Original Research Article

Synthesis and Crystal Structures of Group 10 Metal Bis(dithiolate) Complexes Constructed by 2,3-Naphtho-15-Crown-5 or 2,3-Naphtho-18-Crown-6

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Abstract

Five novel 2,3-naphtho crown ether group 10 metal bis(dithiolate) complexes, $[Na(N15C5)_2]_2[Pd(mnt)_2]$ (**1**), $[Na(N15C5)]_2[Pd(i\text{-}mnt)_2]$ (**2**) and $[K(N18C6)]_2[M(i\text{-}mnt)_2]$ (**3–5**) (where mnt = 1,2-dicyanoethylene-1,2-dithiolate, i-mnt = 1,1-dicyanoethylene-2,2-dithiolate and M = Ni, Pd, Pt for complexes **3–5**, respectively), have been synthesized and characterized by elemental analysis, FT-IR, UV–Visible spectra and single crystal X-ray diffraction. X-ray diffraction analyses reveal that complexes **1** and **2** have different structural features while complexes **3–5** are structurally isomorphous. Complex **1** consists of two $[Na(N15C5)_2]^+$ sandwich complex cations and one $[Pd(mnt)_2]^{2-}$ anion, affording a zero-dimensional structure. For **2**, the $[Na(N15C5)]^+$ mono-capped complex cations act as the bridges linking the $[Pd(i\text{-}mnt)_2]^{2-}$ anions into a 1D infinite chain through Na–N interactions and $S{\cdots}C$ and $S{\cdots}\pi$ interactions are observed in the resulting chain. Complexes **3–5** all consist of two $[K(N18C6)]^+$ complex cations and one $[M(i\text{-}mnt)_2]^{2-}$ (M = Ni, Pd or Pt) anion and the complex molecules are linked into 1D chains by the bridging K–O(ether) interactions between the adjacent $[K(N18C6)]^+$ units. What's novel is that the resulting chains are assembled into novel 2D networks through interchain π–π stacking interactions between the neighboring naphthylene moieties of N18C6. The stack model of naphthylene group in complexes **3–5** is discussed.

Introduction

Since the pioneering work of Pedersen [1], crown ethers and their complexes with metal cations have attracted much attention, which is not only because crown ethers are able to present unusual coordination numbers and arrangements on various metal ions but also because they and their cations, especially those containing aromatic rings, can act as building blocks to form 1D–3D supramolecular structures by coordinate covalent bonds, hydrogen bonds, π–π stacking, cation–π interactions and other weak interactions [2–4]. In recent years, N15C5 has been widely studied in electrochemistry and it's solution coordination behaviors to alkali and alkaline earth metal ions were studied by CV and ESI-MS methods [5, 6]. Among the cyclic polyethers, the ones with six oxygen atoms such as 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6 and dicyclohexano-18-crown-6 are well known to form stable complexes with

alkali metal, alkali earth metal and transition metal ions. The associations of N18C6 with alkali metal, ammonium and alkylammonium ions in solution have been studied by Cram [7]. However, the crystal structures of N15C5 or N18C6 complexes have been rarely studied, including a few examples, such as $[K(N15C5)_2]I$ [8], $[K(N15C5)_2][Cu_2Cl_6]\cdot3H_2O$ [9], $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt) and $[K(N18C6)]_2[M(SCN)_4]$ (M = Pd, Pt) [10], $\{[K(N18C6)]_2(CH_3CN)\}[Ni(mnt)_2]$ [11] and $[(t\text{-}BuNH_3)(N18C6)][ClO_4]\cdot0.25MeCOEt\cdot0.25CH_2Cl_2$ [12]. On the other hand, the new-arising crown ether metal bis(dithiolate) complexes which act as one kind of hybrid inorganic–organic species have attracted widespread interest owing to their novel crystal structures and unusual electrical, magnetic and optical properties [13–15]. We are interested in developing synthetic strategies for the construction of hybrid materials containing crown ethers on the basis of crystal engineering and the supramolecular concept [10, 11]. To study the solid behaviors of N15C5 or N18C6 and to design new crown ether–metal–

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bis(dithiolate) complexes with novel crystal engineering and new supramolecular information, we choose N15C5 or N18C6 as organic building block and Na$_2$[Pd(mnt)$_2$], Na$_2$[Pd(i-mnt)$_2$] or K$_2$[M(i-mnt)$_2$] (M = Ni, Pd or Pt) as inorganic building block and achieve five novel supramolecular complexes, [Na(N15C5)$_2$]$_2$[Pd(mnt)$_2$] (1), [Na(N15C5)]$_2$[Pd(i-mnt)$_2$] (2) and [K(N18C6)]$_2$[M(i-mnt)$_2$] (3–5).

Experimental

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. UV–Visible spectra were performed on HP-8453 UV–Visible spectrophotometer in acetonitrile.

N15C5 [16], N18C6 [17], Na$_2$(mnt) [18], Na$_2$(i-mnt) [19] and K$_2$(i-mnt) [20] were prepared as described in the literature. All reagents and solvents purchased were A.R. grade and used without further purification.

