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# Crystal structures of sandwich-type potassium cation complexes formed from benzo-15-crown-5-based ligand containing a chloromaleimide moiety†

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**We developed a novel benzo-15-crown-5 (B15C5)-based organic ligand containing an *N*-phenylchloromaleimide moiety. Two geometrically different potassium cation (K⁺) complexes with a B15C5/K⁺/B15C5 sandwich structure were prepared and characterised *via* single-crystal X-ray diffraction.**

Crown ethers, which are macrocyclic poly(ethylene glycol) molecules, have been widely used as representative host molecules owing to their ability to encapsulate cations (*e.g.* metal ions and ammonium).[1] The host–guest interactions of crown ethers with these cations enable the development of materials that exhibit catalytic activity,[2] ion transport activity,[3] optical properties,[4] magnetic properties,[5] and phosphorescent properties.[6] Remarkably, crown ethers possess unique and specific inclusion modes for guest species that correspond to the diameters of the cavities within their cyclic structures. For example, benzo-15-crown-5 (B15C5) forms a 2:1 sandwich complex with potassium cations (K⁺; 2.76 Å), *i.e.* B15C5/K⁺/B15C5,[7] whereas the cavity of B15C5 (1.70–2.20 Å) is suitable for the formation of a 1:1 chelate complex with sodium cations (Na⁺; 2.04 Å). Such coordination-mode variation arises from the flexibility of these cyclic structures containing oxygen donor atoms for coordination.

By exploiting the inclusion characteristics of B15C5, we prepared a 2-anilino-3-chloromaleimide (AC)-based chromophore in which the anilino moiety was derivatised to a B15C5 moiety to serve as the K⁺-chelating unit (**B15C5-AC-C6-COO⁻**, Fig. 1A).[8] **B15C5-AC-C6-COO⁻** interacted effectively with K⁺ in an aqueous solvent (0.2 M Tris-HCl buffer, pH 8.0) to form a gel-like molecular assembly (*i.e.* supramolecular hydrogel), resulting in a colour change from orange to yellow. The formation of this supramolecular hydrogel was attributed to molecular assembly induced by the formation of the aforementioned B15C5/K⁺/B15C5 sandwich complex. Although the interactions between **B15C5-AC-C6-COO⁻** and K⁺ were monitored by ¹H nuclear magnetic resonance spectroscopy in CD₃OD and the structure of the host–guest complex was evaluated by density functional theory calculations, the structure was not experimentally determined because of the low crystallinity. Therefore, the molecular-scale mechanism of the assembly process is not yet well understood.

To determine the inclusion mode of the B15C5-AC structure with K⁺, we reviewed the literature on the crystal structures of complexes in which K⁺ is encapsulated by B15C5-based organic ligands. The B15C5 structure exhibited multiple inclusion modes for K⁺ depending on the ligand

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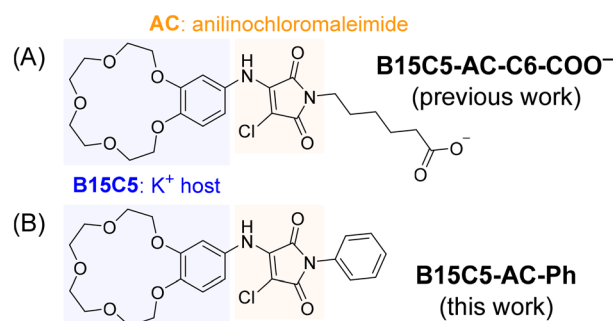
**Fig. 1** Chemical structures of **B15C5-ACC-C6-COO⁻** (A, previous work[8]) and **B15C5-AC-Ph** (B, this work).

structure and counterions (some of which are shown in Fig. 2).[9] For example, a direction difference between two benzo moieties in a B15C5/K$^+$/B15C5 complex in Fig. 2A, B and C are ~180°, ~50°, and ~120°, respectively. Furthermore, in some B15C5 systems, the complexes are oligomerised by another complex unit and/or *via* noncovalent interactions (Fig. 2A and C). This variation in the inclusion mode suggests the importance of developing a crystalline B15C5-AC analogue and its K$^+$ complex formed by the addition of KCl, as in our previous studies.

