

## Synthesis and Characterization of One-dimensional Dicyclohexyl-18-crown-6 Complexes with $M_2[Cd(mnt)_2]$ ( $M = Na, K$ )

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### Abstract

Two supramolecular crown ether complexes  $[Na(DC18C6-A)(H_2O)]\{[Na(DC18C6-A)][Cd(mnt)_2]\}$  (**1**) and  $[K(DC18C6-A)]_2[Cd(mnt)_2]$  (**2**) (DC18C6-A = *cis-syn-cis*-dicyclohexyl-18-crown-6, isomer A; mnt = maleonitriledithiolate) have been synthesized and characterized by elemental analysis, FT-IR spectroscopy and X-ray single crystal diffraction. Complex **1** is composed of one  $[Na(DC18C6-A)(H_2O)]^+$  complex cation and one  $\{[Na(DC18C6-A)][Cd(mnt)_2]\}^-$  complex anion and displays an infinite chain-like structure through N–Na–N interactions. In complex **2**,  $[K(DC18C6-A)]^+$  complex cation and  $[Cd(mnt)_2]^{2-}$  complex anion afford a novel 1D ladder-like structure by N–K–N, N–K–S interactions.

### Introduction

In recent years, crystal engineering and design of solid-state materials involving novel structures have drawn more and more attention [1]. Much effort has been made in this field and the current focus is mainly on understanding the factors that determine the supramolecular self-assembly process [2]. Our studies in this area are focused on the synthesis and characterization of organic-inorganic hybrid crystalline solids containing crown ether cation building blocks. In earlier work, we have chosen  $[M(SCN)_4]^{2-}$  or  $[M(SeCN)_4]^{2-}$  ( $M = Pd, Pt$ ) as inorganic components to react with 18-crown-6 or some substituted 18-crown-6 ether cations and obtained a series of complexes under the similar experimental conditions, such as  $\{[Na(18C6)](H_2O)\}_n[M(SCN)_4]_n$  [3],  $[K(18C6)]_2[M(SeCN)_4](H_2O)$  [4],  $[Na(B18C6)]_2[Pd(SCN)_4](H_2O)$  [5],  $[Na(B18C6)]_2[Pt(SCN)_4] \cdot 0.5C_2H_4Cl_2$  [5],  $[K(DB18C6)]_2[M(SCN)_4]$  [6, 7],  $[Na(DB18C6)]_2[Pd(SCN)_4]$  [8] and  $[K(N18C6)]_2[M(SCN)_4]$  ( $M = Pd, Pt$ ) [9]. The studies demonstrate that many factors are concerned with the topology structures of such crown ether-metal complex. Thereinto, crown ethers, due to their different substitutional groups and hence the variant steric hindrance and flexibility, usually play a very important role in constructing diverse supramolecular self-assembly system. According to our previous work, the complexes of 18C6 are mostly assembled into infinite 1D chains by means of the Na–O(water)–Na or K–O(water)–K contacts [3, 4]. Due to the effect of two symmetrically substitutional phenyls, the sodium or potassium complexes of DB18C6 are easily to form cation– $\pi$  supra-molecular interactions [6–8]. The chain-like

structural assembly of B18C6 complexes needs the support of O atoms of crown ether or water molecule to form Na–O–Na or K–O–K linking forces [5]. More interestingly, two N18C6 complexes [9] are both linked into a 1D chain through the K–O (ether) bonds, and the resulting chains are further into a 2D network by the inter-chain  $\pi$ – $\pi$  stacking interactions, which is mainly due to the larger  $\pi$  electronic system of crown ether molecule.

