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### Inclusion of an anion guest within a molecular host formed by (4,6-dimethyl-1,3-phenylene)bis(N, N-dibenzylmethane) and $[\text{CuCl}_4]^{2-}/[\text{TeCl}_6]^{2-}$ through second-sphere coordination

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## Inclusion of an anion guest within a molecular host formed by (4,6-dimethyl-1,3-phenylene)bis(*N,N*-dibenzylmethane) and $[\text{CuCl}_4]^{2-}/[\text{TeCl}_6]^{2-}$ through second-sphere coordination

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In this work, we have utilized the second-sphere coordination approach toward the construction of supramolecular inclusion solids  $\text{Cl} \cdot 2\text{H}_2\text{O} \subset [\text{H}_2\text{L}1]_{0.5} \cdot [\text{CuCl}_4]_{0.5}$  (Crystal **1**) and  $\text{Cl} \subset [\text{H}_2\text{L}1] \cdot [\text{TeCl}_6]_{0.5}$  (Crystal **2**). The chloride anions can be encapsulated inside the host assemblies formed by the diamine molecule (4,6-dimethyl-1,3-phenylene)bis(*N,N*-dibenzylmethane) (**L1**) and the metal complexes ( $[\text{CuCl}_4]^{2-}$  and  $[\text{TeCl}_6]^{2-}$ ) via second-sphere coordination. The complexes have been structurally characterized by X-ray crystallography, indicating that weak  $\text{C-H} \cdots \text{Cl}$  hydrogen-bonding synthons play a significant role in the construction of second-sphere coordination complexes. 2-D networks are formed in both complexes by the interconnection of 1-D networks through multiple  $\text{C-H} \cdots \text{Cl}$  hydrogen-bonding interactions with  $[\text{CuCl}_4]^{2-}$  and  $[\text{TeCl}_6]^{2-}$ . The guest chlorides are encapsulated inside the host cages through  $\text{N-H} \cdots \text{Cl}$  hydrogen bonds.

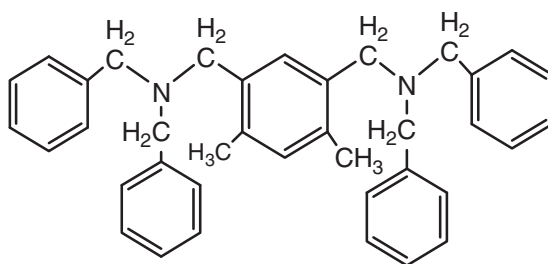
*Keywords:* Anion recognition; Second-sphere coordination; Supramolecular chemistry; X-ray crystallography;  $[\text{CuCl}_4]^{2-}/[\text{TeCl}_6]^{2-}$

### 1. Introduction

Molecular recognition directed by anion receptors has emerged as a major area in supramolecular chemistry [1–3], partly because anions play many essential roles in the environment, industrial, and health-related perspectives [4]. The synthesis of supramolecular solid-state structures with various hosts including anion guest species in the crystalline phase is a subject of intense investigation [5–8]. The binding of anionic species to a host molecule may occur by one of the three effects or act in combination: electrostatic attraction by cationic centers, formation of polar bonds with Lewis-acid centers, and formation of hydrogen bonds.

Recently, the second-sphere coordination approach [9, 10] toward the construction of supramolecular coordination polymers has attracted much attention as they offer

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Scheme 1. Scheme of **L1**.

intriguing possibilities for the inclusion and aggregation of guest molecules [11–15], and as well exhibit intriguing architectures and topologies [16–18]. Second-sphere coordination refers to any intermolecular interactions with the primary coordination sphere of a metal ion [10], in which choice of metal with specific coordination geometries and the suitable design of ligands are key steps in the production of second-sphere coordination complexes. Based on the second-sphere coordination approach, some remarkable supramolecular inclusion complexes with different guest encapsulations have been reported; however, the inclusion of more sophisticated guest molecules or anionic species by exploiting specific host frameworks has thus far been relatively rarely reported [19].

To achieve such inclusion systems, we have recently focused on the design of diamine ligands with metal chloride salts  $MCl_2$  to obtain second-sphere coordination complexes so as to encapsulate varieties of aromatic guest molecules [20]. In this work, we report successful employment of second-sphere coordination approach into the construction of host frameworks to trap the anionic guest. (4,6-Dimethyl-1,3-phenylene)bis(*N,N*-dibenzylmethane) (**L1**, scheme 1) has been synthesized with the following structural features: (1) the two NH functional groups are easily protonated, (2) the NH functional groups are wrapped by five benzyl rings and two acidic N–H protons can be oriented in a centripetal fashion, and (3) the two substituent benzylamine rings are spaced by the core 2,4-dimethylbenzene, with  $N \cdots N$  distance around 5.5 Å. The doubly protonated ligand **L1** serves as a building block because they can offer two positive charges allowing strong electrostatic charge–charge interactions with anions; moreover, the acidic protons are divergently oriented and are capable of forming a hydrogen-bond chelate.

