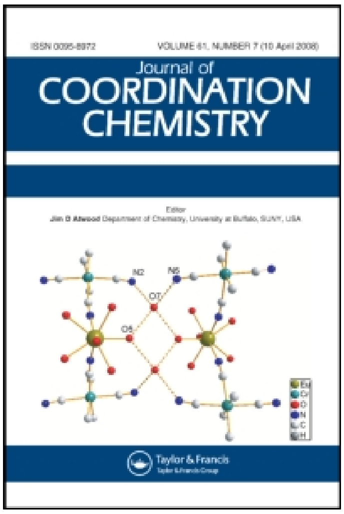

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Layered structures constructed by second-sphere coordination *via* N-H ··· Cl and C-H ··· Cl hydrogen bonding: synthesis and crystal structures of tribenzylamine and [MCl$_6$] (M = Sn, Re, and Te)

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Layered structures constructed by second-sphere coordination *via* N–H $\cdots$ Cl and C–H $\cdots$ Cl hydrogen bonding: synthesis and crystal structures of tribenzylamine and [MCl_6] (M = Sn, Re, and Te)

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A series of second-sphere coordination complexes of tribenzylamine (**L**^{1}) and [MCl_6] (M = Sn, Re, Te) have been synthesized and characterized by spectroscopic techniques (IR, NMR) and single-crystal X-ray diffraction. The main driving force for the encapsulation of [MCl_6] and recognition with **L**^{1} is the second-sphere coordination of metal halides by the amide protons of the ligand *via* hydrogen bonding (N–H $\cdots$ Cl–M and C–H $\cdots$ Cl–M); new layered structures are described. Thermal stability and irreversible behavior of second-sphere coordination complexes [$\mathbf{L}^2$] $\cdot$ 0.5[$TeCl_6$]$^{2-}$ $\cdot$ HCl $\cdot$ (H_3O)$^+$ $\cdot$ 0.5H_2O (**L**^{2} = N,N,N′,N′-tetrabenzyl-ethylenediamine) in contact with water vapor are also described.

Keywords: Second-sphere coordination; Weak hydrogen bonding; Layered structure; Tribenzylamine; Sn, Re, Te, Tribenzylamine

1. Introduction

Second-sphere coordination, referring to any intermolecular interactions with the primary coordination sphere of a metal ion [1, 2], has attracted immense interest due to their unconventional physico-chemical properties [3–6] and novel structures [7–10]. Second-sphere coordination has primarily focused on cationic transition metal complexes and is mainly provided by a host/receptor/ligand with an appropriate set of donors, such as a crown ether or macropolycyclic ligands [11–13]. Supramolecular synthons based on the complementarity of intermolecular interactions, such as N–H $\cdots$ Cl, N–H $\cdots$ N, and N–H $\cdots$ O, have been widely used to construct a diverse range of second-sphere coordination complexes due to its strength and directionality [5–9, 14–16]. One synthon that has proved to be very effective for constructing second-sphere coordination is N–H $\cdots$ Cl–M hydrogen bonding, through the pioneering work of Orpen [17–20]. While weak interactions have more frequently appeared in

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the organic crystal network [21], much less work on the construction of second-sphere coordination complexes *via* weak interactions has been reported [22].

One direction in the design of functional solid materials is to recognize and accommodate guest molecules. A variety of frameworks based on metal–organic framework polymers have been reported [23–26]. Second-sphere coordination recently has also afforded an attractive route to this goal [27], in which the design and synthesis of suitable neutral or charged second-sphere ligands that can coordinate with first-sphere metal ions *via* non-covalent interactions is necessary. We have synthesized two second-sphere ligands, tribenzylamine ($\mathbf{L^1}$), and N,N,N′,N′-tetrabenzylethylenediamine ($\mathbf{L^2}$), and prepared a series of second-sphere coordination complexes with $[MCl_6]^{2-}$ (M = Sn, Re, Te).