Preparation of [Na(N15C5)$_2$]$_2$[Pd(mnt)$_2$] (1)

To a solution of N15C5 (0.50mmol) in 1,2-dichloro-ethane (5ml) was added 5 ml aqueous mixture of PdCl$_2$ (0.125 mmol) and Na$_2$(mnt) (0.25 mmol). The reaction mixture was stirred for 2 hrs at room temperature and then filtered. The precipitate was dissolved in the mixture of CH$_3$CN and CH$_3$COCH$_3$ (v/v = 1/1). The green single crystal was obtained by slowly evaporating the solution. Yield: 177 mg, 83% (based on Pd). m.p. 222–223 °C. Anal. for C$_{80}$H$_{88}$N$_4$Na$_2$O$_{20}$PdS$_4$, Calc. C, 56.67; H, 5.16; N, 3.28. Found: C, 56.32; H, 5.36; N, 3.40. FT-IR (KBr): 3052w (Ar-H), 2924m (CH$_2$CH$_2$), 2871m; 2193ms (CN), 1629m (Ar, CC), 1602w, 1510m; 1484s (C=C), 1452m (CH$_2$CH$_2$), 1383m; 1255vs (C–O–C), 1176ms, 1116vs, 1057m; 865m (CS), 747m (Ar-H) cm^{-1}. UV–Vis (CH$_3$CN, λ_{max}, nm): 232, 320, 437, 642.

Preparation of [Na(N15C5)]$_2$[Pd(i-mnt)$_2$] (2)

The reaction is analogous to that of 1, using Na$_2$(mnt) instead of Na$_2$(i-mnt). Yield the yellow single crystal: 96 mg, 72% (based on Pd), m.p. > 300 °C. Anal. for C$_{44}$H$_{44}$Na$_2$N$_4$PdO$_{10}$S$_4$, Calc. C, 49.37; H, 4.11; N, 5.24. Found: C, 49.06; H, 4.22; N, 5.31. FT-IR (KBr): 3052w (Ar-H), 2927m (CH$_2$CH$_2$), 2874m; 2207s (CN), 1631m (Ar, CC), 1604w, 1510m, 1487ms; 1453m (CH$_2$CH$_2$), 1370vs (C=CS$_2$), 1259s (C–O–C), 1176ms, 1121vs, 1059m, 895m (CS$_2$), 755m (Ar-H), 746m cm^{-1}. UV–Vis (CH$_3$CN, λ_{max}, nm): 234, 325, 379, 585.

Preparation of [K(N18C6)]$_2$[Ni(i-mnt)$_2$] (3)

To a solution of N18C6 (0.50 mmol) in 1,2-dichloro-ethane (5ml) was added 5ml aqueous mixture of NiCl$_2$ (0.125 mmol) and K$_2$(i-mnt) (0.25 mmol). The reaction mixture was stirred for 2 hrs at room temperature and then filtered. The precipitate was dissolved in the mixture of CH$_3$CN and CH$_3$COCH$_3$ (v/v = 1/1). The single crystal was obtained by slowly evaporating the solution. Yield: 0.12 g, 85% (based on Ni). m.p. 230–231 °C. Anal Calc. for C$_{48}$H$_{52}$K$_2$N$_4$NiO$_{12}$S$_4$: C, 50.48; H, 4.59; N, 4.91. Found: C, 50.66; H, 4.78; N, 5.08. Selected FT-IR (cm^{-1}): 3057m (Ar-H), 2896m (CH$_2$CH$_2$), 2878m; 2199s (CN), 1631m (Ar, CC), 1603m, 1510m, 1483m, 1463m; 1448m (CH$_2$CH$_2$), 1399s (C=CS$_2$), 1382s (CH$_2$CH$_2$), 1255s (C–O–C), 1114s, 1066m (CS), 1049m, 943m (CS$_2$), 892m; 748m (Ar−H). UV–Vis (CH$_3$CN, λ_{max}, nm): 239, 340, 457, 642.

Preparation of [K(N18C6)]$_2$[Pd(i-mnt)$_2$] (4)

The reaction is analogous to that of 3, using PdCl$_2$ instead of NiCl$_2$. Yield: 0.10 g, 67% (based on Pd). m.p. 237–238 °C. Anal Calc. for C$_{48}$H$_{52}$K$_2$N$_4$PdO$_{12}$S$_4$:C, 48.46; H, 4.41; N, 4.71. Found: C, 48.46; H, 4.53; N, 4.89. Selected FT-IR (cm^{-1}): 3056m (Ar-H), 2920m (CH$_2$CH$_2$), 2876m; 2198s (CN), 1630m (Ar, CC), 1603m, 1510m, 1483m, 1464m; 1401s (C=CS$_2$), 1382s (CH$_2$CH$_2$), 1255s (C–O–C), 1170s, 1111s, 1066m (CS), 1049m, 949m (CS$_2$), 895m; 749m (Ar–H). UV–Vis (CH$_3$CN, λ_{max}, nm): 236, 322, 380, 450.

Preparation of [K(N18C6)]$_2$[Pt(i-mnt)$_2$] (5)

Complex 5 was prepared by the similar procedure, using K$_2$PtCl$_4$ in place of NiCl$_2$. Yield: 0.11 g, 69% (based on Pt). m.p. 233–234 °C. Anal Calc. for C$_{48}$H$_{52}$K$_2$N$_4$PtO$_{12}$S$_4$:C, 45.10; H, 4.10; N, 4.38. Found: C, 45.39; H, 4.23; N, 4.30. FT-IR (cm^{-1}): 3056m (Ar–H), 2919m (CH$_2$CH$_2$), 2875m; 2197s (CN), 1630m (Ar, CC), 1603m, 1510m, 1483m, 1464m; 1395s (C=CS$_2$), 1255s (C–O–C), 1170m, 1113 s, 1065m (CS), 1048m, 947m (CS$_2$), 891m; 748m (Ar–H). UV–Vis (CH$_3$CN, λ_{max}, nm): 238, 290, 358, 418.

