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# Exploiting Complementary Second-sphere Effects in Supramolecular Coordination Solids

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**In the design of extended supramolecular solids, reliable synthons are a valuable commodity. This work concerns the complementary second-sphere coordination interactions between a highly preorganized hexasulphonated**

## The Future of Supramolecular Chemistry

The number and breadth of extended coordination structures being reported are growing at an exponential rate. There is still much untapped ground with respect to new ligands, varying cation–anion pairs, and altering synthetic conditions to yield new frameworks. Our feeling has been that, while new assembly motifs and structural topologies are of interest, they do represent only a means to an end, that being the development of new families of functional solids. Zeolite mimics with permanent porosity have been heralded as Holy Grails within this domain, and understandably so, given the structural variation incorporation of organic moieties brings. Numerous outstanding examples have been reported which illustrate this feature already. A feature which has been less explored are pliant coordination solids which exhibit reversible phase transitions with guest inclusion (the third-generation solids as defined by Kitagawa). While often not possessing measurable porosity, it can certainly be argued that reversible guest sorption constitutes functional porosity. It is almost a question of philosophy: "If a guest molecule exists in a pore and it can be removed and re-inserted, does it matter that the pore exists in its absence?"

Our recent research has concerned a number of functionally porous solids. The appeal of this class of compounds is not so much that they will replace zeolitic solids, but more that they represent complements to rigid networks. Particularly with the incorporation of metal centres with some physico-chemical activity (magnetism, luminescence, and so on), the idea of solids switchable with guest inclusion is a prospect not available to a rigid network. There are likely many such networks which have been reported but have not been recognized as hosts with such potential as interest was focused on a permanently porous structure. It is important for researchers in the field to recognize and study the sorption properties of "soft" networks as these compounds represent the truly distinctive aspect of coordination solids vs. a metal oxide framework. With these compounds in mind, the domain of possible building units also expands to include "weaker" coordinate covalent and non-covalent interactions, as these would be expected to promote a greater structural flexibility. In this light, we have been examining second-sphere coordination as a means of assembling extended solids, and this is the topic of the following work.

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**Sean Dalrymple** was raised in Coxheath, Nova Scotia, Canada. He completed his BSc at St. Francis Xavier University and moved to Calgary to begin graduate studies in 1999. Sean is presently a PhD student and an NSERC Canada Graduate Scholarship holder.

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**ligand, L, and aquated metal ions. Four second-sphere inclusion complexes $[M(H_2O)_6]_2L\cdot(S)_3$ (M/S: Mg/acetone, 1; Zn/acetone, 2, Mg/dioxane, 3; Zn/dioxane, 4) and three extended networks $\{[(M(H_2O)_3)_2(L)]\cdot(H_2O)_{14.5}\}_\infty$ (M = Cr, 5; Fe, 6; Al, 7) have been structurally characterized by X-ray crystallography. The second-sphere effects on the stabilization of the primary coordination sphere are illustrated by TGA experiments. In these assemblies, the potential of a new supramolecular synthon is illustrated, that being the complementary hydrogen-bonding interaction between *cis*-aquo ligands and sulphonate oxygen atoms.**

*Keywords*: Second-sphere interactions; Supramolecular chemistry; Coordination networks; Porous frameworks

## INTRODUCTION

The self-assembly of molecular building blocks has gained immense interest over the past 10 years as an alternate methodology in the production of porous materials. Research activities within this field of supramolecular chemistry have been directed toward the assembly of inorganic metal clusters [1–3], organic molecules [4–6], and hybrid inorganic–organic materials [7–9]. The desirable properties of the molecular building blocks may be incorporated into the overall structure to create finely tuned bulk materials with a specific function for chemical sensing, gas storage, molecular sieving, or catalysis applications [10]. The ultimate goal of "crystal engineering", a discipline devoted to guiding the assembly of molecules into desirable crystalline architectures, is the a priori structure prediction of potential building blocks with respect to generating porous materials [11]. Although the predictability of solid-state structures has remained elusive to date, prodigious steps have been taken towards smaller synthetic goals to gain information on the delicate assembly process. Establishing connections between molecular and supramolecular structure via intermolecular interactions could allow for the identification of structurally robust motifs to be carried from one crystal structure to another, reminiscent of synthons in molecular chemistry [12]. In addition to the strongly directional metal–ligand coordinate bond, hydrogen-bonding interactions have also been widely employed to assemble organic building blocks bearing the common COOH, OH, F, Cl, Br, CN, NH, $NH_2$, and $NO_2$ functionalities, as acceptors and donors, into desirable solid-state architectures [6,13].

Empirically derived hydrogen bond rules have even appeared in the literature, outlining potentially reliable synthons for organic molecules [14]. Alternatively, the use of second-sphere interactions to produce novel hydrogen bonded complexes has also been investigated [15–18]. Second-sphere coordination refers broadly to any intermolecular interactions with the primary coordination sphere of a metal complex, that is, further interactions with those ligands directly bonded to the metal centre. These inherently supramolecular phenomena are fundamental to the properties of any metal complex in the solid state. A number of excellent reviews on second-sphere complexes, in general, and their effects on molecular complexes have been published [19,20]. The nature of the interactions between the second sphere and the primary coordination sphere with respect to the composition, stability, and solution lifetimes of the second-sphere complexes has been investigated [21,22], while the effects of solvent on second coordination spheres on the relaxivity of Gd(III) complexes as MRI contrast agents have also been reviewed [23].

The molecular recognition and binding of transition metal complexes via second-sphere coordination have been accomplished with a variety of artificial receptor ligands. The traditional ligand classes which have been examined as hosts range from crown ethers [24,25] and dibenzocrown ethers [26,27] to cyclodextrins [28,29] and macropolycyclic ethers [30,31] and sulphonated calixarenes [32–35]. Although, several examples of second-sphere complexes with aquo [36–44] and ammine [45–49] coordination compounds have appeared in the literature, the second-sphere interactions reported were typically only with a fraction of the primary coordination sphere. There is surprisingly very little use of second-sphere interactions in the construction of extended structures. The most studied systems involve hydrogen bonding between metal chloride acceptor groups and protonated N species [50,51]. Additional systems by Hosseini *et al.* have also been reported for metal cyanide donors and bis-amidinium acceptors [52] in extended structures constructed from hydrogen-bonding interactions, while Kitagawa *et al.* have studied metal chloranilic acid structures augmented by hydrogen bonding between aquo and aromatic N ligands [53,54]. The bulk of available structural data on metal sulphonate complexes demonstrates the inability of sulphonate ions to displace solvent, usually water, from the primary coordination sphere [55,56]. Previous work in our group has been focused on the chemistry of the sulphonate ($RSO_3^-$) group in the generation of extended solids via primary and secondary sphere interactions [57–59]. Specifically, we have reported that the trianion of 1,3,5-tris(sulphomethyl)benzene, TSMB (Fig. 1), forms discrete second-sphere complexes with trivalent hexaaquo metal ions through complete encapsulation of the primary coordination sphere [59]. In these complexes, two molecules of TSMB each form six hydrogen

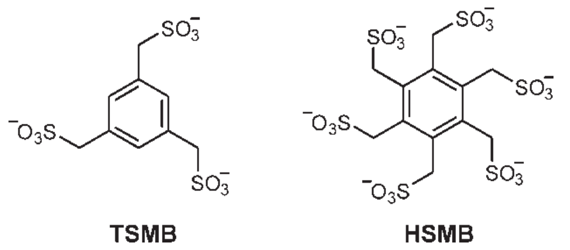

FIGURE 1 Line drawings of the polysulphonated ligands.

bonds to each triangular face of the octahedral metal cations. A high degree of hydrogen-bonding complementarity was observed between sulphonate groups and pairs of aquo ligands oriented in *cis* coordination sites on the metal centre. In order to explore further the potential second-sphere interactions of the sulphonate group, a novel ligand, hexakis(sulphomethyl)benzene (HSMB), henceforth denoted **L**, was synthesized (Fig. 1). Given the previous results with TSMB, **L** was believed to be ideal for generating fully encapsulated second-sphere complexes in a comparable manner to two molecules of TSMB fused at the benzene core. These structures were expected to exhibit extended morphologies sustained solely by second-sphere interactions with hexaaquo transition-metal complexes. Herein, we present four second-sphere complexes of **L** with divalent metals, $[M(H_2O)_6]_2\mathbf{L}\cdot(S)_3$ (M/S: Mg/acetone **1**; Zn/acetone **2**, Mg/dioxane **3**; Zn/dioxane **4**), which have been structurally characterized by X-ray crystallography and examined by thermogravimetric analysis. Indeed, these extended structures exhibit the previously observed *cis*-aquo sulphonate hydrogen-bonding pattern which promotes the complete encapsulation of the hexaaquo metal complexes. In addition, three isostructural three-dimensional networks constructed from **L** with trivalent metal centres, $\{[(M(H_2O)_3)_2(\mathbf{L})]\cdot(H_2O)_{14.5}\}_\infty$ (M = Cr, **5**; Fe, **6**; Al, **7**), will be fully presented. These structures exhibit unexpected primary sphere coordination and cooperative secondary sphere interactions to yield neutral open frameworks with water-filled channels.

## EXPERIMENTAL

### Methods and Materials

Commercial reagents were purchased from Aldrich Chemical Co. and used without further purification. NMR spectra were obtained using a Bruker AC-200 Nuclear Magnetic Resonance spectrometer equipped with a Tecmag PowerMac Data system. ESI-MS were obtained on a Bruker Esquire 3000 spectrometer. FT-IR spectra were run as KBr pellets on a Nicolet Nexus 470 instrument, while elemental analyses (C, H, N) were conducted by the Department of Analytical Services at the University of Calgary. Thermogravimetric Analyses (TGA) were performed on a Netzsch 449C Simultaneous Thermal Analyser under a static $N_2$ atmosphere at a scan rate of 5°C/min.