Dicyclohexyl-18-crown-6 is one of the earliest crown ethers reported by Pedersen [10]. In the past years, the research and application about this macrocycle were established in many areas, such as phase transfer catalysis, ionophore, ion pair extraction, isotope separation and so on, which may be attributed to its various isomers and better solubility in some organic solvents [11–15]. To our best knowledge, up to now, organic-inorganic hybrid complexes containing DC18C6- $Na^+$  or  $K^+$  component characterized by X-ray include  $[Na(DC18C6-A)](ReO_4)$  [16],  $[K(DC18C6-A)][Au(CN)_2]$  [17],  $[K(DC18C6-A)](C_{18}H_{15}N_{12}Ni) \cdot 3(CH_4O) \cdot 2(H_2O)$  [18],  $[K(DC18C6-B)](CuI_2)$  (DC18C6-B = *cis-anti-cis*-dicyclohexyl-18-crown-6, isomer B) [19]. To continue our work, here, the reactions of dicyclohexyl-18-crown-6 with  $M_2mnt$  ( $M = Na, K$ ) and  $CdCl_2$  are researched and two new complexes,  $[Na(DC18C6-A)(H_2O)]\{[Na(DC18C6-A)][Cd(mnt)_2]\}$  (**1**) and  $[K(DC18C6-A)]_2[Cd(mnt)_2]$  (**2**), are presented.

### Experimental

$M_2mnt$  ( $M = Na, K$ ) were synthesized according to the literature [20]. All chemicals were commercially available and used without further purification.

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FT-IR spectra of the complexes were measured on a Nicolet-460 FT-IR spectrometer in the range 4000–400 $\text{cm}^{-1}$  as KBr pellets. The microanalytical data were obtained from a Perkin-Elmer 2400 II analyser. Thermogravimetric analysis was performed on a Perkin-Elmer Pyris I Thermogravimetric Analyzer with the heating rate of 10  $^{\circ}\text{C}/\text{min}$  from 50 to 750  $^{\circ}\text{C}$ . Nitrogen stream was used as an atmosphere.

*Preparation of complex [Na(DC18C6-A)(H<sub>2</sub>O)]<sub>2</sub>{[Na(DC18C6-A)][Cd(mnt)<sub>2</sub>]} (1)*

This complex was prepared by adding 10 ml aqueous mixture of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.0571 g, 0.25 mmol) and  $\text{Na}_2\text{mnt}$  (0.1862 g, 1 mmol) to 10 ml dicyclohexyl-18-crown-6 (0.3722 g, 1 mmol) in 1,2-dichloroethane. The reaction mixture was stirred for 2.5 h at room temperature. The organic phase was separated from the reaction solution. The colorless crystals were obtained from 4:1 diethyl ether/1,2-dichloroethane solution over a period of 7d. Yield, 79% (based on Cd). M.p. 152–153  $^{\circ}\text{C}$ . Anal.  $\text{C}_{96}\text{H}_{148}\text{N}_4\text{Na}_4\text{Cd}_2\text{O}_{26}\text{S}_8$ , Calcd.: C, 47.97; H, 6.21; N, 4.66. found: C, 47.42; H, 6.30; N, 4.50. Selected FT-IR ( $\text{v}/\text{cm}^{-1}$ ): 3524(s, O–H), 2935(s, C–H), 2873(s), 2198(s,  $\text{C}\equiv\text{N}$ ), 1618(m), 1463(s, C=C), 1437(s), 1355(m), 1309(w), 1145(s), 1080(vs, C–O–C), 994(s), 948(m), 921(m), 859(m, C–S), 620(m), 515(m).

*Preparation of complex [K(DC18C6-A)]<sub>2</sub>[Cd(mnt)<sub>2</sub>] (2)*

The synthesis procedure is the same as that for complex 1 with  $\text{K}_2\text{mnt}$  (0.2184 g, 1 mmol) instead of  $\text{Na}_2\text{mnt}$ . Yield, 82% (based on Cd). M.p. 204–205  $^{\circ}\text{C}$ . Anal.

$\text{C}_{48}\text{H}_{72}\text{N}_4\text{K}_2\text{O}_{12}\text{CdS}_4$ , Calcd.: C, 47.42; H, 5.97; N, 4.61. found: C, 47.38; H, 5.82; N, 4.52. Selected FT-IR ( $\text{v}/\text{cm}^{-1}$ ): 2934(s, C–H), 2868(s), 2198(s,  $\text{C}\equiv\text{N}$ ), 1620(m), 1468(s, C=C), 1439(s), 1355(m), 1308(w), 1148(s), 1081(vs, C–O–C), 994(s), 947(m), 920(m), 862(m, C–S), 621(m), 513(m).

