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Halogen anion-directed helical host chain and the effect of halogen anions on the inclusion property

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In this paper, a series of halogen anion-directed complexes $0.5[CH_3OH] \cdot 0.5[H_2O] \subset [L1H_2]^{2+} \cdot 2[Cl^-]$ (crystal 1), $0.5[H_2O]$, $\{[L1H_2]^{2+}\}_{0.5} \cdot [Br^-]$ (crystal 2), $[L2H_2]^{2+} \cdot 2[Br]^-$ (crystal 3), $[L1H_2]^{2+} \cdot 2[I_3^-]$ (crystal 4) and $2[L2H_2]^{2+} \cdot 2[I_3^-]$ (crystal 5) were synthesised (L1 = diamine N, N, N', N'-tetrabenzyl-2-butylyne-1,4-diamine, L2 = N, N, N', N'-tetra-(*p*-tertbutylbenzyl)-ethyl-enediamine), in which the halogen anions act as templates, via N-H···X (halogen) interactions, generating the helical structures. The choice of anion in this process was shown to be crucial for the successful assembly of the host chains and as well the inclusion property, meanwhile, the conformation of L1 and L2 may also exert an important influence on the formation of helical structures. X-ray structure studies have shown that the ability of the halides to template the formation of the helical host chains follows the order Cl⁻ > Br⁻ > l⁻.

Keywords: anion template; helical structure; halogen anion; host-guest; hydrogen bonding

1. Introduction

Helical structures, which are ubiquitous in nature and are the foundation of the genetic code, have received widespread attention because of their importance in biological and supramolecular chemistry (1-3). Many chemists have made great contributions to this field, and the preparation and characterisation of single, double and triple helical structures through the self-assembly of ligands and metal cations have shown significant progress recently (4-9). The factors affecting the formation of helices also have attracted particular interest. For example, molecular shape can determine the helical packing motif (10). The coordination interactions can effectively generate helices (11). Hydrogen bonding interaction is also a versatile and efficient supramolecular synthon in crystal engineering, even the weak interactions such as C-H···O, $\pi - \pi$ stacking and C-H- π interactions may produce helical structures (12-20). However, to our best knowledge, the helical structures constructed via hydrogen bonding interactions are still rare.

The use of anion template to direct the formation of specific molecules and assemblies is an area of supramolecular chemistry (21). The different anions can have influence on the self-assembly of the helices (4, 22). However, the anion-templated formation is particularly rare in the assembly of metal-free helices (23, 24). Gale and co-workers (25) have reported the first example of an anion-templated assembly of a helix formed by two neutral strands (containing amides as hydrogen bond donors). Inspired by the aforementioned consideration,

ISSN 1061-0278 print/ISSN 1029-0478 online © 2012 Taylor & Francis http://dx.doi.org/10.1080/10610278.2012.741686 http://www.tandfonline.com our current synthetic strategy is to acquire metal-free host-guest complexes featuring helical characters. In this work, we have synthesised a new kind of halogen aniondirected helical chain, in which the halogen anions act as templates, via N-H···X (halogen) or C-H···X (halogen) interactions, generating the helical structures. In our strategy, the diamine ligands N, N, N', N'-tetrabenzyl-2butylyne-1,4-diamine (L1) and N,N,N',N'-tetra-(p-tertbutylbenzyl)-ethyl-enediamine (L2) were chosen as the organic ligand based on the following considerations (Scheme 1): (i) two N functionality groups are located in the middle positions, instead of α , ω position; (ii) two N atoms are attached to the substituent benzyl rings, and spaced by different spacers, such as methylene and 2butyne; (iii) two functionality groups are easily double protonated. Such structure can be motivated by geometrical requirements for the recognition of halide anions.

2. Experiment

2.1 Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purifications. IR spectra were obtained with a PerkinElmer 100 FT-IR spectrometer (USA) using KBr pellets. NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz, USA) at 25°C with TMS as the internal reference. Differential scanning calorimetry was performed using a TA Instrument Q100 differential scanning calorimeter.