The key feature of $\mathbf{L^1}$ and $\mathbf{L^2}$ is that the functional groups are located in middle positions of the ligands instead of α, ω, such as 4,4′-bipyridine [18, 19], 1,4-piperazine-bis(ethanesulfonate) [27], and 5,5′-diamino-2,2′-bipyridine [29]. The bulky benzyl rings reside outside, in the hope that the bulky group can be a component of the layer or channel framework, to generate a suitable size of cavity accessible to various guest molecules. The structure determination of resulting complexes of $[\mathbf{L^1}]2H^+\cdot[SnCl_6]^{2-}$ (**1**), $[\mathbf{L^1}]2H^+\cdot[ReCl_6]^{2-}$ (**2**), and $[\mathbf{L^1}]2H^+\cdot[TeCl_6]^{2-}$ (**3**) show that $\mathbf{L^1}$ adopts optimized conformations when recognizing different anion complexes, based on the different shape and size of anions (table 1). Strong N–H ··· Cl and weak C–H ··· Cl hydrogen bonds play significant roles in the construction of layered structures of these complexes. As the interlayered channel structures of second-sphere coordination

Table 1. Crystallographic data and structure refinement summary.

	$[\mathbf{L^1}]2H^+\cdot[SnCl_6]^{2-}$	$[\mathbf{L^1}]2H^+\cdot[ReCl_6]^{2-}$	$[\mathbf{L^1}]2H^+\cdot[TeCl_6]^{2-}$
Empirical formula	$C_{42}H_{44}Cl_6N_2Sn$	$C_{42}H_{44}Cl_6N_2Re$	$C_{42}H_{44}Cl_6N_2Te$
Formula weight	908.18	975.69	915.08
Temperature (K)	294(2)	294(2)	294(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions (Å, °)			
a	11.4358(13)	11.3993(15)	11.018(2)
b	13.1705(15)	13.2331(18)	22.942(5)
c	14.7431(17)	14.706(3)	16.813(4)
α	90.00	90.00	90.00
β	106.187(2)	107.700(2)	90.901(3)
γ	90.00	90.00	90.00
Volume (Å^3), Z	2132.5(4), 2	2113.4(5), 2	4249.5(15), 4
Calculated density (g cm^{-3})	1.414	1.533	1.430
Absorption coefficient (mm^{-1})	1.006	3.286	1.109
$F(000)$	924	974	1848
Crystal size (mm^3)	0.28 × 0.24 × 0.20	0.30 × 0.26 × 0.24	0.30 × 0.26 × 0.20
Reflections collected (unique)	11,886	11,729	20,874
R_{int}	0.0284	0.0276	0.0485
Data/parameters	4368/233	4318/236	7405/460
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0270$, $wR_2 = 0.0614$	$R_1 = 0.0227$, $wR_2 = 0.0452$	$R_1 = 0.0683$, $wR_2 = 0.1672$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.0685$	$R_1 = 0.0418$, $wR_2 = 0.0515$	$R_1 = 0.0957$, $wR_2 = 0.1844$
s	1.021	1.058	1.059

complexes formed by $\mathbf{L^2}$ and [MCl_6] (M = Cu, Co, Mn, Sn, Te) have been reported previously [28]; herein, the thermal stability of $[\mathbf{L^2}] \cdot 0.5[TeCl_6]^{2-} \cdot HCl \cdot (H_3O)^+ \cdot 0.5H_2O$ is reported.

2. Experimental

2.1. *Materials and measurements*

All chemicals were purchased as analytical reagents. IR spectra were obtained with a PerkinElmer 100 FT-IR spectrometer using KBr pellets. ^{1}H-NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz) at 25°C with TMS as internal reference.

2.2. *Preparation of L^1*

Benzylamine (5.6 mL) was added to a stirred solution of 8.5 g $NaHCO_3$ and 10 mL distilled water. Benzyl chloride (14.8 mL; 2–3 drops s^{-1}) was then continuously added to the mixture. After the reaction was heated to 95°C and stirred for 4 h, the mixture was cooled to room temperature giving white precipitate, 11.343 g, yield 79.05%, m.p. 94°C. IR(cm^{-1})ν_{max}(KBr): 3082.77, 3061.78, 3027.22 (s, ArC–H), 2923.29, 2881.02 (s, CH_2), 1601.89, 1583.78, 1493.25, 1451.78 (s, ArC–C); ^{1}H-NMR δH($CDCl_3$): 3.811 (6H, s, CH_2), 7.329–7.346 (15H, m, ArH).

