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## COMMUNICATION

# The crystallographic observation for mesitylene-mesitylene and mesitylene-CH<sub>2</sub>Cl<sub>2</sub>-mesitylene adducts trapped in irregular cavity

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**We report two crystals and one gel formed by a chiral Mo(VI) complex. The particular accumulation of complex molecules creates inert irregular cavities for trapping the solvent adduct. The sp<sup>3</sup>-CH/ $\pi$  interaction models of mesitylene-mesitylene and mesitylene-CH<sub>2</sub>Cl<sub>2</sub>-mesitylene adduct in the irregular accumulation environment are directly observed.**

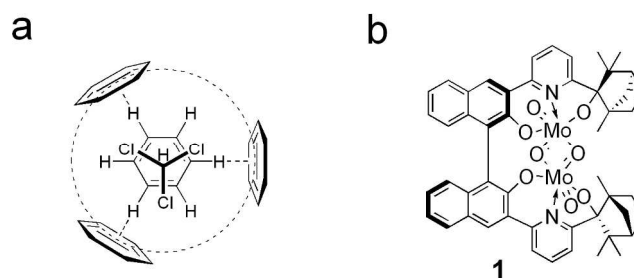
In recent years, the CH/ $\pi$  interaction, i.e., the weak interaction between a soft acid CH and a soft base  $\pi$  system, has attracted considerable interest from scientists because it is believed to play an important role in controlling the structures of molecular assemblies.<sup>1</sup> Many theoretical calculations have supported the existence of the attraction.<sup>1-3</sup> The nature of the typical CH/ $\pi$  interaction is similar to that of London dispersion force.<sup>2</sup> The highly acidic C-H bonds, e.g., in chloroform or acetylene, can activate the CH/ $\pi$  interaction.<sup>3</sup> The optimized geometry of the chloroform-benzene or methane-benzene adduct displays that the interacting C-H bond vertically points towards the centre of the benzene ring.<sup>1a</sup>

In 1952, Tamres first noted that dissolving benzene in chloroform was exothermic and then the CH/ $\pi$  interaction was postulated.<sup>4</sup> Spectroscopic techniques including IR, NMR, circular dichroism and electron spectroscopy, et al., gave further evidences.<sup>5-6</sup> Statistical analysis of the crystal structure database also showed that the C-H bond preferred to point towards the benzene ring.<sup>7</sup> However, the details of these organic crystal structures containing a phenyl and an alkane region may be considered as a result of molecular accumulation. Notably, if a small molecular adduct presumably formed by sp<sup>3</sup>-CH/ $\pi$  interaction might be wrapped in crystal, the convincing geometrical model of this interaction would be obtained by X-ray diffraction technique. Undoubtedly, it is difficult to obtain such crystal since that the sp<sup>3</sup>-CH/ $\pi$  interaction itself is too weak.

Fortunately, Pradyut Ghosh et al. have observed a chloroform-benzene-chloroform adduct within the channel formed by supramolecular assembly.<sup>8</sup> The benzene molecule of the adduct is hooked with three phenyl moieties of channel through edge-to-face aromatic interactions (Scheme 1a). The symmetry of the channel completely matches the adduct. However, the accurate structural information of a small molecular adduct in the irregular environment is urgently needed for sp<sup>3</sup>-CH/ $\pi$  interaction. Furthermore, the

crystallographic exploration for weak adduct such as alkane-benzene is also lacking so far.

Recently, our group has prepared the (*R*)-1,1'-binaphthyl-based bis(dioxo-Mo(VI)) complex **1** with two rigid fenchyl groups (Scheme 1b).<sup>9</sup> The intramolecular MoO<sub>2</sub>Mo structure can steadily exist in inert aromatic solvents such as toluene or mesitylene. Interestingly, when accumulated, the oxygen atom of Mo=O of one complex is prone to contacting with pyridyl of another one. Thus, the fenchyl and binaphthyl parts of complex **1** molecules form the wall of inert cavity.<sup>9</sup> In this communication, we report two crystals and one gel formed by complex **1**. The mesitylene-mesitylene and mesitylene-CH<sub>2</sub>Cl<sub>2</sub>-mesitylene adduct can be trapped in the inert cavities. The sp<sup>3</sup>-CH/ $\pi$  interaction models of these two adducts in the irregular accumulation environment are directly observed.