### *Synthesis of Hexakis(sulphomethyl)benzene (L)*

Hexakis(bromomethyl)benzene (1.024 g, 1.611 mmol) and $Na_2SO_3$ (1.421 g, 11.277 mmol) were placed in a Teflon-lined autoclave along with $H_2O$ (15 mL) and mixed vigorously for 5 min. The hydrothermal apparatus was then assembled and placed in a temperature-programmable oven at 175°C. After 3 days, the autoclave was removed from the oven and cooled to room temperature before filtering the slightly cloudy yellowish solution that had been obtained. To the clear yellow-coloured solution was added $CH_3OH$ (20 mL), which resulted in the immediate precipitation of a beige solid. After sitting for 12 h at 0°C, the off-white solid was then isolated by suction filtration (0.3808 g). The crude product was then dissolved in a minimal amount of $H_2O$ (3 mL). Diffusion of $CH_3OH$ vapor into the aqueous solution triturated out the inorganic contaminants. After approximately 48 h of crystallization, the inorganic salts were removed by suction filtration, and the mother liquor was removed on a rotary evaporator to give pure white hexakis(sulphomethyl)benzene as the sodium salt ($Na_6\mathbf{L}$). Based on TGA and elemental analysis, the sodium salt was formulated as $Na_6\mathbf{L}\cdot 5H_2O$. Yield based on $Na_6\mathbf{L}\cdot 5H_2O$: 0.310 g (0.359 mmol, 23%); IR ($cm^{-1}$, KBr): 3453.7(br), 1651(s), 1481.6(w), 1421.6(w), 1224.9(vs), 1142.94(vs), 1050.1(vs), 979.1(w), 809.7(w), 766.0(m), 678.6(m), 634.9(m), 585.7(m), 525.6(m). TGA: 25–185°C $-10.85\%$ obs. and $-10.42\%$ calcd. for loss of $5H_2O$, 400°C decomposition of **L**. Elemental analysis calcd. for $Na_6\mathbf{L}\cdot 5H_2O$: C 16.67, H 2.62; found: C 16.84, H 2.62.

Conversion of the ligand to the acid form ($H_6\mathbf{L}$) was accomplished by passing an aqueous solution of $Na_6\mathbf{L}$ (0.508 g, 0.588 mmol) down an ion-exchange column (Dowex 50 × 8) previously charged with 6 M HCl. Upon removal of the water *in vacuo*, a beige-brown sticky solid was obtained. Based on TGA and elemental analysis, the acid form of the ligand was formulated as $H_6\mathbf{L}\cdot 12H_2O$. Yield based on $H_6\mathbf{L}\cdot 12H_2O$: 0.458 g (0.534 mmol, 91%); $^1H$ NMR (200 MHz, $D_2O$): $\delta = 4.97$ (s, $CH_2SO_3$); $^{13}C\{^1H\}$: $\delta = 125.94$, (arom.), 51.40 ($CH_2SO_3$); ESI-MS: *m/z*: 640.9 $[H_6\mathbf{L}-H]^-$; TGA: 25–150°C $-26.34\%$ obs. and $-25.20\%$ calcd. for loss of $12H_2O$, 390°C decomposition of L2. Elemental analysis calcd. for $H_6\mathbf{L}\cdot 12H_2O$: C 16.78, H 4.93; found: C 16.04, H 4.63.

### *Preparation of $[(Mg(H_2O)_6)_3(L)]\cdot((CH_3)_2CO)_3$ (1)*

$H_6$**L** (0.201 g, 0.270 mmol) was dissolved in $H_2O$ (10 mL) to give a clear, colourless solution to which was added white crystalline $Mg(OH)_2$ (0.048 g, 0.810 mmol). The clear, colourless solution was stirred for 20 h. The solution was then filtered, and acetone was slowly diffused into the aqueous solution to crystallize the product. A small crop of clear block crystals was observed after 5 days of slow diffusion. The crystals were isolated and dried on filter paper for 1 h before being weighed. Yield: 0.085 g (0.070 mmol, 26%); IR ($cm^{-1}$, KBr): 3366.3(br), 1683.8(s), 1645.5(s), 1476.2(m), 1421.6(m), 1366.9(m), 1230.4(m), 1175.7(w), 1132.0(m), 1033.7(vs), 804.2(m), 766.0(m), 667.7(m), 584.8(m), 509.3(m); TGA: 25–120°C −10.15% obs. and −10.10% calcd. for loss of $2[(CH_3)CO]$, 120–265°C −28.96% obs. and −28.20% calcd. for loss of $18H_2O$, 375°C decomposition of **L**. Elemental analysis calcd. for **1**: C 20.88, H 5.51; found: C 15.36, H 4.72; formulated as $[(Mg(H_2O)_6)_3(\mathbf{L})]\cdot((CH_3)_2CO)_{0.5}$ (C 15.26, H 4.83).

### *Preparation of $[(Zn(H_2O)_6)_3(L)]\cdot((CH_3)_2CO)_3$ (2)*

$H_6$**L** (0.201 g, 0.270 mmol) was dissolved in $H_2O$ (10 mL) to give a clear, colourless solution to which was added white crystalline $Zn(NO_3)_2\cdot6H_2O$ (0.241 g, 0.810 mmol). The clear, colourless solution was stirred for 20 h and then filtered before acetone was slowly diffused into the aqueous solution to crystallize the product. A small crop of clear block crystals was observed after 6 days of slow diffusion. The crystals were isolated and dried on filter paper for 1 h before being weighed. Yield: 0.115 g (0.086 mmol, 24%); IR ($cm^{-1}$, KBr): 3573.9(br), 1618.2(s), 1476.2(m), 1416.1(m), 1388.8(m), 1350.5(w), 1241.3(m), 1175.7(m), 1132.0(m), 1033.7(vs), 809.7(m), 787.9(m), 760.6(s), 673.1(s), 580.3(s), 520.2(m); TGA: 25–110°C −13.88% obs. and −13.09% calcd. for loss of $3[(CH_3)CO]$, 110–265°C −24.99% obs. and −25.47% calcd. for loss of $18H_2O$, 350°C decomposition of **L**. Elemental analysis calcd. for **2**: C 18.94, H 4.99; found: C 10.64, H 3.61; formulated as $[(Zn(H_2O)_6)_3(\mathbf{L})]$ (C 12.46, H 4.18).

### *Preparation of $[(Mg(H_2O)_6)_3(L)]\cdot(C_4H_8O_2)_3$ (3)*

$H_6$**L** (0.201 g, 0.270 mmol) was dissolved in $H_2O$ (10 mL) to give a clear, colourless solution to which was added white crystalline $Mg(OH)_2$ (0.048 g, 0.810 mmol). The clear, colourless solution was stirred for 20 h and then filtered before dioxane was slowly diffused into the aqueous solution to crystallize the product. A small crop of clear block crystals was observed after 18 days of slow diffusion. The crystals were isolated and dried on filter paper for 1 h before being weighed. Yield: 0.078 g (0.060 mmol, 22%); IR ($cm^{-1}$, KBr): 3240.7(br), 1661.9(s), 1476.2(m), 1454.3(w), 1421.6(m), 1383.3(m), 1295.9(w), 1224.9(w), 1110.2(m), 1039.2(vs), 968.1(w), 897.1(m), 864.3(s), 798.8(m), 760.0(m), 667.7(m), 580.3(m), 509.3(m); TGA: 25–330°C −44.62% obs. and −45.33% calcd. for loss of $3(C_4H_8O_2)$ and $18H_2O$, 350°C decomposition of **L**. Elemental analysis calcd. for **3**: C 22.21, H 5.59; found: C 18.69, H 5.46; formulated as $[(Mg(H_2O)_6)_3(\mathbf{L})]\cdot(C_4H_8O_2)_{1.5}$ (C 18.56, H 5.15)

### *Preparation of $[(Zn(H_2O)_6)_3(L)]\cdot(C_4H_8O_2)_3$ (4)*

$H_6$**L** (0.201 g, 0.270 mmol) was dissolved in $H_2O$ (10 mL) to give a clear, colourless solution to which was added white crystalline $Zn(NO_3)_2\cdot6H_2O$ (0.241 g, 0.810 mmol). The clear, colourless solution was stirred for 20 h and then filtered before acetone was slowly diffused into the aqueous solution to crystallize the product. A small crop of clear block crystals was observed after 19 days of slow diffusion. The crystals were isolated and dried on filter paper for 1 h before being weighed. Yield: 0.095 g (0.067 mmol, 25%); IR ($cm^{-1}$, KBr): 3573.9(br), 1623.7(m), 1476.2(w), 1421.6(w), 1257.7(m), 1235.8(m), 1175.7(m), 1132.0(m), 1110.2(m), 1039.2(vs), 886.2(m), 869.8(s), 760.6(m), 673.1(m), 618.5(w), 585.7(m), 547.5(m), 520.2(m); TGA: 25–320°C −41.10% obs. and −41.40% calcd. for loss of $3(C_4H_8O_2)$ and $18H_2O$, 340°C decomposition of **L**. Elemental analysis calcd. for **4**: C 20.28, H 5.11; found: C 17.38, H 4.64; formulated as $[(Zn(H_2O)_6]_3(\mathbf{L})]\cdot(C_4H_8O_2)_{1.5}$ (C 16.77, H 4.69).

### *Preparation of $\{[(Cr(H_2O)_3)_2(L)]\cdot(H_2O)_{14.5}\}_\infty$ (5)*

$Na_6$**L** (0.084 g, 0.113 mmol) was dissolved in $H_2O$ (6 mL) to give a clear, colourless solution to which was added green crystalline $CrCl_3\cdot6H_2O$ (0.061 g, 0.229 mmol). The solution immediately turned forest green in colour and was stirred for an additional 20 h. Over the 20 h period, the solution slowly changed to a slightly violet colour. After 20 h, the solution was filtered, and acetone was slowly diffused into the aqueous solution to crystallize the product. A small crop of purple block crystals was observed after 9 days of slow diffusion. The crystals were isolated and dried on filter paper for 1 h before being weighed. Yield: 0.019 g (0.018 mmol, 31%); IR ($cm^{-1}$, KBr): 3453.7(br), 1645.5(m), 1639.5(m), 1476.2(w), 1421.6(w), 1230.4(s), 1186.6(s), 1142.9(m), 1039.2(vs), 766.0(m), 678.6(m), 591.2(m), 525.6(m); TGA: 25–75°C −18.1% obs. and −18.4% calcd. for loss of $11H_2O$, 75–350°C −9.3% obs. and −10.0% calcd. for loss of $6H_2O$, 400°C decomposition of **L**. Elemental analysis calcd. for **5**: C 13.00, H 4.80; found: C 13.01, H 2.64.

