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Supramolecular Chemistry

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First published on: 27 July 2010

To cite this Article Guo, Fang , Xia, Fang , Lu, Na , Tong, Jian and Guo, Wen-sheng(2010) 'Supramolecular inclusion of a pillared double-layered host by an anion-directed second-sphere coordination', *Supramolecular Chemistry*, 22: 9, 548 – 553, First published on: 27 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/10610278.2010.497210

URL: <http://dx.doi.org/10.1080/10610278.2010.497210>

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Supramolecular inclusion of a pillared double-layered host by an anion-directed second-sphere coordination

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(Received 4 March 2010; final version received 20 May 2010)

In this paper, we have illustrated the utilisation of a second-sphere coordination approach to construct supramolecular inclusion solids with varieties of guest molecules. A flexible molecule *N,N,N',N'*-tetra-*p*-methylbenzyl-ethylenediamine (**L1**) bearing doubly protonated H-bond donors was designed, capable of forming N–H···Cl hydrogen bonds with a crystallographically unique chloride anion, to construct an anion-directed ligand. The pillared double-layered host framework was constructed by an anion-directed ligand and primary coordination sphere [CoCl₄]²⁻ through weak C–H···Cl hydrogen-bonding interactions. A variety of guest molecules, such as *p*-anisaldehyde, 1,4-dimethoxy-2,5-bis(methoxymethyl)benzene, can be included, leading to the formation of novel supramolecular inclusion solids: [**L1**]₄[H]⁺·[CoCl₄]²⁻·2Cl⁻·1.5[C₈H₈O₂]·0.25[CH₃OH] (**1**) and [**L1**]₄[H]⁺·[CoCl₄]²⁻·2Cl⁻·1.5[C₁₂H₂₀O₄]·0.5[CH₃OH] (**2**).

Keywords: second-sphere coordination; anion receptor; inclusion complex; pillared double-layered host; [CoCl₄]²⁻

1. Introduction

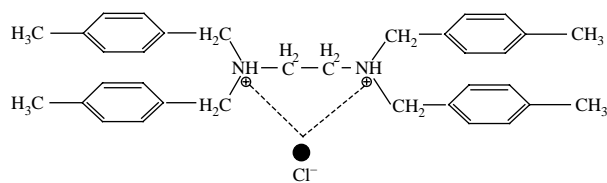
One long-term goal in the design and synthesis of functional solid-state materials is to accommodate and recognise a variety of guest molecules. The concept of second-sphere coordination (1, 2), originating from Alfred Werner's classical works on coordination chemistry, has recently afforded an attractive route to this goal, in which the design and synthesis of suitable neutral or charged second-sphere ligands that can coordinate with the primary coordination sphere via non-covalent interactions is necessarily demanded (3, 4, 5). For example, bis-amidiniums was exploited as tetra- and octa-H-bond donor dicationic tectons, to coordinate with the primary coordination sphere [M(CN₆)]³⁻ (Co, Fe), showing supramolecular enantiomers and the inclusion of water molecules (6). Disulphonate anions, 1,4-piperazine-bis(ethanesulphonate) and 2,6-naphthalenedisulphonate, interacted with [Co(NH₃)₆Cl]²⁺ to construct a pillared layered super-complexes for the inclusion of water or dioxane molecules (7). [4,4'-H₂bipip]²⁺ (8) and 4-carboxy phenylboronic (9) constructed second-sphere coordination complexes with [Pt(CN)₄]²⁻ and Co(H₂O)₆²⁺, including acetonitrile and water, respectively. Recently, a caged supramolecular structure formed with a tripodal tris(3-pyridylurea) receptor has been reported to encapsulate the sulphate ion (10). But even if the second-sphere coordination approach offers us such an opportunity to obtain supramolecular inclusion solids, the inclusion of more sophisticated guest components by exploiting a