The tetrahedral  $[CuCl_4]^{2-}$  or octahedral  $[TeCl_6]^{2-}$  are selected as the primary coordination sphere for two reasons: (1) they serve as hydrogen-bonding acceptors to react with **L1** through second-sphere coordination and (2) they can provide a precise positioning within molecular assemblies by locating the special position of crystallography. Thus the bulky benzyl rings in **L1** can construct layers or channels, generating a suitable size of cavity or void space accessible to anion guest molecules.

Following the above design, supramolecular inclusion solids were constructed by a second-sphere coordination approach. Chloride guest can be included, leading to the formation of  $Cl \cdot 2H_2O \subset [H_2L1]_{0.5} \cdot [CuCl_4]_{0.5}$  (Crystal **1**) and  $Cl \subset [H_2L1] \cdot [TeCl_6]_{0.5}$  (Crystal **2**).

## 2. Experimental

### 2.1. Materials and measurements

All chemicals were analytical reagents and commercially purchased. IR spectra were obtained with a Perkin Elmer 100 FT-IR spectrometer using KBr pellets.  $^1\text{H}$  NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz) at 25°C with TMS as the internal reference. Elemental analysis was obtained with a Thermo Electron SPA, Flash EA 1112.

### 2.2. Preparation of L1

**2.2.1. Synthesis of 1,5-bis(chloromethyl)-*m*-xylene.** 10 g anhydrous  $\text{ZnCl}_2$ , 200 g formaldehyde, 106 g *m*-xylene, and 300 mL concentrated hydrochloric acid were mixed and refluxed at 90°C for 12 h. After cooling overnight, the white precipitate was isolated by filtration. The product is 121 g, yield 60%. Recrystallization from ethanol gave white needle crystals, m.p. 94–98°C [21, m.p. 96–98°C]. IR (KBr,  $\text{cm}^{-1}$ ): 2973 (s), 2924 (m), 1618 (m), 1506 (s), 1451 (s), 1375 (m), 902 (s), 801 (s), 656 (vs);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz),  $\delta$ : 2.385 (s, 6H,  $\text{CH}_3$ ), 4.571 (s, 4H,  $\text{CH}_2$ ), 7.046 (s, 1H, ArH), 7.251 (s, 1H, ArH). Elemental analysis (%): C, 59.14; H, 5.96 calculated from  $\text{C}_{10}\text{H}_{12}\text{Cl}_2$ , observed: C, 59.01; H, 5.97.

**2.2.2. Synthesis of (4,6-dimethyl-1,3-phenylene)bis(*N,N*-dibenzylmethane) (L1).** About 3.5 g  $\text{NaHCO}_3$ , 4 mL  $\text{H}_2\text{O}$  and 11.5 mL dibenzylamine were mixed and heated to 45°C. 1,5-Bis(chloromethyl)-*m*-xylene (6 g) was then added and the solution was refluxed at 95°C for 4 h. The reaction was cooled to room temperature and a white precipitate was formed, 12 g, yield 65.4%, m.p. 100–104°C. IR( $\text{cm}^{-1}$ ) $_{\text{v}_{\text{max}}}$ (KBr): 3062.22, 3027.44, 1602.15, 1494.07, 1451.99; 908.87 (s, Ar-CH), 2925, 2880, 1470 (s,  $\text{CH}_2$ ), 1366.37~1246.35 (Ar-NH); 2918.83, 2794.02 ( $\text{CH}_3$ ); no absorption at 3500–3300, suggesting the existence of tertiary amine.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz),  $\delta$ : 6.846 (1H, ArH), 7.625 (1H, ArH), 7.201–7.334 (20H, ArH), 3.486 (12H,  $\text{CH}_2$ ), 2.176 (6H,  $\text{CH}_3$ ).