*Determination of crystal structure*

The X-ray diffraction experiments for complex 1 and 2 were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo  $\text{K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation at the temperature of 293(2) and 298(2) K, respectively. The structures were solved by direct method and expanded by using Fourier's technique and Shelxl-97 program system. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on  $F^2$ . The water H atoms were located in a difference map and the O–H distances were restrained to about 0.90  $\text{Å}$ ; the  $U_{\text{iso}}(\text{H})$  values were not allowed to refine. All other hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data for complex 1 and 2 are listed in Table 1.

**Results and discussion**

*Synthesis and solubility*

Dicyclohexyl-18-crown-6 was commercially purchased as a mixture of the *cis-syn-cis* and *cis-anti-cis* isomers and directly used without further purification and

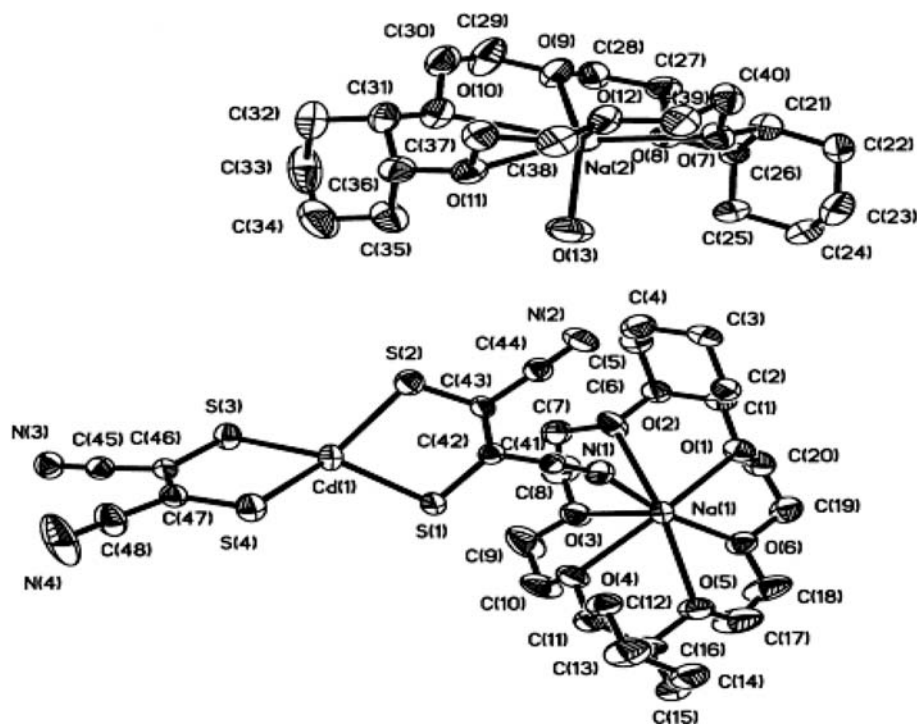


Figure 1. ORTEP drawing of complex 1 with atomic numbering scheme.

