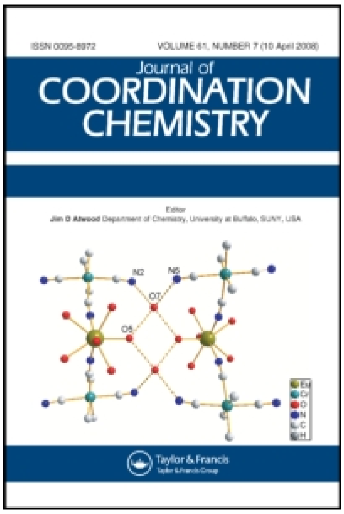

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Novel crystal engineering in the crown ether nickel maleonitriledithiolate complexes, synthesis and crystal structures of $[Na(N15C5)_2]_2[Ni(mnt)_2]$ and $[Na(N15C5)]_2[Ni(mnt)_2]$

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Novel crystal engineering in the crown ether nickel maleonitriledithiolate complexes, synthesis and crystal structures of $[Na(N15C5)_2]_2[Ni(mnt)_2]$ and $[Na(N15C5)]_2[Ni(mnt)_2]$

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Reactions of N15C5 (2,3-naphtho-15-crown-5) with nickel maleonitriledithiolate sodium complex, $Na_2[Ni(mnt)_2]$ (mnt = maleonitriledithiolate) using different molar ratios (2 : 1 and 4 : 1) afforded two structurally different complexes $[Na(N15C5)_2]_2[Ni(mnt)_2]$ (**1**) and $[Na(N15C5)]_2[Ni(mnt)_2]$ (**2**). The sandwich $[Na(N15C5)_2]^+$ and mono-capped $[Na(N15C5)]^+$ organic cations are observed in the crystals of **1** and **2**, respectively, with the same $[Ni(mnt)_2]^{2-}$ inorganic conteranions. It is these structurally different organic cations that lead to the dissimilar structures. Complex **1** exhibits a one-dimensional (1D) chain-like structure assembled by intercantionic $\{[Na(N15C5)_2]^+\}_\infty$ π–π stacking interactions and electrostatic interactions, while **2** displays a novel two-dimensional (2D) corrugated sheet-like structure constructed by Na–N interactions which occur between the $[Na(N15C5)]^+$ inorganic cations and $[Ni(mnt)_2]^{2-}$ inorganic anions.

Keywords: Synthesis and crystal structure; Crystal engineering; 2,3-Naphtho-15-crown-5 (N15C5); Nickel(II) mnt complexes

1. Introduction

Since the pioneering work of Pedersen [1], crown ethers and their complexes with metal cations have attracted much attention, not only because crown ethers present unusual coordination numbers and arrangements on metal ions but also because they and their cations can act as modules to form polymeric supramolecular structures with novel crystal engineering [2–5]. N15C5 (2,3-naphtho-15-crown-5) has been widely used and studied electrochemically and some of its coordinating properties in solutions

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and the gas phase have been studied by cyclic voltammetry (CV) and ESI-MS [6, 7]. To develop synthetic strategies for the construction of hybrid materials using $[Na(N15C5)]^+$ cation as spacer on the basis of crystal engineering and the supramolecular concept [8–10], novel self-assembling supramolecular systems, involving one-dimensional (1D) or two-dimensional (2D) structures and various supramolecular forces, were achieved by reactions of N15C5 with alkali metal salts of size-fitted inorganic complex anions. The reactions of N15C5 with $Na_2[M(SCN)_4]$ (M = Pd, Pt) afforded two 1D zig-zag chain-like structures, $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt) [8], assembled by strong intermolecular π–π stacking interactions. Under similar experimental conditions, the 1D polymeric complex, $[Na(N15C5)]_2[Ni(i\text{-}mnt)_2]$ (mnt = maleonitriledithiolate) [9], containing S···C and S···π interactions was obtained, constructed by Na–N contacts. The differences in size and stereo aspects of inorganic anions have an influence on the final structural features of the complexes. In this article, two new examples, $[Na(N15C5)_2]_2[Ni(mnt)_2]$ (**1**) and $[Na(N15C5)]_2[Ni(mnt)_2]$ (**2**), which show an influence of organic crown ether cations on final topologized structures of the products, are reported. The novel crystal engineering and supramolecular information of complexes **1** and **2** are discussed.