### 2.3. Preparation of $\text{Cl}\cdot 2\text{H}_2\text{O} \subset [\text{H}_2\text{L1}]_{0.5}\cdot [\text{CuCl}_4]_{0.5}$ (Crystal 1)

About 0.131 g L1 and 20 mL ethanol were placed in a 50 mL Erlenmeyer flask and shaken until the contents dissolved; then 5 mL distilled water, 1 mL concentrated hydrochloric acid, and 4 mL solution of  $\text{Na}_2[\text{CuCl}_4]$  were added and the flask was allowed to stand for 2 days at room temperature. After the crystals were separated by filtration, recrystallization from ethanol gave yellow, transparent block crystals, yield 75%, m.p. 170°C–174°C. IR( $\text{cm}^{-1}$ ) $_{\text{v}_{\text{max}}}$ (KBr): 3060.43, 3032.96, 3005.49 (s, ArC-H), 2957.30, 2712.56 (s,  $\text{CH}_2$ ), 2592.87 (s,  $\text{NH}^+$ ), 1640.93, 1499.13 (s, ArC-C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz);  $\delta$ : 1.809 (6H,  $\text{CH}_3$ ), 2.635–4.553 (12H,  $\text{CH}_2$ ), 6.990–8.762 (22H, ArH), 10.782 (2H, s,  $\text{NH}^+$ ).

## 2.4. Preparation of $\text{ClC}[\text{H}_2\text{L1}]\cdot[\text{TeCl}_6]_{0.5}$ (Crystal 2)

The same experimental procedure as for Section 2.3 was carried out, with 0.4 mL solution of  $\text{Na}_2[\text{TeCl}_6]$  added and the flask was allowed to stand for 3 days at room temperature. After the crystals were separated by filtration, recrystallization from ethanol gave yellow-green, transparent crystals, yield 70%, m.p. 238–241°C. IR( $\text{cm}^{-1}$ ) $\nu_{\text{max}}$ (KBr): 3062.77, 3035.03 (s, ArC–H), 2930.23 (s,  $\text{CH}_2$ ), 1622.70, 1499.47, 1456.00 (s, ArC–C);  $^1\text{H}$  NMR ( $\text{D}_3\text{CSOCD}_3$ , 300 MHz);  $\delta$ : 2.113(6H,  $\text{CH}_3$ ), 4.202 ~ 4.382(12H, d,  $\text{CH}_2$ ), 7.055 ~ 8.036 (22H, m, ArH), 10.788 (2H, s,  $\text{NH}^+$ ).

## 2.5. X-ray crystallography

Single-crystal X-ray diffraction measurements of complexes were carried out on a Bruker Smart CCD diffractometer equipped with a graphite-monochromator at 294 K. The determination of unit cell parameters and data collection were performed with Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The unit cell parameters were obtained with least-squares refinements and 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) [22]. Data were reduced by using the Bruker SAINT software. All non-hydrogen atoms were refined with anisotropic displacement. Crystal data, refinement details, and data collection parameters are given in table 1.

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

	<b>1</b>	<b>2</b>
Formula	$\text{C}_{38}\text{H}_{46}\text{Cl}_3\text{N}_2\text{O}_2\text{Cu}_{0.5}$	$\text{C}_{38}\text{H}_{42}\text{N}_2\text{Cl}_4\text{Te}_{0.5}$
Formula weight	700.89	732.34
Temperature (K)	294(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$\text{C}2/c$	$P\bar{1}$
Unit cell dimensions ( $\text{\AA}$ , $^\circ$ )		
$a$	22.391(5)	11.066(3)
$b$	13.636(4)	12.2176(13)
$c$	26.077(6)	14.084(3)
$\alpha$	90	98.715(14)
$\beta$	95.039(4)	95.58(2)
$\gamma$	90	101.334(18)
Volume ( $\text{\AA}^3$ ), $Z$	7931(3), 4	1829.5(7), 2
Calculated density $D_x$ ( $\text{g cm}^{-3}$ )	1.174	1.503
Absorption coefficient, $\mu$ ( $\text{mm}^{-1}$ )	0.866	1.141
$F(000)$	3636	840
Crystal size ( $\text{mm}^3$ )	$0.28 \times 0.24 \times 0.20$	$0.37 \times 0.35 \times 0.23$
$R_{\text{int}}$	0.0341	0.0267
No. of collected data (unique)	7004	4781
No. of data with $I > 2\sigma(I)$	4492	3995
No. of refined parameters	413	409
$R_f/wR_f$	0.0487/0.1360	0.0460/0.1180
All data $R_f/wR_f$	0.0772/0.1474	0.0587/0.1289
Goodness-of-fit	1.054	1.056
CCDC reference numbers	752171	752172

### 3. Results and discussion

#### 3.1. Structure description of **1**

The crystal **1** forms in the  $C2/c$  space group of monoclinic crystal system. The Cu is located at crystallographic inversion centers and **L1** are in a general position. One asymmetric unit of **1** consists of one  $[\mathbf{L1}]2\text{H}^+$ , one  $\text{Cl}^-$ , half of  $[\text{CuCl}_4]^{2-}$ , and two water molecules (figure 1a). Through symmetry operations of the inversion center, Cu(II) is tetrahedrally coordinated by four chlorides with bond lengths of  $\text{Cu1}-\text{Cl11} = 2.253(1) \text{ \AA}$  and  $\text{Cu1}-\text{Cl2} = 2.224(1) \text{ \AA}$ . The  $\text{Cl}-\text{Cu}-\text{Cl}$  bond angles are  $95.63(4)^\circ$  and  $140.42(4)^\circ$ .