Table 1. Crystallographic data of complexes 1 and 2

	1	2
Empirical formula	C <sub>96</sub> H <sub>148</sub> N <sub>4</sub> Na <sub>4</sub> Cd <sub>2</sub> O <sub>26</sub> S <sub>8</sub>	C <sub>48</sub> H <sub>72</sub> N <sub>4</sub> K <sub>2</sub> CdO <sub>12</sub> S <sub>4</sub>
Formula weight	2403.46	1215.94
Crystal size/mm	0.40 × 0.27 × 0.20	0.34 × 0.18 × 0.13
Temperature/K	293(2)	298(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> <sub>1</sub>	<i>P</i> <sub>1</sub>
a/Å	13.547(14)	10.873(9)
b/Å	14.134(15)	13.980(12)
c/Å	16.465 (17)	20.634(17)
α/°	68.021(15)	97.830(13)
β/°	83.919(16)	101.338(14)
γ/°	89.104(16)	108.345(13)
V/Å <sup>3</sup>	2906(5)	2852(4)
Z	1	2
D <sub>calc</sub> /g cm <sup>-3</sup>	1.373	1.416
μ/mm <sup>-1</sup>	0.297	0.734
Data/restraints/parameters	9615/5/649	9948/0/640
F(000)	1256	1268
Theta range/°	2.213 to 25.03	1.57 to 25.03
Reflection collected	14354	14645
Independent reflections	9615	9948
Final R indices [ <i>I</i> > 2σ ( <i>I</i> )]	R <sub>1</sub> = 0.0577, wR <sub>2</sub> = 0.1122	R <sub>1</sub> = 0.0425, wR <sub>2</sub> = 0.0662
Largest diff. peak and hole/e Å <sup>-3</sup>	1.066, -0.289	0.356, -0.364

separation. In the process of preparation of complex, Na<sup>+</sup> and K<sup>+</sup> ions were all selected by *cis-syn-cis* instead of *cis-anti-cis* isomers, which may be attributed to the larger binding constant for the former with all the alkali metal cations relative to the latter [21].

Two complexes in solid state are both very stable in the air. At room temperature, they are difficult to dissolve in water, methanol, diethyl ether and benzene, but soluble in some organic solvents such as acetone, acetonitrile, pyridine, dimethylformamide and dimethylsulfoxide.

#### Structure of complex (1)

As shown in Figure 1, complex 1 consists of one complex cation [Na(DC18C6-A)(H<sub>2</sub>O)]<sup>+</sup> and one complex anion {[Na(DC18C6-A)][Cd(mnt)<sub>2</sub>]}<sup>-</sup>. In the complex anion, the Cd atom is coordinated by four S atoms from

two mnt ligands. The S–Cd–S bond angles (see Tables 2 and 3) indicate a distorted tetrahedral CdS<sub>4</sub> group. The average bond lengths of Cd–S, S–C, C≡N, C–C and C=C are 2.512, 1.735, 1.142, 1.430 and 1.376 Å, respectively, which are consistent with the corresponding values in complex [K(18-C-6)]<sub>2</sub>[Cd(mnt)<sub>2</sub>] [22].

In the [Na(1)(DC18C6-A)] segment, Na(1) atom lies in the crown ether and is coordinated by six O atoms. Bond lengths of Na(1)–O are in the range from 2.562(4) to 2.799(5) Å with an average value of 2.640 Å, which is comparable to that of complex [Na(DC18C6-A)](ReO<sub>4</sub>) (2.630 Å) [16]. Four atoms, O(1), O(2), O(4) and O(5), form a plane with the Na(1), O(3) and O(6) atoms lying 0.327, 1.687 and 1.351 Å out of it, respectively. Na(1) atom also interacts with two N atoms from mnt ligands of two [Cd(mnt)<sub>2</sub>] segments. The distances of Na(1)–N(1) and Na(1)–N(3) #1 are 2.617(6) and 2.547(6) Å, respectively, and the angle of N(1)–Na(1)–N(3)N(3)#1 is

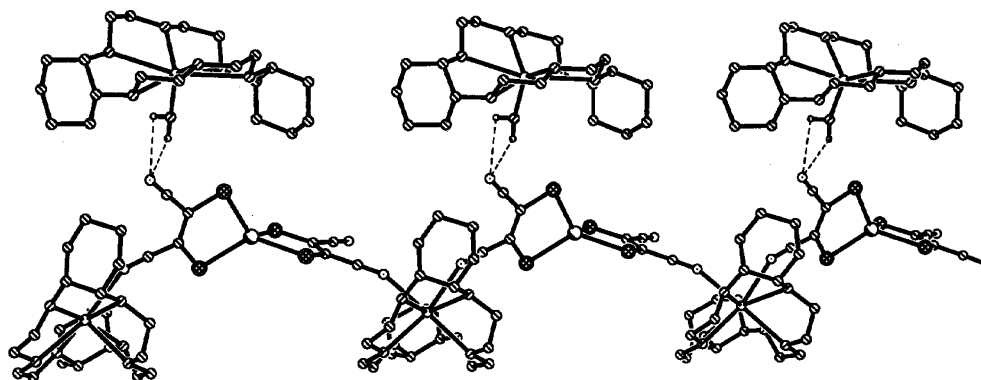


Figure 2. 1D chain-like structure of complex 1, the dot lines show the H-bonds.