2. Experimental

2.1. *Preparations*

N15C5 [11] and $Na_2(mnt)$ [12] were prepared as described in the literature. All reagents and solvents purchased were A.R. grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 II analyzer. FT-IR spectra of the complexes were measured on Nicolet-460 FT-IR spectrometer in the range 4000–400 cm^{-1} as KBr pellets.

2.1.1. Preparation of $[Na(N15C5)_2]_2[Ni(mnt)_2]$ (1). To a solution of N15C5 (0.50 mmol) in 1,2-dichloroethane (5 mL) was added a 5 mL aqueous mixture of $NiCl_2$ (0.125 mmol) and $Na_2(mnt)$ (0.25 mmol). The reaction mixture was stirred for 2 h at room temperature and then filtered. The precipitate was dissolved in CH_3CN and CH_3COCH_3 (v/v = 1 : 1) and a red single crystal was obtained by slowly evaporating the solution. Yield: 172 mg, 83% (based on Ni); melting point (m.p.) 216–217°C. Anal. Calcd for $C_{80}H_{88}N_4Na_2O_{20}NiS_4$ (%): C, 57.88; H, 5.31; N, 3.38. Found: C, 57.92; H, 5.29; N, 3.35. Selected FT-IR (cm^{-1}): 3052 (w), 2904 (m), 2872 (m), 2191 (m), 1628 (m), 1603 (w), 1509 (s), 1484 (m), 1452 (m), 1384 (m), 1259 (vs), 1177 (s), 1122 (vs), 1057 (m), 865 (m), 748 (m).

2.1.2. Preparation of $[Na(N15C5)]_2[Ni(mnt)_2]$ (2). The reaction is analogous to that of **1**, using 0.25 mmol N15C5 instead of 0.50 mmol of N15C5. Red single crystals (89 mg) in 70% yield (based on Ni) were obtained by slowly evaporating the solution; m.p. 283–284°C. Anal. Calcd for $C_{44}H_{44}N_4Na_2NiO_{10}S_4$ (%): C, 51.68; H, 4.31; N, 5.48. Found: C, 51.73; H, 4.27; N, 5.35. Selected FT-IR (cm^{-1}): 3062 (w), 2921 (m), 2876 (m), 2199 (s), 1632 (m), 1602 (w), 1508 (m), 1487 (sh m), 1476 (s), 1451 (m), 1384 (m), 1256 (s), 1172 (s), 1118 (vs), 1045 (m), 863 (m), 750 (m).

Table 1. Crystallographic data for complexes **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{80}H_{88}N_4Na_2NiO_{20}S_4$	$C_{44}H_{44}N_4Na_2NiO_{10}S_4$
Formula weight	1658.47	1021.76
Color and shape	Red block	Red block
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	15.5715 (17)	10.490 (14)
b (Å)	20.562 (2)	19.49 (2)
c (Å)	12.9385 (16)	12.248 (16)
β (°)	103.182 (3)	111.88 (2)
V (Å^3)	4033.5 (8)	2324 (5)
Z	2	2
T (K)	298(2)	298(2)
μ (mm^{-1})	0.428	0.677
Reflections collected	23615	12172
Independent reflections	8354	4108
Crystal size (mm)	0.30 × 0.25 × 0.19	0.38 × 0.31 × 0.22
θ range (°)	1.67–26.53	2.07–25.03
$h/k/l$ (max, min)	−19, 17/ −25, 23/ −13, 16	−8, 12/ −22, 23/ −14, 13
R_{int}	0.0650	0.0703
Goodness-of-fit	1.002	0.907
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_1 and wR_2 [$I > 2\sigma(I)$]	0.0484, 0.0923	0.0472, 0.1082
R_1 and wR_2 (all data)	0.1413, 0.1458	0.0817, 0.1199
Largest diff. peak and hole (e Å^{-3})	0.422, −0.396	0.553, −0.366

2.2. *Crystal structure determination*

Suitable single crystals of **1** and **2** were glued to fine glass fibers and then mounted on a Bruker Smart-1000 CCD diffractometer with Mo-K_α radiation, $\lambda = 0.71073$ Å. The intensity data were collected at 298 ± 2 K. The structures were solved by direct methods and expanded using Fourier techniques with the SHELXL97 program [13]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added, riding on the concerned atoms and not refined. Detailed information about crystal data and structure determinations are summarized in table 1. Selected bond lengths and angles of complexes **1** and **2** are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Synthesis*

