



# One-dimensional Chain Crown Ether Complexes. Synthesis and Crystal Structure of Benzo-18-Crown 6 Complexes with $\text{Na}_2[\text{M}(\text{SCN})_4]$ ( $\text{M} = \text{Pd}, \text{Pt}$ ) \*

DA-CHENG LI<sup>1</sup>, ZENG-XIN LI<sup>1,2</sup>, JIAN-MIN DOU<sup>1,\*\*</sup> and DA-QI WANG<sup>1</sup>

<sup>1</sup>Department of Chemistry, Liaocheng University, Liaocheng 252000, P.R. China; <sup>2</sup>Department of Chemistry, Qingdao Teacher's College, Qingdao University 266000, P.R. China

(Received: 3 October 2002; in final form: 5 February 2003)

**Key words:** one-dimensional chain, benzo-18-crown-6, Pd complex, Pt complex, synthesis and crystal structure

## Abstract

Two benzo-18-crown-6 (B18-C-6) complexes:  $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4](\text{H}_2\text{O})$  (**1**) and  $[\text{Na}(\text{B18-C-6})]_2[\text{Pt}(\text{SCN})_4] \cdot 0.5\text{C}_2\text{H}_4\text{Cl}_2$  (**2**) have been synthesized and characterized by elemental analysis, IR spectrum and X-ray diffraction analysis. The crystal of complex **1** belongs to monoclinic, space group  $\text{P}2_1/n$  with cell dimensions,  $a = 1.0481(3)$ ,  $b = 1.2864(3)$ ,  $c = 1.7003(4)$  nm,  $\beta = 93.626(4)^\circ$ ,  $V = 2.2879(9)$  nm<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.491$  g/cm<sup>3</sup>,  $F(000) = 1060$ ,  $R_1 = 0.0562$ ,  $wR_2 = 0.1412$  and **2** is triclinic, space group  $\text{P}1$  with cell dimensions,  $a = 0.9581(3)$ ,  $b = 1.2173(3)$ ,  $c = 2.1198(6)$  nm,  $\alpha = 79.522(4)^\circ$ ,  $\beta = 77.911(4)^\circ$ ,  $\gamma = 78.617(4)^\circ$ ,  $V = 2.3442(11)$  nm<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.626$  g/cm<sup>3</sup>,  $F(000) = 1154$ ,  $R_1 = 0.0515$ ,  $wR_2 = 0.0612$ . Two complexes show one-dimensional chain of  $[\text{Na}(\text{B18-C-6})]^+$  complex cations and  $[\text{M}(\text{SCN})_4]^{2-}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) complex anion bridged by Na–O–Na interactions of  $\text{H}_2\text{O}$  molecule or Na–O bond of B18-C-6 between adjacent  $[\text{Na}(\text{B18-C-6})]^+$  units respectively.

## Introduction

Since Pedersen reported the synthesis and cation complexing characteristics of the crown ethers [1], there has been increasing interest in these compounds because of their coordination abilities and potential applications in catalysis, solvent extraction, isotope separation and materials science [2–5]. Crown ethers exhibit an extremely versatile range of interaction with alkali metal, alkali earth metal or transition metal cations and various types of complexes were synthesized and characterized structurally by X-ray single crystal structure determination [6–7]. Up to now, benzo-18-crown-6 complexes characterized structurally included:  $[\text{Ba}(\text{B18-C-6})(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ ,  $[\text{Sr}(\text{B18-C-6})(\text{ClO}_4)_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  [8],  $[\text{Ru}_6\text{C}(\text{CO})_{14}\{(\eta^6\text{-C}_6\text{H}_4\text{C}_{10}\text{H}_{20}\text{O}_6)(\text{NH}_4)\}][\text{PF}_6]$  [9],  $[(\text{B18-C-6})(\text{SbF}_3)]$  [10],  $[\text{K}(\text{B18-C-6})]_3$  [11],  $\{[\text{Rb}(\text{B18-C-6})]\text{NCS}\}_2$  [12],  $\{[\text{K}(\text{B18-C-6})]_2[\text{Hg}(\text{SCN})_4]\}_2$  [13]; one-dimensional chain complexes:  $[\text{K}(\text{B18-C-6})]_2\text{I}_8 \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ ,  $[\text{K}(\text{B18-C-6})]_2\text{I}_{12}$  [11],  $[\text{K}(\text{B18-C-6})]_2[\text{Cd}(\text{SCN})_3]$  [13],  $[\text{K}(\text{B18-C-6})]_2[\text{Hg}_2\text{I}_6]$  [14] and multi-dimensional network complexes:  $[\text{K}(\text{B18-C-6})][\text{Zn}(\text{CN})_3] \cdot \text{H}_2\text{O}$  [15],  $[\text{Zn}(\text{CH}_2\text{I})(\text{I})(\text{B18-C-6})]_{0.7}[\text{Zn}(\text{I}_2)(\text{B18-C-6})]_{0.3} \cdot \text{CH}_2\text{Cl}_2$  [16]. We have synthesized and characterized a series of one-dimensional 18-crown-6, B18-crown-6, DB-18-crown-6 complexes and inorganic counterparts are square plane  $[\text{ML}_4]^{2-}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{L} = \text{SCN}, \text{NO}_2$ ) [17–20],  $[\text{Cu}(\text{mnt})_2]^{2-}$  [21] and two-