### *Preparation of* $\{[(Fe(H_2O)_3)_2(L)]\cdot(H_2O)_{14.5}\}_\infty$ *(6)*

$Na_6$**L** (0.080 g, 0.109 mmol) was dissolved in $H_2O$ (6 mL) to give a colourless solution to which was added slightly beige crystalline $Fe(NO_3)_2\cdot 6H_2O$ (0.088 g, 0.217 mmol), which resulted in a clear, yellow solution upon stirring. The reaction was stirred for a total of 20 h and then filtered before ethanol was slowly diffused in to crystallize the product. After 7 days of crystallization, a small crop of yellow block crystals had formed. The crystals were isolated by suction filtration for 1 h before being weighed. Yield: 0.030 g (0.027 mmol, 25%); IR ($cm^{-1}$, KBr): 3442.8(br), 1650.99(m), 1641.3(m), 1388.8(m), 1230.3(s), 1192.1(s), 1142.9(m), 1044.6(vs) 771.5(w), 684.1(m), 591.2(m), 525.6(m); TGA: 25–90°C −19.8% obs. and -19.9% calcd. for loss of $12H_2O$, 150–380°C −9.4% obs. and −9.7% calcd. for loss of $6H_2O$, 405°C decomposition of **L**. Elemental analysis calcd. for **6**: C 12.92, H 4.77; found: C 13.33, H 2.54.

### *Preparation of* $\{[(Al(H_2O)_3)_2(L)]\cdot(H_2O)_{14.5}\}_\infty$ *(7)*

$Na_6$**L** (0.086 g, 0.115 mmol) was dissolved in $H_2O$ (6 mL) to which was added white crystalline $AlCl_3\cdot 6H_2O$ (0.056 g, 0.231 mmol). After 22 h, the solution was filtered, and an acetone slow diffusion was set up to crystallize the product. A small crop of clear, colourless block crystals was observed to have formed on the bottom of the small beaker after 12 days of acetone diffusion. The crystals were isolated from the mother liquor by suction filtration for 1 h before being weighed. Yield: 0.038 g (0.037 mmol, 32%); IR ($cm^{-1}$, KBr): 3453.7(br), 1645.52(m), 1627.8(m), 1230.4(vs), 1192.1(s), 1137.5(m), 1044.6(vs), 809.7(w), 766.0(m), 678.6(m), 591.2(m), 531.1(m); TGA: 25–150°C −24.1% obs. and −24.5% calcd. for loss of $14.4H_2O$, 200–375°C −10.5% obs. and −10.2% calcd. for loss of $6H_2O$, 390°C decomposition of **L**. Elemental analysis calcd. for **7**: C 13.63, H 5.03; found: C 13.60, H 2.50.

## X-ray Crystallography

Crystals suitable for X-ray analysis were chosen under an optical microscope and quickly coated in oil before being mounted in a glass loop and frozen under a stream of liquid nitrogen.

Crystal data, refinement details and data collection parameters are given in Tables I and II. All measurements were made on a Nonius Kappa CCD diffractometer at −100°C using graphite monochromatized MoKα ($\lambda = 0.71073$ Å) radiation. Data were processed, and intensities were corrected for Lorentz and polarization effects and for absorption with DENZO software. The structures were solved by direct methods using SHELXS-97 [60] and refined on $F^2$ by full-matrix least-squares procedures with SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier atoms. Final atomic coordinates, thermal parameters

TABLE I Crystal data and refinement parameters for **1**–**4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Formula | $C_{21}H_{66}O_{39}Mg_3S_6$ | $C_{21}H_{66}O_{39}Zn_3S_6$ | $C_{24}H_{72}O_{42}Mg_3S_6$ | $C_{24}H_{72}O_{42}Zn_3S_6$ |
| $M$ ($g\,mol^{-1}$) | 1208.03 | 1331.21 | 1298.11 | 1421.29 |
| Crystal system | Trigonal | Trigonal | Trigonal | Trigonal |
| $a$ (Å) | 12.738(2) | 12.689(2) | 12.704(2) | 21.719(3) |
| $b$ (Å) | 12.738(2) | 12.689(2) | 12.704(2) | 21.719(3) |
| $c$ (Å) | 18.920(4) | 18.940(4) | 10.088(2) | 10.297(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 90 | 90 | 90 |
| $\gamma$ (°) | 120 | 120 | 120 | 120 |
| $V$ (Å$^3$) | 2658.6(8) | 2641.0(7) | 1409.9(4) | 4206.5(1) |
| $\rho_{calcd}$ ($g\,cm^{-3}$) | 1.509 | 1.674 | 1.529 | 1.683 |
| Space group | $P$-31$c$ | $P$-31$c$ | $P$-3 | $P$-3 |
| $Z$ | 2 | 2 | 1 | 3 |
| Dimensions (mm) | 0.15 × 0.15 × 0.10 | 0.20 × 0.15 × 0.10 | 0.22 × 0.17 × 0.10 | 0.25 × 0.15 × 0.10 |
| $\mu$ ($mm^{-1}$) | 0.394 | 1.690 | 0.381 | 1.602 |
| Temperature (K) | 173(2) | 173(2) | 173(2) | 173(2) |
| $2\theta_{max}$ (°) | 55 | 55 | 55 | 55 |
| No. measured | 7477 | 6761 | 4176 | 11693 |
| No. unique | 2032 | 2015 | 2140 | 6376 |
| $R_{int}$ | 0.0611 | 0.0363 | 0.0440 | 0.0669 |
| No. with $I > 2\sigma(I)$ | 1400 | 1623 | 1267 | 3178 |
| Parameters | 110 | 110 | 102 | 348 |
| $wR$ (all data) | 0.2070 | 0.1806 | 0.2566 | 0.1900 |
| $R1$ [$I > 2\sigma(I)$] | 0.0636 | 0.0609 | 0.0793 | 0.0640 |

TABLE II Crystal data and refinement parameters for **5**–**7**

| | **5** | **6** | **7** |
|---|---|---|---|
| Formula | $C_{12}H_{24}O_{38.33}Cr_2S_6$ | $C_{12}H_{24}O_{38.33}Fe_2S_6$ | $C_{12}H_{24}O_{38.33}Al_2S_6$ |
| $M$ (g mol$^{-1}$) | 1078.01 | 1085.71 | 1027.97 |
| Crystal system | Trigonal | Trigonal | Trigonal |
| $a$ (Å) | 11.988(2) | 11.978(2) | 11.985(2) |
| $b$ (Å) | 11.988(2) | 11.978(2) | 11.985(2) |
| $c$ (Å) | 24.758(5) | 24.671(5) | 24.641(5) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 90 | 90 |
| $\gamma$ (°) | 120 | 120 | 120 |
| $V$ (Å$^3$) | 3081.3(9) | 3065.8(9) | 3065.7(9) |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.743 | 1.764 | 1.670 |
| Space group | *R*-3*m* | *R*-3*m* | *R*-3*m* |
| $Z$ | 3 | 3 | 3 |
| Dimensions (mm) | 0.27 × 0.27 × 0.18 | 0.25 × 0.20 × 0.20 | 0.25 × 0.22 × 0.15 |
| $\mu$ (mm$^{-1}$) | 0.949 | 1.132 | 0.494 |
| Temperature (K) | 173(2) | 173(2) | 173(2) |
| $2\theta_{max}$ (°) | 55 | 55 | 55 |
| No. measured | 4428 | 4376 | 5856 |
| No. unique | 873 | 874 | 877 |
| $R_{int}$ | 0.0282 | 0.0309 | 0.0575 |
| No. with $I > 2\sigma(I)$ | 771 | 760 | 650 |
| Parameters | 63 | 63 | 63 |
| $wR$ (all data) | 0.3223 | 0.3532 | 0.1805 |
| $R1$ [$I > 2\sigma(I)$] | 0.1053 | 0.1173 | 0.0663 |

and complete listing of bond lengths and angles are listed in Supporting Information. CCDC reference numbers for **1**–**4**: 196018–196021; **5**: 196023; **6**: 196024; **7**: 188681.

## RESULTS AND DISCUSSION

### Structures of fully encapsulated species: [M(H$_2$O)$_6$]$_2$L·(S)$_3$ (M/S = Mg/acetone, 1; Zn/acetone, 2; Mg/dioxane, 3; Zn/dioxane, 4)

The single crystal X-ray structure determinations of divalent hexaaquo complexes, **1**–**4**, reveal that the acetone inclusion compounds, **1** and **2**, are isostructural. The overall structural motif of compound **4** is identical to that observed in compound **3**, even though two of the unit cell lengths are significantly longer. Second-sphere capsules are formed in all four compounds as a result of the high complementarity between trisulphonate faces of **L** with the triaquo faces of octahedral $[M(H_2O)_6]^{2+}$ cations. A detailed description of only the Mg acetone and dioxane inclusion complexes, **1** and **3**, respectively, will be presented as the Zn acetone/dioxane inclusion compounds are identical except for very slight variations in structural and thermal parameters, which may be ascertained from the supporting information.

### Acetone Inclusion Compounds

The asymmetric unit of **1** (Fig. 2) consists of one-sixth of a molecule of **L**, one-half of a molecule of acetone, one-third of one Mg centre with two bound water molecules, and one-sixth of another Mg centre bearing one water molecule. Of the two types of hexaaquo $Mg^{2+}$ centres in compound **1**, the first, Mg1, is not encapsulated by **L** and as such is referred to as a "naked" metal centre, which is involved in charge-balancing the second-sphere complex. Mg1 contains two crystallographically unique water molecules [Mg1–O5 = 2.059(4) Å and Mg1–O4 = 2.075(4) Å], which are used to generate the hexaaquo coordination sphere by related symmetry operations. Even though Mg1 is not encapsulated, it still participates in significant hydrogen-bonding interactions which serve to

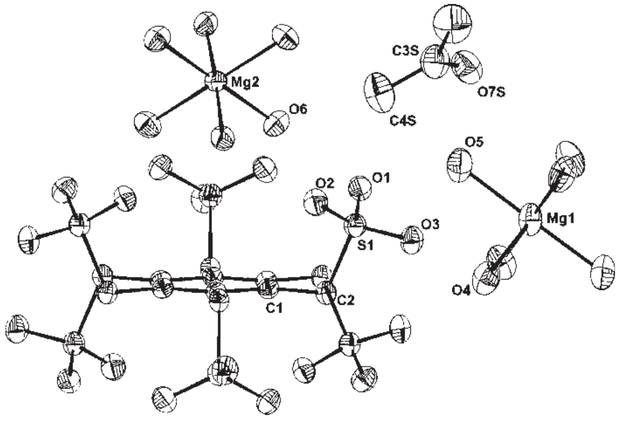

FIGURE 2 ORTEP plot of **1** showing the numbering scheme and the fully encapsulated hexaaquo Mg2 centre as well as the intrachannel hexaaquo Mg1 centre and acetone molecule. Thermal ellipsoids of 50% probability are represented.