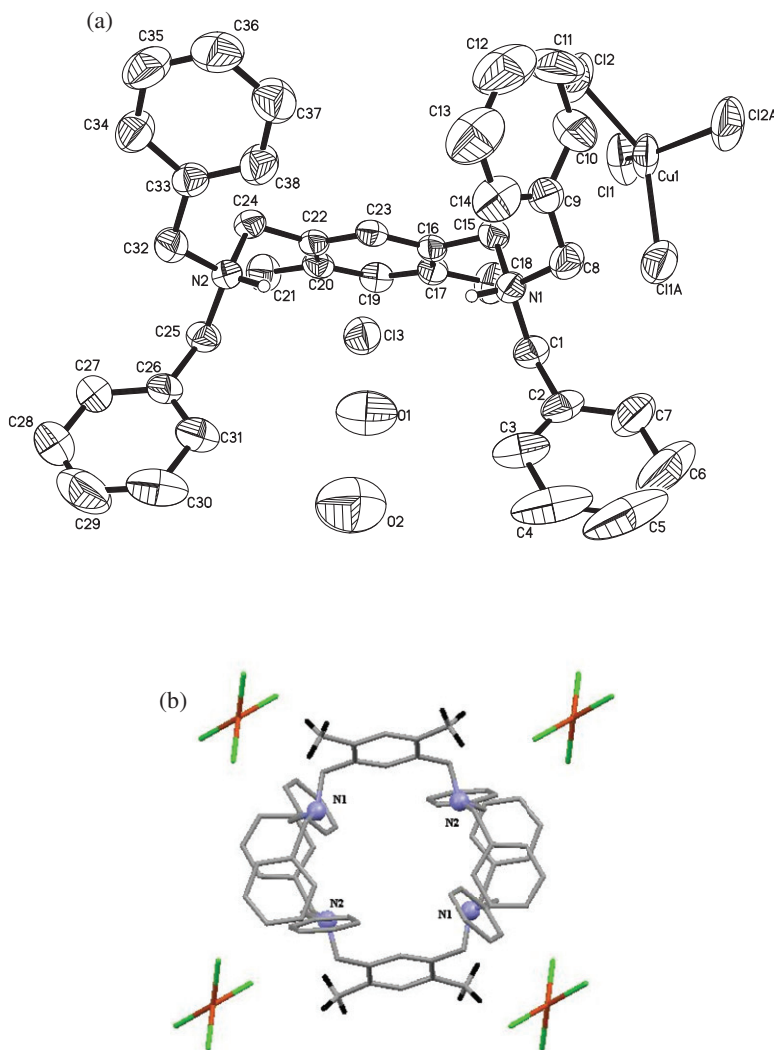


Figure 1. (a) Crystal structure of **1**; (b) encapsulation assembly formed by neighboring ligand; (c) the formation of 1-D molecular layer along the  $ab$  plane; and (d) crystal packing of **1** along the  $b$ -axis. For the sake of clarity only hydrogens involved in H-bonding are represented.