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Scheme 1. Structures of L1 and L2.

2.2 Preparation of L1

Dibenzylamine (43 ml) was slowly added into the solution of 17 g NaHCO₃ and 23 ml distilled water. 1,4-Dichloro-2butyne of 13 ml (2-3 drops/s) was 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 by diethyl ether, and then washed with distilled water. Recrystallisation using acetone and drying in vacuo, produced white crystals 27 g, yield 60.8%. m.p. 109–112°C. IR (KBr), λ_{max} (cm⁻¹): 3028 (w, ArH), 1600, 1494, 1452 (s, Ar), 2911 (s, CH₂); ¹H NMR (CDCl₃, 300 MHz) &: 3.36 (4H, s, CH2), 3.78 (8H, s, CH2), 7.26-7.45 (20H, m, ArH). ¹³C NMR (CDCl₃, 75.45 MHz) δ: 41.461 (CH₂ attached to alkyne bond), 57.605 (CH₂ attached to benzyl group), 79.831 (C≡C), 127.091 (p-C of monosubstituted benzene), 128.278 (m-C of monosubstituted benzene), 128.961 (o-C of monosubstituted benzene), 138.889 (C of monosubstituted benzene attached to CH₂).

2.3 Preparation of L2

Ethylene diamine (7 ml) was slowly added into the solution of 8 g NaOH and 20 ml distilled water. p-Tertbutyl-benzyl chloride of 40 ml (2-3 drops/s) was then continuously added into the mixture solution. After the reaction was heated to 95°C and stirred for 3 h, the mixture was cooled to room temperature. The white reaction product was separated by chloroform and then washed with distilled water. Recrystallisation using acetone and drying in vacuo, produced white crystals 21.6 g, yield 67.1%. m.p. 156–158°C, IR (KBr), λ_{max} (cm⁻¹): 3059 (w, ArH), 1602, 1513, 1462 (s, Ar), 2869 (s, CH₂), 2960 (s, CH₃); ¹H NMR (CDCl₃ 300 MHz) δ: 1.30–1.31 (18H, d, CH₃), 2.63 (2H, s, CH₂), 3.50 (4H, s, CH₂), 7.22-7.30 (8H, m, ArH). ¹³C NMR (CDCl₃, 75.45 MHz) δ: 31.476 (CH₃ of tert-butyl), 34.391 (quaternary carbon attached to benzene ring), 51.340 (CH₂), 58.174 (CH₂ of benzyl ring), 124.947 (o-C of tert-butyl-benezene), 128.343 (m-C of *tert*-butyl-benezene), 136.783 (benzene ring attached to CH_2), 149.333 (benzene ring attached to *tert*-butyl).

2.4 Preparation of $0.5[CH_3OH] \cdot 0.5[H_2O] \subset [L1H_2]^{2+} \cdot 2[Cl]^{-}$ (crystal 1)

L1 (0.22 g), 25 ml methanol, 1.5 ml concentrated hydrochloric acid and 3 ml water were placed in a 50-ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 5 days at room temperature. Recrystallisation produced white block crystals, m.p. 219–224°C; IR (KBr), λ_{max} (cm⁻¹): 3419 (s, N⁺H), 3040 (w, ArH), 2516 (s, N⁺H), 1498, 1458 (s, Ar), 2915 (s, CH₂), 1087 (m, C–O). ¹H NMR (DMSO, 300 MHz) &: 3.85 (6H, d, CH₂), 4.40 (8H, s, CH₂), 7.44– 7.71 (20H, m, ArH), 12.37 (2H, s, N⁺H).