Determination of crystal structure

Suitable single crystals of 1–5 were glued to fine glass fibers respectively and were then mounted on a Bruker Smart-1000 CCD diffractometer with MoK$_\alpha$ radiation, $\lambda = 0.71073$ Å. The intensity data were collected at room temperature. The structures were solved by direct method and expanded using Fourier techniques with Shelxl-97 program [21]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and not refined. Detailed information about crystal data and structure determinations are summarized in Table 1. The selected bond lengths and angles of complexes 1, 2 and 3–5 are listed in Tables 2, 3 and 4, respectively.

Table 1. Crystal data and structure refinement for complexes **1–5**

Complex	1	2	3	4	5
Empirical formula	$C_{80}H_{88}N_4Na_2PdO_{20}S_4$	$C_{44}H_{44}N_4Na_2PdO_{10}S_4$	$C_{48}H_{52}K_2N_4NiO_{12}S_4$	$C_{48}H_{52}K_2N_4PdO_{12}S_4$	$C_{48}H_{52}K_2N_4PtO_{12}S_4$
Formula weight	1706.16	1069.45	1142.09	1189.78	1278.47
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	15.612(9)	8.298(3)	12.848(12)	12.942(9)	12.957(7)
b (Å)	20.566(12)	12.856(5)	12.943(12)	12.937(9)	12.947(8)
c (Å)	12.931(8)	12.909(5)	16.386(15)	16.504(12)	16.458(10)
α	90	115.456(6)	90	90	90
β (°)	103.301(12)	105.453(6)	106.287(15)	106.656(10)	106.849(8)
γ	90	91.307(6)	90	90	90
V (Å^3)	4040(4)	1183.4(8)	2616(4)	2647(3)	2642(3)
Z	2	1	2	2	2
D_{cald}(g cm^{-3})	1.402	1.501	1.450	1.493	1.607
μ (mm^{-1})	0.417	0.647	0.753	0.728	3.034
$F(000)$	1776	548	1188	1224	1288
Crystal size (mm)	0.25 × 0.20 × 0.12	0.28 × 0.12 × 0.09	0.34 × 0.24 × 0.18	0.42 × 0.35 × 0.26	0.30 × 0.25 × 0.23
θ range (°)	2.39–25.03	1.78–25.02	2.59–25.03	2.03–25.04	1.64–25.02
Reflections collected	21036	6316	12838	13057	13684
Independent reflections	7113	4130	4568	4579	4664
R_{int}	0.1093	0.0267	0.0888	0.0302	0.0409
R_1, wR_2 [$I > 2\sigma(I)$]	0.0450, 0.0503	0.0393, 0.0805	0.0594, 0.1313	0.0322, 0.0857	0.0319, 0.0677
R_1, wR_2 (all data)	0.1725, 0.0675	0.0704, 0.1099	0.1126, 0.1528	0.0534, 0.0968	0.0638, 0.1031
Largest diff. peak and hole (eÅ^{-3})	0.293 and −0.382	0.317 and −0.343	1.318 and −0.555	0.406 and −0.335	0.645 and −0.524

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

Na(1)–O(1)	2.772(3)	Na(1)–O(8)	3.005(4)	S(1)–C(38)	1.737(5)
Na(1)–O(2)	2.790(3)	Na(1)–O(9)	2.593(4)	S(2)–C(39)	1.694(6)
Na(1)–O(3)	2.872(4)	Na(1)–O(10)	2.552(4)	C(37)–C(38)	1.433(7)
Na(1)–O(4)	2.611(4)	Pd(1)–S(1)	2.2786(16)	C(38)–C(39)	1.355(6)
Na(1)–O(5)	2.613(3)	Pd(1)–S(2)	2.2787(16)	C(39)–C(40)	1.441(6)
Na(1)–O(6)	2.796(4)	N(1)–C(37)	1.149(6)		
Na(1)–O(7)	3.109(4)	N(2)–C(40)	1.146(6)		
S(1)–Pd(1)–S(1)#1	180.0	O(10)−Na(1)–O(6)	60.80(11)		
S(2)–Pd(1)–S(2)#1	180.0	O(9)−Na(1)–O(6)	94.45(12)		
S(1)–Pd(1)–S(2)	90.32(7)	O(5)−Na(1)–O(6)	166.32(12)		
C(38)–S(1)–Pd(1)	101.3(2)	O(1)−Na(1)–O(6)	121.59(11)		
C(39)–S(2)–Pd(1)	101.95(19)	O(2)−Na(1)–O(6)	78.14(10)		
O(10)–Na(1)–O(9)	66.18(13)	O(10)−Na(1)–O(3)	69.90(12)		
O(10)–Na(1)–O(5)	120.51(12)	O(9)−Na(1)–O(3)	134.15(14)		
O(9)–Na(1)–O(5)	75.15(12)	O(5)−Na(1)–O(3)	118.82(12)		
O(10)–Na(1)–O(4)	74.01(11)	O(4)−Na(1)–O(3)	62.27(11)		
O(10)–Na(1)–O(1)	167.55(12)	O(1)−Na(1)–O(3)	98.45(11)		
O(9)–Na(1)–O(4)	93.03(13)	O(2)−Na(1)–O(3)	56.10(10)		
O(5)–Na(1)–O(4)	64.57(11)	O(6)−Na(1)–O(3)	74.79(10)		
O(9)–Na(1)–O(1)	123.81(13)	O(9)−Na(1)–O(2)	165.65(13)		
O(5)–Na(1)–O(1)	60.52(11)	O(5)−Na(1)–O(2)	109.95(12)		
O(4)–Na(1)–O(1)	96.97(12)	O(4)−Na(1)–O(2)	101.28(13)		
O(10)–Na(1)–O(2)	118.78(12)	O(1)−Na(1)–O(2)	53.68(10)		
O(4)–Na(1)–O(6)	125.86(12)	O(10)—Na(1)–O(8)	120.94(13)		
O(9)–Na(1)–O(8)	61.16(12)	O(2)−Na(1)–O(8)	107.34(12)		
O(4)–Na(1)–O(8)	131.50(13)	O(6)−Na(1)–O(8)	98.19(12)		
O(5)–Na(1)–O(8)	69.14(11)	O(3)−Na(1)–O(8)	162.73(12)		
O(1)–Na(1)–O(8)	71.44(10)				

Symmetry code for complex **1**: #1−x + 1,−y + 1, −z + 2.