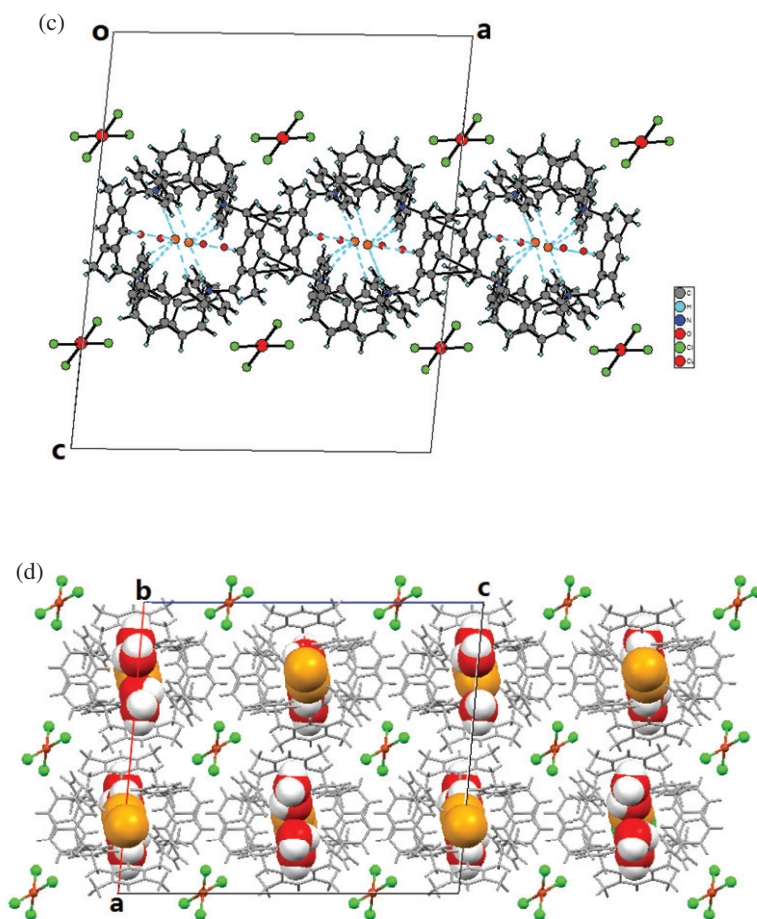


Figure 1. Continued.

The crystallographically unique chloride is held in place between two protonated nitrogens of the same ligand. The localization of two acidic protons on **L1** and the  $N \cdots N$  distance of 5.58(1) Å between two nitrogens ensures recognition between chloride and the protonated ligand through dihapto  $N-H \cdots Cl$  interactions [ $N-H \cdots Cl$  hydrogen bonds ( $N1-H1 \cdots Cl3$ : 3.285(1) Å, 169.15°;  $N2-H2 \cdots Cl3$ : 3.275(1) Å, 170.50°)]. Two neighboring **L1** molecules construct an encapsulation assembly by van der Waals force ( $C36-H36 \cdots C4$ : 3.769(1) Å, 132.2(1)°, figure 1b). In addition to the encapsulation of two  $Cl^-$ 's, the two disordered water molecules encapsulate inside the assembly by self-association through  $O-H \cdots O$  interactions ( $O1 \cdots O2 = 2.796(1)$  Å,  $O1 \cdots O1 = 2.749(1)$  Å). The approximate region for the inclusion of guest molecules is 6.9 Å (defined by H23 and H2A)  $\times$  4.0 Å (defined by H13 and H14).

The interconnection between the encapsulation assemblies through weak  $C-H \cdots \pi$  interactions [ $C24-H24B \cdots C17$ : 3.573 Å, 130.4°,  $H24 \cdots C17 = 2.867$  Å;  $C24-H24B \cdots C19$ : 3.741 Å, 147.5°,  $H24B \cdots C19 = 2.887$  Å] leads to an infinite 1-D molecular layer along the *ab* plane (figure 1c). These 1-D networks are further connected into a 2-D network (figure 1d) through multiple  $C-H \cdots Cl$  hydrogen-bonding



Table 2. Selected weak C–H...Cl hydrogen bonding lengths (Å) and angles (°) for **1** and **2**.

	D	A	$d(\text{D}-\text{H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}-\text{A})$	$\angle\text{DHA}$
<b>1</b>	C1	C11 ( $x, y, z$ )	0.970	2.804	3.685	151.5
	C15	C11 ( $x, y, z$ )	0.971	2.872	3.748	150.6
	C24	C12 ( $1-x, 1-y, 1-z$ )	0.970	2.897	3.801	155.5
	C25	C12 ( $1-x, 1-y, 1-z$ )	0.969	2.754	3.683	160.8
	C32	C11 ( $1-x, 1-y, 1-z$ )	0.970	2.868	3.797	160.7
	C34	C11 ( $1-x, 1-y, 1-z$ )	0.929	2.860	3.680	147.8
<b>2</b>	C3	C13 ( $-x, -y, 1-z$ )	0.93	2.836	3.670	149.8
	C8	C12 ( $-x, -y, 1-z$ )	0.971	2.770	3.713	163.9
	C22	C12 ( $-1+x, -1+y, z$ )	0.960	2.892	3.785	155.1
	C38	C13 ( $-1-x, -1-y, 1-z$ )	0.930	2.874	3.738	154.9

D, donor; A, acceptor.