2.5 Preparation of $0.5[H_2O] \subset \{[L1H_2]^{2+}\} \ 0.5[Br]^{-1}$ (crystal 2)

L1 (0.11 g), 20 mlmethanol, 2.0 ml hydrobromine and 2 ml water were placed in a 50-ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 2 days at room temperature. Recrystallisation produced white transparent crystals, m.p. 200–206°C; IR (KBr), λ_{max} (cm⁻¹): 3441 (s, N⁺H), 3031 (w, ArH), 2509 (s, N⁺H), 1496, 1458 (s, Ar), 2911 (s, CH₂), 1625 (w, H₂O). ¹H NMR (DMSO, 300 MHz) δ : 3.94 (4H, s, CH₂), 4.45 (8H, s, CH₂), 7.47–7.64 (20H, m, ArH).

2.6 Preparation of $2[H_2O] \subset [L2H_2]^{2+} \cdot 2[Br]^{-}$ (crystal 3)

L2 (0.15 g), 30 ml methanol, 1.0 ml hydrobromine and 3 ml water were placed in a 50-ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 4 days at room temperature, producing white transparent block crystals. m.p. 216– 220°C; IR (KBr), λ_{max} (cm⁻¹): 3632 (w, H₂O), 3442 (s, N⁺H), 2687, 2512 (s, N⁺H), 1615, 1516, 1456 (s, Ar), 2960, 2869 (s, CH₃), 2903 (s, CH₂); ¹H NMR (CDCl₃, 300 MHz) δ : 1.25 (36H, s, CH₃), 1.70 (5H, s, H₂O), 3.82 (4H, s, CH₂), 3.97–4.03 (4H, q, CH₂), 4.17–4.21 (4H, q, CH₂), 7.41–7.54 (16H, m, ArH).

2.7 Preparation of $[L1H_2]^{2+} \cdot 2[I_3]^-$ (crystal 4)

L1 (0.10 g), 25 ml methanol and 0.5 ml hydroiodic acid were placed in a 50-ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 2 days at room temperature, producing red block crystals, m.p. 190–196°C; IR (KBr), λ_{max} (cm⁻¹): 2695, 2600 (s, N⁺H), 1498, 1454 (s, Ar), 2934 (s, CH₂);

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¹H NMR (DMSO, 300 MHz) δ: 3.86 (4H, s, CH₂), 4.34 (8H, s, CH₂), 7.49–7.53 (20H, m, ArH).

2.8 Preparation of $2[L2H_2]^{2+} \cdot 2[I_3]^-$ (crystal 5)

L2 (0.10 g), 25 ml methanol and 0.5 ml hydroiodic acid were placed in a 50-ml Erlenmeyer flask and shaken until the contents were dissolved. The flask was allowed to stand for over 2 days at room temperature, producing red block crystals. m.p. 189–194°C. IR (KBr), λ_{max} (cm⁻¹): 3431 (s, N⁺H), 1613, 1513, 1462 (s, Ar), 2960, 2865 (s, CH₃), 2903 (s, CH₂); ¹H NMR (CDCl₃, 300 MHz) δ : 1.25 (36H, s, CH₃), 3.16 (4H, s, CH₂), 3.71 (8H, s, CH₂), 5.06 (2H, s, N⁺H), 7.20–7.22 (8H, d, ArH), 7.38–7.41 (8H, m, ArH).

2.9 Crystallography

Single-crystal X-ray diffraction measurements of complexes were carried out on a Bruker Smart CCD diffractometer equipped with a graphite monochromator. The determination of unit cell parameters and data collection was performed with MoK α 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-square methods (SHELXTL 97) (26). The details of data collection, data reduction and crystallographic data are summarised in Table 1. CCDC 889241–889245 contain the supplementary crystallographic data for this paper.

3. Results and discussion

3.1 Structure of crystals 1–5

Crystal structures of 1-3 are halogen anion-directed host– guest complexes, in which the halogen anions act as templates, via N-H···X (halogen) or C-H···X (halogen) interactions, generating the helical host, within which the guest molecules are included.