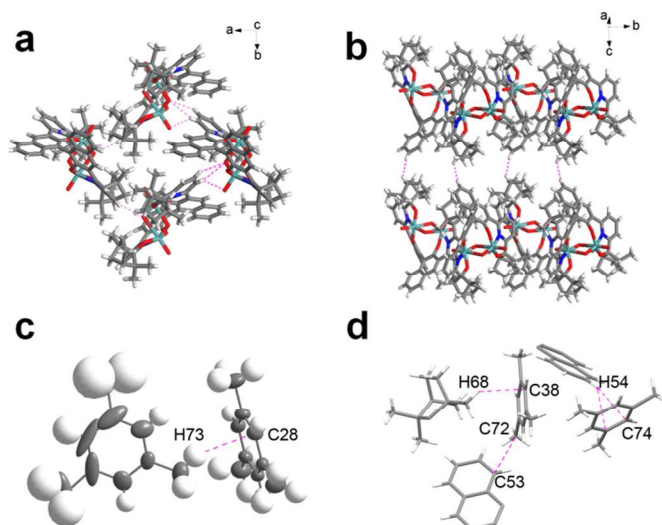


**Scheme 1** The C<sub>3</sub>-symmetrical chloroform-benzene-chloroform adduct and the channel around it<sup>8</sup> (a) (the chloroform molecule behind the benzene ring omitted for clarity); (*R*)-1,1'-binaphthyl-based bis(dioxo-Mo(VI)) complex **1** (b). The dashed circle denotes the channel.

Complex **1** as amorphous yellow powder is almost insoluble in mesitylene at room temperature (solubility, < 0.1 mg/mL). To our surprise, it can gradually swell in mesitylene, and then be transformed into the **1**•mesitylene crystal. The single crystal X-ray diffraction analyses indicated that one complex **1** molecule co-crystallized with two mesitylene ones in a monoclinic crystal system ( $\dagger$ ). The binaphthyl and fenchyl parts of two adjacent complex **1** molecules are reversely arranged. An accumulation plane parallel to (001) plane is formed by the short contacts mainly between Mo=O and pyridyl of complex **1** (Fig. 1a). These accumulation planes

further form a lamellar 3D structure by short contacts between fenchyl and naphthyl units (Fig. 1b).

A solvent adduct containing two mesitylene molecules was observed, in which there existed short contact (H73...C28, 2.757 Å) between one methyl of one mesitylene and phenyl ring of the other one (Fig. 1c). The distance between the carbon atom of methyl and the plane of phenyl ring is about 3.483 Å. The interacting methyl group is located above the submarginal region of phenyl ring. Notably, the computational results on the CH/ $\pi$  interaction model of methane-benzene adduct showed that the interaction potential would be relatively low when the carbon atom of methane is located above the centre of phenyl ring.<sup>10</sup> The deviation from the ideal state could be characteristic of the adduct in an irregular environment. In two adjacent adducts, there is one weak short contact (C<sub>methyl</sub>...C<sub>methyl</sub>, 3.866 Å) between methyl groups. There are also weak short contacts (C53...C72, 3.377 Å; H54...C74, 2.777 Å; H68...C38, 2.881 Å) between complex **1** and mesitylene adduct (Fig. 1d). These show that the adduct is not tightly fastened in the cavity. According to the thermal ellipsoid picture, the atomic vibration amplitude of the interacting methyl group is relatively small as compared to adjacent another two, suggesting the existence of sp<sup>3</sup>-CH/ $\pi$  interaction (Fig. 1c).