specific host framework has thus far been reported to be relatively few.¹

Molecular recognition directed by anion receptors is a chemical incident that has occurred over the past decade (11). Since the first design and synthesis of an inorganic 'tennis-ball' encapsulated by the BF₄⁻ anion (12), the use of anions to template assemblies is becoming a new area in supramolecular chemistry (13). In the present study, we wish to report on our successful employment of the anion-directed ligand to construct a novel type of a second-sphere coordination complex. Furthermore, this second-sphere coordination complex can construct an interesting host framework to trap different aromatic guest molecules. The molecule *N,N,N',N'*-tetra-*p*-methylbenzyl-ethylenediamine (**L1**) was designed with the following structural features: (i) two N functional groups are located in the middle positions, instead of the α, ω position which appeared in most of the reported ligands, and (ii) two N atoms are protonated and the substituent bulky benzyl rings are properly spaced by ethylenediamine, with the measuring N–N distance around 3.3 Å. Such a structure may ensure the recognition between the chloride anion (as a template acceptor) and the doubly protonated **L1** through N–H···Cl···H–N interactions, to form an anion-directed ligand. The anion-directed ligand exhibits a cationic moiety, as shown in Scheme 1.

Because the doubly protonated **L1**, behaving as the only strong H-bond donors, participates in the formation of the anion-directed ligand with Cl⁻ via N–H···Cl hydrogen bonding, the other weak H-bond sites of **L1**,

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Scheme 1. Anion-directed ligand **L1**.

such as methylene or phenyl rings, can provide the propensity for the formation of second-sphere coordination complexes with the primary coordination sphere $[\text{CoCl}_4]^{2-}$ through weak $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonding. Another significant merit of such a design for **L1** is that the substituent bulky benzyl rings residing on the outside of **L1** can act as the component of constructing layers or channels, and can generate a suitable size of region or void space accessible to various guest molecules.

Following the above design, a pillared double-layered host framework was constructed by a second-sphere coordination approach. A variety of guest molecules, such as *p*-anisaldehyde, 1,4-dimethoxy-2,5-bis(methoxymethyl)benzene, can be included, leading to the formation of supramolecular inclusion solids: $[\text{L1}]\cdot 4[\text{H}]^+\cdot [\text{CoCl}_4]^{2-}\cdot 2\text{Cl}^- \cdot 1.5[\text{C}_8\text{H}_8\text{O}_2]\cdot 0.25[\text{CH}_3\text{OH}]$ (**1**) and $[\text{L1}]\cdot 4[\text{H}]^+\cdot [\text{CoCl}_4]^{2-}\cdot 2\text{Cl}^- \cdot 1.5[\text{C}_{12}\text{H}_{20}\text{O}_4]\cdot 0.5[\text{CH}_3\text{OH}]$ (**2**).

2. Experimental section

2.1 Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purifications. IR spectra were obtained with a Perkin-Elmer 100 FT-IR spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz) at 25°C with TMS as the internal reference.

2.2 Preparation of ligand **L1**

Seven millilitres of ethylenediamine were slowly added into the solution of 8 g of NaOH and 20 ml of distilled water. Thirty millilitres of *p*-methylbenzyl chloride (2–3 drops/s) were then continuously added into the mixture solution. After the reaction was heated to 95°C and stirred for 4 h, the mixture was cooled to room temperature. The white reaction product was separated from diethyl ether, and then washed with distilled water. Recrystallisation using anhydrous ethanol and drying *in vacuo* produced white crystals of 18.5 g, yield 77%. Mp 95–97°C. IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3045 (w, ArH), 1615, 1513, 1450 (s, Ar), 2924 (s, CH_2), 2948 (s, CH_3); ^1H NMR (CDCl_3 , 300 MHz) δ : 2.32 (6H, s, CH_3), 2.57 (2H, s, CH_2), 3.45 (4H, s, CH_2), 7.05–7.16 (8H, m, ArH).