In crystal **1**, there are one double-protonated L1, two chloride anions, half methanol and half water molecule in one asymmetric unit. The two crystallographically independent chloride anions Cl1 and Cl2, acting as templates, bind simultaneously double-protonated L1 through two strong N-H···Cl interactions (N1-H1···Cl1: 3.058 Å, 170.8°; N2-H2···Cl2: 3.088 Å, 176.7°), forming a double anion-directed unit, as seen in Figure 1(a). An anion-directed helical chain along *c*-axis is formed, involving the above N-H···Cl hydrogen bonds (Figure 1(b)). However, there are no short contacts between the helical chains, and the helical chains are isolated.

The guest molecules of methanol and water are filled between the neighbouring helical chains and stabilised by the O-H···Cl interactions [water···Cl⁻: 3.213 Å (O1w···Cl1) and methanol···Cl⁻: 3.316 Å (O1M···Cl2)] with the two chloride anions. The guest molecules are connected with each other through O···O interactions [2.481 Å (O1w···O1M)] between the methanol and the water, forming a trapezoidal-shaped hydrogen bonded network, as seen in Figure 1(c). The overall 3D structural framework is given in Figure 1(d).

Table 1. Crystal data and refinement summary for crystals 1–5.

	1	2	3	4	5
Temperature (K)	294	294	294	113	113
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P2/c	$P2_1/c$	P-1	<i>C</i> 2
Z	4	4	4	2	4
<i>a</i> (Å)	8.889(2)	9.0083(16)	11.2294(15)	9.4807(19)	9.4241(19)
<i>b</i> (Å)	23.792(5)	11.566(2)	12.4585(15)	9.5065(19)	18.800(4)
c (Å)	14.681(3)	15.164(3)	33.103(4)	11.255(2)	26.836(5)
α (°)	90	90	90	104.13(3)	90
β (°)	90.277(4)	90.265(3)	94.128(2)	110.58(3)	92.50(3)
γ (°)	90	90	90	91.92(3)	90
$V(Å^3)$	3104.9(13)	1579.9(5)	4619.1(10)	913.0(3)	4750.1(16)
$D_x (g {\rm cm}^{-3})$	1.214	1.294	1.212	2.197	1.436
$F(0\bar{0}0)$	1208	630	1784	558	2056
R _{int}	0.0506	0.0452	0.0574	0.0274	0.0808
No. of total reflns	15,938	7766	22,935	5579	12,736
No. of unique reflns	5472	2789	8142	3192	6857
No. of obsd refins $I > 2\sigma(I)$	2905	2088	5443	2672	5792
No. of refined parameters	389	172	581	181	469
$R_{\rm f}/wR_{\rm f}$	0.0647/0.1689	0.0436/0.1274	0.0669/0.1442	0.0269/0.0626	0.0858/0.2191
All data $R_{\rm f}/wR_{\rm f}$	0.1306/0.2110	0.0642/0.1417	0.1056/0.1587	0.0330/0.0656	0.0927/0.2269
S	1.026	1.07	1.087	0.984	1.036



Figure 1. Crystal 1: (a) a double anion-directed unit, (b) the formation of anion-directed helical chain along *c*-axis, (c) the inclusion of guest molecules and the interactions between the guest and host chains and (d) the overall 3D structural framework.

In the crystal 2, there are half double-protonated L1, one bromine anion and one water molecule in one asymmetric unit. The bromine anion, as a template, binds directly with L1 molecules through N–H···Br (3.259 Å, 171.1°), forming a similar anion-directed unit to crystal 1 (Figure 2(a)). A helical chain is also formed, in which the $R_4^2(10)$ hydrogen bonding arrays are involved to stabilise the chain, whilst Br1 forms a bifurcated hydrogen bonds (N1-H1···Br1: 3.259 Å, 171.1° and C1-H1B···Br1: 3.849 Å, 156.2°) (Figure 2(b)). Similar to crystal 1, the helical chains are also isolated, and no short contacts between the helical chains are involved. Water molecules are filled into the helical chains, in which a similar trapezoidal-shaped hydrogen-bonded network is present, with the distances of bromine · · · water and water · · · water being 3.365 Å (Br1 \cdots O1) and 2.934 Å (O1 \cdots O1), respectively (Figure 2(c)). The overall 3D structural framework is given in Figure 2(d).