Results and discussion

Synthesis and UV–Vis spectra studies

The group 10 metal bis(dithiolate) alkali metal salts Na₂[Pd(mnt)₂], Na₂[Pd(i-mnt)₂] or K₂[M(i-mnt)₂] (M = Ni, Pd, Pt) were completely formed in water. The reactions of N15C5 or N18C6 with Na₂[Pd(mnt)₂], Na₂[Pd(i-mnt)₂] or K₂[M(i-mnt)₂] (M = Ni, Pd, Pt) in the mixed phases (1,2-dichloroethane/water) afforded the solid products **1**–**5**. Crystals of **1**–**5** are air and moisture stable. The complexes are soluble in polar organic solvents, such as CH₃CN, DMF, DMSO, CH₃COCH₃ and CH₃OH, but are insoluble in water, diethyl ether and hexane. However, for complexes **1** and **2**, the similar experimental conditions did not afford the similar results. Complex **1** contains the sandwich 2:1 complex cation [Na(N15C5)₂]⁺ while complex **2** has the 1:1 complex cation [Na(N15C5)]⁺, indicating that the 'size and stereo' factors of the complex anions have an

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

Pd(1)–S(1)	2.3182(15)	Na(1)–O(5)	2.476(3)	S(1)–C(19)	1.713(4)
Pd(1)–S(2)	2.3302(13)	Na(1)−N(1)	2.526(5)	S(2)–C(19)	1.716(4)
Na(1)–O(1)	2.604(3)	Na(1)–N(2)#2	2.430(4)	C(19)–C(20)	1.376(5)
Na(1)–O(2)	2.561(3)	N(2)–Na(1)#2	2.430(4)	C(20)−C(21)	1.413(6)
Na(1)–O(3)	2.450(3)	N(1)–C(21)	1.138(6)	C(20)−C(22)	1.425(6)
Na(1)–O(4)	2.435(3)	N(2)–C(22)	1.142(5)		
S(1)–Pd(1)–S(1)#1	180.0	C(22)–N(2) −Na(1)#2	171.2(4)		
S(1)–Pd(1)–S(2)	74.82(4)	S(1)−C(19)−S(2)	110.9(2)		
S(2)#1–Pd(1)–S(2)	180.0	N(1)−C(21)−C(20)	179.0(5)		
N(1)–Na(1)–N(2)#2	80.43(15)	N(2)−C(22)−C(20)	178.9(5)		
C(21)–N(1)–Na(1)	141.9(5)	C(21)−C(20)−C(22)	117.6(4)		

Symmetry code for complex **2**: #1−x + 2, −y + 2, −z + 2 #2 −x + 2, −y + 1, −z + 1.

Table 4. Selected bond lengths (Å) and bond angles (°) for complexes **3–5** with M = Ni, Pd, Pt, respectively

	3	4	5
M(1)–S(1)	2.1956(19)	2.3241(15)	2.3186(19)
M(1)–S(2)	2.209(2)	2.3331(17)	2.325(2)
M–S (average)	2.202	2.329	2.322
K(1)—O(1)	2.732(3)	2.738(2)	2.730(4)
K(1)—O(2)	2.734(3)	2.737(2)	2.737(4)
K(1)—O(3)	2.710(4)	2.710(3)	2.692(5)
K(1)—O(4)	2.679(4)	2.686(3)	2.680(5)
K(1)—O(5)	2.903(4)	2.904(3)	2.898(5)
K(1)—O(6)	2.686(4)	2.719(3)	2.709(5)
K(1)—O (average)	2.741	2.749	2.741
K(1)—O(5)#2	2.969(4)	2.983(3)	2.963(5)
K(1)—N(1)	2.889(6)	2.920(5)	2.878(8)
N(1)–C(23)	1.129(7)	1.138(5)	1.137(9)
N(1)–C(24)	1.140(6)	1.135(4)	1.131(8)
N–C (average)	1.135	1.137	1.134
S(1)—C(21)	1.719(5)	1.730(3)	1.721(6)
S(2)—C(21)	1.721(5)	1.717(3)	1.715(6)
S–C (average)	1.720(5)	1.724(3)	1.718(6)
C(21)–C(22)	1.385(7)	1.376(4)	1.399(8)
C(22)–C(24)	1.409(7)	1.418(5)	1.436(10)
C(22)–C(23)	1.424(8)	1.425(5)	1.445(10)
S(1)—M(1)–S(1)#1	180.0	180.0	180.0
S(1)—M(1)–S(2)	78.59(6)	74.96(5)	74.37(6)
S(2)# 1–M(1)—S(2)	180.0	180.0	180.0
O(5)—K(1)—O(5)#2	83.79(10)	83.25(7)	83.17(13)
K(1)—O(5)–K(1)#2	96.21(10)	96.75(7)	96.83(13)
C(23)–N(1)–K(1)	146.0(5)	143.1(4)	142.8(7)
S(1)—C(21)–S(2)	108.4(3)	110.62(17)	109.5(3)
N(1)–C(23)–C(22)	175.3(7)	178.7(5)	178.1(8)
N(2)–C(24)–C(22)	177.5(6)	177.9(4)	179.6(10)

Symmetry codes for **3**: #1 − x + 1, − y + 1, − z + 1; #2 − x + 1, − y+ 1, − z, for **4**: #1 −x, −y + 2, −z + 1; #2 −x, −y + 2, −z and for **5**: #1 − x + 1, −y + 1, −z + 2; #2 −x + 1, −y + 1, −z + 1.

influence on the final structural features. Comparing with **1**, the higher melting point and less solubility of **2** may be assigned to its polymeric structure.