Table 2. Selected bond lengths (Å) and angles (°) of complex 1

Cd(1)–S(1)	2.512(3)	Na(2)–O(9)	2.476(5)	S(2)–C(43)	1.737(6)
Cd(1)–S(2)	2.522(2)	Na(2)–O(10)	2.877(6)	S(3)–C(46)	1.742(5)
Cd(1)–S(3)	2.516(2)	Na(2)–O(11)	2.838(5)	S(4)–C(47)	1.721(5)
Cd(1)–S(4)	2.501(2)	Na(2)–O(12)	2.471(5)	C(41)–C(42)	1.421(7)
Na(1)–O(1)	2.571(4)	Na(2)–O(13)	2.275(6)	C(42)–C(43)	1.369(7)
Na(1)–O(2)	2.799(5)	Na(1)–N(1)	2.617(6)	C(43)–C(44)	1.453(7)
Na(1)–O(3)	2.596(5)	Na(2)–N(3)#1	2.547(6)	C(45)–C(46)	1.416(7)
Na(1)–O(4)	2.562(4)	N(1)–C(41)	1.136(6)	C(46)–C(47)	1.383(7)
Na(1)–O(5)	2.724(5)	N(2)–C(44)	1.136(6)	C(47)–C(48)	1.429(8)
Na(1)–O(6)	2.589(5)	N(3)–C(45)	1.158(7)	O(13)⋯N(2)	2.950(7)
Na(2)–O(7)	2.672(5)	N(4)–C(48)	1.140(7)	H(1)⋯N(2)	2.644(2)
Na(2)–O(8)	2.571(5)	S(1)–C(42)	1.741(5)	H(2)⋯N(2)	2.460(2)
S(4)–Cd(1)–S(1)	116.71(8)		N(2)–C(44)–C(43)	178.2(6)	
S(4)–Cd(1)–S(3)	88.52(8)		N(3)–C(45)–C(46)	176.0(6)	
S(1)–Cd(1)–S(3)	125.10(8)		N(4)–C(48)–C(47)	178.0(7)	
S(4)–Cd(1)–S(2)	124.77(8)		N(1)–Na(1)–N(3)#1	79.50(2)	
S(1)–Cd(1)–S(2)	88.44(7)		O(13)–Na(2)–O(11)	66.80(17)	
S(3)–Cd(1)–S(2)	117.27(8)		O(13)–H(1)⋯N(2)	110(2)	
C(41)–N(1)–Na(1)	154.6(5)		O(13)–H(2)⋯N(2)	114(2)	

Symmetry transformations used to generate equivalent atoms: #1  $x, y - 1, z$ ; #2  $x, y + 1, z$ .

79.50(2)°. It is noteworthy that Na(1) atom is coordinated by two N atoms only on the ‘closed’ side of the ether ring (i.e. between two cyclohexyl rings), which is different from that of reported complexes (DC18C6-A) $\cdot$ 2NaOPh [23] and Ba(SCN) $_2$  $\cdot$ H $_2$ O $\cdot$ DC18C6 [24]. In those complexes, the metal ion in the center of crown ether is coordinated by ligands either on the ‘open’ side [23] or on two sides of the ether ring [24].