The nickel maleonitriledithiolate sodium complex, $Na_2[Ni(mnt)_2]$, was formed in water by reaction of 2 : 1 $Na_2(mnt)$ with $NiCl_2$. The reactions of N15C5 with $Na_2[Ni(mnt)_2]$ under 2 : 1 and 4 : 1 molar-ratios in mixed phases (1,2-dichloroethane/water) afforded solid $[Na(N15C5)_2]_2[Ni(mnt)_2]$ (**1**) and $[Na(N15C5)]_2[Ni(mnt)_2]$ (**2**), respectively. The amount of crown ether used in the synthesis affects the final composition and solid-structure of the complexes. Crystals of **1** and **2** are very stable when exposed to air. Both are soluble in CH_3OH, CH_3COCH_3, CH_3CN, dimethylformamide (DMF) and dimethylsulfoxide (DMSO), but insoluble in diethyl ether and hexane.

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

Na(1)–O(1)	2.767(3)	Na(1)–O(8)	3.031(3)	N(2)–C(40)	1.130(6)
Na(1)–O(2)	2.782(3)	Na(1)–O(9)	2.592(3)	S(1)–C(38)	1.724(5)
Na(1)–O(3)	2.874(3)	Na(1)–O(10)	2.554(3)	S(2)–C(39)	1.725(4)
Na(1)–O(4)	2.627(3)	Ni(1)–S(1)	2.1642(11)	C(37)–C(38)	1.428(6)
Na(1)–O(5)	2.614(3)	Ni(1)–S(2)	2.1618(12)	C(38)–C(39)	1.358(5)
Na(1)–O(6)	2.818(3)	N(1)–C(37)	1.145(5)	C(39)–C(40)	1.426(7)
Na(1)–O(7)	3.131(3)				
S(1)–Ni(1)–S(1)#1	180.0		O(9)–Na(1)–O(2)	164.92(12)	
S(2)–Ni(1)–S(2)#1	180.00(4)		O(5)–Na(1)–O(2)	110.53(10)	
S(1)–Ni(1)–S(2)	92.20(5)		O(4)–Na(1)–O(2)	102.05(10)	
C(38)–S(1)–Ni(1)	102.86(15)		O(1)–Na(1)–O(2)	54.16(8)	
C(39)–S(1)–Ni(1)	103.43(17)		O(10)–Na(1)–O(6)	60.83(10)	
O(10)–Na(1)–O(9)	66.56(12)		O(9)–Na(1)–O(6)	94.45(10)	
O(10)–Na(1)–O(5)	120.71(10)		O(5)–Na(1)–O(6)	165.87(11)	
O(9)–Na(1)–O(5)	74.88(10)		O(1)–Na(1)–O(6)	121.41(10)	
O(10)–Na(1)–O(4)	74.22(10)		O(2)–Na(1)–O(6)	77.61(9)	
O(10)–Na(1)–O(1)	167.91(11)		O(10)–Na(1)–O(3)	69.44(10)	
O(9)–Na(1)–O(4)	92.98(11)		O(9)–Na(1)–O(3)	134.07(12)	
O(5)–Na(1)–O(4)	64.48(10)		O(5)–Na(1)–O(3)	119.21(10)	
O(9)–Na(1)–O(1)	123.27(12)		O(4)–Na(1)–O(3)	62.54(9)	
O(5)–Na(1)–O(1)	60.48(9)		O(1)–Na(1)–O(3)	99.18(9)	
O(4)–Na(1)–O(1)	97.17(10)		O(2)–Na(1)–O(3)	56.64(8)	
O(10)–Na(1)–O(2)	118.49(11)		O(6)–Na(1)–O(3)	74.86(9)	
O(4)–Na(1)–O(6)	126.39(11)				

Symmetry code for complex **1**: #1 $-x$, $-y+1$, $-z+1$.