2.3. *Preparation of $[L^1]2H^+ \cdot [SnCl_6]^{2-}$*

Protonated $\mathbf{L^1}$ (0.3042 g) and 15 mL ethanol were placed in a 50 mL Erlenmeyer flask and shaken until the contents dissolved; then 14 mL of distilled water, 2 mL of concentrated hydrochloric acid, and 4 mL solution of $(NH_4)_2[SnCl_6]$ were added and the flask was allowed to stand for 3 days at room temperature. Collecting the crystals by filtration and recrystallization gave a sizeable amount of colorless and transparent crystals, m.p. 205–210°C. IR(cm^{-1})ν_{max}(KBr): 3539.66, 3344.81 (s, NH), 3062.77, 3034.15, 3003.85 (s, ArC–H), 2957.24, 2906.00 (s, CH_2), 2684.03, 2557.76 (s, NH^+), 1643.07, 1586.02, 1496.24, 1455.92 (s, ArC–C). ^{1}H-NMR δH (DMSO): 4.263–4.364 (6H, t, CH_2), 7.200–7.524 (15H, m, ArH), 10.813 (H, s, NH^+).

2.4. *Preparation of $[L^1]2H^+ \cdot [ReCl_6]^{2-}$*

$\mathbf{L^1}$ (0.1441 g) and 15 mL ethanol were placed in a 50 mL Erlenmeyer flask and shaken until the contents dissolved; then 14 mL of distilled water, 3 mL of concentrated hydrochloric acid, and 7 mL solution of $K_2[ReCl_6]$ were added and the flask was allowed to stand for 3 days at room temperature. After the crystals were separated by filtration, recrystallization gave green, transparent crystals, m.p. 246–250°C. IR (cm^{-1})ν_{max}(KBr): 3468.13 (s, NH), 3115.14, 3065.30 (s, ArC–H), 2953.49, 2763.44 (s, CH_2), 2600.18, 2326.64 (s, NH^+), 1606.32, 1586.48, 1498.63, 1457.56 (s, ArC–C).

^{1}H-NMR δH(DMSO): 4.017–4.186 (6H, d, CH_2), 7.403–7.502 (15H, m, ArH), 11.096 (1H, s, NH^+).

2.5. *Preparation of $[L^1]2H^+ \cdot [TeCl_6]^{2-}$*

$\mathbf{L^1}$ (0.1435 g) and 20 mL ethanol were placed in a 50 mL Erlenmeyer flask and heated until the contents dissolved; 7 mL of distilled water, 11 mL of concentrated hydrochloric acid, and 10 mL solution of $(NH_4)_2[TeCl_6]$ were added and the flask allowed to stand for 3 days at room temperature. Collecting the crystals by filtration and recrystallization gave transparent yellow-green crystals, m.p. 210–213°C. IR(cm^{-1})ν_{max}(KBr): 3445.05 (s, NH), 3031.75 (s, ArC–H), 2795.48 (s, CH_2), 2599.78 (s, NH^+), 1602.59, 1585.95, 1495.20, 1454.89 (s, ArC–C). ^{1}H-NMR δH(DMSO): 4.227–4.358 (6H, t, CH_2), 7.394–7.589 (15H, m, ArH), 10.600 (1H, s, NH^+).