interactions with  $[\text{CuCl}_4]^{2-}$ . The chloride of the long Cu1–C11 bond is a hydrogen-bond acceptor, participating in four C–H...Cl interactions, two of which with two methylene groups attach to the same NH in one molecule of ligand at ( $x, y, z$ ) [C1–H1B...C11: 3.687 Å, 151.4°, H1B...C11 = 2.805 Å; C15–H15B...C11: 3.747 Å, 150.6°, H15B...C11 = 2.871 Å] and the other two with one methylene and CH in one phenyl ring of the ligand at ( $1-x, 1-y, 1-z$ ) [C32–H32B...C11: 3.799 Å, 160.8°, H32B...C11 = 2.869 Å; C34–H34...C11: 3.679 Å, 147.7°, H34...C11 = 2.858 Å]. The other chloride (short Cu1–C12 bond) is a hydrogen-bond acceptor involving two C–H...Cl interactions with the methylene attached to the same NH of ligand at ( $1-x, 1-y, 1-z$ ) [C25–H25A...C12: 3.683 Å, 160.8°, H25A...C12 = 2.752 Å; C24–H24A...C12: 3.800 Å, 155.5°, H24A...C12 = 2.895 Å]. As a result of crystal symmetry, the overall hydrogen-bonding number around the metal complex is 12 (table 2).

### 3.2. Structure description of **2**

Complex **2** was crystallized in a triclinic crystal system  $P\bar{1}$ . One asymmetric unit of **2** contains one complete ligand, half of  $[\text{TeCl}_6]^{2-}$ , and one  $\text{Cl}^-$  (figure 2a). Te lies on a special position and has an overall octahedral coordination derived from the symmetry operations (Te1–Cl1 = 2.509(2) Å, Te1–Cl2 = 2.526(2) Å, Te1–Cl3 = 2.5455(16) Å). The Cl–Te–Cl bond angles between two *trans* Te–Cl bonds are 180°, whereas those for *cis* Te–Cl bonds deviate slightly from the ideal 90°, in the range of 88.45(7)–93.05(12)°.

The structure of **2** also reveals the formation of a 2-D network and may be described as the interconnection of 1-D networks composed of **L1** assemblies by  $[\text{TeCl}_6]^{2-}$ . The crystallographically unique chloride is again held between two protonated amine nitrogens of **L1**. The N...N distance of 5.2 Å between two nitrogens in one ligand and localization of two acidic protons on **L1** allows recognition of chloride, as template acceptor, through a chelating mode of N–H...Cl interactions with protonated **L1** (N1–H1...Cl4 = 3.105 Å, 172.7°; N2–H2...Cl4 = 3.244 Å, 165.03°). Similar as **1**, the interconnection of neighboring **L1**'s also forms an encapsulation assembly through weak C–H...Cl hydrogen bonds, in which every two chlorides are encapsulated by two **L1**'s, and the approximate region for the inclusion of chloride is 6.9 Å (defined by H34 and H34)  $\times$  6.2 Å (defined by H31A and H31A). The encapsulation assemblies are