2.3 Crystal preparation of

$[\text{L1}]\cdot 4[\text{H}]^+\cdot [\text{CoCl}_4]^{2-}\cdot 2\text{Cl}^- \cdot 1.5[\text{C}_8\text{H}_8\text{O}_2]\cdot 0.25[\text{CH}_3\text{OH}]$ (**1**) and

$[\text{L1}]\cdot 4[\text{H}]^+\cdot [\text{CoCl}_4]^{2-}\cdot 2\text{Cl}^- \cdot 1.5[\text{C}_{12}\text{H}_{20}\text{O}_4]\cdot 0.5[\text{CH}_3\text{OH}]$ (**2**)

In a 50 ml Erlenmeyer flask, 0.12 g of **L1**, 20 ml of methanol and 0.5 ml of *p*-anisaldehyde were placed, and then 1 ml of concentrated hydrochloric acid and 0.11 g of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ were added and shaken until the contents were dissolved. The flask was allowed to stand for over 10 days at room temperature. After the crystals were separated out by filtration, recrystallisation gave a sizeable amount of blue and transparent block crystals (**1**). Mp 161–166°C; IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3431 (s, OH), 2732, 2565 (s, N^+H), 1680 (s, $\text{C}=\text{O}$); ^1H NMR (D_3CSOCD_3 , 300 MHz) δ : 2.32 (12H, s, CH_3), 3.18 (1H, s, CH_3), 3.36 (4H, s, CH_2), 3.86 (2.3H, s, $-\text{OCH}_3$), 4.10 (8H, s, CH_2), 7.12–7.34 (17.5H, m, ArH), 7.86–7.88 (1.5H, m, ArH), 9.87 (0.7H, s, CHO), 11.33 (2H, s, N^+H). The same experimental procedure was carried out for the crystal preparation of **2**, with 0.5 ml of 1,4-dimethoxy-2,5-bis(methoxymethyl)benzene (synthesised) added into the flask. Mp 148–153°C; IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 2894, 2664 (s, N^+H), 1280, 1080 (s, $\text{Ar}-\text{O}-\text{CH}_3$); ^1H NMR (D_3CSOCD_3 , 300 MHz) δ : 2.34 (12H, s, CH_3), 3.68 (4H, s, CH_2), 3.24 (4.5H, s, $-\text{OCH}_3$), 3.75 (4.5H, s, $-\text{OCH}_3$), 4.60 (3H, s, CH_2), 4.05 (8H, s, CH_2), 7.12–7.34 (16H, m, ArH), 6.8–6.9 (1.4H, m, ArH), 11.85 (2H, s, N^+H).

2.4 X-ray crystallographic study

Single crystals were mounted on a Bruker Smart 1000 CCD X-ray diffractometer equipped with a graphite-monochromated Mo $\text{K}\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected at 294 K. The unit cell parameters were obtained with least-squares refinements and the data were collected for absorption using the SADABS program. The structures were determined using direct methods and refined (based on F^2 using all independent data) by full-matrix least-squares methods (SHELXTL 97). Data were reduced using the Bruker SAINT software (14). All non-hydrogen atoms were directly located from different Fourier maps and refined with an isotropic displacement parameter. CCDC 735382 and 748441 contain the supplementary crystallographic data.

3. Results and discussion

3.1 Crystal structures of **1** and **2**

The structure of **1** crystallises as a triclinic crystal system, and the space group is $\text{P}\bar{1}$ (Table 1). One asymmetric unit contains one dianion $[\text{CoCl}_4]^{2-}$, two doubly protonated **L1**, two anions of Cl^- , 1.5 molecules of *p*-anisaldehyde and 0.25 molecule of methanol.

Table 1. Crystal data and refinement summary for **1** and **2**.