dimensional network complexes  $[\text{K}(\text{18-C-6})]_2[\text{Cd}(\text{mnt})_2]$ ,  $[\text{Na}(\text{DB18-C-6})(\text{H}_2\text{O})_2][\text{Na}(\text{DB18-C-6})(\text{SCN})_2]$ ,  $[\text{Na}(\text{B15-C-5})]_2[\text{Pt}(\text{SCN})_6]$  and  $[\text{Na}(\text{DB18-C-6})]_2[\text{Pt}(\text{SCN})_6]$  [22–24]. In this presentation, the synthesis and characterization of one-dimensional chain benzo-18-crown-6 complexes:  $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4](\text{H}_2\text{O})$  (**1**) and  $[\text{Na}(\text{B18-C-6})]_2[\text{Pt}(\text{SCN})_4] \cdot 0.5\text{C}_2\text{H}_4\text{Cl}_2$  (**2**) have been reported based on the basis of previous work.

## Experimental

IR spectra of the complexes in KBr pellets were measured on Nicolet-460 FT-IR spectrometer in the range 4000–400  $\text{cm}^{-1}$ . The microanalytical data were obtained from a Perkin-Elmer 2400 II analyser.

Benzo-18-crown-6 was supplied friendly by Prof. Qin Sheng-Ying of Department of Chemistry, Sichuan University. All other chemicals were commercial products and were used as supplied.

### Preparation of $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4](\text{H}_2\text{O})$ (**1**)

The complex **1** was prepared by adding 10 mL aqueous mixture of  $\text{PdCl}_2$  (0.025 mol L<sup>-1</sup>) and  $\text{NaSCN}$  (2 mol L<sup>-1</sup>) to 10 mL benzo-18-crown-6 (0.1 mol L<sup>-1</sup>) in 1,2-dichloroethane solution. The reaction mixture was stirred for 2 hours at room temperature and then organic phase was separated. The single crystal was obtained from 4:1 diethyl ether/1,2-dichloroethane solution, m.p. 124–125°C (Anal.:  $\text{C}_{36}\text{H}_{50}\text{N}_4\text{O}_{13}\text{S}_4 \text{Na}_2\text{Pd}$ , Calcd. C, 42.08; H, 4.87; N, 5.45;

\* Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82303 (13 pages).