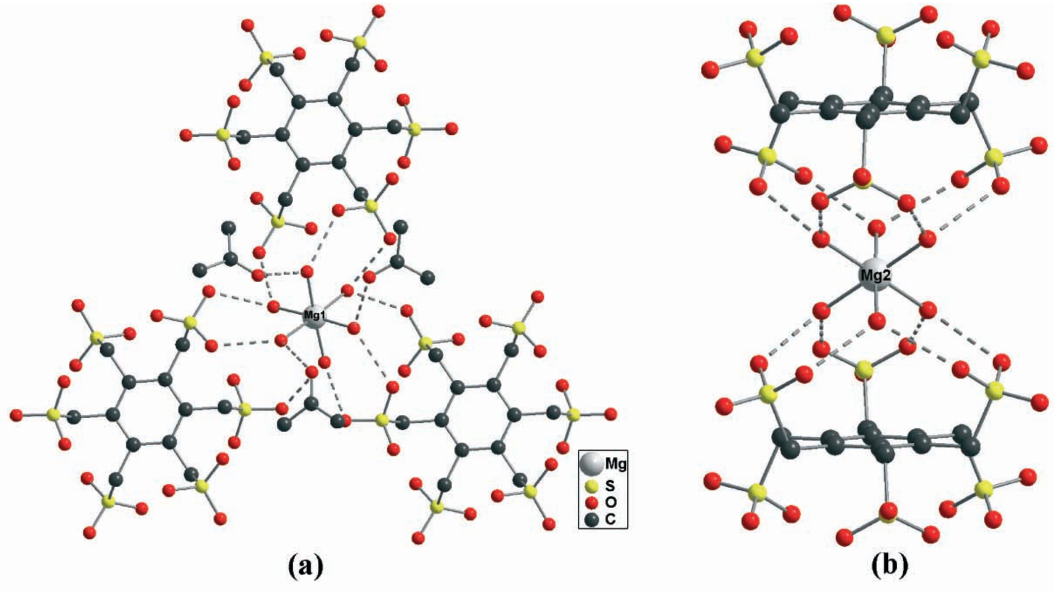

FIGURE 3 Hydrogen-bonding environments around Mg1(a) and Mg2(b) in **1**. Dashed lines represent the hydrogen-bonding interactions. (See colour plate 5 at the end of this issue.)

stabilize the overall structure. There are two charge-assisted hydrogen bonds between the coordinated water molecule, O4, on Mg1 and O3, the sulphonate oxygen atom which is not involved in hydrogen bonding to the encapsulated Mg2 centre [O4···O3 = 2.764(4) Å, O4···O3* = 2.847(4) Å]. In addition, the second crystallographically unique water molecule on Mg1, O5, also undergoes charge-assisted hydrogen-bonding interactions with one of the encapsulating sulphonate oxygen atoms [O5···O1 = 2.738(4) Å], as well as to the acetone solvate molecule [O5···O7S = 2.793(4) Å]. As a result of the symmetry operations within the crystal, each hexaaquo Mg1 centre is H-bonded, in total, to nine different sulphonate oxygen atoms from three different **L** and to three acetone molecules (Fig. 3a).

The second metal centre, Mg2, is completely encapsulated by two trisulphonate faces of two different **L** through a total of 12 charge-assisted hydrogen bonds, six to each molecule of **L** (Fig. 3b). The methylsulphonate groups on each molecule of **L** adopt a *cis*–*trans*–*cis* orientation, which places the 1,3,5- and 2,4,6- substituents on opposite sides of the planar benzene core. This ligand orientation promotes the capping of two triangular faces of two different octahedral hexaaquo Mg2 metal centres by one molecule of **L**. The two triangular triaquo faces of each Mg2 complex are then staggered with respect to either the 1,3,5- or 2,4,6- substitution pattern of **L**. All six water molecules of Mg2 are crystallographically equivalent [Mg2–O6 = 2.057(3) Å]. Both H atoms of the coordinated water molecule form hydrogen bonds to two sulphonate oxygen atoms from two different sulphonate groups [O6···O1 = 2.768(4) Å, O6···O2 = 2.733(4) Å]. The hydrogen-bonding environment about one of the segregated tris(sulphomethyl) faces of **L** is depicted in Fig. 7a. In total, each molecule of **L** undergoes 30 charge-assisted hydrogen-bonding interactions with eight surrounding hexaaquo $Mg^{2+}$ metal centres. A regular feature observed in these second-sphere aquo complexes is the hydrogen-bonding pattern which functions between two oxygen atoms of each $SO_3$ group and two water molecules occupying *cis* coordination sites on the metal centres. Interestingly, if one envisions $RNH_2$ in place of $M(H_2O)$, the hydrogen-bonding motif observed for each triaquo face is identical to that in the quasi-hexagonal layers observed by Ward *et al.* in their guanidinium sulphonate structures [61–65].

The overall packing of **1** is shown in Fig. 4. The columns of encapsulated hexaaquo Mg2 centres align along the *c*-axis, while two columns of "naked" hexaaquo Mg1 centres, interspersed by acetone solvates, separate adjacent encapsulated Mg2-**L** columns. Around each column of encapsulated Mg1 centres then lie six columns of naked Mg1 centres and six columns of acetone solvate, which give the overall hexagonal pattern of hydrogen-bonding interactions. The naked hexaaquo Mg1 centres appear slightly staggered with respect to the arrangement of triangular triaquo faces along the *c*-axis. This is a direct result of the preferred hydrogen-bonding motif which is in operation to stabilize the structure in the solid state. If this arrangement was not incurred by the crystal structure, the *cis*-aquo sulphonate hydrogen-bonding interactions could not be realized. In terms of a three-dimensional hydrogen-bonded network built from **L** and hexaaquo Mg centres,

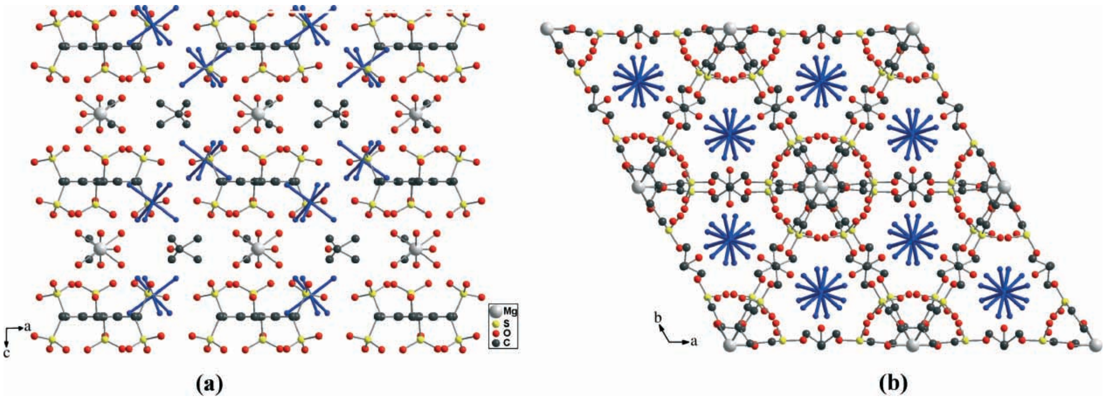

FIGURE 4 Views of **1**: (a) down the *b*-axis showing the alignment of the second-sphere encapsulation of Mg2 and the relative positioning of the "naked" hexaaquo Mg1 centres and acetone molecules. For clarity, the hydrogen atoms have been removed, and the hexaaquo Mg1 centres are shown in blue. (b) Looking down the *c*-axis showing the hexagonal H-bonded net with intrachannel $[Mg(H_2O)_6]^{2+}$ and acetone moieties. (See colour plate 5 at the end of this issue.)

the crystallized acetone moieties then serve as guest molecules. The acetone guests reside within small cages stabilized by hydrogen bonding with the naked $Mg(H_2O)_6^{2+}$ centres.

## Dioxane Inclusion Compounds

As previously mentioned, the overall structural motif of the dioxane inclusion compound **4** is essentially identical to that of **3**, even though the *a* and *b* unit cell axis are approximately 8 Å longer (Tables I and II). As a result, the asymmetric units will be reported for both **3** and **4**, although a detailed description of the extended networks will be limited to **3**. Pertinent structural information will be presented on compound **4**. The variations in thermal and structural parameters can be ascertained from the supporting information.

The asymmetric unit of **3** (Fig. 5a) consists of one-sixth of a molecule of **L**, one-half molecule of dioxane, one-third of one Mg centre with two bound water molecules, and one-sixth of another Mg centre bearing one water molecule. In the crystal structure of **3**, the first crystallographically unique Mg centre, Mg1, is again the "naked" metal centre, which is involved in charge-balancing the second-sphere complex. Mg1 contains two types of crystallographically unique water molecules [Mg1–O5 = 2.057(4) Å and Mg1–O4 = 2.059(4) Å], which, through symmetry, generate the hexaaquo octahedral coordination sphere. The coordinated water molecule, O4, undergoes two charge-assisted hydrogen-bonding interactions with the sulphonate oxygen atom, O1, which is not involved in hydrogen bonding with the encapsulated Mg2 centre [O4···O1 = 2.913(5) Å, O4···O1* = 2.781(5) Å]. The second crystallographically unique water molecule participates in hydrogen bonding to one of the encapsulating sulphonate oxygen atoms [O5···O2 = 2.721(5) Å] as well as to the crystallized dioxane molecule [O5···O7S = 2.632(7) Å]. Through symmetry operations, each hexaaquo Mg1 centre is

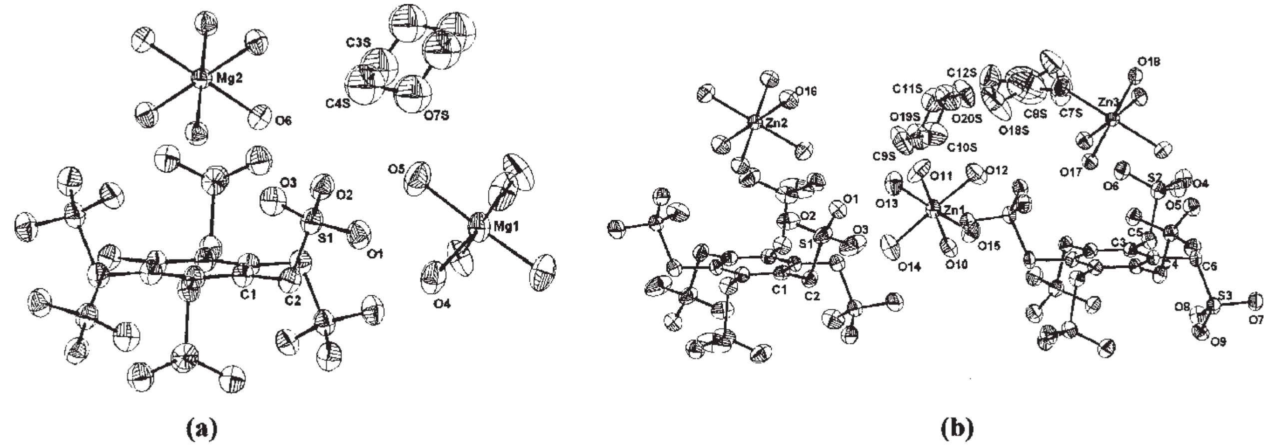

FIGURE 5 ORTEP plot of **3**(a) and **4**(b) showing the numbering scheme of the asymmetric units. Thermal ellipsoids have been drawn at the 50% probability level.