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

Ni(1)–S(1)	2.160(2)	Na(1)–O(5)	2.561(4)	S(1)–C(20)	1.728(4)
Ni(1)–S(2)	2.173(2)	Na(1)–N(1)	2.487(4)	S(2)–C(21)	1.731(4)
Na(1)–O(1)	2.590(4)	Na(1)–N(2)#1	2.533(4)	C(19)–C(20)	1.426(5)
Na(1)–O(2)	2.492(4)	N(1)–C(19)	1.136(4)	C(20)–C(21)	1.350(5)
Na(1)–O(3)	2.550(5)	N(1)–C(22)	1.140(5)	C(21)–C(22)	1.435(5)
Na(1)–O(4)	2.397(4)	N(2)–Na(1)#3	2.533(4)		
S(1)–Ni(1)–S(1)#1	180.0		N(1)–Na(1)–N(2)#2	85.72(13)	
S(1)–Ni(1)–S(2)	92.23(8)		C(19)–N(1)–Na(1)	162.7(3)	
S(2)–Ni(1)–S(2)#1	180.000(18)		C(22)–N(2)–Na(1)#3	161.6(3)	
C(20)–S(1)–Ni(1)	102.98(14)		N(1)–C(19)–C(20)	177.1(4)	
C(21)–S(2)–Ni(1)	102.70(14)		N(2)–C(22)–C(21)	177.9(4)	

Symmetry code for **2**: #1 $-x+2$, $-y$, $-z+2$; #2 x, $-y+1/2$, $z-1/2$; #3 x, $-y+1/2$, $z+1/2$.

3.2. *FT-IR spectral study*

The FT-IR spectra of **1** and **2** display several sharp bands of different intensities, which may be classified into those emerging from N15C5 and those originating from the mnt ligand. The bands at 3062 or 3052 cm^{-1} and 750 or 748 cm^{-1} are clearly assigned to the ν(Ar–H) and δ(Ar–H) vibrations of the naphthylene moieties. The $\nu(CH_2CH_2)$ and $\delta(CH_2CH_2)$ vibrations of N15C5 in both complexes took place at 2872–2921 cm^{-1} (double peak) and 1384, $\sim$1450 cm^{-1}, respectively. The C–O–C groups afford four bands in the range of 1045–1259 cm^{-1}, which are comparable to those of $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt) (1041–1261 cm^{-1}) [8] and in the region two terminal bands are assigned to the ν(Ar–O–C) vibrations. For both complexes, the ν(CC) vibrations of the naphthylene groups of **1** and **2** are comparable

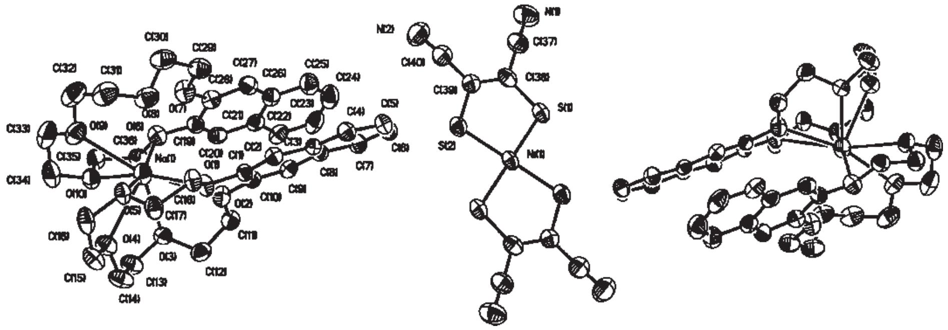

Figure 1. Molecular structure of **1** with 30% probability ellipsoids.

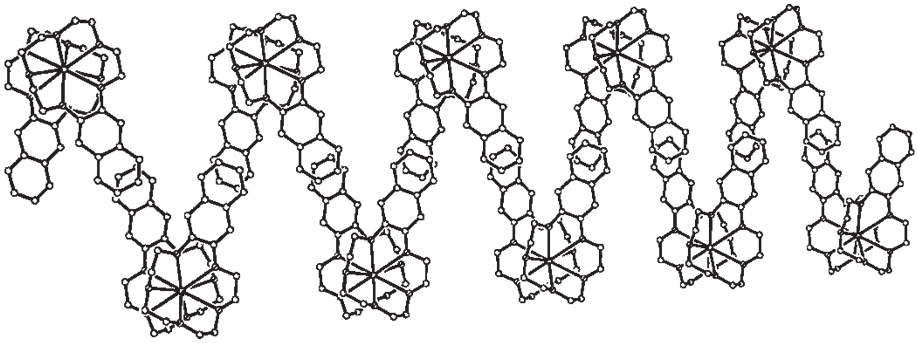

Figure 2. The 1D cationic chain of complex cations of **1**.

to each other and to $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt) (1484–1632 cm^{-1}) [8], giving four bands between 1484–1632 cm^{-1}. For complex anions, the stretching vibrations of multiple C≡N bonds in complexes **1** and **2** are observed at 2191 and 2199 cm^{-1}, respectively. The band due to ν(C=C) vibrations of mnt in **2**, appear at 1476 cm^{-1}, but those of **1** were not clearly observed because of overlay by the band at 1484 cm^{-1}. The bands at 863 and 865 cm^{-1} may be assigned to ν(CS) vibrations [14].