Solution electronic spectra of the complexes were measured in acetonitrile in the UV–Vis region (190–1000 nm). For complex **1**, four absorption peaks were observed with λ_{max} = 231, 320, 440 and 642 nm (very weak), in which the former two bands may be attributed to π–π^* transitions of naphthylene group and the latter two correspond to the ligand-to-metal ($L_\pi \rightarrow xy$) and metal d–d ($x^2 − y^2 \rightarrow xy$) transitions, respectively [22]. The electronic spectrum of **2** also consists of four bands at 234, 325, 379 and 570 nm. The high-energy bands at 234 and 325 nm are due to π–π^* transitions of naphthylene group and the metal-to-ligand charge transition appears at 379 nm which is consistent with that of [TBA][Pd(i-mnt)$_2$] (377 nm) [23]. The very weak band at 570 nm indicates d–d transition of the Pd atom and is quite blue-shift comparing with that of [TBA][Pd (i-mnt)$_2$] (448 nm).

For complex **3–5**, the high-energy bands at 236–239 nm are attributed to π–π^* transitions of naphthylene group. The absorption bands at 322–358 nm and 380–457 nm are attributed to the intraligand (L $\rightarrow$ L*) and metal-to-ligand (M $\rightarrow$ L*) charge transfers, respectively, with the decreasing wavelength λ_{max} along the series Ni(II) > Pt(II) > Pd(II), which are comparable to the corresponding values in [TBA]$_2$[M(i-mnt)$_2$] (M = Ni, Pd, Pt) (314–352 nm and 377–452 nm) [23]. Furthermore, the very weak bands at 642 nm for **3** and 450 nm for **4** show the d–d transitions of the Ni and Pd atoms, respectively. However, the d–d transition band of complex **5** was not observed.

Crystal structure description and discussion

Complex 1
The molecular crystal structure of **1** is shown in Figure 1 and its selected bond lengths and angles are listed in Table 2. Complex **1** consists of two [Na(N15C5)$_2$]$^+$ sandwich complex cations and one [Pd(mnt)$_2$]$^{2−}$ complex anion, there are no obvious contacts between the cations and the anion and **1** affords a zero-dimensional structure. For the [Pd(mnt)$_2$]$^{2−}$ complex anion, the PdS$_4$
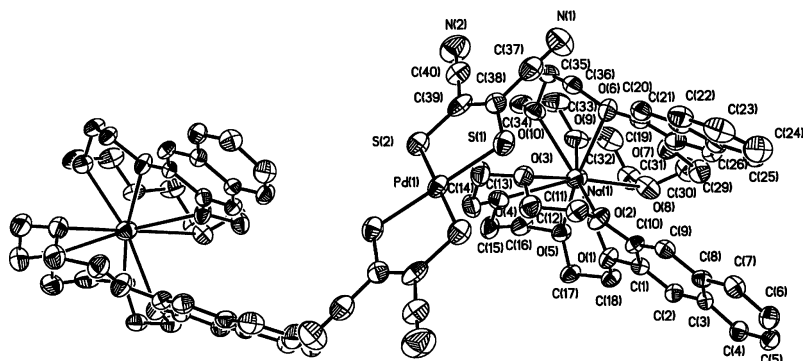
Figure. 1. Molecular structure of **1** with Na–O distances <3.01 Å and 30% probability ellipsoids.

group is square planar and tilted slightly at the angle of 3.3 ° with respect to the plane of mnt ligand. Four Pd–S bonds give two identical distances (2.2786(16) Å and 2.2787(16) Å), which are on average consistent with that of MV[Pd(mnt)$_2$] (average 2.30 Å) [24]. The average bond lengths of S–C, C=C, C–C, C≡N are 1.716, 1.355, 1.437, 1.148 Å, respectively.

In the [Na(N15C5)$_2$]$^+$ sandwich complex cation, the arrangement of N15C5 to metal ion is similar to that of [K(N15C5)$_2$]$^+$ in complexes [K(N15C5)$_2$]I and [K(N15C5)$_2$][Cu$_2$Cl$_6$]·3H$_2$O [8, 9]. There are two N15C5 molecules surrounding the sodium ion in the sandwich structure, with ten Na–O distances in the region of 2.552(4)–3.109(4) Å, which is comparable to that of [Na(B15C5)$_2$][BPh$_4$] (2.482(17)–3.304(18) Å) [25]. The ether oxygen planes O(1)–O(5) (mean deviation 0.1815 Å) and O(6)–O(10) (mean deviation 0.2215 Å) are not parallel with the dihedral angle of 8.1° and the deviations of Na(1) atom from the ether oxygen planes are 1.485 and 1.585 Å, respectively. In the sandwich complex the macrocycles are twisted around the axis which passes through the centers of their cavities. The dihedral angle between the planes determined by two centers of two six-member rings of each naphthylene group and the sodium ion equals 42.1 °.