In this study, we designed and synthesised a novel B15C5-AC analogue, **B15C5-AC-Ph** (Fig. 1B and Scheme S1, ESI†) and obtained crystal structures of an inclusion complex of this ligand with KCl. We attributed the low crystallinity of the previously reported **B15C5-AC-C6-COO**$^-$ to (1) diversification of possible conformations as a result of the flexibility of the alkyl (C6) chain and (2) electrostatic repulsion arising from the terminal carboxylate moiety. Furthermore, owing to the presence of this carboxylate moiety, the 2:1 complex was anionic at pH 8.0 and the flexible Tris·H$^+$ used as the buffer was a possible countercation. Thus, to increase the crystallinity, we replaced the alkyl chain containing a terminal carboxyl group (C6-COO$^-$) with a rigid, charge-neutral phenyl (Ph) group. We expected that the Ph group would induce a regular molecular orientation *via* π–π and/or CH–π interactions. The chloro group was selected as a halogeno group introduced in the maleimide backbone. The halogeno group is thought to play roles in the molecular packing and the absorption change upon the molecular assembly. The former was demonstrated in our recent publication, where a bromo group substituted for a chloro group contributed to crystallisation *via* the strong halogen bond.[10] We have expected that the chloro group exhibiting weaker halogen bond enlarges the impact of the B15C5 moiety and complexation with K$^+$ on the molecular packing.

Single crystals of non-clathrate **B15C5-AC-Ph** (**1**) were prepared by evaporation from a methanol/water mixture (ESI†). The crystal structure is shown in Fig. 3, and the crystallographic data (Table 1) indicated that **1** crystallised in the monoclinic $P2_1/n$ space group. The benzo–AC and AC–*N*-Ph dihedral angles in a **B15C5-AC-Ph** molecule are 40.2(2)° and 45.8(2)°, respectively. The
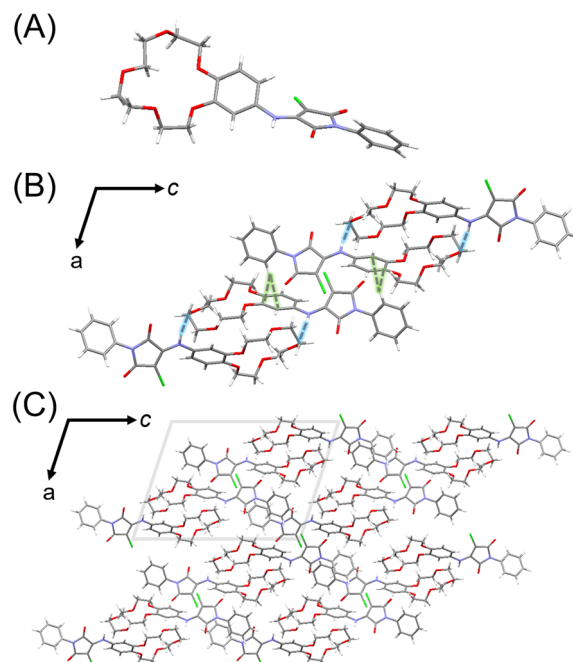


**Fig. 3** Crystal structures of **B15C5-AC-Phe**. Monomer (A), molecular interactions (B) and packing (C). Red represents oxygen; blue, nitrogen; gray, carbon; and white, hydrogen.

ether oxygens of two B15C5 moieties hydrogen-bonded to the secondary amines of the AC–Ph moieties (light blue broken lines in Fig. 3B). Furthermore, the Ph group on the ring nitrogen in the maleimide (*N*-Ph) moiety interacted with the benzene ring of the B15C5 moiety in another **B15C5-AC-Ph** *via* CH–π interactions (light green broken lines in Fig. 3B). Thus, **B15C5-AC-Ph** participated in three-dimensional packing (Fig. 3C), and in the crystal structure of **1**, the *N*-Ph group influenced the molecular orientation and crystallinity despite the flexible ether structure.