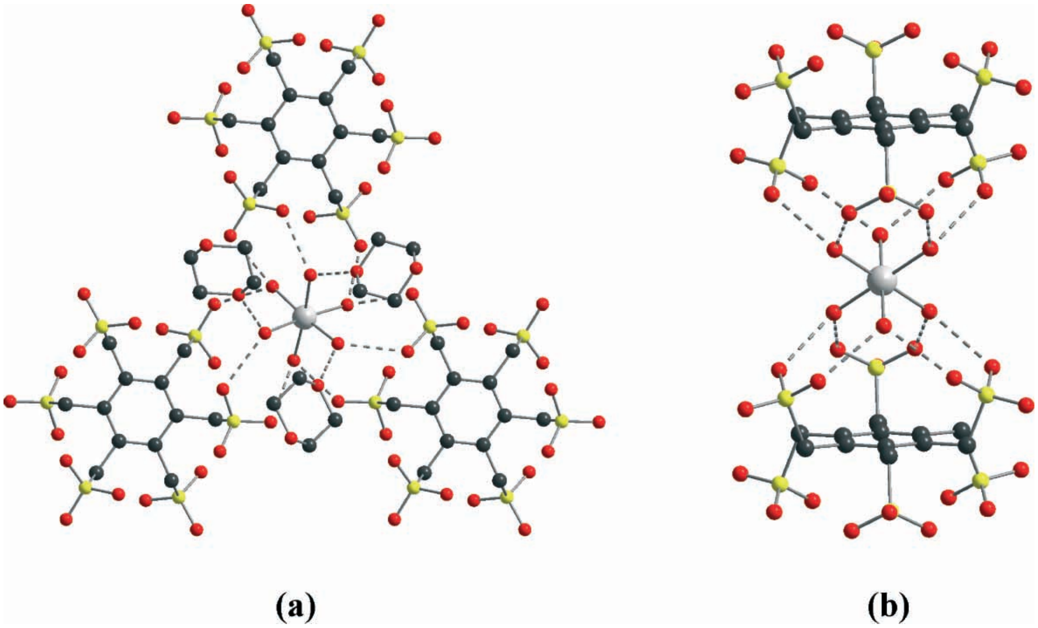

FIGURE 6 Hydrogen-bonding environments around Mg1 (a) and Mg2 (b) in **3**. Dashed lines represent the hydrogen-bonding interactions. (See colour plate 6 at the end of this issue.)

hydrogen-bonded, in total, to nine sulphonate oxygen atoms and three dioxane molecules (Fig. 6a). Although Mg1 is not encapsulated by **L**, the hydrogen-bonding interactions which are in operation help to stabilize the overall structure. As observed in the crystal structure of **1**, the encapsulated hexaaquo metal centre, Mg2, participates in a total of 12 charge-assisted hydrogen bonds, six to each molecule of **L** (Fig. 6). The methylsulphonate groups on each molecule of **L** again adopt a *cis–trans–cis* orientation, which promotes the capping of two triangular faces of two different octahedral hexaaquo Mg2 metal centres. The two triangular triaquo faces of each Mg2 are similarly staggered with respect to the methylsulphonate substitution pattern of **L**. The coordination sphere around Mg2 consists of six crystallographically equivalent water molecules [Mg2–O6 = 2.068(3) Å]. Two oxygen atoms from two different sulphonate groups form hydrogen bonds to each of the coordinated water molecules [O6···O3 =2.804(5) Å, O6···O2 = 2.775(4) Å] to generate the second-sphere complex. Fig. 7b depicts the hydrogen-bonding environment about one of the tri(sulphomethyl) faces of **L**. The hydrogen bonding about **L** in **3** is exactly the same as that observed in **1**. As such, the complete hydrogen-bonding picture about **L**, a total of 30 hydrogen bonds to eight surrounding hexaaquo $Mg^{2+}$ metal centres, can be visualized by combining the top and bottom faces in the two

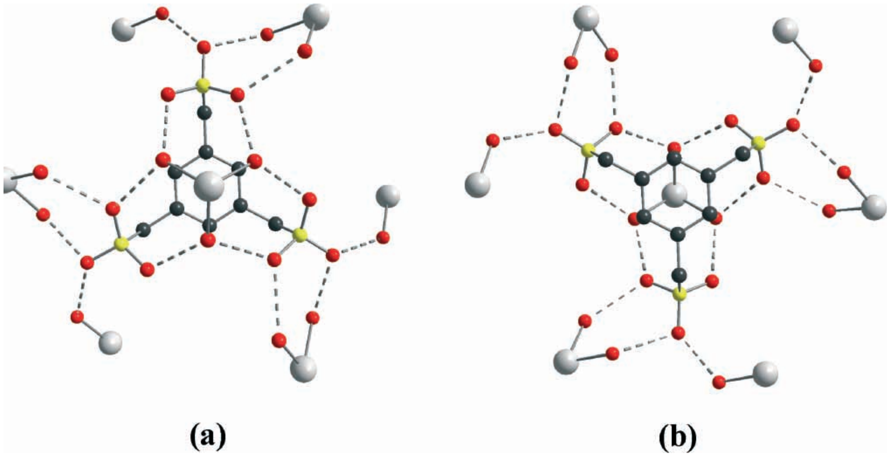

FIGURE 7 (a) Hydrogen-bonding environment about the top tri(sulphomethyl) face of **L** in **1**. A total of 15 hydrogen bonds are depicted by the dashed lines. The complete hydrogen-bonding environment about **L** could be generated by an inversion centre placed at the centre of the benzene core. (b) Hydrogen-bonding environment about the bottom tri(sulphomethyl) face of **L** in **3**. (See colour plate 6 at the end of this issue.)

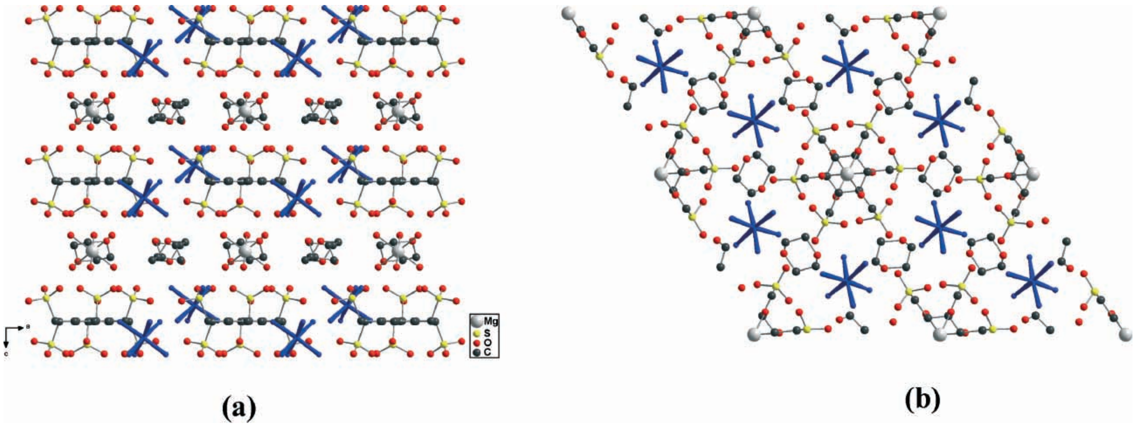

FIGURE 8 Views of **3**: (a) down the *b*-axis showing the alignment of the second-sphere encapsulation of Mg2 and the relative positioning of the "naked" hexaaquo Mg1 centres and dioxane molecules. For clarity, the hydrogen atoms have been removed, and the hexaaquo Mg1 centres are shown in blue. (b) Looking down the *c*-axis showing the hexagonal H-bonded net with intrachannel $[Mg(H_2O)_6]^{2+}$ and dioxane moieties. (See colour plate 7 at the end of this issue.)

images from Fig. 7. Hydrogen bonding of *cis*-aquo water molecules on the metal centres to two oxygen atoms from the same $SO_3$ group is also prevalent throughout these dioxane inclusion compounds.

The extended structure of **3** can be viewed in Fig. 8. The columns of encapsulated hexaaquo Mg2 centres are in a strikingly similar arrangement as was seen in the structure of **1**. The second-sphere encapsulation is aligned along the *c*-axis where adjacent columns are separated by two columns of "naked" hexaaquo Mg1 centres interspersed with one column of dioxane solvate molecules, as can be seen upon viewing the extended structure perpendicular to the columns. Six columns of naked metal centres and six columns of dioxane solvate surround each column of Mg2-L to give the overall hexaganal hydrogen-bonding array. With the inclusion of dioxane molecules, the slightly staggered orientation of the naked metal centres which was seen in the extended structure of **1** is not required to attain stable networks. In these structures, the crystallized dioxane molecules can also be viewed as guests in the three-dimensional hydrogen-bonded network to which dioxane is hydrogen-bonded solely to the naked $Mg(H_2O)_6^{2+}$ centres.