Similar to crystals 1 and 2, there are one doubleprotonated L2, two bromine anions and two water molecules in one asymmetric unit in crystal 3. The two crystallographically independent bromine anions Br1 and Br2, as templates, also bind simultaneously with doubleprotonated L2 simultaneously through two strong N-H···Br interactions (N1-H1···Br2: 3.205 Å, 167.2°; N2–H2···Br1: 3.192 Å, 164.2°), forming a double aniondirected unit, as seen in Figure 3(a). Such units are further linked to a helical chain along *b*-axis, as seen in Figure 3(b). Interestingly, the helical chains are linked into a 3D network. The main difference between crystals 3 and 1/2 is that the template Br anions are located at the outside of the chains and connect with the neighbouring helical chains via N-H···Br interactions. The water molecules are filled inside the channel between the neighbouring helical chains, with O1-H1c···Br1 (3.515 Å, 152.4°) and O1-H1D···Br2 $(3.652 \text{ \AA}, 156.1^{\circ})$ stabilising the helical chains and the guest molecules (Figure 3(c)). It is necessary to mention that the four tert-butyl groups of L2 ligand are greatly disordered, with the C atom of each methyl refined anisotropically as two closely situated positions for the sake of overall convergence with the most reasonable $R_{\rm f}$ factor. The occupancies of two sites are refined as 0.230/0.770, 0.818/0.182, 0.606/0.394, 0.647/0.353, for the four tertbutyl groups, respectively.

In contrast to crystals 1-3, an interesting variation occurs in the crystals 4-5, although the ligands L1 and L2



Figure 2. Crystal **2**: (a) a anion-directed unit, (b) the formation of helical chain, (c) the inclusion of water molecules and the interactions between the guest and host chains and (d) the overall 3D structural framework.

are reacted with HI in identical experimental conditions. In crystal 4, there are half double-protonated L1 and one discrete triiodide anion I_3^- in one asymmetric unit. In the discrete triiodide anion (labeled I1–I2–I3), the I₂ units have a distance of 2.884 (1) Å (I2–I3), and I⁻ with I2 units has a distance of 2.954 (1) Å (I1–I2). The angle of I–I–I is 176.7°. The triiodide in this crystal is comparable with those found in the triiodide anions of [Fe(phen)₃](I₃)₂ (solvent) (27). As the potential energy surfaces of I₃⁻ are flat (28, 29), the anion I₃⁻ is positioned on the surfaces of the molecule of L1 through N1–H1···I1 (3.588 Å, 166.1°). The extension of the hydrogen-bonding linkages resulted in 1D-layered network along (011), and is then sandwiched with I₃⁻ species, as seen in Figure 4.

In crystal 5, one asymmetric unit comprises two independently double-protonated L2 and two discrete triiodide anions. The two crystallographically independent discrete triiodide anions (labeled I4-I3-I4 and I2-I1-I2), with I-I distances being 2.820 (1) Å (I1-I2) and 2.925 (1) Å (I3–I4), and I–I–I angle being 176.1° (I2–I1–I2) and 176.8° (I4-I3-I4), respectively. One triiodide anion I_2^- (I4–I3–I4) is positioned on the surfaces of one molecule of L2 in the asymmetric unit through van der Waals force [the nearest distance is C24-H24···I4 $(4.131 \text{ \AA}, 176.5^{\circ})$], whereas the other triiodide anion I_3^{-1} (I2-I1-I2) sits on the surface of the other crystallographically independent molecule of L2 through van der Waals force [the nearest distance is C19-H19...I2 $(4.201 \text{ \AA}, 160.6^{\circ})$]. The two discrete triiodide anions, as templates, linking the neighbouring L2 molecules along caxis into a helical chain through shot contacts between tert-butyl groups (H11A···H15: 2.8 Å, H34B···H45B: 2.1 Å), as seen in Figure 5, but no guest molecules are included.