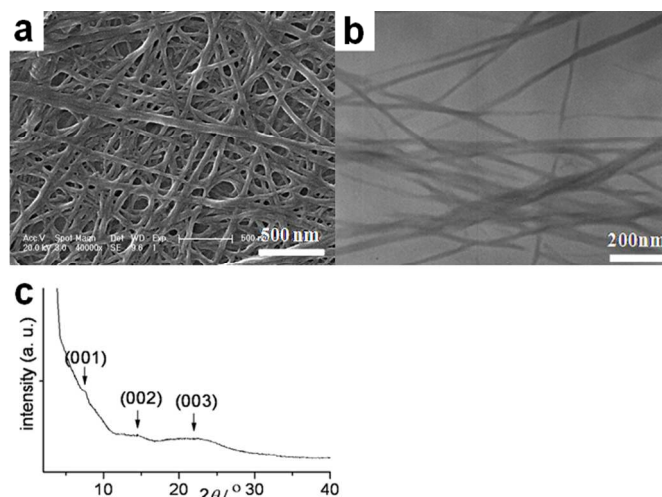


**Fig. 1** In **1**•mesitylene crystal, the accumulation plane formed by short contacts mainly between Mo=O and pyridyl of complex **1** (a), the lamellar structure (b), the mesitylene-mesitylene adduct (ellipsoid model) (c), and the short contacts between complex **1** and mesitylene (d) (only partial structures of complex **1** presented for clarity). Gray, C; white, H; blue, N; red, O; cyan, Mo. Dashed line, short contact.

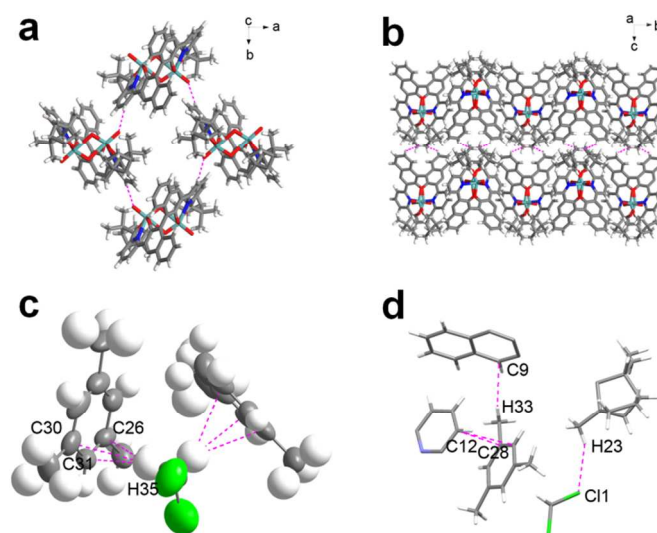
Notably, the  $\pi$ - $\pi$  stacking interaction between two mesitylene molecules is very weak because of the existence of three bulky methyl groups. This is favourable for observing the CH/ $\pi$  interaction. The CH/ $\pi$  interaction energy in mesitylene-mesitylene adduct calculated at the MP2/aug-cc-pVDZ level was about -3.94 kcal/mol.<sup>6</sup> The value is higher than the computational one of methane-benzene adduct (-1.45 kcal/mol).<sup>10</sup> Three electron-donating methyl groups of mesitylene can moderately increase the  $\pi$  electron cloud density of central phenyl ring. In contrast, mesitylene has higher acidity (pK<sub>a</sub> value in DMSO: toluene, ~43; methane, ~56).<sup>11</sup>

In a sealed bottle, complex **1** suspension of 1.0 wt% in mesitylene was heated for 5 minutes at 160 °C, thus forming a transparent solution. After cooled to room temperature, the solution gradually became turbid, and then was quickly transformed into a translucent gel with a little precipitate. The gel kept unchanged for at

least one year at room temperature. The scanning electron microscopy (SEM) picture from mesitylene xerogel of complex **1** showed typical three-dimensional network structure with long fibre bundles (Fig. 2a). This is characteristic of small molecular gel.<sup>12</sup> Furthermore, the transmission electron microscopy (TEM) image from mesitylene gel of complex **1** exhibited the subtle structure of the fibre bundle (Fig. 2b). The powder X-ray diffraction (PXRD) pattern of mesitylene xerogel gave three broad peaks at d-spacings of 1.19 nm, 0.61 nm and 0.41 nm (Fig. 2c), corresponding to a lamellar structure with the reciprocal spacing ratio of 1:1/2:1/3. We estimated that the gel structure could be similar to that of **1**•mesitylene crystal with the similar lamellar characteristic. However, the true accumulation structure keeps still elusive since that no adaptable technique can be used to observe it directly at a molecular level.



**Fig. 2** SEM image of mesitylene xerogel (a), TEM image of mesitylene gel (b), and PXRD diagram of mesitylene xerogel (c) of complex **1**.