The reaction of **15C5-AC-Ph** with KCl in a methanol/water mixture afforded two crystallographically different **B15C5-AC-Ph⊃K$^+$** crystals, namely, [K(**B15C5-AC-Ph**)$_2$·(CH$_3$OH)$_{1.75}$(H$_2$O)$_{2.4}$]$_n$ (**2**) and [K(**B15C5-AC-Ph**)$_2$·(H$_2$O)$_{2.8}$]$_n$ (**3**) (ESI†). The crystals used in this study were obtained from a sample bottle from a different batch that was prepared under identical conditions. **2** crystallised in the triclinic $P\bar{1}$ space group (Table 1). In the crystal structure of **2** (Fig. 4), two molecules of **B15C5-AC-Ph** and one
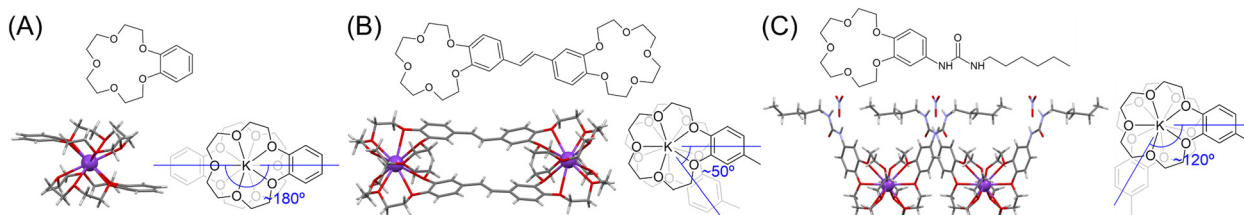


**Fig. 2** Reported crystal structures of B15C5/K$^+$/B15C5-type complexes: benzo-15-crown-5 (B15C5, A),[9i] bis(15-crown-5)stilbene (B)[9e] and hexylureidobenzo-15-crown-5 (C).[9f] Purple represents potassium; red, oxygen; blue, nitrogen; gray, carbon; and white, hydrogen.

**Table 1** Crystallographic data for crystals **1**–**3**

| Compound | **B15C5-AC-Ph (1)** | **B15C5-AC-Ph⊃K⁺ (2)** | **B15C5-AC-Ph⊃K⁺ (3)** |
|---|---|---|---|
| Formula | $C_{24}H_{25}ClN_2O_7$ | $C_{48}H_{50}ClKN_4O_{14} \cdot (CH_3OH)_{1.75}(H_2O)_{2.4}$ | $C_{48}H_{50}Cl_3KN_4O_{14} \cdot (H_2O)_{2.8}$ |
| Formula weight | 488.91 | 1151.17 | 1151.17 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ |
| $a/\text{Å}$ | 14.6695(5) | 12.0536(4) | 15.1444(4) |
| $b/\text{Å}$ | 8.4232(2) | 14.4733(5) | 23.9026(5) |
| $c/\text{Å}$ | 19.7536(6) | 17.4640(5) | 15.8158(6) |
| $\alpha/\text{deg.}$ | 90 | 90.685(2) | 90 |
| $\beta/\text{deg.}$ | 108.105(4) | 105.563(2) | 103.663(3) |
| $\gamma/\text{deg.}$ | 90 | 108.209(3) | 90 |
| $V/\text{Å}^3$ | 2319.99(13) | 2772.69(16) | 5563.2(3) |
| $Z$ | 4 | 2 | 4 |
| Crystal size/mm³ | 0.281 × 0.081 × 0.021 | 0.235 × 0.111 × 0.018 | 0.237 × 0.166 × 0.032 |
| $T/\text{K}$ | 113.15 | 113.15 | 103.15 |
| $D_c/\text{g cm}^{-3}$ | 1.400 | 1.379 | 1.371 |
| $F_{000}$ | 1024.0 | 1206.0 | 2395.0 |
| $\lambda/\text{Å}$ | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ (Mo Kα)/mm⁻¹ | 0.213 | 0.315 | 0.315 |
| $R_1 [I > 2.00\sigma(I)]^a$ | 0.0384 | 0.0689 | 0.0549 |
| $R$ (all reflections)$^a$ | 0.0532 | 0.0941 | 0.0845 |
| $wR_2$ (all reflections)$^b$ | 0.1000 | 0.2030 | 0.1561 |
| GOF | 1.055 | 1.043 | 1.022 |
| Number of observations | 16 615 | 34 566 | 38 344 |
| Number of variables | 4744 | 11 304 | 11 373 |
| CCDC number | 2428279 | 2428376 | 2428377 |

$^a R_1 = R = \sum||F_o| - |F_c||/\sum|F_o|.$ $^b wR_2 = [(\sum w(|F_o|^2 - |F_c|^2)^2)/\sum w(F_o^2)^2]^{1/2}.$