2.6. *Preparation of $[L^2] \cdot 0.5[TeCl_6]^{2-} \cdot HCl \cdot (H_3O)^+ \cdot 0.5H_2O$*

$\mathbf{L^2}$ (0.1103 g) and 15 mL ethanol were placed in a 50 mL Erlenmeyer flask and heated until the contents dissolved; 8 mL of distilled water, 10 mL of concentrated hydrochloric acid, and 0.5 mL of $(NH_4)_2[TeCl_6]$ were added and the flask was allowed to stand for 3 days at room temperature. After collecting the crystals, recrystallization gave transparent yellow-green crystals, m.p. 154°C. IR(cm^{-1})ν_{max}(KBr): 3434.27 (s, NH), 3006.65 (s, CH_2), 2585.70 (s, NH^+), 1621.12, 1499.17, 1456.90 (s, ArC–C). ^{1}H-NMR ($CDCl_3$): 3.868 (4H, s, CH_2), 4.200 (8H, s, CH_2), 7.203–7.609 (20H, m, ArH), 11.358 (2H, s, NH), 2.573 (1H, s, H_2O).

2.7. *X-ray crystallography*

Single-crystal X-ray diffraction measurements 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-Kα radiation ($\lambda = 0.71073$ Å). 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 (SHELXTL 97). Data were reduced using the Bruker SAINT software.

3. Results and discussion

3.1. *Spectroscopic analyses*

IR and ^{1}H-NMR data for both ligands and four complexes are listed in section 2. In the complexes, proton resonances on the methylene CH_2 in $\mathbf{L^1}$ significantly shift to lower fields compared to those in the free ligand, 3.811 (6H, s, CH_2) → 4.263–4.364 (6H, t, CH_2, **1**) → 4.017–4.186 (6H, d, CH_2, **2**) → 4.227–4.358 (6H, t, CH_2, **3**), indicating that these groups participate in weak hydrogen bonding, further ascertained by the structure determination from the single-crystal X-ray diffraction analysis.

3.2. *Layer structures constructed by L^1 and [MCl$_6$] (M = Sn, Re, Te)*

Complexes **1** and **2** crystallize in the $P2_1/n$ space group of the monoclinic system. The metal ions (Sn and Re) are located at crystallographic inversion centers and **L^1** are in a general position. Complexes **1** and **2** consist of half ion of $[SnCl_6]^{2-}$ (or $[ReCl_6]^{2-}$) and one protonated **L^1** in one asymmetric unit, thus the molar ratio of $[SnCl_6]^{2-}$ (or $[ReCl_6]^{2-}$) to **L^1** is 1 : 2. Complex **3** crystallizes in the $P2_1/c$ space group of the monoclinic system and contains two protonated **L^1** molecules and one $[TeCl_6]^{2-}$ anion in one asymmetric unit, thus the molar ratio of $[TeCl_6]^{2-}$ to **L^1** is also 1 : 2.

3.2.1. $[L^1]2H^+ \cdot [MCl_6]^{2-}$ (M = Sn, Re) ($C_{21}H_{22}N \cdot 0.5SnCl_6$, $C_{21}H_{22}N \cdot 0.5ReCl_6$). A detailed description will be presented only for **1**, as **2** is similar to **1** except for slight variations in structural and thermal parameters which may be ascertained from the Supplementary material.

The molecular structure of **1** with the atom numbering scheme is shown in figure 1(a). The Sn lying on a crystallographic inversion center at (0, 1/2, 0) is bonded to six chlorides, having four short Sn–Cl bonds (2.3850(7) Å, 2.4145(7) Å) and two longer bonds(2.4927(6) Å). The three benzyl groups of **L^1** are located on the pyramidal side of nitrogen, in which one benzyl (C2–C7) is significantly tilted with respect to the other benzyl group (C9–C14) with the distance of centroids of 4.030 Å and the dihedral angle of 30° between the phenyl rings. The primary sphere $[SnCl_6]^{2-}$ is encapsulated by four **L^1** through a total of 12 hydrogen bonds, including two strong N–H $\cdots$ Cl hydrogen bonds and 10 weak C–H $\cdots$ Cl interactions to construct the building block, as seen in figure 1(b).

The tilted benzyl ring of **L^1** is not involved in interactions with Cl^-, but has π–π stacking to connect the building blocks with 3.667 Å centroid–centroid distance of phenyls, forming a 1-D chain along (1 0 1). The 1-D chain expands along *b* to construct a layer structure (figure 1c). Within a layer, the Sn align along (1 0 1) at a distance of 10.339 Å.