The asymmetric unit of **4** (Fig. 5b) contains half of a molecule of **L**, one and a half molecules of dioxane, one Zn centre bonded to six unique water molecules, one-third of another Zn centre bound to two unique water molecules, and one-sixth of a third Zn centre with one unique water molecule. The two encapsulated $Zn(H_2O)_6^{2+}$ centres, Zn2 and Zn3, have one [Zn2–O16 = 2.094(4) Å] and two [Zn3–O17 = 2.104(3) Å and Zn3–O18 = 2.106(3) Å] crystallographically unique water molecules, respectively, which are acted upon by symmetry to generate the full hexaaquo coordination sphere around the metals. Each water oxygen atom participates in two hydrogen bonds with sulphonate oxygen atoms to generate the completely encapsulated species [for Zn2: O16···O1 = 2.746(6) Å and O16···O2 = 2.773(5) Å; for Zn3: O17···O6 = 2.779(5) Å, O17···O4 = 2.782(5) Å, O18···O8 = 2.784(5) Å, O18···O9 = 2.762(5) Å]. This hydrogen-bonding pattern is identical to that depicted in Figs. 3b and 6b. The naked metal centre, Zn1, has six crystallographically unique bound water molecules with bond lengths ranging from 2.048(4) Å to 2.122(4) Å. Three of the water molecules, O11–O13, each form one hydrogen bond to a dioxane molecule [O11···O20S = 2.637(6) Å, O12···O18S = 2.676(7) Å, O13···O19S = 2.659(6) Å] and one hydrogen bond to a sulphonate oxygen atom involved in the second-sphere encapsulation [O11···O9 = 2.728(6) Å, O12···O4 = 2.793(6) Å, O13···O2 = 2.741(6) Å]. The remaining three water molecules, O10, O14 and O15, each form two hydrogen bonds to the sulphonate oxygen atoms, which are not involved in second-sphere encapsulation [O10···O3 = 2.705(6) Å and O10···O5 = 2.815(5) Å, O14···O3 = 2.988(7) Å and O14···O5 = 2.790(5) Å, O15···O7 = 2.750(5) Å and O15···O7* = 2.840(5) Å]. A depiction of the hydrogen bonding around Zn1 is presented in Fig. 9. The difference in hydrogen bonding in this structure compared with the hydrogen bonding observed in the previously reported structures is that O14 on Zn1 does not participate in *cis*-aquo sulphonate hydrogen bonding because of the orientation of the second type of crystallized dioxane molecule. As a result of this, the aymmetric unit contains three times the amount of atoms that was observed in the structure of **3**. The hydrogen-bonding environments about both crystallographically unique molecules of **L** are presented in Fig. 10. In total, each molecule of **L** undergoes 30 charge-assisted hydrogen-bonding interactions with eight surrounding hexaaquo $Mg^{2+}$ metal centres. Although additional dioxane molecules were crystallized within this network, the *cis*-aquo sulphonate

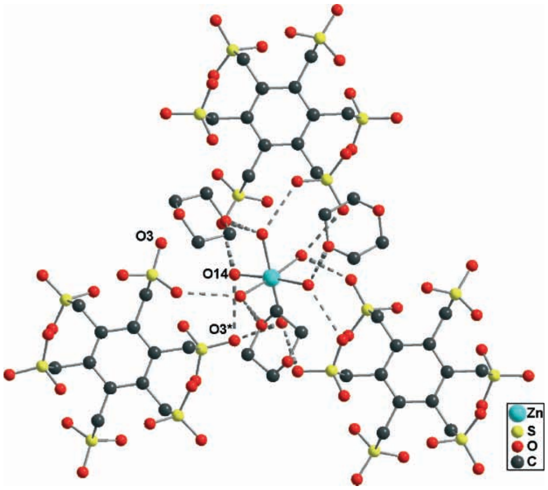

FIGURE 9 Hydrogen-bonding environments around the naked hexaaquo Zn1 metal centre in **4**. Dashed lines represent the hydrogen-bonding interactions. The missing *cis*-aquo sulphonate hydrogen bond should exist between labelled atoms O14 and O3. In addition, the hydrogen bond between O14 and O3* is absent in previous structures. (See colour plate 7 at the end of this issue.)

hydrogen-bonding motif was still observed to be in operation.

## Structures of Extended Networks: $\{[(M(H_2O)_3)_2(L)]\cdot(H_2O)_{14.5}\}_\infty$ (M = Cr, 5; Fe, 6; Al, 7)

The single crystal X-ray structures for **5**–**7** reveal that these compounds are completely isostructural. The higher residual values which were observed for the crystal structures of **5** and **6** are not unreasonable given that an excessive number of disordered water molecules (14.4 per structural unit) are occupying the elaborate channel systems within the porous networks. In addition, the residual values calculated for the isostructural **7** ($R = 6.63\%$, $R_w = 18.05\%$), with exactly the same position, number, and occupancy of non-coordinated water molecules, were found to be quite low. As a result, it was believed that the data sets collected for **5** and **6** were most likely of a poorer quality compared with **7**, and hence resulted in the observed moderate $R$ values for these networks. Extended two-dimensional sheets were constructed from coordinate bonding of the sulphonate groups to the trivalent metal centres. Extension of these networks into the third dimension was afforded through second-sphere encapsulation of the triaquo faces by tri(sulphomethyl) substituents from **L** in adjacent two-dimensional sheets. Owing to the isostructural morphologies, only the complete structural description for the $Al^{3+}$ containing compound **7** will be given. The very slight variations in structural and thermal parameters for compounds **5** and **6** may be ascertained from the supporting information.

The highly symmetric space group, $R$-3$m$, within which **7** crystallized is supported by the extremely small asymmetric unit containing one-sixth of an $Al^{3+}$ centre bearing a half occupied water molecule, one-twelfth of a molecule of **L**, and a total of 1.2 water molecules spread over five crystallographically unique positions (Fig. 11). Remarkably, the coordination sphere around the one crystallographically unique $Al^{3+}$ centre, Al1, is composed of three symmetry equivalent sulphonate oxygen atoms [Al1–O2 = 2.382(4) Å] and three symmetry equivalent water molecules [Al1–O3 = 2.374(5) Å]. As such, one triangular face on the Al1 centre consists of oxygen atoms from three sulphonate groups on three different ligands, while three coordinated water

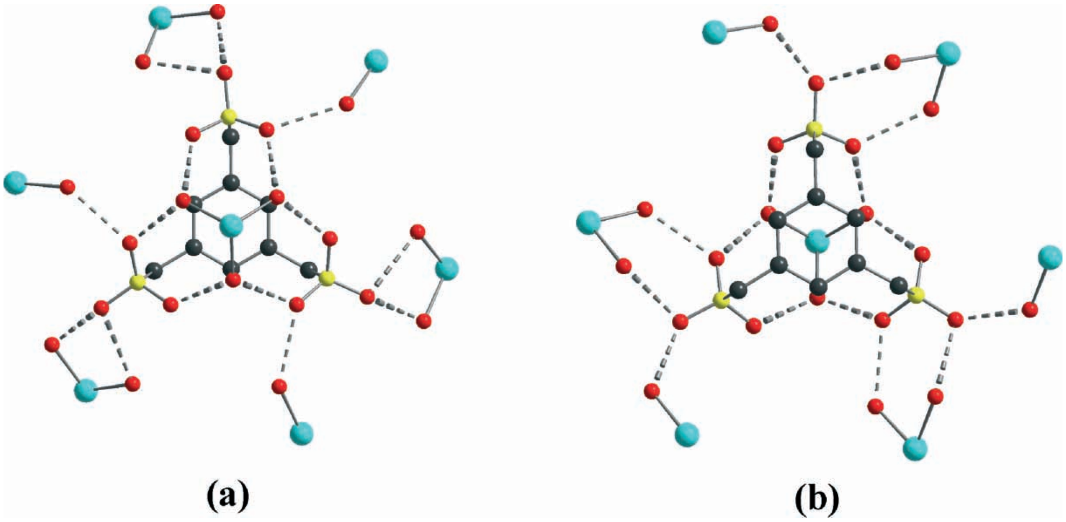

FIGURE 10 (a) Hydrogen-bonding environment about the top tri(sulphomethyl) face of one molecule of **L** in **4**. A total of 15 hydrogen bonds are depicted by the dashed lines. (b) Hydrogen-bonding environment about the top tri(sulphomethyl) face of the second type of **L** in **4**. The complete hydrogen-bonding environment about both crystallographically unique molecules of **L** could be generated by an inversion centre placed at the centre of the benzene core. (See colour plate 8 at the end of this issue.)

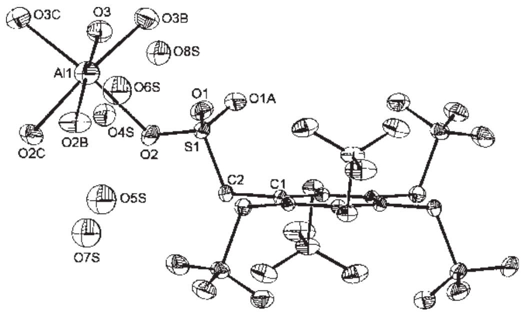

FIGURE 11 ORTEP plot of **7** showing the numbering scheme of the asymmetric unit. Thermal ellipsoids have been drawn at the 50% probability level.

molecules construct the opposite triangular face. A mirror plane runs through each sulphonate group along S1 to O2 and relates the equivalent O1 atoms which are not involved in coordinate bonding to the metal centres. The ligand is in the *cis*–*trans*–*cis* conformation where alternating methylsulphonate groups are located above and then below the plane of the aromatic ring. Owing to the extraordinarily high symmetry observed within the crystal structure, each **L** undergoes $\eta^6$, $\mu^6$ coordinate bonding with the surrounding $Al^{3+}$ metal centres. Although, based on proximity, numerous hydrogen-bonding interactions between the sulphonate groups and the non-coordinated water molecules are most likely present within the structure of **7**, these hydrogen bonds were unable to be confirmed as the hydrogen atoms on these water molecules could not be located within the crystal structure. However, one hydrogen-bonding interaction was found to exist between a coordinated water molecule and one of the non-coordinated guest water molecules [O3···O8S = 3.076(19) Å].

A view of the extended two-dimensional network formed by the assembly of **L** with trivalent aluminium metal centres in the solid state can be seen in Fig. 12. The layers within the crystal structure of **7** are held together by means of second-sphere encapsulation of the triangular triaquo faces on Al1 centres from one layer with the perfectly orientated **L** from an adjacent layer. As a result, each triaquo face undergoes a total of six charge-assisted hydrogen-bonding interactions with the symmetry equivalent oxygen atoms on the sulphonate groups [three sets of O3···O1 = 2.787(4) Å, O3···O1 = 2.787(4) Å]. The previously mentioned *cis*-aquo sulphonate hydrogen-bonding motif is again maximized to afford the second-sphere complex. The two-dimensional coordinate architecture is thereby effectively extended into the third dimension by the extensive hydrogen-bonding interactions operating between the layers.

Examining the crystal structure on a 45° angle to the *ab*-plane revealed the formation of a porous channel system within which the non-coordinated water molecules reside (Fig. 12b). The square channels are constructed from two $Al^{3+}$ centres in conjunction with two **L** and have dimensions of 7.495(1) Å by 7.495(1) Å (~4.1 by 4.1 Å with van der Waals considerations), as measured by the transannular S1–S1 distances. For each molecule of **L**, 14.5 molecules of water are found in the channels, as was determined crystallographically and corroborated by TGA data. The sulphonate oxygen atoms which are involved with the second-sphere encapsulation are also oriented for effective hydrogen bonding to the guest water molecules which reside within the host framework. Overall, there are six equivalent channels around each molecule of **L**.