3.3. *Description of the crystal structure*

3.3.1. Complex 1. The crystal structure of **1** and the packing diagram are shown in figures 1 and 2, respectively. The complex molecule consists of two $[Na(N15C5)_2]^+$ sandwich complex cations and one $[Ni(mnt)_2]^{2-}$ complex anion. For the $[Ni(mnt)_2]^{2-}$ complex anion, the NiS_4 group is square planar and tilted slightly at an angle of 4.3° with respect to the plane of mnt ligand. Four Ni–S bonds have two distances [2.1618(12) and 2.1642(11) Å], which are slightly shorter than those of $Rb_2[Ni(mnt)_2] \cdot H_2O$ [2.172(2) and 2.178(3) Å] [15]. The average bond lengths of S–C, C=C, C–C, C≡N are 1.737, 1.343, 1.431, and 1.123 Å, respectively.

In $[Na(N15C5)_2]^+$ sandwich complexes cation, the arrangement of N15C5 to metal ion is similar to that of $[K(N15C5)_2]^+$ for $[K(N15C5)_2]I$ [16] and $[K(N15C5)_2][Cu_2Cl_6] \cdot 3H_2O$ [17]. There are two N15C5 molecules surrounding the sodium ion in a sandwich structure, with 10 Na–O distances in the region of 2.554(3)–3.131(3) Å,

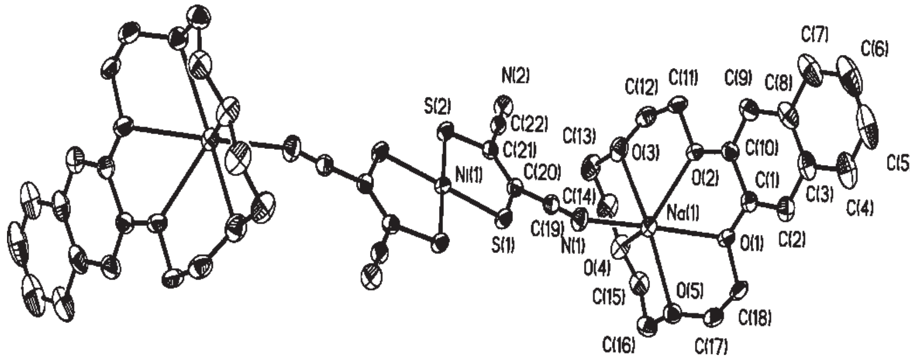

Figure 3. Molecular structure of complex **2** with 30% probability ellipsoids.

comparable to $[Na(B15C5)_2][BPh_4]$ (2.482(17)–3.304(18) Å) [18]. The ether oxygen planes O(1)–O(5) (mean deviation 0.185 Å) and O(6)–O(10) (mean deviation 0.221 Å) are not parallel with a dihedral angle of 8.1° and the deviations of Na(1) from the ether oxygen planes are 1.475 and 1.594 Å, respectively. In the sandwich structure, the macrocycles are twisted around the axis through the center of their cavities. The dihedral angle between the planes determined by the centers of two six-member rings of each naphthylene group and the sodium ion equals 41.6°.