$[SnCl_6]^{2-}$ are completely encapsulated by **L^1** and can be considered to be located inside the channel surrounded by **L^1** (figure 1c). The adjacent distance of Sn inside the channel is 13.170 Å. There is no space to accommodate solvent molecules between the layers.

Complex **2** has similar layered structure: within a layer, the Re align along (1 0 1) at a distance of 10.240 Å and along the *b*-axis 13.233 Å. **L^1** in **2** exhibits a slightly different conformation compared with **1**. One benzyl (C2–C7) is also tilted with respect to the other benzyl (C9–C14) with 3.983 Å distance of centroids and 29° dihedral angle between the phenyls.

3.2.2. $[L^1]2H^+ \cdot [TeCl_6]^{2-}$ ($(C_{21}H_{22}N)_2 \cdot TeCl_6$). Complex **3** is different from **1** and **2**. The coordination geometry around Te is significantly distorted octahedral with Te–Cl distances varying between 2.413(2) Å and 2.766(2) Å. The primary sphere $[TeCl_6]^{2-}$ is encapsulated by five molecules of **L^1** through a total of nine hydrogen bonds, including two strong N–H $\cdots$ Cl interations and seven C–H $\cdots$ Cl weak interactions, as seen in figure 2(b); $\pi \cdots \pi$ stacking was not found in **3**.

The anions of $[TeCl_6]^{2-}$ are related to the 2_1 symmetry operation, making the molecules of **L^1** arrange in a helical chain along the *c*-axis, with the Te centers at