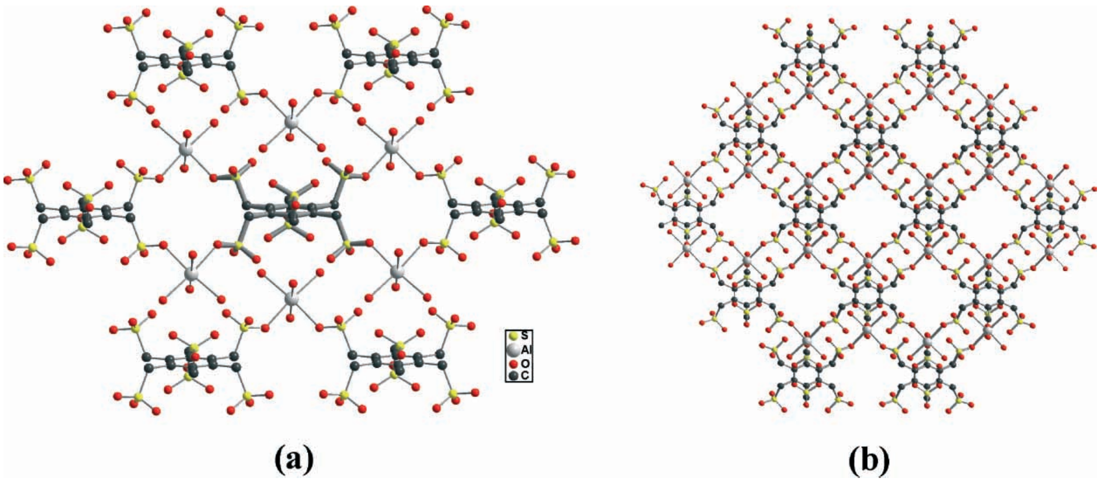

FIGURE 12 (a) Packing view of the infinitely extending two-dimensional layers in **7** perpendicular to the *c*-axis showing the connectivity of a single molecule of **L** in three dimensions. One molecule of **L**, situated centrally, is shown with thickened bonds. The non-coordinated water molecules and hydrogen atoms have been omitted for clarity. (b) Packing view of **7** at a 45° angle on to the *ab*-plane depicting the channel system which runs through the extended structure. (See colour plate 8 at the end of this issue.)

## Complementary Hydrogen-bonding Motifs

The propensity for *cis*-aquo ligands to hydrogen bond with the sulphonate functionality appears to be a reliable synthon for the construction of supramolecular coordination solids. The encapsulation of triaquo metal faces by the 1,3,5- and 2,4,6-tri(sulphomethyl) substituents on **L** maximizes the occurrence of this type of hydrogen-bonding motif. Furthermore, the non-encapsulated metal centres in compounds **1–4** also participate in second-sphere interactions. The aquo ligands on these metal centres, however, only exhibit partial *cis*-aquo sulphonate hydrogen-bonding interactions as a result of the crystallized solvent molecules. In essence, the complementary second-sphere interactions are disrupted because of the additional hydrogen bonding to the solvent molecules. As will be discussed later, this disruption adversely effects the stabilization of the dehydration temperature for the naked hexaaquo metal centres. In compounds **5–7**, the complementary second-sphere interactions between **L** and the triaquo face of trivalent metal centres serve to extend the coordination network into the third dimension. A search of the Cambridge Structural Database revealed that, in the absence of structural constraints, the *cis*-aquo sulphonate hydrogen-bonding motif is unquestionably prevalent [66–79]. Metal complexes with *cis*-aquo ligands and sulphonate anions were examined, employing the Mercury program to elucidate hydrogen bonding. Of 226 compounds, over half (127 or 56.2%) showed the hydrogen-bonding motif between the aquo ligands and two adjacent sulphonate oxygen atoms. The next most common motif involves hydrogen bonds to a single sulphonate oxygen atom. It should be noted that these statistics represent the occurrence of this interaction when they have not been specifically targeted as a supramolecular synthons. The structural constraints imposed by the sterically demanding orientation of six sulphomethyl groups about a benzene core in **L** then appears to have a beneficial effect for maximizing the complementary hydrogen-bonding motif.

## Thermogravimetric Analysis

The loss of solvent molecules, both coordinated and non-coordinated, from within the crystal structures of **1–7** was measured and quantified by thermogravimetric analysis. As expected, similar trends were observed in the mass losses for structurally related compounds. Specifically for **1** and **2**, the guest acetone molecules were lost rapidly at ambient conditions and up to ~110°C (−13.09% calcd., −13.88% obs.). This merges with a second mass loss of the 18 bound water molecules up to a temperature of 265°C (−25.47% calcd., −24.99% obs.). The second mass loss is rapid at the beginning of the run but becomes more gradual toward the end of the heating program. The final mass loss, above 350°C, corresponds to decomposition of **L**. Typically, aquo ligands in transition metal complexes are lost at temperatures below 150°C [80–83]. The TGA data correlate well with the naked metal centres being dehydrated early on in the heating process while the encapsulated hexaaquo metal centres are more resistant to dehydration because of the maximized number of complementary second-sphere interactions with the ligand. This postulation is also supported by the fact that the asymmetric unit contains twice the number of naked metal ions than encapsulated ions. As a result, the initial dehydration step should have been twice as large as the final dehydration mass loss. Indeed, this general detail is discernible from the TGA data as the second mass loss trails well into the heating program, almost to the ligand decomposition temperature. Comparatively, the aquo ligands of the encapsulated metal centre have been stabilized by >100°C through the secondary coordination sphere, a very significant value given that only weak interactions are involved. Undoubtedly, the disruption of *cis*-aquo sulphonate hydrogen bonding by the incorporation of the more volatile acetone molecules plays a significant role in facilitating the loss of the aquo ligands on the naked metal centre.

Complexes **3** and **4** also show similar trends in TGA data, but individual mass losses could not be ascertained as only one large broad mass loss was observed between 100°C and 330°C. The majority of this mass loss occurs between 100°C and 175°C, followed by a very slow loss to 330°C. The overall mass loss corresponds to the complete desolvation of 3 dioxane and 18 water molecules (−45.33% calcd., −44.62% obs.) from the compounds. The final mass loss, above 350°C, corresponds to the decomposition of **L**. The larger initial mass loss is assigned to the loss of dioxane guests and water molecules bound to the naked metal centres. The remainder of the gradual mass loss to 330°C is then assigned to the dehydration of the encapsulated metal centres. As seen in **1** and **2**, the asymmetric units for **3** and **4** also contain twice the number of naked metal centres as encapsulated metal centres, adding further validity to the assignments made in the TGA data.

The TGA data for extended structures **5–7** are remarkably similar, reflecting the isostructural nature of these compounds. Early in the heating program, 25–150°C, a large mass loss is observed, which corresponds to the complete removal of all 14.4 water molecules (−24.5% calcd., −24.1% obs.) from the channels of the extended structures. The remaining coordinated water molecules are then slowly lost up to a temperature of 375°C. The last mass loss, at 390°C, corresponds to the ligand decomposition temperature. The aquo ligands in these compounds have been stabilized by $>200$°C through complementary second-sphere interactions. Undoubtedly, the added stability is associated with the coordination of **L** in the formation of the extended structure. As a result of this coordination, both the 1,3,5- and 2,4,6-tri(sulphomethyl) faces of **L** become ideally positioned to undergo hydrogen-bonding interactions with the remaining triaquo faces of the coordinated metal centres from adjacent layers. The result extends the structure into the third-dimension by essentially "locking" the second-sphere interactions into place. The structurally stability of the extended structures was examined by powder X-ray diffraction analysis. Upon removal of the 14.4 water molecules from the channels, it was observed that the solids undergo a structural change to a second ordered phase which retains the coordinated aquo ligands and is stable up to 300°C.

A key point in determining the stabilization of the primary coordination sphere by the hydrogen bonding to sulphonates is the freedom of the benzylic carbons to rotate. Rotation about the aryl-benzyl bond decreases the preorganization of **L** and hence destabilizes the hydrogen bonding. In **1–4**, the "external" hydrogen-bonding faces of each $SO_3$ group interact with volatile included solvent, resulting in considerable destabilization. In **5–7**, the "external" sulphonate oxygen atom is involved in coordinate bonding with a trivalent metal centre so it is rigidly fixed in place.

## CONCLUSIONS

The predictable ordering of molecular species in the solid state is the fundamental premise of the discipline known as crystal engineering [11]. Given that two commonly employed approaches to the generation of extended supramolecular solids are to sustain the network via metal–ligand interactions [84–88] and/or by complementary hydrogen-bonding interactions [15–18,89–96], the use of second-sphere interactions to assemble supramolecular solids seems almost a corollary. It is surprising then that extended solids generated deliberately utilizing these interactions are rare. The complementary second-sphere coordination chemistry of a novel hexasulphonated ligand has been presented. The persubstituted benzene derivative provides two segregated trisulphonated faces with 1,3,5- and 2,4,6-tri(sulphomethyl) substituents adopting mutually *syn* orientations. This conformational preference has frequently been described as "steric gearing" for its utility in preorganizing supramolecular hosts [97]. With divalent hexaaquo ions, complete second-sphere encapsulation of $M(H_2O)_6^{2+}$ centres was realized in **1–4** through 12 charge-assisted hydrogen-bonding interactions. The primary aquo coordination sphere was stabilized by over 100°C owing to the electrostatic pairing of the constituents and to the high complementarity of the ligand with the triangular aquo faces of the metal complexes. The dominant hydrogen-bonding motif observed in these systems is the complementarity between adjacent oxygen atoms of a sulphonate group and *cis*-oriented aquo ligands on the metal centre. Given the recurrent nature of this interaction in aquated metal complexes with sulphonate-based ligands, it has promise as a new supramolecular synthon. Indeed, this work illustrates that second-sphere interactions involving sulphonate moieties have considerable potential in the construction of designed solids. For those interested in generating coordination solids, the use of a binding group, such as the sulphonate functionality, that frequently will not displace solvent from the primary coordination sphere of a metal complex, seems counterintuitive. However, we have shown that with proper ligand design, the extended coordinate networks **5–7** can be constructed which exploit both primary and cooperative secondary sphere interactions. These neutral frameworks exhibit porous channel systems which are filled with guest water molecules. These results serve to illustrate many of the core principles of supramolecular chemistry, those being the importance of preorganization, complementarity, and cooperativity between numerous intermolecular interactions. In a more general sense, these results have implications for the assembly and stabilization of both extended and discrete metal complexes in the solid state.