Complex 2

The molecular crystal structure and packing diagram of **2** are shown in Figures 2 and 3. The selected bond lengths and angles are listed in Table 3. Complex **2** is composed of two mono-capped [Na(N15C5)]$^+$ complex cations and one [Pd(i-mnt)$_2$]$^{2-}$ complex anion. For the complex anion, the PdS$_4$ group is square planar and tilted slightly at the angle of 5.6 ° with respect to the

plane of i-mnt ligand. The average bond lengths of Pd–S, S–C, C=C, C–C, C≡N are 2.3241, 1.715, 1.376, 1.419, 1.140 Å, respectively, which are consistent with those of complex [TBA][Pd(i-mnt)$_2$] [26].

In the [Na(N15C5)]$^+$ complex cation, the five oxygen atoms of crown ether are approximately coplanar with the mean deviation of 0.256 Å and Na$^+$ ion is about 1.06 Å out of the ether oxygen plane, displaying a basket-like structure. The five Na–O distances vary from 2.435(3) to 2.604(3) Å (average 2.505 Å). The remainders of the coordinating sphere of Na(1) atom are 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 80.43(15)°. The Na(1)–N(1) and Na(1)–N(2)#2 bond lengths are 2.526(5) and 2.430(4) Å (average 2.478 Å), respectively, which are much shorter than the sum (2.81 Å) of the van der Waals radii [27] of N atom and the effective ionic radii [28] of seven-coordinated Na$^+$, indicating strong Na–N contacts. The strong Na–N contacts lead to the even stable polymeric structure and the very high melting point.

The self-assembly of **2** is similar to that of [Na(B15C5)]$_2$[M(i-mnt)$_2$] (M = Ni, Pd) reported by Long *et al.* [29, 30]. However, the expanded aryl (naphthylene ring) endows complex **2** with new structural features. The shorter S···C distances occur at S(1) #1···C(6) #2 (3.460 Å), S(2)···C(3) #2 (3.588 Å) and S(2)···C(8) #2 (3.602 Å), which are all shorter than the non-bonded C···S contact distance observed in organic crystal structures (3.61 Å) [31]. The shortest C···N interaction is found between N(2) and C(1) #2 (3.22 Å) and shorter than the non-bonded C···N distance (3.31 Å) [31]. The distances from the S(2) atom to the centers of the corresponding naphthylene ring and
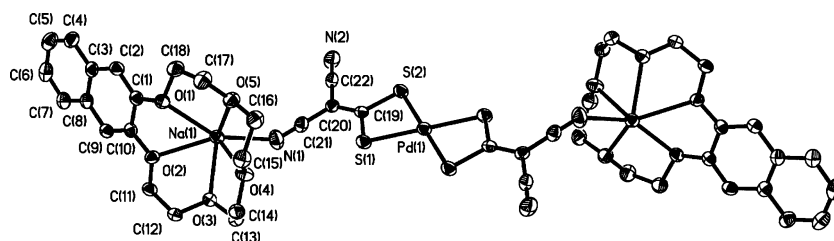

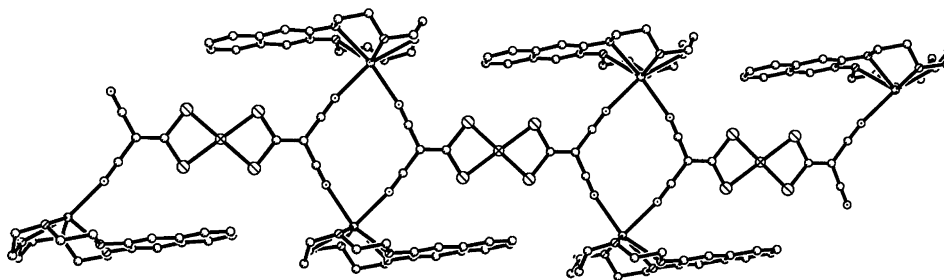*Figure. 2.* Molecular structure of **2** with 30% probability ellipsoids.

Figure. 3. Packing diagram of the complex **2**.

its outer and inner six-member rings are 3.52, 3.60 and 3.83 Å, respectively, indicating the existence of S···π interactions.

Complexes 3–5

ORTEP drawing of complex **3** is shown in Figure 4 and those of **4** and **5** are not given owing to the isomorphous nature. Figure 5 displays a 2D network of complex **3**, the packing diagrams of **4** and **5** are essentially identical owing to the isomorphous complexes. Complexes **3**–**5** have the analogous composition of two [K(N18C6)]$^+$ complex cations and one [M(i-mnt)$_2$]$^{2-}$ (M = Ni, Pd or Pt) complex anion and they are contacted together by

the K–N interactions between two diagonal cyano groups of the complex anion and the potassium ions of [K(N18C6)]$^+$ units. The Ni, Pd or Pt atom lies on inversion center and two naphthylene moieties of N18C6 in complex molecule are *trans* arrangement with respect to the group 10 metal atom.