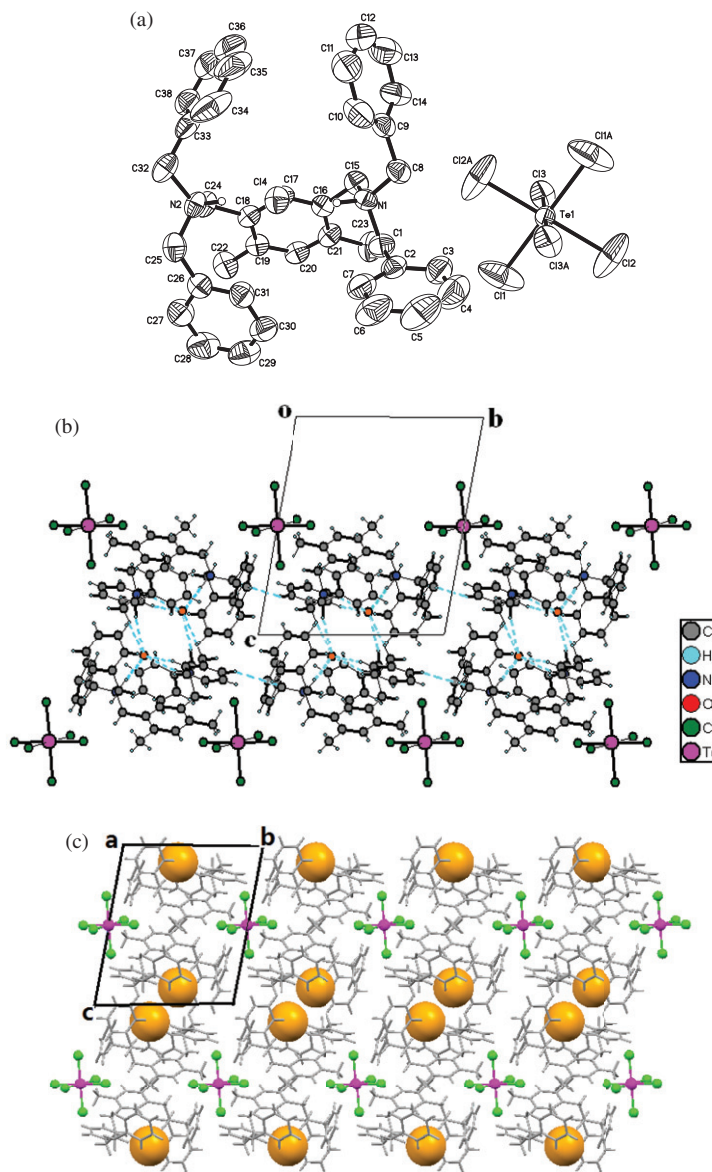


Figure 2. (a) Crystal structure of **2**; (b) the formation of 1-D molecular layer along the *ac* plane; and (c) crystal packing of **2** along the *a*-axis. For the sake of clarity only hydrogens involved in H-bonding are represented.

connected through C–H $\cdots$  $\pi$  interactions (C27–H27A $\cdots$ C9: 3.609 Å, 135.3°, H27A $\cdots$ C9: 2.888 Å), leading to an infinite 1-D network along the *ac* plane, as seen in figure 2(b).

Due to the different conformation of **L1** in **2** and the different choice of primary metal ions compared with **1**, the crystal **2** gives different crystal packing (figure 2c).

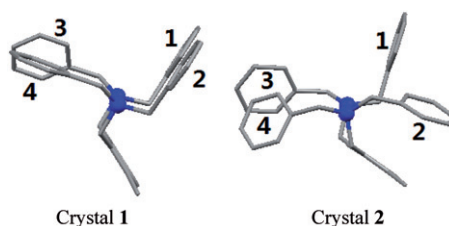


Figure 3. The conformation comparison of **L1** in crystals **1** and **2**.

In **2**, eight weak C–H...Cl hydrogen bonds construct the second-sphere coordination between  $[\text{TeCl}_6]^{2-}$  and the ligand (table 2). The chloride of the longest Te–Cl bond, Cl3, is a hydrogen-bond acceptor, linking molecules of ligand at  $(-x, -y, 1-z)$  and  $(1+x, 1+y, z)$  through two weak C–H...Cl interactions [C3–H3A...Cl3: 3.670 Å, 149.8°, H3A...Cl3 = 2.836 Å; C38–H38A...Cl: 3.738 Å, 154.9°, H38A–Cl = 2.874 Å]. In addition, the chloride of the second longest Te–Cl bond, also a hydrogen-bond acceptor, has two weak C–H...Cl interactions [C8–H8B...Cl2: 3.713 Å, 163.9°, H8B–Cl2 = 2.770 Å; C22–H22B...Cl3: 3.785, 155.1°, H22B–Cl3 = 2.892 Å] with the molecules of ligand at  $(-x, -y, 1-z)$  and  $(1+x, 1+y, z)$ . The remaining short Te–Cl bond was not involved in any interactions.

### 3.3. Conformation comparison of **L1** in crystals **1** and **2**

Molecules of diprotonated **L1** exhibit distinct conformations in the two crystals viewed from the projection of the Newman-type overlay of two nitrogens (figure 3). For **1**, the two phenyl rings (denoted 1 and 2) on one side are parallel with the dihedral angle of 3.4°, and the other two phenyl rings (denoted 3 and 4) on the other side are crossed with the dihedral angle of 54.2°, whereas for **2**, the two phenyl rings on one side are almost vertical, with the dihedral angle of 85.8°, and the other two phenyl rings on the other side are arranged with the dihedral angle of 68.4°. Such different conformation of **L1** results in the different crystal packing in **1** and **2**.

### 3.4. Thermal analysis

Thermogravimetric analyses (TGA) were carried out on **1** and **2**. In figure 4, loss of  $\text{H}_2\text{O}$  from the cavity of **1** was slow, beginning at room temperature to 190°C (5.14% calcd, 5.48% obsd). This merges with a second mass loss from 190°C to 500°C, which was considered decomposition of the ligand and HCl (80.21% Calcd, 79.52% obsd). The mass loss above 500°C was further decomposition of  $\text{CuCl}_4$ . TGA of **2** shows a weight loss from 200°C to 400°C, as seen in figure 4(b), from decomposition of the ligand and HCl (76.76% calcd, 74.44% obsd). The mass loss above 400°C was decomposition of  $\text{TeCl}_6$ .