	1	2
Formula	C _{80.25} H ₉₇ Cl ₆ Co ₁ N ₄ O _{3.25}	C ₈₁ H ₁₀₂ Cl ₆ Co ₁ N ₄ O _{3.5}
Formula weight	1441.25	1459.30
Crystal size (mm)	0.26 × 0.20 × 0.14	0.24 × 0.20 × 0.18
Temperature	294(2)	294(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	4
<i>a</i> (Å)	15.7128(19)	16.591(4)
<i>b</i> (Å)	16.1717(19)	27.469(6)
<i>c</i> (Å)	17.988(2)	18.978(4)
α (°)	69.687(2)	90
β (°)	67.616(2)	109.351(4)
γ (°)	89.617(2)	90
<i>V</i> (Å ³)	3921.9(8)	8160(3)
<i>D</i> _x (g cm ⁻³)	1.220	1.188
μ (mm ⁻¹)	0.471	0.454
<i>F</i> (000)	1523	3092
<i>R</i> _{int}	0.0233	0.1168
No. of collected data (unique)	13758	14412
No. of data with <i>I</i> > 2σ(<i>I</i>)	8492	5163
No. of refined parameters	872	881
<i>R</i> _p / <i>wR</i> _f	0.0530/0.1572	0.0787/0.1985
All data <i>R</i> _p / <i>wR</i> _f	0.0992/0.1954	0.2236/0.2642
<i>s</i>	1.067	1.086

[CoCl₄]²⁻ forms a distorted tetrahedron with Co–Cl bond lengths in the range of 2.2564(17)–2.2767(12) Å, and Cl–Co–Cl bond angles in the range of 105.94(5)°–112.47(6)°. The second-sphere coordination is constructed by [CoCl₄]²⁻ and four molecules of **L1** via eight C–H···Cl weak interactions, as shown in Figure 1(a).

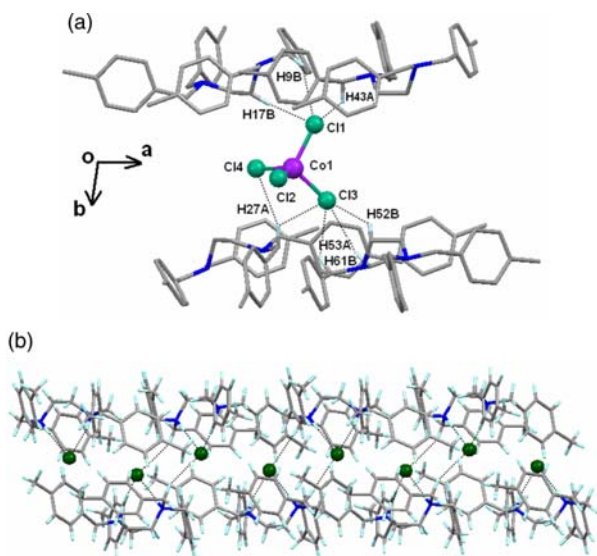


Figure 1. Crystal **1**: (a) construction of a second-sphere coordination through C–H···Cl weak hydrogen bonding interactions and (b) the linear layer formed by anion-directed ligands.

The doubly protonated **L1** is a divalent cation. The crystallographically unique chloride anion is held in place between two protonated amine N atoms of **L1**. The N–N distances (3.264(1) Å in one ligand and 3.237(1) Å in the other ligand) ensure the recognition between the chloride anion and the doubly protonated **L1** through N–H···Cl interactions [N1–H1···Cl5: 3.071(1) Å, 175.7(1)°; N2–H2···Cl5: 3.121(1) Å, 163.9(1)°; N3–H3···Cl6: 3.062 Å, 162.9(1)°; N4–H4···Cl6: 3.092(1) Å, 176.7(1)°], forming an anion-directed ligand. A pair of anion-directed ligands arrange along the *c*-axis to form a linear double chain through C–H···Cl weak interactions (3.747(1) Å, 156.9(1)°) (Figure 1(b)), and are further extended along the *a*-axis into 2D double layers. The 2D layers are linked by [CoCl₄]²⁻ as molecular pillars to form a pillared double-layered structure (Figure 2).

