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Complexation behavior and crystal structure of a dithia[16.3.3](1,2,6)cyclophane: a novel one-dimensional coordination polymer with perchlorate anions as linkers†

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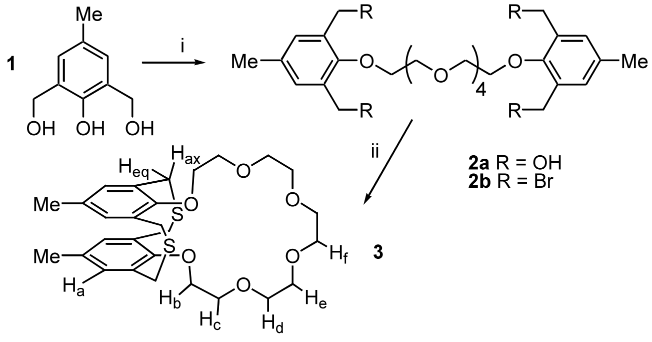
Abstract—The synthesis of 20,28-dimethyl-24,33-dithia-1,4,7,10,13,16-hexaoxa[16.3.3](1,2,6)cyclophane **3** was achieved by cesium carbonate-assisted high dilution cyclization. Cyclophane **3** exhibited strong complexation towards all alkali metal ions. The change in chemical shift for the bridge methylene protons upon addition of alkali metal ions correlated to log K_a. The crystal structure of cyclophane **3** as well as its sodium and potassium complexes was studied. Cyclophane **3** formed a novel one-dimensional coordination polymer with potassium perchlorate using anions as the linkers, while the complex of **3** with sodium perchlorate had a dimeric structure. © 2002 Elsevier Science Ltd. All rights reserved.

The term crownophane is defined as a macrocycle in which a mobile polyether chain and a rigid cyclophane unit are present.[1] Crownophanes, combining a flexible moiety with complexation ability, exhibit some interesting properties.[2–4] Dithia[3.3]metacyclophane shows conformational diversity in solution.[5] Besides *syn–anti* isomerization, it undergoes bridge-wobbling, ring-flipping and ring-tilting processes. In this article, we report the synthesis, complexation properties and structural study of a *syn*-dithia[3.3]metacyclophane-fused crownophane.

Crownophane **3** was synthesized as shown in Scheme 1. Tetraol **2a**[6] was prepared in a good yield of 66% by the reaction of bis(2,6-hydroxymethyl)-4-methylphenol **1** with pentaethylene glycol dibromide in dry acetone. Conversion of **2a** to tetrabromide **2b**[7] could be achieved in 74% yield using phosphorus tribromide in dry 1,4-dioxane at low temperature. The corresponding crownophane **3**[8] was obtained in 51% yield when **2b** underwent intramolecular cyclization with $Na_2S{\cdot}9H_2O$ in the presence of Cs_2CO_3 under high dilution conditions. The single-crystal X-ray structure of **3** was determined[9] (Fig. 1). The two thia-bridges in **3** adopt a *pseudochair–pseudochair* conformation. Both aromatic rings do not deviate from planarity, but tilt at an angle of 12.8°, which is less than that in *syn*-2,11-dithia[3.3]metacyclophane (20.6°)[10] because the internal crown ring forces the aromatic rings to be inclined to favor 'inward tilting'. The average diameter of the crown part is estimated to be ca. 2.81 Å. The crownophane **3** exhibits strong complexation ability towards all alkali metal cations. Its logarithm of association constants (K_a)[11] are 3.57, 4.26, 5.77, 5.21 and 4.55, respectively, for Li^+, Na^+, Rb^+, and Cs^+. Log K_a for K^+ is the largest, which is as expected in accordance with the size complementarity. In comparison with 18-crown-6,[12] K^+/Na^+ selectivity for **3** decreases by a



Scheme 1. *Reagents and conditions*: (i) **2a**, $Br(CH_2CH_2O)_4$–CH_2CH_2Br, acetone, K_2CO_3; **2b**, PBr_3, 1,4-dioxane, 0–10°C; (ii) $Na_2S{\cdot}9H_2O$, Cs_2CO_3, benzene/ethanol, high dilution conditions.

Keywords: cyclophane; crownophane; synthesis; complexation; crystal structure.

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† Taken in part from the J. Xu's dissertation.