In the [Na(DC18C6-A)(H $_2$ O)] $^+$  complex cation, Na(2) atom is coordinated by six ether O atoms and one water oxygen. The mean Na–O(ether) distance is 2.650 Å. From the plane defined by O(7), O(8), O(10) and O(11), the deviations of Na(2), O(9) and O(12) are 0.024, 1.173, 1.116 Å, respectively. The distance of Na(2)–O(water) is 2.275 Å. In addition, the water molecule also acts as H-donor and bridges one nitrogen atom of mnt ligand. The distances of O(13)⋯N(2), H(1)⋯N(2) and H(2)⋯N(2) are 2.950(7), 2.644(2) and 2.460(2) Å, and the O(13)–

H(1)⋯N(2) and O(13)–H(2)⋯N(2) bond angles are 110(2)° and 114(2)°, respectively. As displayed in Figure 2, the {[Na(DC18C6-A)][Cd(mnt) $_2$ ]} $^-$  complex anions are assembled into an infinite 1D chain-like structure through N–Na–N interactions, and the counter [Na(DC18C6-A)(H $_2$ O)] $^+$  complex cations cling to the chain through the O–H⋯N hydrogen bonds.

#### Structure of complex (2)

Complex 2 is composed of two [K(DC18C6-A)] $^+$  complex cations and one [Cd(mnt) $_2$ ] $^{2-}$  complex anion. The coordinating manner of Cd atom is similar to that of complex 1. The mean bond lengths of Cd–S, S–C, C  $\equiv$  N, C–C and C = C are 2.511, 1.729, 1.133, 1.441 and 1.364 Å, respectively.

In each complex cation [K(DC18C6-A)] $^+$ , K atom sits in the DC18C6-A molecule and is coordinated by six

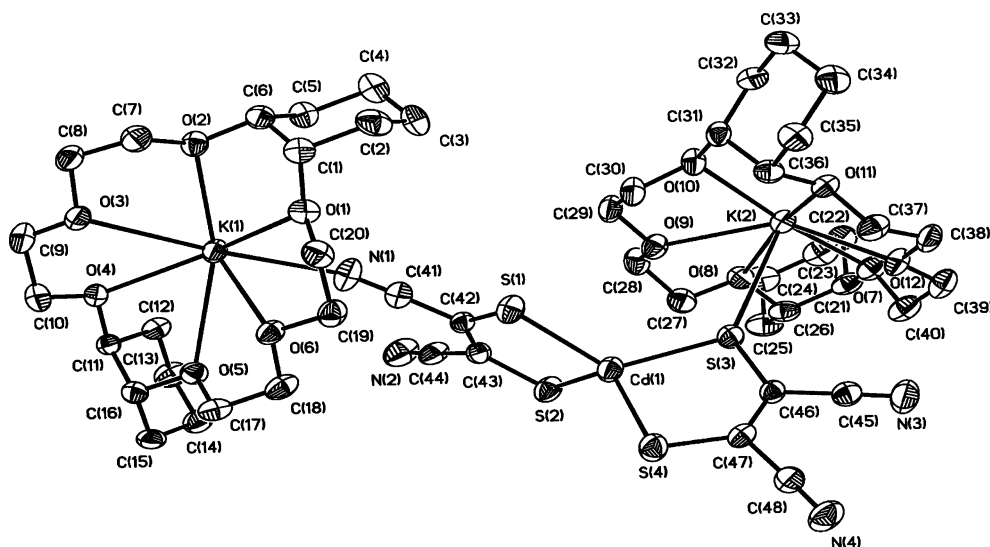


Figure 3. ORTEP drawing of complex 2 with atomic numbering scheme.