The pillared double-layered structure, as a host framework, generates two regions accessible to guest molecules, as shown in Figure 3(a). The dimension size of the smaller region is approximately 3.698(1) × 7.66(1) Å (defined by Cl4–Cl4 and H21–H21, respectively), and the Co···Co distance between the pillars is 14.9297(1) Å. The approximate dimension of the larger region is 10.52(1) × 5.51(1) Å, defined by Cl2–Cl2 and H51B–H51B, respectively. The Co···Co distance between the pillars is 10.7967 Å. The guest molecules *p*-anisaldehyde and methanol are disorderly accommodated inside the two regions. C–H···O, C–H···π and C–H···Cl weak interactions between the guest and the

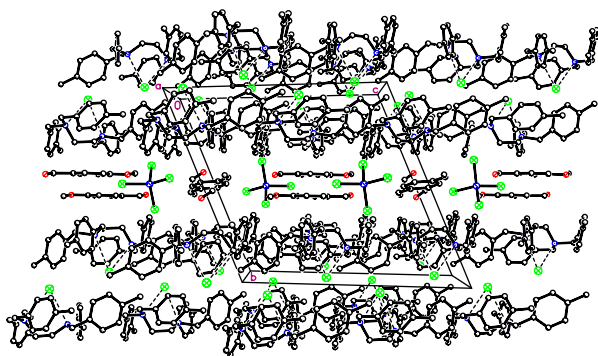


Figure 2. Pillared double-layered host framework of crystal **1**.

host framework reinforce the stability of the resulting supramolecular inclusion complex (Figure 3(b)).

In crystal **1**, the molecule **L1** adopts a linear conformation, in which the substituent benzyl groups attached to N are aligned in a straight arrangement viewed from the projection of the Newman-type overlay of the two N atoms, with the torsion angles of the benzyl rings and N1–N2 (or N3–N4) are 168.5° (C10–N1–N2–C20) and 168.1° (C2–N1–N2–C28) for one **L1**; 175.0° (C36–N3–N4–C62) and 169.4° (C44–N3–N4–C54) for the other **L1**. Such conformation of **L1** facilitates the formation of linear layers.

Crystal **2** crystallises as a monoclinic crystal system, and the space group is $P2_1/c$ (Table 1). One asymmetric unit comprises one dianion $[\text{CoCl}_4]^{2-}$, two doubly protonated **L1**, two Cl^- anions, 1.5 molecules of 1,4-dimethoxy-2,5-bis(methoxymethyl)benzene and 0.5 molecule of methanol. $[\text{CoCl}_4]^{2-}$ shows four almost equal Co–Cl bond lengths (2.271(2), 2.272(3), 2.275(3) and 2.279(2) Å), and the Cl–Co–Cl bond angles are in the range of 104.57(12)°–113.32(10)°.

Similar to crystal **1**, the dianions $[\text{CoCl}_4]^{2-}$ are also sandwiched between neighbouring layers formed by doubly protonated **L1**. The crystallographically unique chloride anion is again held in place between two protonated amine N atoms of **L1**. The N–N distances of 3.295(1) Å and 3.297(1) Å between two nitrogen atoms in two **L1** and localisation of two acidic protons on **L1** allow the recognition of chloride anions. The extended 2D zigzag-shaped layers are formed by the molecules of **L1** via N–H...Cl bidentate hydrogen bonds with Cl^- anions (Figure 4(a)). $[\text{CoCl}_4]^{2-}$ serve as molecular pillars between the adjacent double layers, generating the space for the inclusion of guest molecules, as shown in Figure 4(b). The dimensions of the regions are about 7.02(1) × 11.76(1) Å, and the Co...Co distance between the pillars is 13.63(1) Å, as shown in Figure 4(c). The guest molecules of 1,4-dimethoxy-2,5-bis(methox-