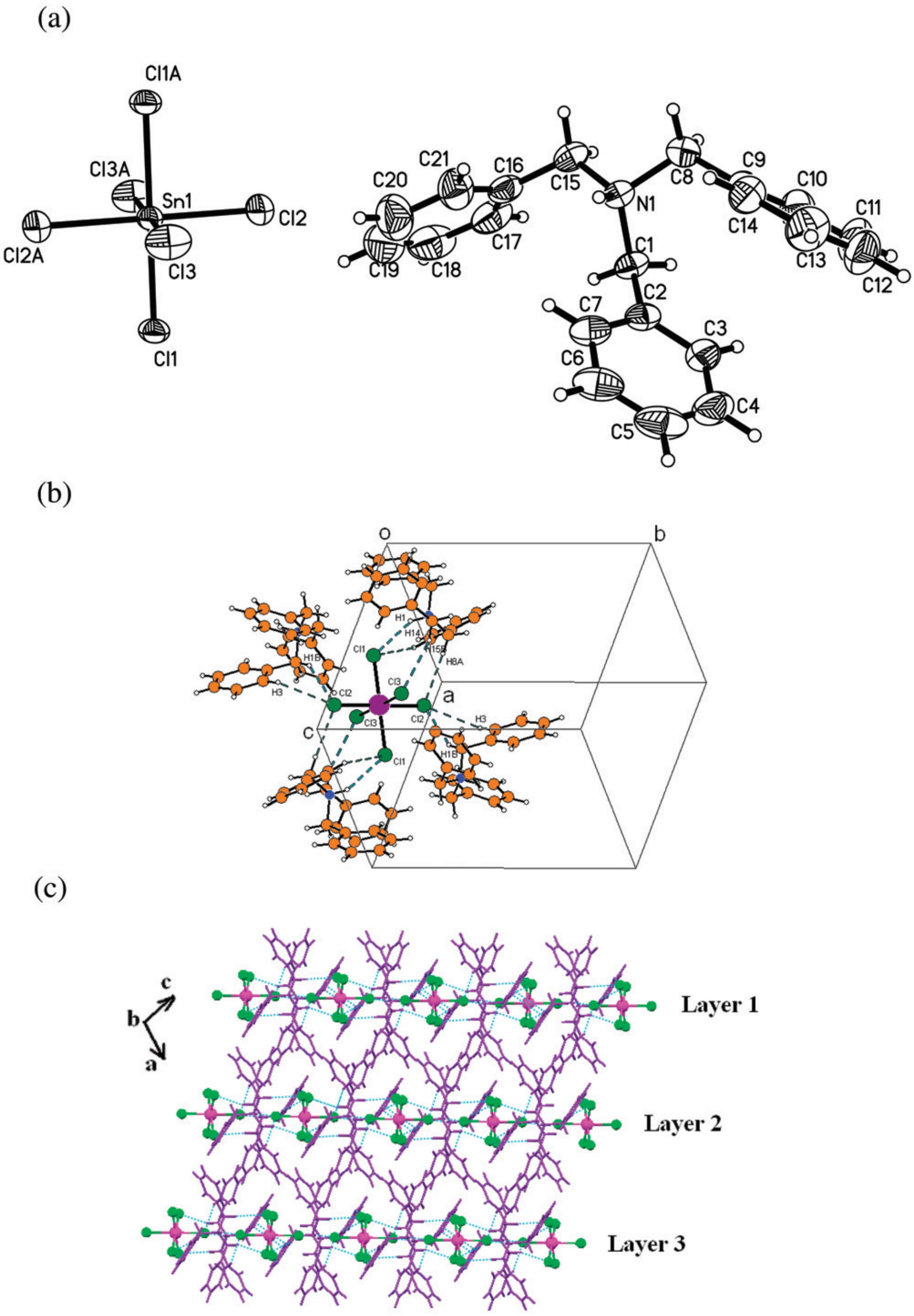

Figure 1. Structure of $[\mathbf{L^1}]2H^+ \cdot [SnCl_6]^{2-}$.