\*\* Author for correspondence, E-mail: jmdou@lake.lctu.edu.cn

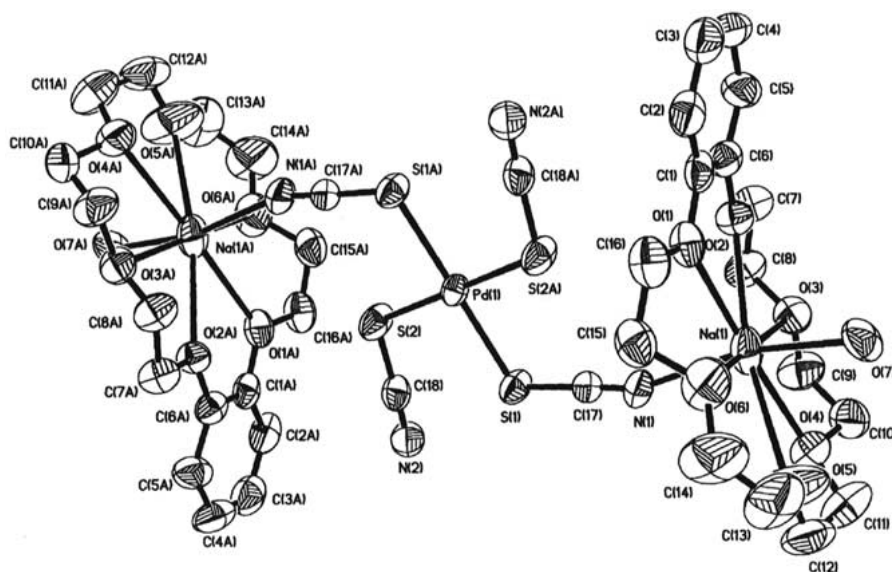


Figure 1. The structure of complex 1.

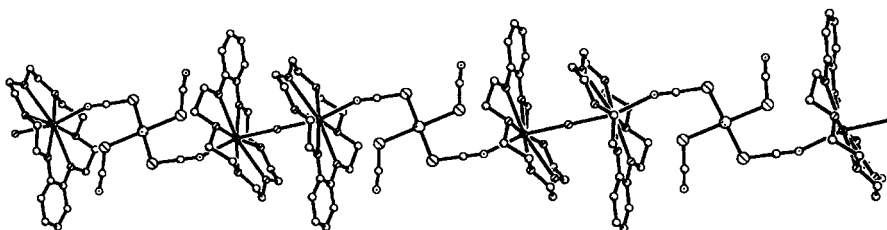


Figure 2. Packing diagram of complex 1.

Table 1. X-ray diffraction data for complexes 1 and 2

Complex	1	2
Empirical formula	C <sub>36</sub> H <sub>50</sub> N <sub>4</sub> O <sub>13</sub> S <sub>4</sub> Na <sub>2</sub> Pd	C <sub>37</sub> H <sub>50</sub> N <sub>4</sub> O <sub>12</sub> S <sub>4</sub> Na <sub>2</sub> Pt
Formula weight	1027.42	1147.57
Crystal size/mm	0.25 × 0.20 × 0.10	0.30 × 0.20 × 0.20
Temperature/K	293 (2)	298 (2)
Crystal system	monoclinic	triclinic
Space group	P2 <sub>1</sub> /n	P1
a/nm	1.0481(3)	0.9581(3)
b/nm	1.2864(3)	1.2173(3)
c/nm	1.7003(4)	2.1198(6)
α/°	90	79.522(4)
β/°	93.626(4)	77.911(4)
γ/°	90	78.617(4)
V/nm <sup>3</sup>	2.2879(9)	2.2442(11)
Z	2	2
D/g cm <sup>-3</sup>	1.491	1.626
F(000)	1060	1154
Theta range/°	1.99 < θ < 23.35	2.11 < θ < 25.03
Reflection collected	10232	11966
Unique reflections	3314	7909
R <sub>1</sub>	0.0562	0.0515
wR <sub>2</sub>	0.1412	0.0612
Largest diff. peak and hole/×10 <sup>2</sup> e nm <sup>-3</sup>	2.86, -4.78	9.79, -7.79

S, 12.46. Found: C, 42.55; H, 4.90; N, 5.46; S, 12.48). Selected FT-IR ( $\nu/\text{cm}^{-1}$ ): 2906 (m), 2110 (s), 1448 (m), 1351 (m), 1248 (m), 1105 (s), 963 (m), 838 (m), 510 (m).

#### Preparation of $[\text{Na}(\text{B18-C-6})]_2[\text{Pt}(\text{SCN})_4] \cdot 0.5\text{C}_2\text{H}_4\text{Cl}_2$ (**2**)

The reaction is analogous to that of **1** using  $\text{Na}_2\text{PtCl}_4$  instead of  $\text{PdCl}_2$ , m.p. 117–118 °C. Anal.  $\text{C}_{37}\text{H}_{50}\text{ClN}_4\text{O}_{12}\text{S}_4$   $\text{Na}_2\text{Pt}$ , Calcd. C, 38.72; H, 4.36; N, 4.88, S; 11.15. Found: C, 38.71; H, 4.57; N, 4.56; S, 11.60). FT-IR  $\nu/\text{cm}^{-1}$ : 2910 (m), 2112 (s), 1438 (m), 1353 (m), 1247 (m), 1110 (s), 964 (s), 837 (m), 514 (m).

