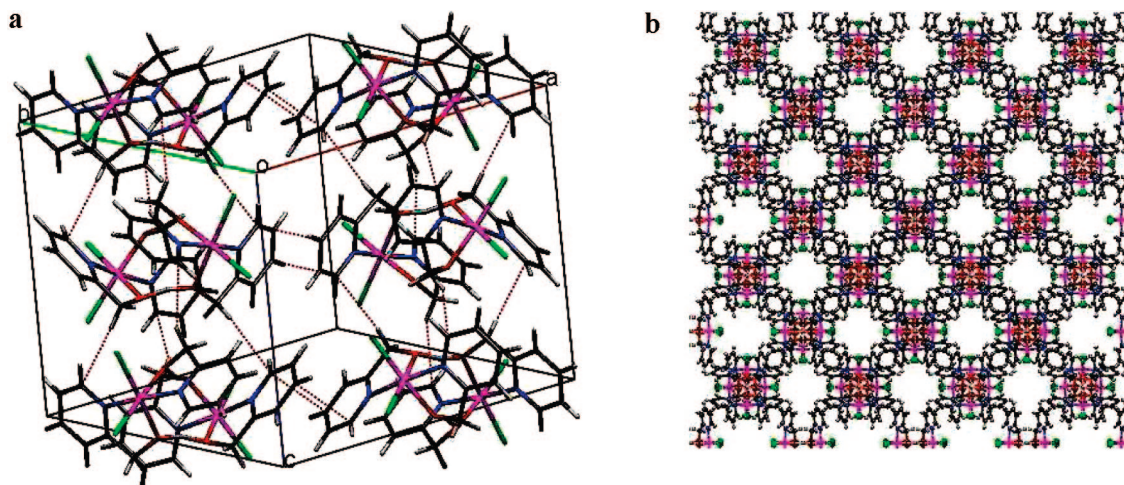
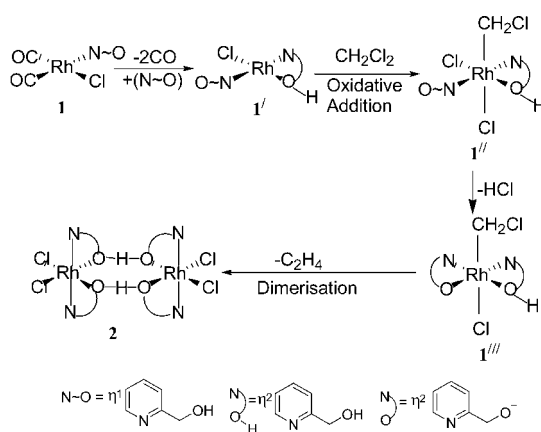


Figure 2. (a) The crystal packing in complex **2** showing π - π stacking and CH/ π interactions of aromatic rings; (b) aggregation in complex **2** by aromatic π - π stacking and CH/ π interactions, viewed along the crystallographic c axis (H atoms are omitted for clarity).

Scheme 1. Probable Mechanism for the Formation of the Complex **2**



analysis (TGA) data; the weight loss at around 50 °C in the TG curve corresponds to the removal of disordered solvent molecules (dichloromethane), which is also supported by elemental analyses. The powder X-ray diffraction (PXRD) pattern also demonstrated that the crystallinity of the framework was retained upon removal of the guest solvent molecule (see Supporting Information).

The architectural stability and porosity of **2** are confirmed by gas adsorption results at 77 K (Figure 3), which indicates that there is a preferential absorption of H₂ over N₂. Complex **2** adsorbs 17 mL of N₂ per gram at 77 K and 1 atm, and fitting the BET equation

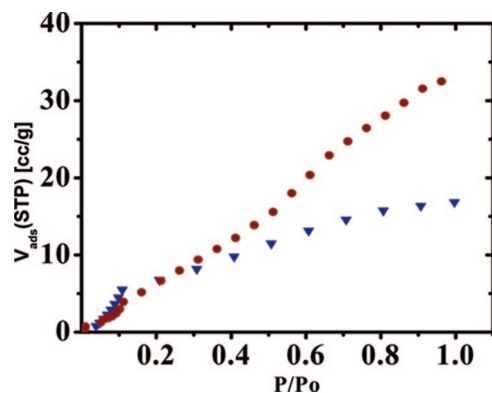


Figure 3. Gas adsorption isotherms of **2** at 77 K (H₂, red; N₂, blue).

to the resulting isotherm gives a surface area of 214 m²/g. Notably, **2** can take up 33 mL of H₂ per gram at 77 K and 1 atm, exhibiting highly selective sorption of H₂ over N₂. This type of selective adsorption of hydrogen over nitrogen is rarely reported in the literature.^{25c} To our knowledge, this is the first example of a hydrogen bonded dimer that exhibits permanent porosity and selective adsorption properties which might be attributable to the interaction between H₂ molecules and the framework by multiple contacts with aromatic rings or the small aperture of channels in **2**, which discriminates H₂ (kinetic diameter 2.8 Å) from N₂ (kinetic diameter 3.64 Å).

In conclusion, we have synthesized and structurally characterized a novel rhodium dimer stabilized by strong intermolecular hydrogen bonding (O \cdots O = 2.42 Å), which further self-assembles through aromatic π - π stacking and CH/ π interactions to form a nanoporous supramolecular assembly that exhibits permanent porosity and selective adsorption properties. It is worth noting that such type of porous material is of special interest for their potential applications in separation and purification of gas molecules. Further research on the rational design and construction of a series of tunable microporous metal-organic frameworks for separation of gas molecules is currently underway.

Acknowledgment. We are grateful to Dr. P. G. Rao, Director, North-East Institute of Science & Technology (CSIR), Jorhat, India, for his kind permission to publish the work. Thanks are also to DST, New Delhi, India, for financial support (Grant: SR/S1/IC-05/2006). B.J.S. thanks CSIR (India) for a senior research fellowship.

Supporting Information Available: Representative synthetic procedures, CIF file, ORTEP view and table of crystal data, TGA plot, PXRD pattern for the complex **2**. This material is available free of charge via Internet at <http://pubs.acs.org>.

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