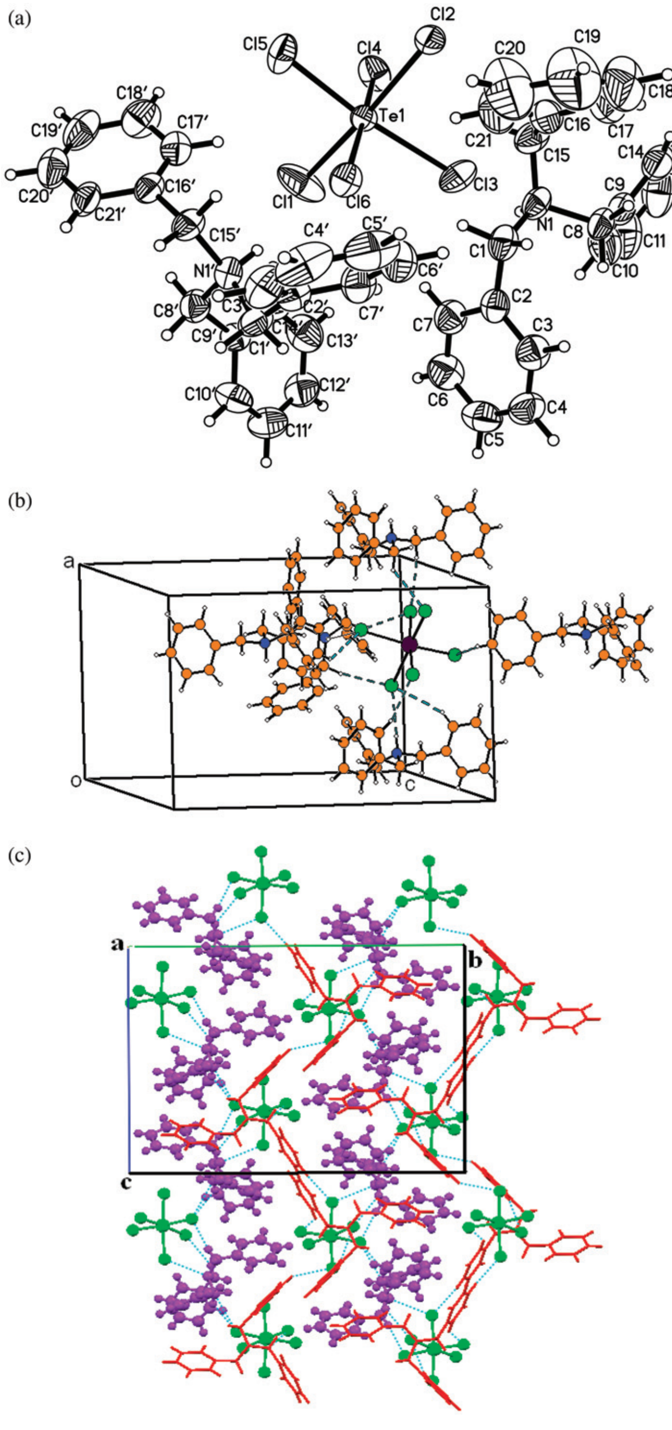

Figure 2. Structure of [$\mathbf{L^1}$]$2H^+ \cdot [TeCl_6]^{2-}$.

10.090 Å, and expanding along the *a*-axis to construct the 2-Dlayer, with Te centers at a distance of 11.018 Å, as seen in figure 2(c).

3.3. *Interlayer channel constructed by L^2 and [$TeCl_6$]*

3.3.1. The struture of the complex $[\mathbf{L^2}]\cdot0.5[TeCl_6]^{2-}\cdot HCl\cdot(H_3O)^+\cdot0.5H_2O$. The complex $[\mathbf{L^2}]\cdot0.5[TeCl_6]^{2-}\cdot HCl\cdot(H_3O)^+\cdot0.5H_2O$ has an interlayer structure [28]. The asymmetric unit is half of $[TeCl_6]^{2-}$ and one molecule of $\mathbf{L^2}$, one molecule of hydrochloric acid, and 1.5 molecules of water (including one protonated water) (figure 3a). The coordination around Te is not like that in **3**, with Te–Cl distances almost equal, 2.516(2)–2.539(2) Å. $[TeCl_6]^{2-}$ is surrounded by eight $\mathbf{L^2}$ through 10 weak C–H $\cdots$ Cl hydrogen bonds between the methylene or CH in the phenyl of $\mathbf{L^2}$ and chloride of $[TeCl_6]^{2-}$. The building block forms a 1-D chain along the *a*-axis, and then expands along *b* to construct the layer structure. Within the layer, the Te centers align along *a* at a distance of 10.350 Å, which is exactly the distance of the *a*-axis, and align