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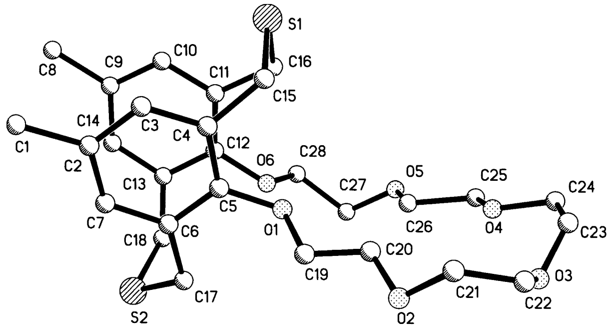

Figure 1. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity.

factor of 6.4, indicating that aromatic ring-tilting and thia-bridge wobbling processes in the cyclophane part have an effect on the selectivity.

Induced chemical shifts upon addition of alkali metal ions were measured in CD_3CN and the results are summarized in Table 1. Interestingly, the oxyethylene protons show only small changes relative to the bridge methylene protons (axial H_{ax} and equatorial H_{eq}). The changes in chemical shift of the methylene protons in the thia-bridges exhibit a correlation to the log K_a for the alkali metal ions: the higher the log K_a, the larger the change in chemical shift (Fig. 2). For example, crownophane **3**, which has the largest log K_a for K^+, showed the largest downfield shift (0.21 ppm) for H_{ax} and the largest upfield shift (−0.27 ppm) for H_{eq}. In fact the order of the chemical shift changes for H_{ax} in **3** (K^+>Rb^+>Na^+>Cs^+>Li^+) follows the same trend as the order of the log K_a values. The thia-bridges in **3** undergo wobbling processes[13] in solution, however, complexation may reduce or disrupt the free wobbling motion due to steric hindrance thus leading to conformational and geometrical changes in the cyclophane part. This may account for the large change in chemical shift for the bridge methylene protons upon addition of alkali metal ions.

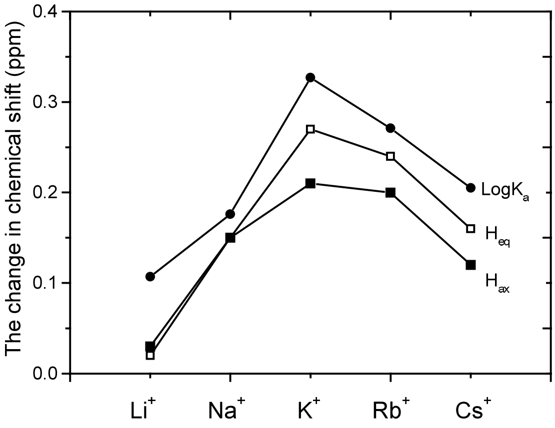

Figure 2. The chemical shift changes for H_{eq} and H_{ax} upon addition of an alkali cation correlated to log K_a. The $\Delta\delta$ are taken as their absolute values in the plot.

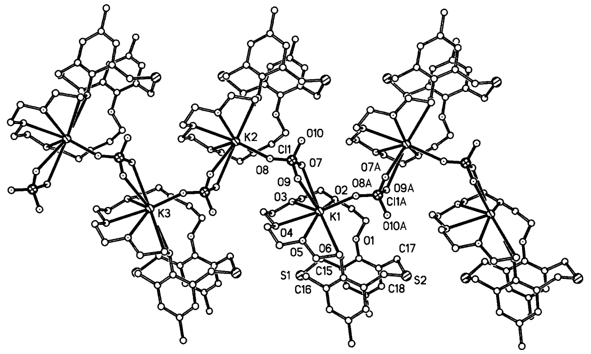

Figure 3. ORTEP drawing of the coordination polymer formed by $3{\cdot}KClO_4$ at the 50% probability level. Hydrogen atoms are omitted for clarity.

The complex $3{\cdot}KClO_4$ for X-ray crystallographic analysis was obtained by vapor diffusion in a mixture of 1:1 stoichiometric crownophane **3** and $KClO_4$ in acetonitrile.[14] The drawing of $3{\cdot}KClO_4$ is portrayed in Fig. 3. Each K^+ is eight-coordinated to oxygen atoms, five from six crown ring oxygen atoms and three from two independent perchlorate anions. Each complex unit is linked to other two host–guest moieties through the perchlorate anions to generate an infinite wave chain (Fig. 3). The infinite zig-zag chain formed by the potassium atoms with K···K distance of 6.75 Å and a K···K···K angle of 102.6° is parallel or antiparallel to other chains and extends along the crystallographic *a* axis. In particular, it is noteworthy that the interlayer of chains interacts through hydrogen bonding between O8 of the anion and the H–C of the polyether chain (Fig. 4). The C–H···O interaction, with distances of 3.375 and 2.576 Å, for the C···O and H···O, respectively, and an angle of 137.7° for C–H···O, dominates the interchain packing and thus stabilizes the crystal.