Figure 3. Crystal 3: (a) a double anion-directed unit, (b) the formation of a helical chain along *b*-axis and (c) the inclusion of guest molecules and the interactions between the guest and host chains.



Figure 4. Crystal 4: the 1D layered network along (0 1 1) and I_3^- species as sandwich between the layers.

3.2 The effect of halogen anions on the inclusion property and thermal analysis

From the X-ray structural analysis, we found that the choice of halogen anions may have effect on the inclusion property. The inclusion property follows the order $Cl^- > Br^- > I^-$. In the case of Br^- as templateds, the helical host can accommodate the guest molecules of water, whereas in the case of Cl^- anions as templates, the host can include both methanol and water guest molecules.



Figure 5. Crystal 5: helical structural packing along c-axis.

However, due to the relatively larger anion radius of I_3^- than Br⁻ and Cl⁻, no guest molecules were included inside the host formed by I_3^- . Therefore, the size of the anion may exert an important influence on the inclusion property.

In addition, in the case of I_3^- as templates, although the ligands L1 and L2 are reacted with HI in identical experimental conditions, the ligand L2 is more favourable to the formation of helical structures than the ligand L1. There are two main differences between two ligands: (1) the two methylene groups as spacers between N atoms in L2 are more flexible than the 2-butyne groups in L1, thus facilitating conformational change to produce the helices instead of the rigid linear arrangement. (2) The substituent tert-butyl groups, which have short contacts between the neighbouring L2 ligands, are key to the formation of helices. Therefore, the choice of ligands, with different conformation and substituent groups, may also exert an important influence on the generation of helical structures.

The thermogravimetric analysis (TGA) was carried out on crystals 1-4 (see Figure 6). The crystal specimens having a nominal mass between 15 and 20 mg were placed in ceramic sample pans. Samples were equilibrated at 25°C for 5 min, and then ramped to 800°C at 10°C/min. In crystal 1, the decomposition could mainly proceed in three stages. The first two stages in the range from 30 to 200°C probably corresponds to the elimination of HCl gas (which was speculated from the previous studies of solid-state interconversions of coordination networks and hydrogenbonded salts (30)) and the weight loss of included water and methanol (18.5% obsd; 18.1% calcd). The subsequent weight loss was considered to be a result of the further decomposing of the ligand. In crystal 2, 3.2% weight loss beginning from 30 to 90°C corresponds to the loss of the included water (calcd 2.9%). The subsequent weight loss above 90°C was considered to be a result of the further



Figure 6. TGA of crystals 1-4.

decomposing of the ligand and HBr. In crystal **3**, one stage in the range from 30 to 220°C, corresponding to the weight loss of included water (4.0% obsd; 4.2% calcd). The subsequent weight loss above 220°C was the further decomposing of the ligand. In crystal **4**, the first stage in the range from room temperature to 180°C could correspond to the sublimation of iodine, and the subsequent weight loss above 185°C was the decomposing of the compound.

4. Conclusion

Herein, we have synthesised a series of halogen aniondirected host–guest complexes, in which the halogen anions act as templates, via N–H···X (halogen) or C– H···X (halogen) interactions, generating the helical host, within which the guest molecules are included. The choice of anion in this process was shown to be crucial for the successful assembly of the host chains and as well the inclusion property, meanwhile, the conformation of L1 and L2 may also exert an important influence on the formation of helical structures. X-ray structure studies have shown that the ability of the halides to template the formation of the helical host chains follow the order Cl⁻ $> Br^- > I^-$.

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A new kind of halogen anion-directed helical chain has been synthesised, in which the halogen anions act as templates, via $N-H \cdots X$ (halogen) interactions, generating the helical structures.



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