#### Determination of crystal structure

The X-ray diffraction experiments for complexes **1** and **2** were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.071073$  nm) radiation. The structure was solved by direct method and expanded using Fourier techniques with Shelxl-97 program. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations. Crystallographic data for complexes **1** and **2** are listed in Table 1.

### Crystal structure description and discussion

#### Complex 1

The crystal structure and stereogram of the complex **1** are shown in Figures 1 and 2. Atomic coordinates and thermal parameters are listed in Table 2 and the selected bond lengths and angles are shown in Table 3. It consists of two  $[\text{Na}(\text{B18-C-6})]^+$  complex cations and a  $[\text{Pd}(\text{SCN})_4]^{2-}$  complex anion. The Pd atom is located on the twofold axis and does not bond directly to any O atom of the crown ether. Pd atom is coordinated by four S atoms from four SCN groups and  $[\text{Pd}(\text{SCN})_4]^{2-}$  is in square planar configuration. The average bond lengths of Pd–S, S–C, C–N are 0.2329, 0.1661, 0.1134 nm respectively, which are consistent with the corresponding values in compound  $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4](\text{H}_2\text{O})$  [25].

In the complex cation  $[\text{Na}(\text{B18-C-6})]^+$ , sodium ion lies within the crown ether. Lengths of Na–O bond are in the range from 0.2587 to 0.2864 nm.  $\text{Na}^+$  ion is 0.01853 nm out of the ether oxygen plane formed by six ether oxygen atoms.  $\text{Na}^+$  ion is also coordinated by one N atom from the SCN group at the distance of 0.2395(8) nm, which is consistent with the corresponding value in complex  $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4](\text{H}_2\text{O})$  [25] [0.2417(4) nm]. The remainder of its coordinating sphere is occupied by O atom of water molecule at the distance of 0.2389(3) nm. The same O atom of the water molecule also connects one of  $\text{Na}^+$  ion of another  $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4]$  group, forming one-dimensional infinite chain structure. The Na–O–Na bond angle is 180°. Two phenyl rings of  $[\text{Na}(\text{B18-C-6})]_2[\text{Pd}(\text{SCN})_4]$  group are *trans* arrangement with respect to Pd atom.

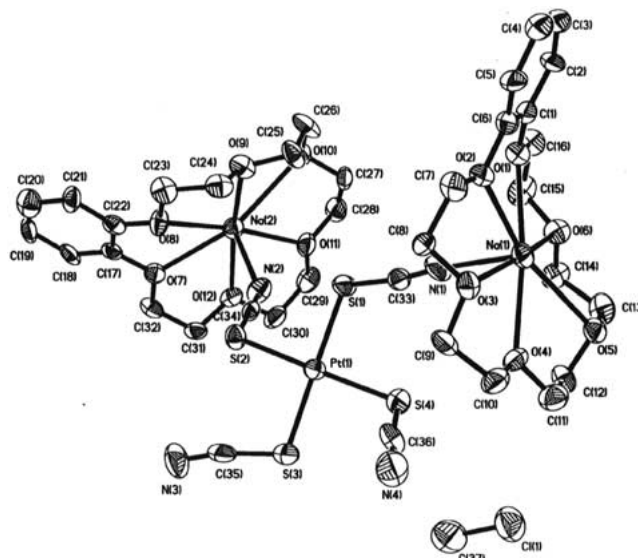


Figure 3. The crystal structure of complex **2**.

#### Complex 2

Atomic coordinates and thermal parameters of complex **2** are listed in Table 4 and the selected bond lengths and angles are shown in Table 5. The crystal structure and packing in a crystal unit cell of **2** is shown in Figures 3 and 4. It also consists of two  $[\text{Na}(\text{B18-C-6})]^+$  complex cations and a  $[\text{Pt}(\text{SCN})_4]^{2-}$  complex anion. Pt atom is coordinated by four S atoms from four SCN groups and  $[\text{Pt}(\text{SCN})_4]^{2-}$  is distorted square planar configuration. The average bond lengths of Pt–S, S–C, C–N are 0.2319, 0.1645, 0.1148 nm respectively.