The K^+ in $(3{\cdot}KClO_4)_n$ lies significantly above the average plane defined by O2, O3, O4, O5 and O6 by 1.033

Table 1. Changes in chemical shift ($\Delta\delta$)[a] upon addition of alkali cations in CD_3CN at 25°C

Metal ion	H_{eq}	H_{ax}	$H_{a\ (Ar)}$	$H_{(Me)}$	H_b	H_c	H_d	H_e	H_f
Li^+	−0.02	0.03	0.01	0.01	0.05	−0.01	0.05	0.05	0.05
Na^+	−0.15	0.15	0.01	0.03	−0.01	−0.04	0.02	0.02	0.08
K^+	−0.27	0.21	0.02	0.04	−0.04	−0.04	−0.03	−0.03	−0.05
Rb^+	−0.24	0.20	0.02	0.05	−0.05	−0.04	−0.04	−0.03	−0.05
Cs^+	−0.16	0.12	0.04	0.05	0.00	−0.03	−0.05	−0.05	‘0.21

[a] $\Delta\delta$ (ppm) = δ(M^+Pic^-+Crownophane)−δ(Crownophane); [M^+Pic^-] = [Crownophane].

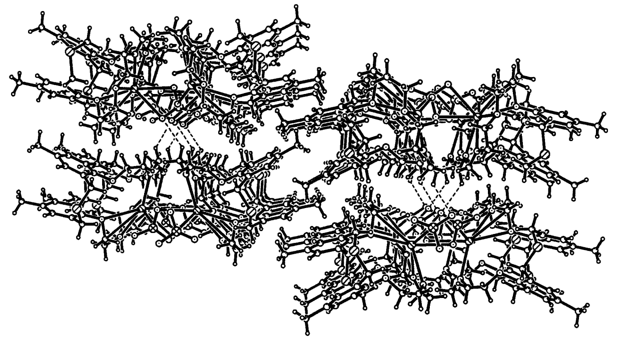

Figure 4. The packing of $(\mathbf{3}\cdot KClO_4)_n$ along the crystallographic *a* axis. The hydrogen bonds are indicated by dashed lines.

Å. This is very different from the 18-crown-6-K^+ complex[15] in which K^+ is coordinated to all six oxygen atoms and embedded perfectly in the plane. On the other hand, the crown part bends towards one of the thia-bridges. This steric arrangement in $(\mathbf{3}\cdot KClO_4)_n$ places the potassium ion in a more favorable spatial environment able to coordinate to oxygen atoms from another perchlorate anion thus extending the chain according to the observed pattern. The thermogravimetric analysis of $(\mathbf{3}\cdot KClO_4)_n$ shows that the coordination polymer was relatively stable and started to decompose at about 270°C.

For comparison, we also examined the reaction of **3** and $NaClO_4$ and determined the structure of complex $\mathbf{3}\cdot NaClO_4$.[16] Since the Na^+ ion, with a diameter of 1.90 Å, is smaller than that of the host cavity, it resulted instead in the formation of a dimeric complex $(\mathbf{3}\cdot NaClO_4)_2$, in which Na^+ is coordinated to four oxygen atoms from the polyether chain and perchlorate anions again act as linkers (Fig. 5). In $\mathbf{3}\cdot NaClO_4$, the thia-bridges adopt *pseudochair–pseudochair* conformations similar to those observed in the free crownophane **3** and $\mathbf{3}\cdot KClO_4$.

Classic crown ethers form stable complexes with metal ions, however, crown ethers and main group metal cations are rarely employed to construct coordination polymers. Some reported coordination polymers consisting of crown ethers are in fact the inorganic polymer with organic spaces which on the basis of the help from the transition metal ions,[17] or crown ethers, were used solely as supporting units.[18] A recent paper[19] reported an example of an extended chain structure with the polymeric unit consisting of lithium and a bridging halogen. In this respect, the supramolecular assembly in $(\mathbf{3}\cdot KClO_4)_n$ observed in our study seems to be a unique example.

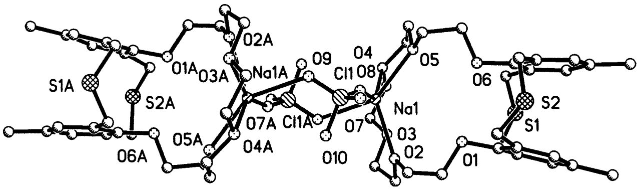

Figure 5. ORTEP drawing of the dimeric $(\mathbf{3}\cdot NaClO_4)_2$ at the 50% probability level. Hydrogen atoms are omitted for clarity.

Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-184025-184027. Copies of the data can be obtained free of charge upon application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-33603; email: deposit@ccdc.cam.ac.uk).