**Fig. 3** In **1**•mesitylene•CH<sub>2</sub>Cl<sub>2</sub> crystal, the accumulation plane formed by short contacts mainly between Mo=O and pyridyl of complex **1** (a), the lamellar structure (b), the C<sub>2</sub>-symmetrical mesitylene-CH<sub>2</sub>Cl<sub>2</sub>-mesitylene adduct (ellipsoid model) (c), and the short contacts between complex **1** and mesitylene/CH<sub>2</sub>Cl<sub>2</sub> (d) (only partial structures of complex **1** and a half short contacts presented for clarity). Gray, C; white, H; blue, N; red, O; cyan, Mo; green, Cl. Dashed line, short contact.



Interestingly, after 0.1 mL of  $\text{CH}_2\text{Cl}_2$  was added to 2.0 g of complex **1** gel in mesitylene of 1.0 wt%, the partial gel was dissolved and then some novel **1**•mesitylene• $\text{CH}_2\text{Cl}_2$  crystals were slowly formed in about one day. As the gradual dissolution-crystallization procedure, similar gel-to-crystal phase transitions have been reported.<sup>13</sup> The single crystal X-ray diffraction analyses indicated that one complex **1** molecule co-crystallized with one  $\text{CH}_2\text{Cl}_2$  and two mesitylene ones in an orthorhombic crystal system ( $\dagger$ ). The binaphthyl and fenchyl parts of two adjacent complex **1** molecules are also reversely arranged in **1**•mesitylene• $\text{CH}_2\text{Cl}_2$  crystal (Fig. 3a). An accumulation plane is formed by the short contacts between  $\text{Mo}=\text{O}$  and pyridyl, then 3D crystal by short contacts between naphthyl and fenchyl groups (Fig. 3b).

A separate  $\text{C}_2$ -symmetrical solvent adduct containing two mesitylene and one  $\text{CH}_2\text{Cl}_2$  molecule was observed, in which there existed short contacts (H35...C30, 2.830 Å; H35...C31, 2.503 Å; H35...C26, 2.749 Å) between hydrogen atom of  $\text{CH}_2\text{Cl}_2$  and phenyl ring of mesitylene (Fig. 3c). Two C-H bonds of  $\text{CH}_2\text{Cl}_2$  approximately vertically direct towards two phenyl rings, respectively, thus forming a sandwich-like structure. The distance between the carbon atom of  $\text{CH}_2\text{Cl}_2$  and the plane of phenyl ring is about 3.329 Å. The carbon atom of  $\text{CH}_2\text{Cl}_2$  is also located above the submarginal region of phenyl ring. There are weak short contacts (C12...C28, 3.330 Å; C9...H33, 2.879 Å; C11...H23, 2.829 Å) between complex **1** and solvent adduct (Fig. 3d). This shows that the adduct is not fastened tightly in the cavity. The thermal ellipsoid picture of the adduct exhibits that the atomic vibration amplitude in the region close to the hydrogen atom of  $\text{CH}_2\text{Cl}_2$  in mesitylene is relatively small, suggesting the existence of  $\text{sp}^3\text{-CH}/\pi$  interaction (Fig. 3c).

The  $\text{CH}/\pi$  interaction energy in mesitylene- $\text{CH}_2\text{Cl}_2$ -mesitylene adduct calculated at the MP2/aug-cc-pVDZ level was about -6.87 kcal/mol.<sup>6</sup> The value is higher than that of mesitylene-mesitylene adduct. This is mainly due to the existence of two chlorine atoms with large dispersion term.<sup>3</sup> The high acidity of C-H of  $\text{CH}_2\text{Cl}_2$  can increase the electrostatic interaction and cause the strong directionality.<sup>3</sup> It is noted that the computational values of  $\text{CH}/\pi$  interaction energy of  $\text{CH}_2\text{Cl}_2$ -benzene and chloroform-benzene adduct are -4.54 kcal/mol and -5.64 kcal/mol, respectively.<sup>3</sup> The three electron-donating methyl groups on phenyl ring can evidently strengthen the  $\text{sp}^3\text{-CH}/\pi$  interaction.