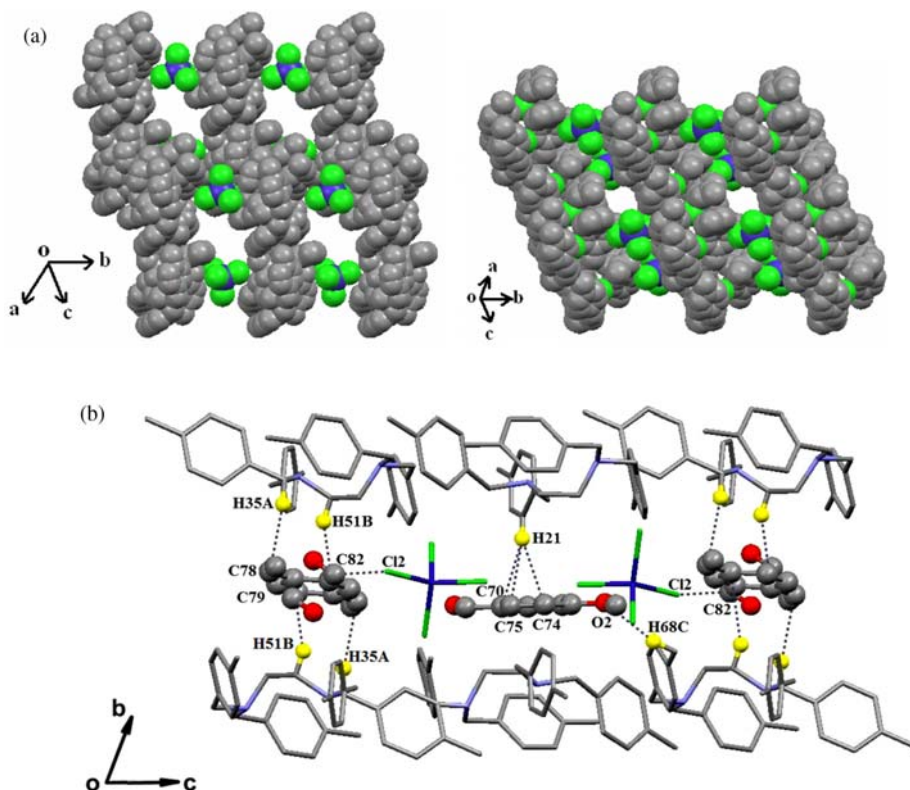


Figure 3. Crystal **1**: (a) two regions accessible to guest molecules and (b) interactions between guest molecules and the host framework.