In the complex cation  $[\text{Na}(\text{B18-C-6})]^+$ , sodium atom lies within the crown ether ring.  $\text{Na}(1)^+$  ion is 0.00294 nm out of the ether oxygen plane formed by six ether oxygen atoms. The five  $\text{Na}(1)$ –O bond lengths are in the range from 0.2544 to 0.2701 nm. However, the bond lengths of  $\text{Na}(1)$ –O(5) is 0.3000(5) nm, which are longer than other  $\text{Na}(1)$ –O values. This situation is also found in complex  $\{[\text{Na}(\text{B18-C-6})][\text{Na}(\text{B18-C-6})(\text{H}_2\text{O})]\}[\text{Cu}(\text{mnt})_2]$  [21].  $\text{Na}(1)^+$  ion is also coordinated by N atom from SCN ligand of  $[\text{Pt}(\text{SCN})_4]^{2-}$  complex anion and the distance of  $\text{Na}(1)$ –N(1) is 0.2400(7) nm.

The  $\text{Na}(2)$ –O bond lengths are in the range from 0.2507 to 0.2887 nm.  $\text{Na}(2)^+$  ion is 0.00484 nm out of the ether oxygen plane formed by six ether oxygen atoms.  $\text{Na}(2)^+$  ion is coordinated by N atom from SCN ligand of  $[\text{Pt}(\text{SCN})_4]^{2-}$  complex anion and the distance of  $\text{Na}(2)$ –N(2) is 0.2417(7) nm. Two  $[\text{Na}(\text{B18-C-6})]^+$  complex cations are *cis* orientation with respect to Pt atom. The dihedral angle of two ether-oxygen planes is 128.4°. The remainders of coordinating sphere of  $\text{Na}(1)$ ,  $\text{Na}(2)$  atoms are made up of one oxygen atom O(5)#1, O(10)#2 from another B18-C-6 ligand of the complex cation  $[\text{Na}(\text{B18-C-6})]^+$  at the distance of 0.2648(5) and 0.2562(5) nm respectively. Thus  $[\text{Na}(\text{B18-C-6})]^+$  complex cations and  $[\text{Pt}(\text{SCN})_4]^{2-}$  complex anion form an one-dimensional chain structure bridged by Na–O interactions between adjacent  $[\text{Na}(\text{B18-C-6})]^+$  units.

Table 2. Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^5$  nm<sup>2</sup>) of complex **1**

atom	x	y	z	U (eq)	atom	x	y	z	U (eq)
Pd(1)	10000	0	5000	58(1)	C(4)	3426(13)	845(8)	6518(10)	127(5)
Na(1)	6537(3)	3740(3)	4645(2)	102(1)	C(5)	3735(10)	1065(7)	5725(7)	105(3)
S(1)	10189(2)	1280(2)	4041(1)	78(1)	C(6)	4771(9)	1753(7)	5636(6)	79(2)
S(2)	11571(3)	-974(2)	4438(1)	93(1)	C(7)	4563(9)	1516(7)	4236(5)	88(3)
N(1)	8426(7)	2855(6)	4289(4)	98(2)	C(8)	5309(10)	1812(7)	3547(5)	99(3)
N(2)	12514(8)	60(6)	3151(5)	98(2)	C(9)	5624(11)	3246(9)	2717(5)	117(4)
O(1)	6390(6)	2858(5)	6089(3)	84(2)	C(10)	5547(10)	4405(11)	2726(6)	118(4)
O(2)	5170(5)	2053(4)	4906(3)	78(2)	C(11)	6749(17)	5796(10)	3246(8)	149(5)
O(3)	5216(5)	2913(5)	3469(3)	92(2)	C(12)	7719(15)	6148(9)	3811(11)	146(5)
O(4)	6585(7)	4760(5)	3263(4)	115(2)	C(13)	7964(17)	6228(10)	5206(13)	187(7)
O(5)	7530(12)	5806(8)	4542(7)	221(6)	C(14)	8358(18)	5573(14)	5842(10)	200(7)
O(6)	7672(8)	4674(7)	5932(5)	141(3)	C(15)	8210(10)	3843(9)	6411(6)	108(3)
O(7)	5000	5000	5000	110(3)	C(16)	7205(10)	3243(8)	6751(6)	102(3)
C(1)	5436(9)	2188(7)	6274(6)	79(2)	C(17)	9136(8)	2208(6)	4199(4)	69(2)
C(2)	5131(11)	1982(9)	7043(5)	106(4)	C(18)	12116(8)	-328(6)	3682(5)	77(2)
C(3)	4109(14)	1289(11)	7143(8)	125(4)					