The most interesting structural feature for **1** is intra- and inter-cationic π–π interactions. The $C(9)\cdots C(20)$ contact is the closest atom–atom distance between two naphthylene rings in the sandwich structure (3.418 Å), significantly smaller than the sum of van der Waals radii for two aromatic carbons (3.54 Å) [19], indicating the existence of intra-cationic π–π interactions. As shown in figure 2, the $[Na(N15C5)_2]^+$ sandwich cations are assembled into a novel 1D zig-zag chain through alternating π–π interactions between the outer six-membered rings of the stacking naphthylene moieties. The stacking naphthylene groups give another stacking model other than the parallel face-to-face geometry [8] or a T-shape array [10] and can be described as a slip displaced arrangement. The rings are inclined by 22.4° and the mean interplanar separation is 3.426 Å with a centroid–centroid distance of 4.212 Å, in which the mean interplanar separation lies within the common stacking region (3.3–3.8 Å) [20]. Although the centroid–centroid distance (4.212 Å) is much larger than that of $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt) (3.6 Å) [8], it is still shorter than reported values for the nearest six-membered rings of the stacking naphthylene groups (4.6 Å [21] and 4.83 Å [22]).

3.3.2. Complex 2.

The ORTEP drawing of **2** is shown in figure 3. Complex **2** consists of two $[Na(N15C5)]^+$ complex cations and one $[Ni(mnt)_2]^{2-}$ complex anion. For $[Ni(mnt)_2]^{2-}$, the NiS_4 group is square planar and tilted slightly at an angle of 7.2° with respect to the plane of the mnt ligand, which is larger than that of **1** (4.3°), and the poor coplanarity may be due to the Na–N contacts. The average bond lengths of Ni–S, S–C, C=C, C–C and $C\equiv N$ are 2.167, 1.730, 1.350, 1.431, 1.138 Å, respectively, of which most are slightly different from **1**.

In the $[Na(N15C5)]^+$ complex cation, the five oxygen atoms of the crown ether are approximately coplanar with maximum deviation of 0.353 Å and Na^+ is 1.09 Å out of the ether oxygen plane, displaying a basket-like conformation. The five Na–O

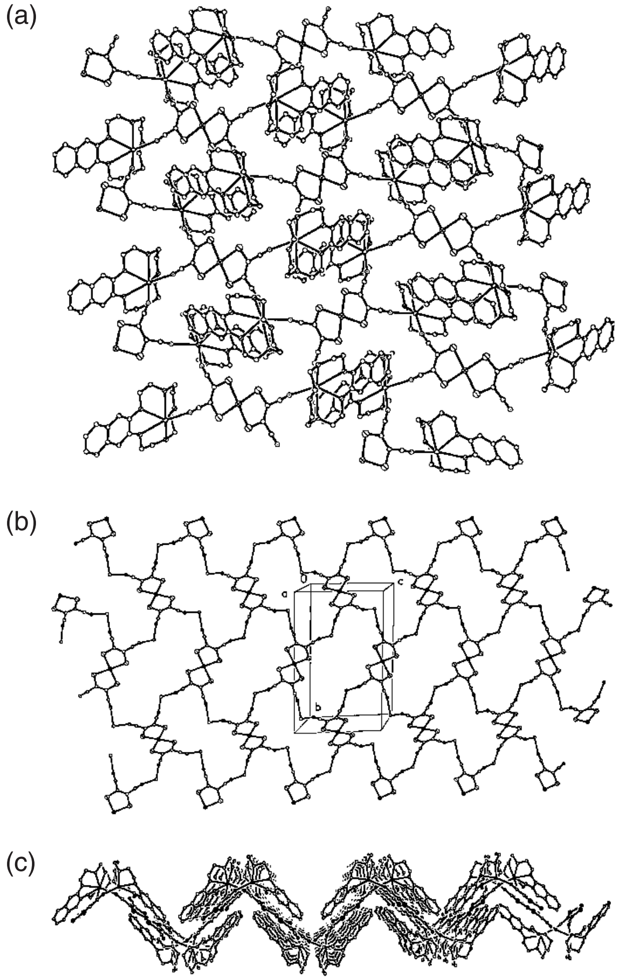

Figure 4. (a) A view of the network of **2** on the *ac* plane; (b) a view of the network of **2** on the *ac* plane in which the crown ethers are omitted for clarity; (c) a view of the network of **2** on the *bc* plane.

distances vary from 2.397(4) to 2.590(4) Å (average 2.518 Å), which are comparable to that of $[Na(N15\text{-}C\text{-}5)]_2[Ni(i\text{-}mnt)_2]$ [9] containing the seven-coordinate sodium ion (2.444(3)–2.607(3) Å, average 2.510 Å). The remainder of the coordination sphere of Na(1) is occupied by N(1) and N(2)#2 atoms from two complex anions, with the N(1)–Na(1)–N(2)#2 bond angle of 85.72(13)°. The Na(1)–N(1) and Na(1)–N(2)#2 bond lengths are 2.487(4) and 2.533(4) Å (average 2.510 Å), respectively; the mean value is consistent with that in $[Na(18\text{-}C\text{-}6)(H_2O)]_2[Ni(mnt)_2] \cdot (18\text{-}C\text{-}6)$ (2.503 Å) [23].