## 4. Conclusions

A number of complexes containing  $\text{CuX}_2$  have been published in the past years. One type is  $\text{A}_2[\text{CuX}_4]$  [23, 24], where A is usually organic protonated bases and X is Cl

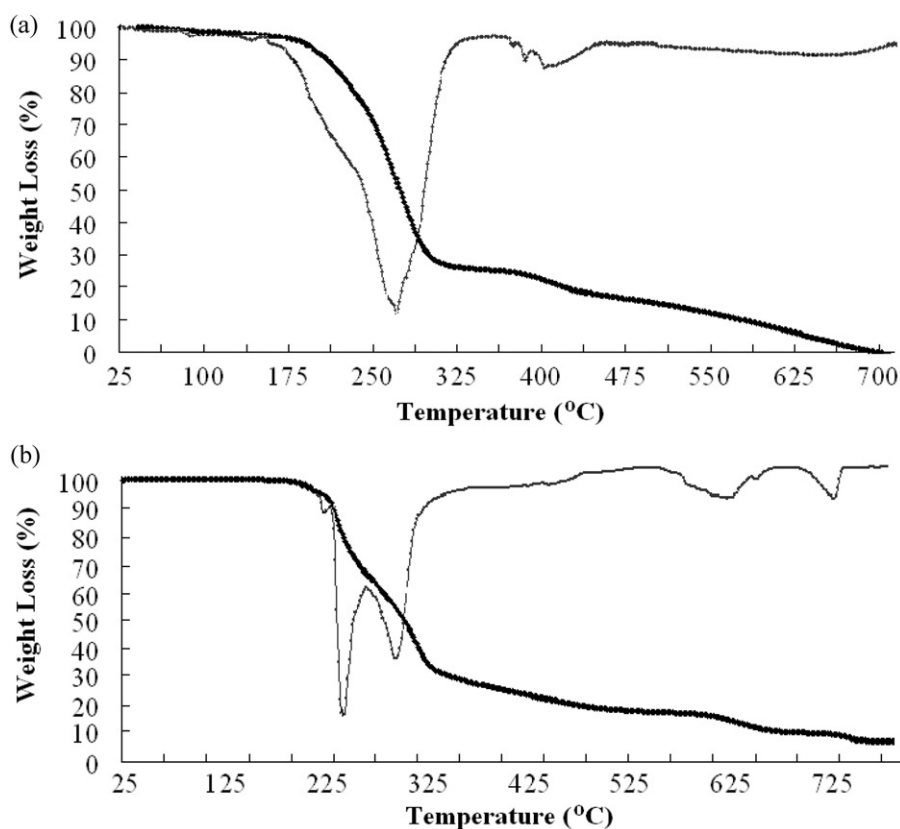


Figure 4. The TG of 1 (a) and 2 (b).

or Br. In addition, using the “plasticity” of the coordination sphere of Cu(II), various coordination polymers containing  $[\text{CuX}_4]$  have also been constructed, such as the structure of  $\{[\text{Cu}(\text{bpea})\text{Cl}]_2\text{CuCl}_4\}$  (bpea = *N*-bis(2-pyridylmethyl)ethylamine) [25]. These molecules containing  $[\text{CuX}_4]^{2-}$  are well-studied because they can offer possible mechanisms for magnetic exchange. With regard to the anion recognition supramolecules, some metal ions, as guest molecules, can be encapsulated inside the designed host, for example, the ucurbit[5]uril as the macrocyclic cryptand can include  $[\text{PbCl}_6]^{4-}$  or  $[\text{HgCl}_4]^{2-}$  [26]. Meanwhile, metal coordination receptors can be specifically designed as artificial hosts for polyatomic anion recognition [27], such as  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ , and  $\text{SO}_4^{2-}$ . Herein, we have proposed the approach of second-sphere coordination into the construction of supramolecular inclusion solids with anion species using a diamine ligand and  $[\text{CuCl}_4]^{2-}$  and  $[\text{TeCl}_6]^{2-}$  to form inclusion host, in which guest molecules, such as chloride anions and water, were contained.

The structure determination revealed that 2-D networks are formed in both complexes by interconnection of 1-D networks through multiple  $\text{C-H}\cdots\text{Cl}$  hydrogen bonding between metal ions and ligands. Future objectives are directed toward the design of other ligands that comprise larger space so as to encapsulate a variety of anions with different sizes and geometries.

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