K⁺ formed a **B15C5-AC-Ph**/K⁺/**B15C5-AC-Ph** sandwich complex. In this sandwich complex, the K–O distances were 2.79–3.00 Å, and direction difference between the benzo moieties was 43°. The AC–Ph moieties of each **B15C5-AC-Ph** ligand were oriented in the same direction relative to B15C5 and the chloro groups were oriented in the opposite direction relative to the central axis of the complex (Fig. 4A). The dihedral angles between benzo and AC moieties being 44.2(3)° and 45.8(3)° resulted in parallel orientation of two maleimides. In contrast, the N-Ph groups are not parallel to each other owing to the maleimide–N-Ph dihedral angles (80.1(4)° and 55.9(5)°). The sandwich complexes dimerised by forming π–π interactions between the N-Ph group and the benzene ring of the B15C5 moiety (light green broken lines in Fig. 4B) and hydrogen bonds between the maleimide oxygen (C=O) and the secondary amine hydrogen (NH; light blue broken lines in Fig. 4B). Furthermore, these dimers contained hydrogen bonds between the maleimide oxygen and $CH_2$ moieties in B15C5 and with incorporated solvents ($H_2O$ and MeOH; Fig. 4C).

In the crystal structure of **3**, which belonged to the monoclinic $P2_1/n$ space group (Table 1), the formation of a **B15C5-AC-Ph**/K⁺/**B15C5-AC-Ph** sandwich complex (K–O distances: 2.59–3.15 Å, benzo direction difference: 48°), similar to that in **2**, was confirmed (Fig. 5A). In contrast to the crystal structure of **2**, as structures overlaid in Fig. 6, the chloro groups in **3** were oriented in the same direction relative to the central axis of the complex. The AC and N-Ph moieties in the sandwich complex were stacked via π–π interactions (dihedral angles for benzo–AC: 46.1(3)° and

46.4(3)°, those for AC–N-Ph: 47.5(4)° and 50.5(4)°). The sandwich complexes were packed via complex CH–π interactions and hydrogen bonds via the incorporation of water molecules (Fig. 5B and C). This geometric variation of the K⁺ complex of **B15C5-AC-Ph** was attributed to the asymmetry of the AC moiety, the presence of non-covalent interactions with the N-Ph moiety and the flexibility of the B15C5 moiety.

Here we compare the halogen bonds in the crystals. As mentioned in the molecular design section, halogen bonds are an important factor in inducing molecular packing in this system. In crystal **1**, the distance between the two Cl atoms in the B15C5-AC structure was 4.434 Å and the two C–Cl⋯Cl angles of them were 95.50°, indicating the presence of type-I halogen bonds.[11] In crystal **2**, there are no halogen bonds because the Cl atoms are oriented in opposite directions. In crystal **3**, the distance between the two Cl atoms in the B15C5-AC structure was 3.922 Å and the two C–Cl⋯Cl angles of them were 75.17° and 107.96° respectively, indicating the presence of type-II halogen bonds.[11] These results suggests that the halogen-bonding ability is not dominant in the present molecular system and that such weak interactions afford flexibility in the molecular packing pattern. Recently, an analysis of halogen–halogen (X1⋯X2, X = Cl, Br and I) contacts in solids using a large data set reported that type-II contacts occur most frequently in iodinated derivatives, less frequently in brominated derivatives and least frequently in chlorinated derivatives.[11b,12] This suggests that the Cl⋯Cl contacts
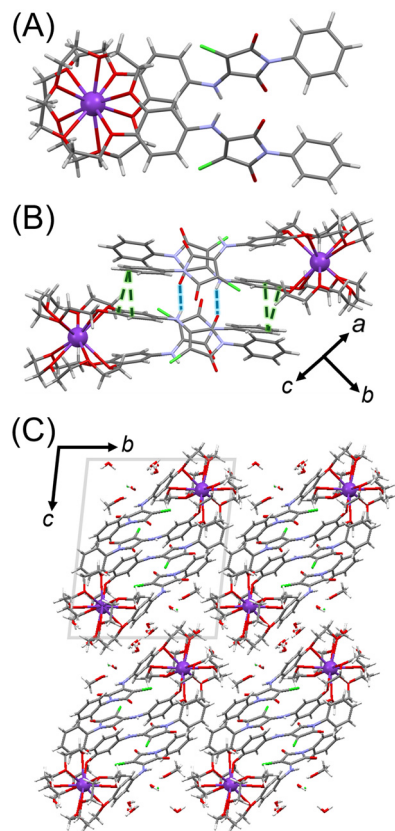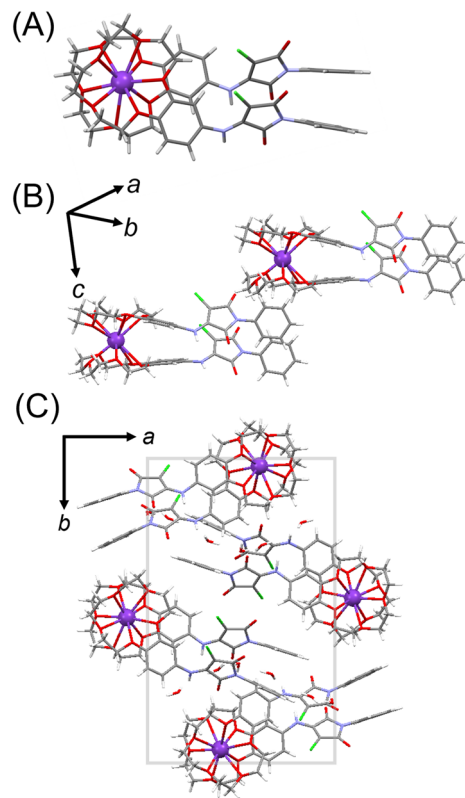
**Fig. 4** Crystal structures of **B15C5-AC-Phe⊃K⁺** [K(**B15C5-AC-Ph**)$_2$·(CH$_3$OH)$_{1.75}$(H$_2$O)$_{2.4}$]$_n$ (**2**). Sandwich complex (A), molecular interactions (B, counterion and solvents omitted) and packing (C). Purple represents potassium; red, oxygen; blue, nitrogen; gray, carbon; and white, hydrogen.