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6. **2a**: ^1H NMR (300 MHz) in $CDCl_3$ δ 2.28 (s, 6H), 3.16 (t, $J=6.0$ Hz, 4H), 3.68–3.71 (m, 12H), 3.73–3.81 (m, 4H), 4.06–4.08 (m, 4H), 4.64 (d, $J=6.0$ Hz, 8H) 7.07 (s, 4H);

IR (neat) 3400, 2916, 2876, 1596, 1474, 1456, 1353, 1245, 1209, 1125, 1059, 989, 948, 901, 868 cm^{-1}; MS (EI) (*m*/*z*) 502 (M$^+$−2H$_2$O, 0.3), 484 (M$^+$−3H$_2$O, 0.5); anal. calcd for $C_{28}H_{42}O_{10}$: C, 62.44; H, 7.86. Found: C, 62.38; H, 7.90%.

7. **2b**: ^{1}H NMR (300 MHz) in CDCl$_3$ δ 2.29 (s, 6H), 3.72–3.80 (m, 12H), 3.87–3.90 (m, 4H), 4.23–4.26 (m, 4H), 4.59 (s, 8H), 7.16 (s, 4H); IR (KBr) 3051, 2878, 1589, 1481, 1461, 1246, 1217, 1137, 1109, 1041, 902, 868, 797, 603 cm^{-1}; MS (EI) (*m*/*z*) 786 (M$^+$, 0.1) 788 (M$^+$+2, 0.2), 790 (M$^+$+4, 0.4), 792 (M$^+$+6, 0.1), 549 (M$^+$−3^{79}Br, 0.4), 470 (M$^+$−4^{79}Br, 2.0); anal. calcd for $C_{28}H_{38}Br_4O_6$: C, 42.56; H, 4.85. Found: C, 42.78; H, 4.60%.
8. **3**: ^{1}H NMR (300 MHz) in CDCl$_3$ δ 2.11 (s, 6H), 3.28 (d, 4H, $J = 14.6$ Hz), 3.64–3.67 (m, 4H), 3.78–3.84 (m, 16H), 4.45 (d, 4H, $J = 14.6$ Hz), 6.79 (s, 4H); ^{13}C NMR (300 MHz) in CDCl$_3$ δ 20.63, 30.19, 70.08, 70.86, 71.06, 71.21, 74.59, 129.93, 130.36, 133.08, 153.53. IR (KBr) 2909, 2878, 1606, 1472, 1419, 1353, 1299, 1259, 1212, 1199, 1117, 1092, 952, 858, 575 cm^{-1}; MS (EI) (*m*/*z*) 534 (M$^+$, 66); anal. calcd for $C_{28}H_{38}O_6S_2$: C, 62.89; H, 7.16; S, 11.99. Found: C, 63.10; H, 7.00; S, 12.10%.
9. *Crystal data* for **3**: $C_{28}H_{38}O_6S_2$, 534.70 g mol^{-1}, triclinic, $a = 8.8831(1)$, $b = 10.2001(2)$, $c = 15.5568(4)$ Å, $\alpha = 100.111(1)$, $\beta = 91.664(1)$, $\gamma = 90.542(1)°$, $V = 1386.95$ (5) Å^3, $T = 293(2)$ K, P-1, $Z = 2$, μ[XJW1]($= 0.231$ mm^{-1}, 8836 reflections collected, 6290 independent reflections, $R_{\text{int}} = 0.0152$. The final wR_2 $(F^2) = 0.2098$ (all data).
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14. *Crystal data* for **3**·KClO$_4$: $C_{28}H_{38}ClKO_{10}S_2$, 673.25 g mol^{-1}, orthorhombic, $a = 10.5597(2)$, $b = 16.5602(3)$, $c = 36.8430(5)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 6442.76(19)$ Å^3, $T = 293(2)$ K, *Pbca*, $Z = 8$, $\mu = 0.430$ mm^{-1}, 29329 reflections collected, 5667 independent reflections, $R_{\text{int}} = 0.0432$. The final wR_2 $(F^2) = 0.2432$ (all data).
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16. *Crystal data* for **3**·NaClO$_4$: $C_{28}H_{38}ClNaO_{10}S_2$, 657.14 gmol^{-1}, orthorhombic, $a = 20.8073(7)$, $b = 9.7163(3)$, $c = 16.2025(6)$ Å, $\alpha = 90$, $\beta = 105.930(1)$, $\gamma = 90°$, $V = 3149.2(2)$ Å^3, $T = 295(2)$ K, $P2(1)/c$, $Z = 4$, $\mu = 0.321$ mm^{-1}, 15611 reflections collected, 5531 independent reflections, $R_{\text{int}} = 0.0335$. The final wR_2 $(F^2) = 0.1566$ (all data).
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