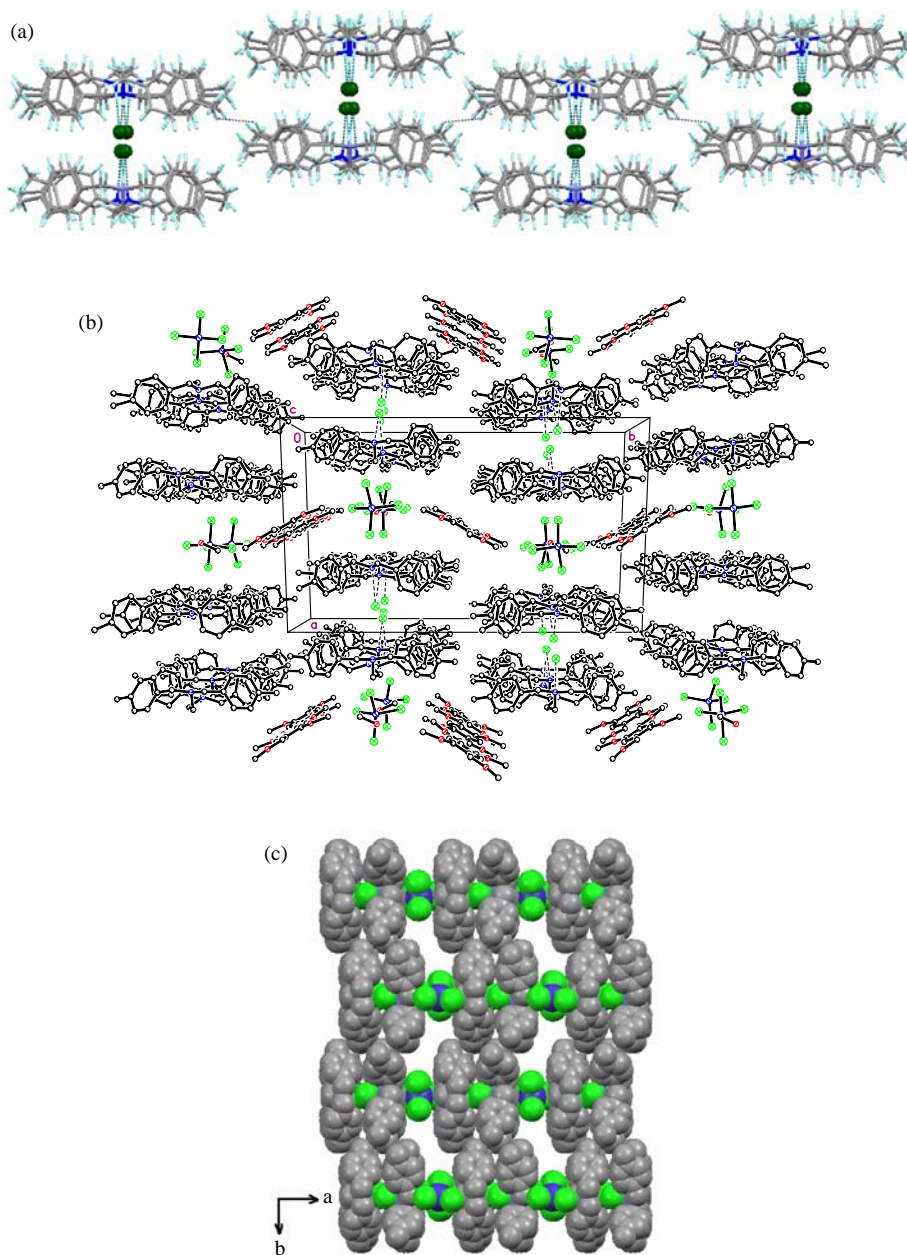


Figure 4. Crystal **2**: (a) zigzag layer formed by anion-directed ligands, (b) pillared double-layered structure and (c) regions accessible to guest molecules.

ymethyl)benzene and methanol are located inside the region through C—H··· π interactions.

The molecule **L1** adopts a similar conformation as that of **1**, viewed from the projection of the Newman-type overlay of the two N atoms, with the torsion angles between the benzyl rings and N1—N2 (or N3—N4) being 173.48° (C10—N1—N2—C20) and 167.47° (C2—N1—N2—C28) for one molecule of **L1**; 167.76° (C36—N3—N4—C62) and 171.88° (C44—N3—N4—C54) for the other molecule of **L1**, respectively.

3.2 Thermal analysis

Thermogravimetric analysis was carried out on crystals of **1**. The result shows that the crystals of **1** are thermally stable up to about 125°C, which is the onset temperature for guest desorption. The mass loss above 235°C was considered to be a result of the further decomposing of the host framework.

3.3 Inclusion properties

The available channel dimensions calculated for a pillared double-layered host framework can match the size of

accommodated guest molecules, such as *p*-anisaldehyde (a), providing a good candidate of a host framework to act as a 'zeolite-like' material and selectively include other certain aromatic guest molecules. Experiments with other guest molecules, such as *o*-salicylaldehyde (b), benzaldehyde (c), 4-hydroxy-3-methoxybenzaldehyde (vanillin, d) and *p*-hydroxybenzaldehyde (e), were carried out, leading to the formation of different adducts or inclusion complexes of the formula $[\mathbf{L1}\cdot\text{CoCl}_4] \times (\text{guest})$.² FT-IR spectra and ¹H NMR of all inclusion complexes confirmed the presence of the solvent molecules with different host-guest stoichiometries. The examination of the FT-IR spectra shows the characteristic bands of ligand and solvent guest bands as indicated below: (1) *o*-salicylic aldehyde bands at 1659 cm⁻¹ (s, C=O) for $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ (b); (2) benzaldehyde bands at 1695 cm⁻¹ (s, C=O) for $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ (c); (3) vanillin bands at 1676 cm⁻¹ (s, C=O) for $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ (d); and (4) *p*-hydroxybenzaldehyde bands at 1685 cm⁻¹ (s, C=O) for $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ (e).