**Fig. 5** Crystal structures of **B15C5-AC-Phe⊃K⁺** [K(**15C5-AC-Ph**)$_2$·(H$_2$O)$_{2.8}$]$_n$ (**3**). Sandwich complex (A), molecular interactions (B, counterion and solvents omitted) and packing (C). Purple represents potassium; red, oxygen; blue, nitrogen; gray, carbon; and white, hydrogen.
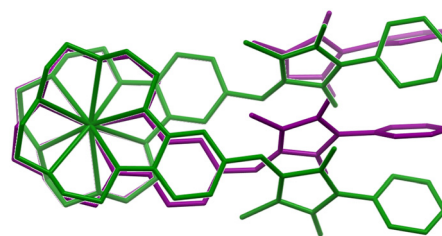
observed in this molecular system may be primarily driven by molecular assembly due to potassium encapsulation in B15C5-AC structure.

## Conclusions

In summary, we determined the crystal structures of a non-clathrate crystal of **B15C5-AC-Ph** (**1**) and two types of K⁺ clathrate crystals of **B15C5-AC-Phe⊃K⁺** (**2** and **3**). It was hypothesised that the *N*-Ph group induced efficient molecular packing and increased the crystallinity by providing an interaction site. Notably, two K⁺ complexes in which the chloro groups were arranged in the different directions were successfully characterised, revealing different crystal structures. The molecular assembly patterns of the B15C5-AC backbone were relatively vague and flexible, making these structures potentially useful for the design of flexible molecular assemblies, such as supramolecular gels, liquid crystals and soft crystals. Crystalline phase transition might occur due to changes in the external environment (*e.g.* solvent removal by heating) as well. We are currently investigating the physical properties of this molecular system as soft materials, such as supramolecular gels, liquid crystals and soft crystals that respond to external stimuli.



**Fig. 6** Overlaid structure comparison between [K(**B15C5-AC-Ph**)$_2$·(CH$_3$OH)$_{1.75}$(H$_2$O)$_{2.4}$]$_n$ (**2**, green) and [K(**B15C5-AC-Ph**)$_2$·(H$_2$O)$_{2.8}$]$_n$ (**3**, purple).

## Data availability

The data supporting this article have been included as part of the PDF and CIF files in the ESI.†

## Author contributions

Conceptualization: Y. H. and R. O.; synthesis and structural analysis: Y. H.; single-crystal XRD analysis: A. I.; writing—original draft: Y. H. and R. O.; writing—review and editing: A. I. and R. O.

## Conflicts of interest

There are no conflicts to declare.

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