In conclusion, we have observed two different  $\text{sp}^3\text{-CH}/\pi$  interaction models of mesitylene-mesitylene and mesitylene- $\text{CH}_2\text{Cl}_2$ -mesitylene adduct in crystal. In the former adduct, one methyl of one mesitylene interacts with the phenyl ring of the other one. In the latter one, two C-H bonds of  $\text{CH}_2\text{Cl}_2$  approximately vertically direct towards two phenyl ring, respectively. In these two adducts, the carbon atoms of the interacting C-H bonds are located above the submarginal region of phenyl ring. The complex **1** molecule can adjust its accumulation mode according to the shape of molecular adduct. We believe that the crystallization of complex **1** also could wrap other interesting molecular adducts with weak interaction.

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## Notes and references

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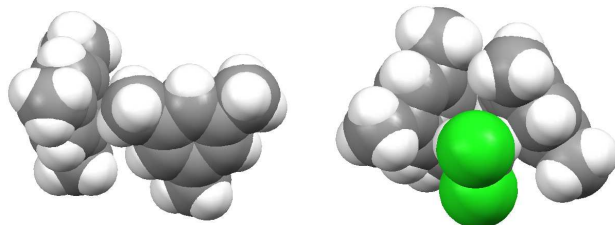
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<sup>c</sup>State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, China, 130022.

<sup>†</sup>Crystal data for **1**•mesitylene (CCDC 992734):  $\text{C}_{68}\text{H}_{72}\text{Cl}_{10}\text{Mo}_2\text{N}_2\text{O}_8$ ;  $M_r = 1237.16$ ; Monoclinic; space group  $P2_1$ ;  $a = 15.7215(16)$  Å,  $b =$

$12.0839(12)$  Å,  $c = 16.2077(17)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 106.856(2)^\circ$ ;  $U = 2946.8(5)$  Å<sup>3</sup>;  $Z = 2$ ;  $\rho_{\text{calcd}} = 1.394$  g cm<sup>-3</sup>;  $\mu(\text{Mo}_{\text{K}\alpha}, \lambda = 0.71073 \text{ Å}) = 0.484$  mm<sup>-1</sup>;  $T = 273(2)$  K;  $2\theta_{\text{max}} = 52.08^\circ$ ;  $F(000) = 1284$ ; 18996 reflections collected, 9024 unique ( $R_{\text{int}} = 0.0436$ ), which were used in all of the calculations; Final  $R_1 = 0.0428$ ,  $wR_2 = 0.0863$  for  $I > 2\sigma(I)$ ;  $R_1 = 0.0513$ ,  $wR_2 = 0.0910$  for all data;  $\text{GoF} = 1.014$ . Crystal data for **1**•mesitylene• $\text{CH}_2\text{Cl}_2$  (CCDC 803680):  $\text{C}_{69}\text{H}_{74}\text{Cl}_2\text{Mo}_2\text{N}_2\text{O}_8$ ;  $M_r = 1322.08$ ; Orthorhombic; space group  $P2_12_12_1$ ;  $a = 14.6862(18)$  Å,  $b = 15.6249(18)$  Å,  $c = 13.2871(16)$  Å;  $U = 3049.0(6)$  Å<sup>3</sup>;  $Z = 2$ ;  $\rho_{\text{calcd}} = 1.440$  g cm<sup>-3</sup>;  $\mu(\text{Mo}_{\text{K}\alpha}, \lambda = 0.71073 \text{ Å}) = 0.557$  mm<sup>-1</sup>;  $T = 185(2)$  K;  $2\theta_{\text{max}} = 50.14^\circ$ ;  $F(000) = 1368$ ; 16874 reflections collected, 5391 unique ( $R_{\text{int}} = 0.0818$ ), which were used in all of the calculations; Final  $R_1 = 0.0591$ ,  $wR_2 = 0.1202$  for  $I > 2\sigma(I)$ ;  $R_1 = 0.0989$ ,  $wR_2 = 0.1372$  for all data;  $\text{GoF} = 1.022$ . Electronic Supplementary Information (ESI) available: experimental details of SEM, TEM, PXRD, single crystal X-ray diffraction, and the theoretical computation. See DOI: 10.1039/c000000x/