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### *References*

[1] Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145.
[2] Wachhold, M.; Rangan, K. K.; Lei, M.; Thorpe, M. F.; Billinge, S. J. L.; Petkov, V.; Heising, J.; Kanatzidis, M. G. *J. Solid State Chem.* **2000**, *152*, 21.
[3] Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13.
[4] Aoyama, Y. *Top. Curr. Chem.* **1998**, *198*, 131.
[5] Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107.
[6] Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

[7] Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.

[8] Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

[9] Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

[10] Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431.

[11] Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

[12] Desiraju, G. R. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E., MacNicol, D. D., Vögtle, F., Eds.; Elsevier: New York, 1996; Vol. 6, p 1.

[13] Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357.

[14] Etter, M. *Acc. Chem. Res.* **1990**, *23*, 120.

[15] Beatty, A. M. *CrystEngComm* **2001**, *51*, 1.

[16] Kurth, D. G.; Fromm, K. M.; Lehn, J. M. *Eur. J. Inorg. Chem.* **2001**, *6*, 1523.

[17] Burrows, A. D.; Chan, C. W.; Chowdhry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, *24*, 329.

[18] Beauchamp, D. A.; Loeb, S. J. *Chem. Eur. J.* **2002**, *8*, 5084.

[19] Loeb, S. J. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E., MacNicol, D. D., Vögtle, F., Eds.; Elsevier: New York, 1996; Vol. 1, p 733.

[20] Raymo, F. M.; Stoddart, J. F. *Chem. Ber.* **1996**, *129*, 981.

[21] Crumbliss, A. L.; Batinic-Haberle, I.; Spasojevic, I. *Pure Appl. Chem.* **1996**, *68*, 1225.

[22] Zamaraev, K. *New J. Chem.* **1994**, *18*, 3.

[23] Botta, M. *Eur. J. Inorg. Chem.* **2000**, *3*, 399.

[24] Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J.; Westenholme, J. B.; Zarzycki, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1051.

[25] Amini, M. M.; Rheingold, A. L.; Taylor, R. W.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 7289.

[26] Colquhoun, H. M.; Doughty, S. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 235.

[27] Colquhoun, H. M.; Doughty, S. M.; Stoddart, J. F.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1639.

[28] Alston, D. R.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1602.

[29] Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 846.

[30] Alston, D. R.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 821.

[31] Alston, D. R.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J.; Zarzycki, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 693.

[32] Dalgarno, S. J.; Raston, C. L. *Chem. Commun.* **2002**, *19*, 2216.

[33] Atwood, J. L.; Ness, T.; Nichols, P. J.; Raston, C. L. *Cryst. Growth Des.* **2002**, *2*, 171.

[34] Atwood, J. L.; Barbour, L. J.; Hardie, M. J.; Raston, C. L. *Coord. Chem. Rev.* **2001**, *222*, 3.

[35] Webb, H. R.; Hardie, M. J.; Raston, C. L. *Chem. Eur. J.* **2001**, *7*, 3616.

[36] Eller, P. G.; Penneman, R. A. *Inorg. Chem.* **1976**, *15*, 2439.

[37] Bombieri, G.; de Paoli, G.; Immirzi, A. *Inorg. Chim. Acta* **1976**, *18*, 23.

[38] Beer, P. D.; Drew, M. G. B.; Ogden, M. J. *J. Chem. Soc., Dalton Trans.* **1997**, 1489.

[39] Junk, P. C.; Atwood, J. L. *J. Organomet. Chem.* **1998**, *565*, 179.

[40] Amini, M. M.; Rheingold, A. L.; Taylor, R. W.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 7289.

[41] Jarrin, J.; Dawans, F.; Robert, F.; Jeannin, Y. *Polyhedron* **1982**, *1*, 409.

[42] Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 61.

[43] Vance, T. B.; Holt, E. M.; Pierpont, C. G.; Holt, S. L. *Acta Crystallogr. Sect. B* **1980**, *36*, 153.

[44] Rogers, R. D.; Kurihara, L. K. *Inorg. Chim. Acta* **1987**, *130*, 131.

[45] Colquhoun, H. M.; Lewis, D. F.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1983**, 607.

[46] Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1051.

[47] Cameron, B. R.; Corrent, S. S.; Loeb, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2689.

[48] Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1995**, *36*, 5656.

[49] Ando, I.; Higashi, M.; Ujimoto, K.; Kurihara, H. *Inorg. Chim. Acta* **1999**, *282*, 247.

[50] Lewis, G. R.; Orpen, A. G. *Chem. Commun.* **1998**, 1873.

[51] Rivas, J. C. M.; Brammer, L. *Inorg. Chem.* **1998**, *37*, 4756.

[52] Ferlay, S.; Félix, O.; Hosseini, M. W.; Planeix, J. M.; Kyritsakas, N. *Chem. Commun.* **2002**, 702.

[53] Kawata, S.; Kitagawa, S.; Kumagai, H.; Kudo, C.; Kamesaki, H.; Ishiyama, T.; Suzuki, R.; Kondo, M.; Katada, M. *Inorg. Chem.* **1996**, *35*, 4449.

[54] Kawata, S.; Kitagawa, S.; Kumagai, H.; Ishiyama, T.; Honda, K.; Tobita, H.; Adachi, K.; Katada, M. *Chem. Mater.* **1998**, *10*, 3902.

[55] Johnson, C. P.; Atwood, J. L.; Steed, J. W.; Bauer, C. B.; Rogers, R. D. *Inorg. Chem.* **1996**, *35*, 2602.

[56] Shubnell, A. J.; Kosnic, E. J.; Squattrito, P. J. *Inorg. Chim. Acta* **1994**, *216*, 101.

[57] Dalrymple, S. A.; Parvez, M.; Shimizu, G. K. H. *Chem. Commun.* **2001**, 2672.

[58] Dalrymple, S. A.; Shimizu, G. K. H. *Chem. Commun.* **2002**, 2224.

[59] Dalrymple, S.A., Parvez, M., Shimizu, G.K.H. *Inorg. Chem.* In press.

[60] *SHELXS-97*; Bruker AXS: Madison, WI, 1997.

[61] Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.

[62] Holman, K. T.; Martin, S. M.; Parker, D. P.; Ward, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 4421.

[63] Swift, J. A.; Pivovar, A. M.; Reynolds, A. R.; Ward, M. D. *J. Am. Chem. Soc.* **1998**, *120*, 5887.

[64] Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107.

[65] Holman, K. T.; Pivovar, A. M.; Ward, M. D. *Science* **2001**, *294*, 1907.

[66] Hagen, K. S. *Inorg. Chem.* **2000**, *39*, 5867.

[67] Walsh, B.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1980**, 681.

[68] Atwood, J. L.; Orr, G. W.; Means, N. C.; Hamada, F.; Zhang, H.; Bott, S. G.; Robinson, K. D. *Inorg. Chem.* **1992**, *31*, 603.

[69] Takahashi, Y.; Akita, M.; Kichi, S. H.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186.

[70] Hernandez-Molina, R.; Dybtsev, D. N.; Fedin, U. P.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *Inorg. Chem.* **1998**, *37*, 2995.

[71] Tandon, S. S.; Mandel, S. K.; Thompson, L. K.; Hynes, R. K. *Inorg. Chem.* **1992**, *31*, 2215.

[72] Airey, S.; Drljaca, A.; Hardie, M. J.; Raston, C. L. *Chem. Commun.* **1999**, 1137.

[73] Johnson, C. P.; Atwood, J. L.; Steed, J. W.; Bauer, C. B.; Rogers, R. D. *Inorg. Chem.* **1996**, *35*, 2602.

[74] Funaioli, T.; Cavezza, C.; Marchetti, F.; Fachinetti, G. *Inorg. Chem.* **1999**, *38*, 3361.

[75] Gunderman, B. J.; Kabell, I. D.; Squattrito, P. J.; Dubey, S. N. *Inorg. Chim. Acta* **1997**, *258*, 237.

[76] Turokowski, P. N.; Bino, A.; Lippard, S. *J. Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 811.

[77] Sakane, G.; Hachimoto, K.; Takahashi, M.; Takeda, M.; Shibahara, T. *Inorg. Chem.* **1998**, *37*, 4231.

[78] Holt, D. G. L.; Larkworthy, C. F.; Povey, D. C.; Smith, G. W.; Leigh, G. J. *Inorg. Chim. Acta* **1990**, *169*, 201.

[79] Ruiz, J.; Florenciano, F.; Vicente, C.; Ramirez de Arellano, M. C.; Lopez, G. *Inorg. Chem. Comm.* **2000**, *3*, 73.

[80] Apblett, A. W.; Cubano, L. A.; Georgieva, G. D.; Mague, J. T. *Chem. Mater.* **1996**, *8*, 650.

[81] Maleki, A.; Gajerski, R.; Labus, S.; Prochowska-Klisch, B.; Wojciechowski, K. T. *J. Therm. Anal. Cal.* **2000**, *60*, 17.

[82] Langfelderova, H. *J. Therm. Anal.* **1994**, *41*, 955.

[83] Maneva, M.; Kovandjiev, P. *J. Therm. Anal.* **1993**, *39*, 1347.

[84] Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

[85] Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13.

[86] Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117.

[87] Moulton, B.; Zaworotko, B. *Chem. Rev.* **2001**, *101*, 1629.

[88] Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.

[89] Hollingsworth, M. D.; Brown, M. E.; Hillier, A. C.; Santarserio, B. D.; Chaney, J. D. *Science* **1996**, *273*, 1355.

[90] Horner, M. J.; Holman, K. T.; Ward, M. D. *Angew. Chem., Int. Ed.* **2001**, *40*, 4045.
[91] Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem., Soc.* **1997**, *119*, 2737.
[92] Endo, K.; Sawaki, T.; Koyonagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341.
[93] Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894.
[94] Thallapally, P. K.; Chakraborty, K.; Katz, K.; Carrell, H. L.; Kotha, S.; Desiraju, G. R. *CrystEngComm* **2001**, *3*, 1.
[95] Aakeroy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 1815.
[96] Aakeroy, C. B.; Beatty, A. M.; Leinen, D. S.; Lorimer, K. R. *Chem. Commun.* **2000**, 935.
[97] Hennrich, G.; Anslyn, E. V. *Chem. Eur. J.* **2002**, *8*, 2219.