The structures of the [K(N18C6)]$^+$ cations in complexes **3**–**5** are similar to each other. In the [K(N18C6)]$^+$ complex cation, potassium ion lies within the crown ether and is bonded by six ether oxygen atoms. The remainders of the coordinating sphere of K(1)$^+$ ion are occupied by one nitrogen atom from a cyano group of complex anion [M(i-mnt)$_2$]$^{2-}$ and one bridging oxygen
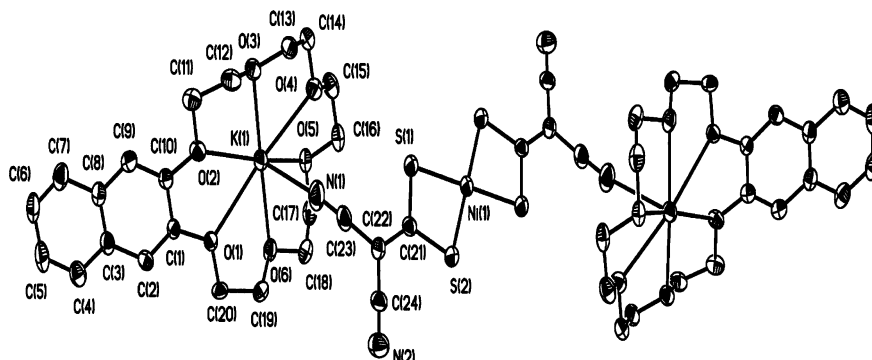

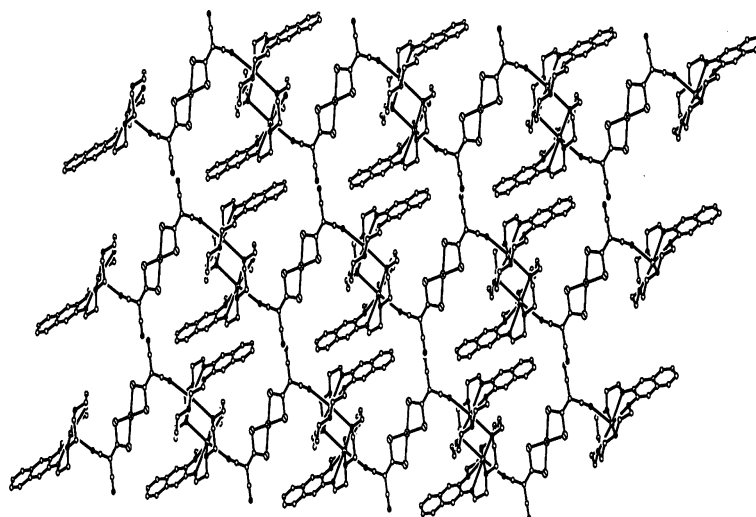*Figure. 4.* Molecular structure of complex **3** with 30% probability ellipsoids.

Figure. 5. The 2D network of complex **3** along b axis.

atom from adjacent $[K(N18C6)]^+$ unit with the $N(1)$–$K(1)$–$O(4)\#2$ bond angles falling into the range $172.3(2)$–$173.45(14)°$ for three complexes. Thus, the coordination environment of $K(1)^+$ ion in **3**–**5** is a distorted hexagonal bipyramid.

In each structure, six ether oxygen atoms of N18C6 near to coplanar with the maximum deviation not larger than 0.55 Å from the least-squares plane and the K^+ ion is about 0.04 Å out of the plane. The equatorial K–O (ether) distances in three structures fall in the range from 2.679(4) to 2.983(3) Å and have a mean value of 2.744 Å, which is comparable to that of $[K(N18C6)]_2[M(SCN)_4]$ (M = Pd, Pt) (2.760 Å) [10] and $\{[K(N18C6)]_2(CH_3CN)\}[Ni(mnt)_2]$ (2.750 Å) [11]. The axial $K(1)$–$N(1)$ and $K(1)$–$O(5)\#2$ bond lengths for complexes **3**–**5** are in the ranges of 2.878(8)–2.920(5) Å and 2.963(5)–2.983(3) Å, respectively. The bridging oxygen atoms of N18C6 in three complexes give the longest K–O bonds and the maximum deviations from the ether oxygen plane, similar result was also found in $[K(N18C6)]_2[M(SCN)_4]$ (M = Pd, Pt) [10]. The dihedral angles of naphthylene ring and ether oxygen plane of N18C6 in complexes **3**–**5** are in the range 38–39°, which are consistent with that of $[K(N18C6)]_2[M(SCN)_4]$ (M = Pd, Pt) (38°) [10] and that of $\{[K(N18C6)]_2(CH_3CN)\}[Ni(mnt)_2]$ (39.4°) [11]. For complex anions $[M(i\text{-}mnt)_2]^{2-}$ (M = Ni, Pd, Pt), the bond angles of $S(1)$–M–$S(1)\#1$ and $S(2)$–M–$S(2)\#1$ are both 180°, indicating that the MS_4 group is square planar. The plane of the i-mnt ligand is tilted slightly at angle of $\sim 4°$ with respect to the MS_4 metal square plane, indicating the coplanar feature of the $[M(i\text{-}mnt)_2]^{2-}$ complex anions. In complexes **1**–**3**, the bond angles of $S(1)$–$C(21)$–$S(2)$, 108.4 – 110.6°, are much smaller than that of Na_2(i-mnt) (122.8°) [32] and K_2 (i-mnt) (121.3°) [33], implying a chelating coordination nature of the i-mnt ligand to group 10 metal atom.

The remarkable structural features of complexes **3**–**5** are attributed to their supramolecular architectures. As shown in Figure 5, the complex molecules are linked into 1D chains by the bridging K–O(ether) interactions between the adjacent $[K(N18C6)]^+$ units. In each bridging cationic dimer$\{[K(N18C6)]_2\}^{2+}$, there is a square planar K_2O_2 group with K$\cdots$K distance of ~ 4.4 Å, indicating a weak repulsive force. What's novel is that the resulting chains pack into novel 2D networks through interchainπ–π stacking interactions between the neighboring naphthylene moieties of N18C6.