- a) S. Tsuzuki, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, 2012, **108**, 69; b) K. Kobayashi, Y. Asakawa, Y. Kato and Y. Aoyama, *J. Am. Chem. Soc.*, 1992, **114**, 10307; c) D. B. Amabilino, P. R. Ashton, C. L. Brown, E. Córdova, L. A. Godínez, T. T. Goodnow, A. E. Kaifer, S. P. Newton, M. Pietraszkiewicz, D. Philp, F. M. Raymo, A. S. Reder, M. T. Rutland, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 1271; d) P. Sozzani, A. Comotti, S. Bracco and R. Simonutti, *Chem. Commun.*, 2004, **40**, 768; e) Y. Yamamoto, A. Yamamoto, S. Furuta, M. Horie, M. Kodama, W. Sato, K. Akiba, S. Tsuzuki, T. Uchimar, D. Hashizume and F. Iwasaki, *J. Am. Chem. Soc.*, 2005, **127**, 14540; f) E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem. Int. Ed.*, 2003, **42**, 1210; g) G. R. Desiraju and T. Sterner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, IUC-Oxford Univ. Press, New York, 2001.
- S. Tsuzuki and A. Fujii, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2584.
- S. Tsuzuki, K. Honda, T. Uchimar, M. Mikami and K. Tanabe, *J. Phys. Chem. A*, 2002, **106**, 4423.
- M. J. Tamres, *J. Am. Chem. Soc.*, 1952, **74**, 3375.
- M. Nishio, M. Hirota and Y. Umezawa, *The CH/π Interaction. Evidence, Nature, and Consequences*, Wiley-VCH, New York, 1998.
- a) A. Fujii, K. Shibasaki, T. Kazama, R. Itaya, N. Mikami and S. Tsuzuki, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2836; b) M. Schauer and E. R. Bernstein, *J. Chem. Phys.*, 1985, **82**, 726.
- a) Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa and M. Nishio, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1207; b) Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa and M. Nishio, *Tetrahedron*, 1999, **55**, 10047; c) A. Matsumoto, T. Tanaka, T. Tsubouchi, K. Tashiro, S. Saragai and S. Nakamoto, *J. Am. Chem. Soc.*, 2002, **124**, 8891; d) M. Nishio, *CrystEngComm*, 2004, **4**, 130.
- P. S. Lakshminarayanan, D. K. Kumar and P. Ghosh, *J. Am. Chem. Soc.*, 2006, **128**, 9600.
- a) L. Ma, R. Jin, Z. Bian, C. Kang, Y. Chen, J. Xu and L. Gao, *Chem. Eur. J.*, 2012, **18**, 13168; b) L. Ma, R. Z. Jin, G. H. Lv, Z. Bian, M. X. Ding and L. X. Gao, *Synthesis*, 2007, **16**, 2461.
- S. Tsuzuki, K. Honda, T. Uchimar, M. Mikami, *J. Am. Chem. Soc.*, 2000, **122**, 3746.
- a) F. G. Bordwell, D. Algrim and N. R. Vanier, *J. Org. Chem.*, 1977, **42**, 1817; b) F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456.
- P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133.
- a) D. K. Kumar, D. A. Jose, A. Das and P. Dastidar, *Chem. Commun.*, 2005, **41**, 4059; b) O. Lebel, M.-É. Perron, T. Maris, S. F. Zalzal, A. Nanci and J. D. Wuest, *Chem. Mater.*, 2006, **18**, 3616; c) Y. Wang, L. Tang and J. Yu, *Cryst. Growth Des.*, 2008, **8**, 884; d) P. Terech, N. M. Sangeetha and U. Maitra, *J. Phys. Chem. B*, 2006, **110**, 15224; e) Y. He, Z. Bian, C. Kang and L. Gao, *Chem. Commun.*, 2010, **46**, 5695; f) Y. He, Z. Bian, C. Kang and L. Gao, *Chem. Commun.*, 2011, **47**, 1589; g) Y. Xu, C. Kang, Y. Chen, Z. Bian, X. Qiu, L. Gao and Q. Meng, *Chem. Eur. J.*, 2012, **18**, 16955.

**Entry for the Table of Contents**

mesitylene-mesitylene

mesitylene-CH<sub>2</sub>Cl<sub>2</sub>-mesitylene

We report two crystals and one gel formed by a chiral Mo(VI) complex. The particular accumulation of complex molecules creates inert irregular cavities for trapping the solvent adduct. The  $\text{sp}^3\text{-CH}/\pi$  interaction models of mesitylene-mesitylene and mesitylene-CH<sub>2</sub>Cl<sub>2</sub>-mesitylene adduct in the irregular accumulation environment are directly observed.