Table 3. Selected bond lengths (nm) and angles (°) of complex **1**

Pd(1)–S(1)	0.2335(2)	Na(1)–N(1)	0.2395(8)	O(3)–C(8)	0.1426(10)
Pd(1)–S(2)	0.2322(2)	S(1)–C(17)	0.1659(9)	O(3)–C(9)	0.1439(10)
Na(1)–O(1)	0.2717(7)	S(2)–C(18)	0.1662(10)	O(4)–C(10)	0.1450(12)
Na(1)–O(2)	0.2653(7)	N(1)–C(17)	0.1134(9)	O(4)–C(11)	0.1344(13)
Na(1)–O(3)	0.2587(7)	N(2)–C(18)	0.1134(9)	O(5)–C(12)	0.1345(15)
Na(1)–O(4)	0.2694(8)	O(1)–C(1)	0.1372(10)	O(5)–C(13)	0.1308(17)
Na(1)–O(5)	0.2864(9)	O(1)–C(16)	0.1456(10)	O(6)–C(14)	0.1376(15)
Na(1)–O(6)	0.2705(8)	O(2)–C(6)	0.1389(9)	O(6)–C(15)	0.1438(12)
Na(1)–O(7)	0.2389(3)	O(2)–C(7)	0.1445(9)		
S(1)–Pd(1)–S(1)#1	180.0	C(17)–S(1)–Pd(1)	107.9(3)		
S(1)–Pd(1)–S(2)#1	90.02(8)	C(18)–S(2)–Pd(1)	109.6(3)		
S(1)#1–Pd(1)–S(2)#1	89.98(8)	N(1)–C(17)–S(1)	178.1(8)		
S(1)–Pd(1)–S(2)	90.02(8)	N(2)–C(18)–S(2)	176.1(8)		
S(1)#1–Pd(1)–S(2)	89.98(8)	N(1)–Na(1)–O(3)	91.1(3)		
S(2)#1–Pd(1)–S(2)	180.0	N(1)–Na(1)–O(4)	87.1(2)		
N(1)–Na(1)–O(1)	97.2(2)	N(1)–Na(1)–O(5)	96.7(4)		
N(1)–Na(1)–O(2)	96.8(2)	N(1)–Na(1)–O(6)	95.0(3)		

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

## Conclusion

The complexes of B18-C-6 with Na<sub>2</sub>[M(SCN)<sub>4</sub>] (M = Pd, Pt): [Na(B18-C-6)]<sub>2</sub>[Pd(SCN)<sub>4</sub>](H<sub>2</sub>O) (**1**) and [Na(B18-C-6)]<sub>2</sub>[Pt(SCN)<sub>4</sub>].0.5C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (**2**) were synthesized in the same condition and characterized by elemental analysis, IR and X-ray diffraction analysis. **1** and **2** are made up of two [Na(B18-C-6)]<sup>+</sup> complex cations and one [M(SCN)<sub>4</sub>]<sup>2-</sup> complex anion. **1** displays an one-dimensional chain of [Na(B18-C-6)]<sup>+</sup> complex cations and [Pd(SCN)<sub>4</sub>]<sup>2-</sup> complex anion bridged by O atom of H<sub>2</sub>O molecule between adjacent [Na(B18-C-6)]<sup>+</sup> units. **2** also shows an one-dimensional chain of [Na(B18-C-6)]<sup>+</sup> complex cations and [Pt(SCN)<sub>4</sub>]<sup>2-</sup> complex anion bridged by Na–O interactions between adjacent [Na(B18-C-6)]<sub>2</sub>[Pt(SCN)<sub>4</sub>] groups. The crystal structures of **1** and **2** are different, indicating that Pd,

Pt atoms have an influence on their types of crystal structures. This situation occurred in other Pd, Pt complexes: [Na(B15-C-5)]<sub>2</sub>[Pd(SCN)<sub>4</sub>] and {[Na(B15-C-5)] [Na(B15-C-5)(H<sub>2</sub>O)]}[Pt(SCN)<sub>4</sub>] [26].