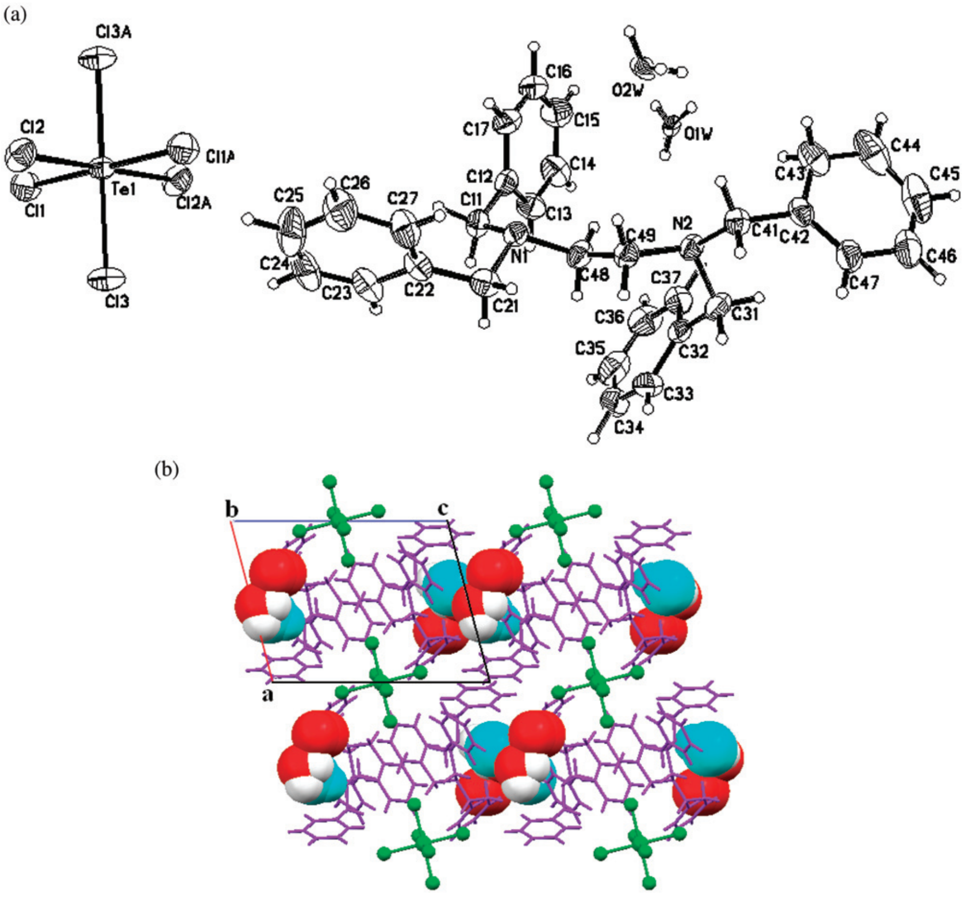

Figure 3. Structure of $[\mathbf{L^2}]\cdot0.5[TeCl_6]^{2-}\cdot HCl\cdot(H_3O)^+\cdot0.5H_2O$.

along the *b*-axis at a distance of 11.687 Å, which is the distance of the *b*-axis. The knaggy phenyls between neighboring layers construct a 4.1 × 5.8 Å channel with hydrochloric acid and water within the channel between the layers (figure 3b).

3.3.2. Thermal analysis and irreversible transformation of the complex. Thermogravimetric analyses (TGA) were carried out on $[\mathbf{L^2}] \cdot 0.5[TeCl_6]^{2-} \cdot HCl \cdot (H_3O)^+ \cdot 0.5H_2O$ from the room temperature and 230°C (Supplementary material). The first stage at 25–210°C corresponds to loss of water and HCl (9.81% Calcd, 10.89% Obs.). The second stage above 210°C were further decomposing of the structure. The PXRD pattern reveals significant changes in peak positions upon heating the powder to 80°C *in vacuo* for 2 h (Supplementary material). Further heating to 120°C for 2 h, the powder becomes identical to the changed solid. Heating the powder to 150°C for 2 h gave a PXRD pattern with a very weak signal relative to the background, but the small peaks did correlate with the changed solid. As supported by TGA data, guest molecules are lost from the interlayer region at this temperature. To further study the complex, we performed a solid–gas experiment in which the changed product was introduced into a sealed vessel containing water and placed in equilibrium with its vapor for about 2 weeks; the dehydrated material cannot change back to the crystalline structure and exhibits irreversible behavior in contact with the vapor of water.

4. Concluding remarks

Design of second-sphere coordination *via* reliable supramolecular synthons has gained interest. Herein, tribenzylamine ($\mathbf{L^1}$) and N,N,N′,N′-tetrabenzyl-ethylenediamine ($\mathbf{L^2}$) have been used to encapsulate [MCl$_6$] by second-sphere coordination *via* hydrogen bonds, involving strong N–H ⋯ Cl–M and weak C–H ⋯ Cl–M. The methylene or phenyl rings of $\mathbf{L^1}$ and $\mathbf{L^2}$ provide for the construction of second-sphere coordination complexes through C–H ⋯ Cl interactions. The second-sphere coordination by $[TeCl_6]^{2-}$ with $\mathbf{L^2}$ provides an interlayered framework. $[TeCl_6]^{2-}$ locate at the crystallography inversion centers, and the channels are constructed between the ligand parts of neighboring layers with size of 4.1 × 5.8 Å, in which water and hydrochloric acid are accommodated. Thermogravimetric studies reveal that all waters can be removed from the channel above 80°C. The crystal structure of $[L2] \cdot 0.5[TeCl_6]^{2-} \cdot HCl \cdot (H_3O)^+ \cdot 0.5H_2O$ cannot be recovered after the removal of water, as confirmed by their PXRD patterns.

Supplementary material

For more information, refer to CCDC reference numbers 720919, 720920, 720921, and 72544.

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