As shown in figure 4(b), the remarkable structural feature for **2** is that the sodium ions act as joint points and $[Ni(mnt)_2]^{2-}$ complex anions as building blocks to form a novel 2D network through the Na–N bonds. In the network, there are 34-member macrocycles linked by four sodium ions and four complex anions and as shown in figure 4(a), in each macrocycle there are two parallel offset stacking naphthylene moieties of N15C5 with interplanar separation of 3.36 Å. These π–π stacking

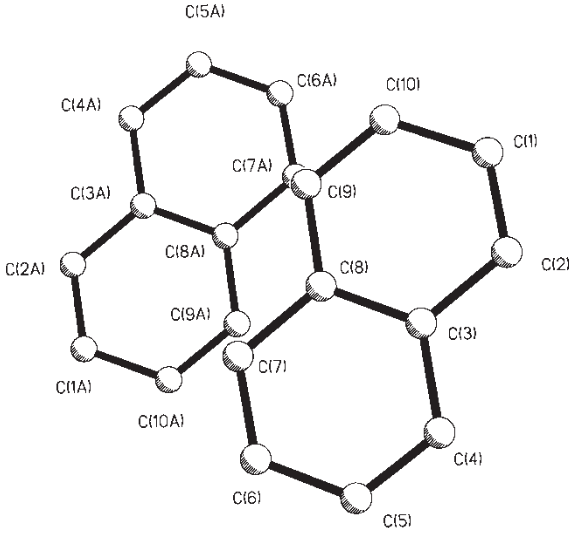

Figure 5. A top view of one pair of the stacking naphthylene moieties of **2**.

Table 4. Selected distances (Å) of the closer atom–atom contacts for the stacking naphthylene moieties of N15C5 in **2**.

Atom–atom contacts		Atom–atom distances
C(7)···C(9A)	C(9)···C(7A)	3.519
C(7)···C(10A)	C(10)···C(7A)	3.691
C(8)···C(9A)	C(9)···C(8A)	3.685
C(9)···C(9A)		3.833

interactions can be described as "parallel edge-to-edge" or "parallel much displaced" geometry (see figure 5) and π–δ attraction dominates in this model [20, 24]. To describe this stacking model, close atom–atom contacts provide for a better criterion. Common atom–atom contacts of stacking aromatic groups are 3.3–3.8 Å [20]; closer atom–atom contacts (3.5–3.84 Å) are given in table 4. It is interesting that the 2D network displays a corrugated sheet on the *bc* plane (see figure 4c). The angle of the V-shaped unit of the sheet is 72.4°, calculated as the dihedral angle of two bond-jointed $[Ni(mnt)_2]^{2-}$ anions. The parallel stacking naphthylene moieties look like the caps of the corrugated sheet. On each side of the V-shape unit of the sheet, the caps are shoulder to shoulder arrayed, and the caps from two sides of the V-shape unit give the T-shape arrays, with a dihedral angle of 92.3°.

4. Conclusion

Reactions of N15C5 with $Na_2[Ni(mnt)_2]$ under different molar ratios (2 : 1 and 4 : 1) afforded two structurally different complexes $[Na(N15C5)_2]_2[Ni(mnt)_2]$ (**1**) and $[Na(N15C5)]_2[Ni(mnt)_2]$ (**2**), indicating an influence of the amount of crown ether used on the structures of complexes. Two types of N15C5-sodium organic cations with ligand-to-sodium ratios of 2 : 1 and 1 : 1 are presented in the crystals of **1** and **2**, respectively. It is these structurally different organic cations that act as spacers, leading to the different structures. Complex **1** shows a 1D structure assembled by π–π stacking interactions and electrostatic interactions while complex **2** displays a novel 2D polymeric structure constructed by Na–N contacts.

Supplementary data

Crystallographic data for the structures in this article have been deposited with Cambridge Crystallographic Data Center (CCDC), CCDC Nos 209437 (**1**) and 227553 (**2**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ ccdc.cam.ac.uk).

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