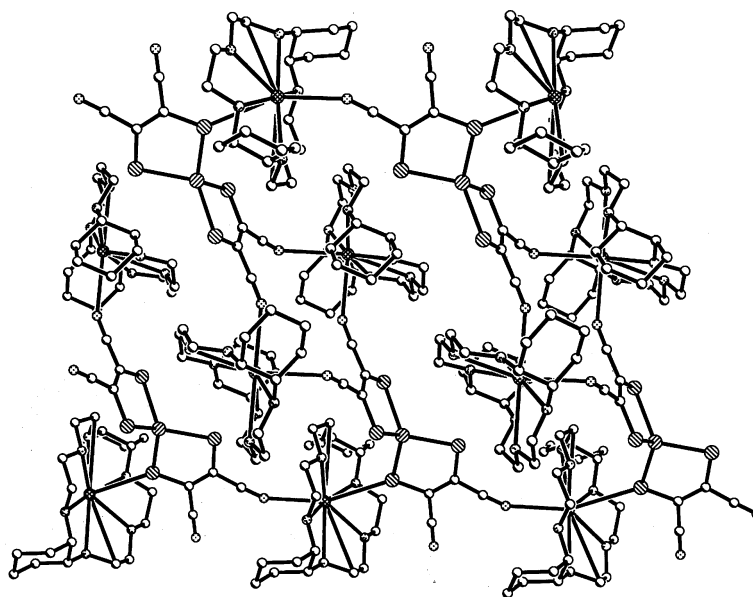


Figure 4. 1D ladder-like structure of complex 2.

O atoms. The K–O bond lengths lie in the range of 2.948(3)–2.654(3) Å, with the mean value of 2.818 Å which is comparable to that of [K(DC18C6-A)]OC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-2 (2.851 Å) [25]. K(1) atom interacts with two N atoms from two mnt ligands. The K(1)–N(1) and K(1)–N(2)#1 distances are 2.860(4) and 3.008(8) Å, respectively, falling into the corresponding K–N region of compound K<sub>2</sub>[Pt(SCN)<sub>4</sub>] (2.766–3.081 Å) [26]. The N(1)–K(1)–N(2) N(2)#1 bond angle is 87.43 (11)°. However, the coordination environment of K(2) atom is different from that of K(1). From one side of the ether ring, K(2) atom interacts with one S atom of one mnt ligand with the K(2)–S(3) distance of 3.430(3) Å, which is consistent with the predicated value (3.45 Å) [27, 28].

From the other side, K(2) atom is linked with one N atom of another mnt ligand with the K(2)–N(4)#2 distance of 2.765(4) Å and N(4)#K(2)–S(3) bond angle of 154.32(9)° (Table 3).

As displayed in Figure 4, [K(DC18C6-A)]<sup>+</sup> complex cations and [Cd(mnt)<sub>2</sub>]<sup>2-</sup> complex anions are constructed into a novel 1D ladder-like structure through N–K–N, N–K–S interactions.

#### Thermal analysis

The measurements show the different thermogravimetric behaviors of two complexes. Complex 2 exhibits a two-stage weight loss in the limited temperature. The

Table 3. Selected bond lengths (Å) and angles (°) of complex 2

Cd(1)–S(1)	2.506(2)	K(2)–O(9)	2.704(3)	S(2)–C(43)	1.726(4)
Cd(1)–S(2)	2.513(2)	K(2)–O(10)	2.766(3)	S(3)–C(46)	1.737(4)
Cd(1)–S(3)	2.503(19)	K(2)–O(11)	2.844(3)	S(4)–C(47)	1.717(4)
Cd(1)–S(4)	2.522(2)	K(2)–O(12)	2.654(3)	C(41)–C(42)	1.444(5)
K(1)–O(1)	2.933(3)	K(1)–N(1)	2.860(4)	C(42)–C(43)	1.366(4)
K(1)–O(2)	2.772(3)	K(1)–N(2)#1	3.008(8)	C(43)–C(44)	1.441(5)
K(1)–O(3)	2.883(3)	K(2)–N(4)#2	2.765(4)	C(45)–C(46)	1.432(6)
K(1)–O(4)	2.797(3)	N(1)–C(41)	1.132(4)	C(46)–C(47)	1.363(5)
K(1)–O(5)	2.948(3)	N(2)–C(44)	1.136(5)	C(47)–C(48)	1.446(5)
K(1)–O(6)	2.867(3)	N(3)–C(45)	1.134(5)	K(2)–S(3)	3.430(3)
K(2)–O(7)	2.784(3)	N(4)–C(48)	1.129(4)	O(1)–C(1)	1.4332(4)
K(2)–O(8)	2.862(3)	S(1)–C(42)	1.736(4)	O(1)–C(20)	1.414(4)
S(4)–Cd(1)–S(1)	117.59(4)	N(2)–C(44)–C(43)	177.4(6)		
S(4)–Cd(1)–S(3)	87.16(5)	N(3)–C(45)–C(46)	178.2(6)		
S(1)–Cd(1)–S(3)	125.04(6)	N(4)–C(48)–C(47)	177.4(5)		
S(4)–Cd(1)–S(2)	123.26(5)	N(1)–K(1)–N(2)#1	87.43(11)		
S(1)–Cd(1)–S(2)	88.07(5)	N(4)#2–K(2)–S(3)	154.32(9)		
S(3)–Cd(1)–S(2)	119.77(5)	C(44)–N(2)–K(1)#1	137.1(4)		
C(41)–N(1)–K(1)	153.6(3)	C(48)–N(4)–K(2)#3	152.1(4)		
N(1)–C(41)–C(42)	177.8(5)	O(2)–K(1)–O(4)	113.10(10)		