4. Conclusions

The examples we have presented herein illustrate the utilisation of a second-sphere coordination approach to construct supramolecular inclusion solids with a variety of guest molecules. Based on the concept developed in the field of molecular recognition of anions, we have designed and synthesised a doubly protonated molecule with the N functional groups located in the middle, capable of forming N—H...Cl hydrogen bonding with chloride anions, to construct the anion-directed ligands. The anion-directed ligands interact with $[\text{CoCl}_4]^{2-}$ through C—H...Cl interactions to construct a pillared double-layered host framework. The bulky benzyl rings of **L1** give rise to a suitable size of void space for the inclusion of guest molecules, such as *p*-anisaldehyde, 1,4-dimethoxy-2,5-bis(methoxymethyl)benzene, leading to the formation of supramolecular inclusion solids **1** and **2**. In addition, the host framework can also include other aromatic guest molecules, such as *o*-salicylaldehyde, benzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and *p*-hydroxybenzaldehyde.

Acknowledgement

This work was supported by the National Science Foundation of China (Nos. 20772054, 20903052).

Notes

- Based on the search from the Cambridge Structural Database system, Version 5.30.
- The same experimental procedures were carried out for the crystal preparations of $[\mathbf{L1}\cdot\text{CoCl}_4] \times (\text{guest})$, with a suitable amount of *p*-anisaldehyde (a), salicylic aldehyde (b), benzaldehyde (c), vanillin (d), *p*-hydroxybenzaldehyde (e)

added into the flasks separately. $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ [b]: mp 144–149°C; IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3427 (s, OH), 2732, 2558 (s, N⁺H), 1659 (s, C=O); ¹H NMR (D₃CSOCD₃, 300 MHz) δ : 2.33 (12H, s, CH₃), 3.17 (1H, s, CH₃), 3.39 (4H, s, CH₂), 4.16 (8H, s, CH₂), 6.96–7.67 (18H, m, ArH), 10.27 (0.5H, s, CHO), 10.76 (0.5H, s, —OH), 11.27 (2H, s, N⁺H). $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ [c]: mp 148–154°C; IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3434 (s, OH), 2732, 2592 (s, N⁺H), 1695 (s, C=O); ¹H NMR (D₃CSOCD₃, 300 MHz) δ : 2.32 (12H, s, CH₃), 3.17 (0.8H, s, CH₃), 3.39 (4H, s, CH₂), 4.14 (8H, s, CH₂), 7.21–7.34 (16H, m, ArH), 7.59–7.75 (2.3H, m, ArH), 7.91–7.93 (1.5H, m, ArH), 10.02 (0.8H, s, CHO), 11.32 (2H, s, N⁺H). $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ [d]: mp 131–137°C; IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3431 (s, OH), 2732, 2592 (s, N⁺H), 1676 (s, C=O); ¹H NMR (D₃CSOCD₃, 300 MHz) δ : 2.32 (12H, s, CH₃), 3.17 (0.9H, s, CH₃), 3.38 (4H, s, CH₂), 3.83 (2.3H, s, —OCH₃), 4.11 (8H, s, CH₂), 6.99 (0.7H, m, ArH), 7.22–7.35 (17.5H, m, ArH), 9.77 (0.7H, s, CHO), 11.35 (2H, s, N⁺H). $[\mathbf{L1}\cdot\text{CoCl}_4]\cdot 1.5$ [e]: mp 165–171°C; IR (KBr), $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3423 (s, OH), 3298 (w, Ar—OH), 2732, 2562 (s, N⁺H), 1685 (s, C=O); ¹H NMR (D₃CSOCD₃, 300 MHz) δ : 2.33 (12H, s, CH₃), 3.17 (1H, s, CH₃), 3.39 (4H, s, CH₂), 4.15 (8H, s, CH₂), 6.93–6.96 (1.5H, m, ArH), 7.22–7.35 (16H, m, ArH), 7.75–7.77 (1.5H, m, ArH), 9.79 (0.75H, s, CHO), 10.67 (0.75H, s, OH), 11.31 (2H, s, N⁺H).

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