## Supplementary material

Crystallographic data for the structural analysis of complexes **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 180705, 180706. Copies of this 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 or www: http://www.ccdc.cam.ac.uk).

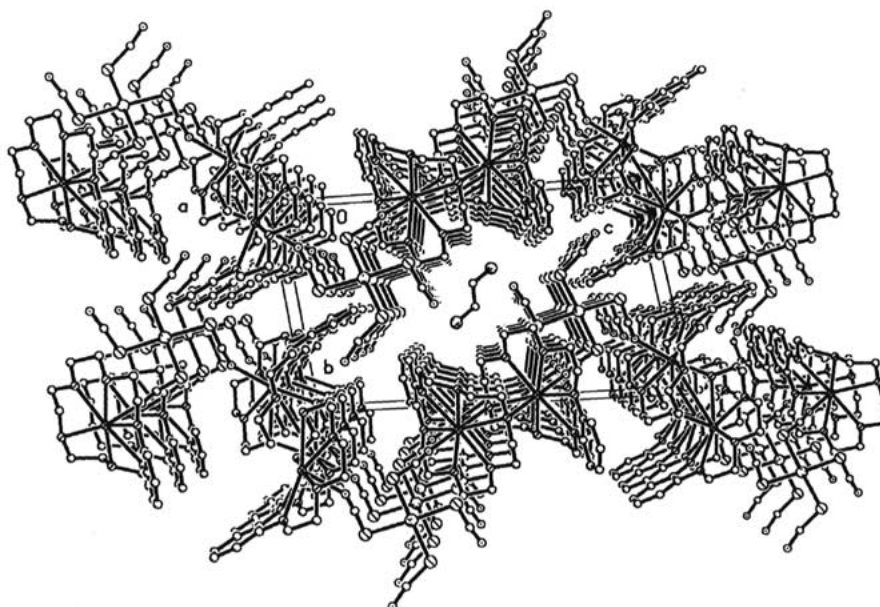


Figure 4. Packing diagram of complex 2.

Table 4. Atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^5 \text{ nm}^2$ ) of complex 2