π–π Stacking interactions of benzene or phenyl as ideal models have been extensively studied in theory and experiments. However, so far, π–π interaction of naphthylene group has been rarely studied and there are several examples with few details [34–36], we recently engaged in this study. The reported stacking geometries of naphthylene group include slip much displaced [34], parallel roughly face-to-face [10], parallel much displaced [10, 35], parallel displaced face-to-face [11] and T-shape geometry [36, 37]. In this paper, complexes **3**–**5** display a typical stacking model of

naphthylene group which is similar to that of $\{[K(N18C6)]_2(CH_3CN)\}[Ni(mnt)_2]$ [11]. To describe the π–π interactions in complexes **3**–**5** and as shown in Scheme 1, the naphthylene moiety of N18C6 is divided into two six-member rings, i.e. the inner six-member ring (A or A′) and the outer one (B or B′). The data of the π–π stacking interactions in complexes **3**–**5** are summarized in Table 5. For complex **3**, π–π stacking interactions occur between two adjacent parallel naphthylene moieties with the interplanar separation of 3.46 Å, lying within the common stacking region for aromatic groups (3.3–3.8 Å) [38]. The centroid–centroid distance of two stacking inner rings (A and A′) is 3.66 Å which is much shorter than that of the stacking inner–outer rings (4.91 Å for A–B′ or A′–B) and some other reported values (4.6 Å [34], 4.83 Å [35] and $[K(N18C6)]_2[M(SCN)_4]$ (M = Pd, Pt) (4.0 Å) [10]). The displaced angles for stacking inner–inner (A–A′) and outer–inner (A–B′ or B–A′) rings are 19° and 45.2°, respectively. Thus, it could be found that significant π–π interactions mainly take place between two stacking inner six-member rings (A–A′) and two stacking naphthylene groups are much displaced, exhibiting a parallel offset face-to-face arrangement. The same results take place in complex **3** and **5** (see Table 5 for stacking data).

Conclusion

The crystal structure studies in this paper together with those of some previous papers show that the coordination behaviors of N15C5 with Na$^+$ are changeful while those of N18C6 with K$^+$ are almost changeless. For the complexes of N15C5 with Na$^+$, such as **1**, **2** and $[Na(N15C5)]_2[M(SCN)_4]$ (M = Pd, Pt), the differences are shown as the coordination numbers of sodium atoms (ranging from 6 to 7 and even higher) and as the arrangements of N15C5 to sodium ions (mono-caped shape and sandwich manner). However, the N18C6 potassium complexes, such as **3**–**5**, $[K(N18C6)]_2[M(SCN)_4]$ (M = Pd, Pt) and $\{[K(N18C6)]_2(CH_3CN)\}[Ni(mnt)_2]$, give the same coordination number (8), and the similar arrangements of N18C6 to potassium ions (the distorted
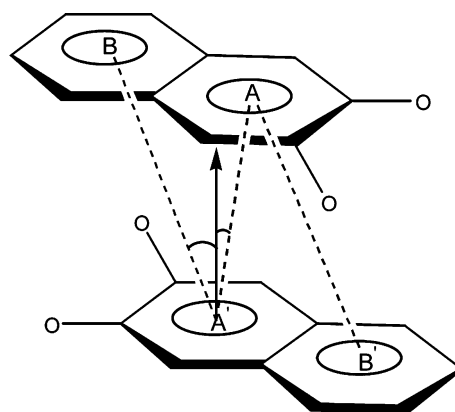
Scheme 1. The stacking model of the naphthylene group of N18C6 in complexes **3**–**5**, symmetry codes: for **3**, $-x + 2$, $-y + 1$, $-z$. for **4**, $-x + 2$, $-y + 1$, $-z + 1$. for **5**, $-x + 1$, $-y + 2$, $-z$.

Table 5. Data of π–π stacking interactions in complexes **3–5**

Complex	Interplanar separation[a] (h /Å)	centroid–centroid distance (d/Å)		displaced angle[b] ($\theta/°$) (cos $\theta = h/d$)	
		A···A′[c]	A···B′[c] or B···A′[c]	A···B′[c] or B···A′[c]	
1	3.46	3.66	4.91	19	45.2
2	3.48	3.67	4.90	18.5	44.7
3	3.47	3.64	4.84	17.6	44.2

[a] The interplanar separations of the stacking naphthylene groups are given instead of that of the divided six-member rings owing to the parallel feature of naphthylene rings. [b] It is formed between the ring-centroid vector and the ring normal to one of the six-member rings. [c] Symmetry codes: for 3, −x + 2, −y + 1, −z. for 4, −x + 2, −y + 1, −z + 1. for 5, −x + 1, −y + 2, −z.

hexagonal bipyramid). For the supramolecular assemblies, the N15C5 sodium complexes with different counter-dianions, such as $[M(SCN)_4]^{2-}$ (M = Pd, Pt), $[Pd(mnt)_2]^{2-}$ and $[Pd(i\text{-}mnt)_2]^{2-}$, display various supramolecular assemblies. On the contrary, the supramolecular assemblies of N18C6 potassium complexes containing different counter-dianions, such as $[M(SCN)_4]^{2-}$ (M = Pd, Pt), $[M(i\text{-}mnt)_2]^{2-}$ (M = Ni, Pd, Pt) and $[Ni(mnt)_2]^{2-}$, afforded similar 2D supramolecular assemblies, i.e. the 1D chains constructed by K–O or/and K–N bonds are further assembled into a 2D network by inter-chain π–π stacking interactions. Moreover, the stacking model of naphthylene group in N18C6 potassium complexes are slightly influenced by different complex anions.

Supplementary material

Crystallographic data for the structural analysys of complexes **1–5** have been deposited with Cambridge Crystallographic Data Center, CCDC Nos. 216846, 216864, 216840, 216867 and 216848, respectively. 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; E-mail: deposit@ccdc.cam.ac.uk).

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