Symmetry transformations used to generate equivalent atoms: #1– $x + 1, -y + 1, -z + 2$ ; #2  $x - 1, y, z$ ; #3  $x + 1, y, z$ .

first stage begins at about 290 °C and ends around 447 °C with the maximum rate at about 358 °C. The weight loss is 63.00%, corresponding to the theoretical value 61.27% of two crown ether molecules per formula unit within the error limit. Based on the shape of curves and value of weight loss, this stage may be regarded as a dissociation and evaporation process of crown ether [29]. The second stage corresponds to the complicated decomposition of mnt ligands and does not completely finish at 750 °C. However, complex **1** presents a multi-step process and begins to lose one water molecule (observed and theoretical losses are 1.44 and 1.42 wt%, respectively) at the temperature of 90 °C, and this endothermic process of dehydration is not over until 161 °C. During the second step (161–375 °C) and the third (375–459 °C), the observed total weight loss (56.95%) is less than the theoretical value 61.99%, corresponding to giving off two crown ether molecules. On the basis of the shapes of TG-DTG curves and these values, it shows two crown ether molecules probably progressively decompose to smaller segments, which is similar to that of complex  $(\text{FeCl}_4)_3[\text{Fe}(\text{H}_2\text{O})_6](18\text{-crown-6})_3(\text{H}_2\text{O})_2$  [30]. The overlapping decompositions of crown ether and mnt ligands occur in the remainder stages and still continue above 750 °C.

## Conclusion

Two organic-inorganic hybrid dicyclohexyl-18-crown-6 complexes,  $[\text{Na}(\text{DC18C6-A})(\text{H}_2\text{O})]\{[\text{Na}(\text{DC18C6-A})][\text{Cd}(\text{mnt})_2]\}$  (**1**) and  $[\text{K}(\text{DC18C6-A})]_2[\text{Cd}(\text{mnt})_2]$  (**2**), have been synthesized by the reactions of dicyclohexyl-18-crown-6 with  $\text{CdCl}_2$  and  $\text{Na}_2\text{mnt}$  or  $\text{K}_2\text{mnt}$  and characterized by elemental analysis, FT-IR and X-ray diffraction analysis. The structural analysis shows that complex **1** displays an infinite 1D chain-like structure constructed by  $\{[\text{Na}(\text{DC18C6-A})][\text{Cd}(\text{mnt})_2]\}^-$  complex anions through N–Na–N interactions, and the counter  $[\text{Na}(\text{DC18C6-A})(\text{H}_2\text{O})]^+$  complex cations cling to it through the O–H···N hydrogen bonds. Complex **2** affords a novel 1D ladder-like structure formed by complex cation  $[\text{K}(\text{DC18C6-A})]^+$  and complex anion  $[\text{Cd}(\text{mnt})_2]^{2-}$  through N–K–N and N–K–S interactions. Thermal analysis indicates that two complexes have two different ways in ejecting the crown ether molecules.

## Supplementary material

Crystallographic data for the structural analysis of complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 216859, 227547. Some information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (Fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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