Atom	x	y	z	U (eq)	Atom	x	y	z	U (eq)
Pt(1)	5201(1)	5982(1)	7495(1)	52(1)	C(8)	11479(8)	7403(7)	6996(4)	65(2)
Na(1)	9575(3)	9373(2)	6013(1)	62(1)	C(9)	10776(9)	6520(7)	6230(4)	78(2)
Na(2)	516(3)	8443(2)	9644(1)	59(1)	C(10)	10604(10)	6728(8)	5520(4)	78(3)
S(1)	5509(2)	7685(2)	7733(1)	67(1)	C(11)	9084(9)	7843(8)	4835(4)	85(3)
S(2)	4220(2)	5565(2)	8592(1)	61(1)	C(12)	7820(8)	8742(8)	4823(4)	69(2)
S(3)	4750(3)	4326(2)	7240(1)	83(1)	C(13)	7053(9)	10754(8)	4850(4)	83(3)
S(4)	6041(3)	6491(2)	6389(1)	92(1)	C(14)	6359(8)	10832(8)	5560(4)	82(3)
Cl(1)	6347(3)	6151(3)	4432(1)	127(1)	C(15)	6821(8)	11515(8)	6474(4)	85(3)
N(1)	7707(8)	8611(6)	6816(3)	94(3)	C(16)	7959(8)	11975(7)	6670(4)	69(2)
N(2)	1921(7)	7365(6)	8806(3)	71(2)	C(17)	43(9)	6160(6)	10864(4)	56(2)
N(3)	4833(9)	2589(8)	8317(4)	115(3)	C(18)	-833(9)	5644(6)	11389(4)	72(2)
N(4)	8220(10)	4724(8)	6000(3)	129(4)	C(19)	-286(11)	5241(7)	11972(4)	77(3)
O(1)	9168(6)	11060(4)	6709(2)	63(1)	C(20)	1079(12)	5359(8)	12020(5)	92(3)
O(2)	11147(5)	9364(5)	6873(2)	61(1)	C(21)	2000(9)	5861(7)	11488(4)	71(2)
O(3)	11307(5)	7489(4)	6340(2)	61(1)	C(22)	1450(8)	6265(6)	10901(4)	57(2)
O(4)	9532(5)	7707(5)	5449(2)	62(1)	C(23)	3606(7)	7011(7)	10413(4)	72(2)
O(5)	8249(5)	9820(5)	4809(2)	66(2)	C(24)	4119(8)	7794(8)	9822(4)	71(2)
O(6)	7427(5)	11139(4)	5826(3)	68(2)	C(25)	3595(9)	9690(8)	9304(4)	91(3)
O(7)	-329(4)	6586(5)	10249(2)	58(1)	C(26)	2612(10)	10754(7)	9444(5)	92(3)
O(8)	2180(5)	6827(4)	10363(2)	67(2)	C(27)	962(11)	11083(6)	8727(4)	81(3)
O(9)	3107(5)	8815(5)	9802(3)	71(2)	C(28)	-585(12)	10920(8)	8672(4)	89(3)
O(10)	1141(6)	10725(4)	9382(2)	75(2)	C(29)	-1812(9)	9543(9)	8524(4)	85(3)
O(11)	-585(6)	9756(5)	8755(2)	75(2)	C(30)	-1714(9)	8255(9)	8630(4)	86(3)
O(12)	-1762(5)	7865(4)	9298(2)	62(1)	C(31)	-1648(8)	6629(7)	9444(4)	61(2)
C(1)	10342(9)	11317(7)	6854(3)	54(2)	C(32)	-1640(7)	6287(6)	10129(4)	65(2)
C(2)	10587(9)	12380(7)	6904(4)	72(2)	C(33)	6804(8)	8178(6)	7164(4)	56(2)
C(3)	11864(13)	12482(9)	7063(4)	90(3)	C(34)	2869(8)	6614(7)	8695(3)	47(2)
C(4)	12995(10)	11571(10)	7167(4)	84(3)	C(35)	4805(9)	3376(8)	7910(5)	75(3)
C(5)	12795(8)	10511(8)	7091(4)	70(2)	C(36)	7304(10)	5444(8)	6199(5)	81(3)
C(6)	11423(9)	10401(8)	6945(3)	64(2)	C(37)	4649(12)	5523(8)	4867(6)	137(4)
C(7)	12168(8)	8390(9)	7037(4)	69(2)					

Table 5. Selected bond lengths (nm) and angles (°) of complex 2

Pt(1)–S(1)	0.2309(2)	Na(1)–O(6)	0.2701(5)	O(4)–C(11)	0.1427(9)
Pt(1)–S(2)	0.2319(2)	Na(1)–N(1)	0.2400(7)	O(5)–C(12)	0.1445(8)
Pt(1)–S(3)	0.2323(2)	Na(1)–O(5)#1	0.2648(5)	O(5)–C(13)	0.1447(8)
Pt(4)–S(4)	0.2325(2)	Na(2)–O(7)	0.2578(6)	O(6)–C(14)	0.1406(8)
S(1)–C(33)	0.1662(9)	Na(2)–O(8)	0.2725(5)	O(6)–C(15)	0.1489(9)
S(2)–C(34)	0.1639(8)	Na(2)–O(9)	0.2707(6)	O(7)–C(17)	0.1405(8)
S(3)–C(35)	0.1663(10)	Na(2)–O(10)	0.2887(6)	O(7)–C(32)	0.1456(8)
S(4)–C(36)	0.1620(10)	Na(2)–O(11)	0.2507(6)	O(8)–C(22)	0.1352(8)
N(1)–C(33)	0.1158(8)	Na(2)–O(12)	0.2694(6)	O(8)–C(23)	0.1456(7)
N(2)–C(34)	0.1173(7)	Na(2)–N(2)	0.2417(7)	O(9)–C(24)	0.1418(8)
N(3)–C(35)	0.1168(10)	Na(2)–O(10)#2	0.2562(5)	O(9)–C(25)	0.1430(9)
N(4)–C(36)	0.1180(10)	O(1)–C(1)	0.1332(8)	O(10)–C(26)	0.1451(9)
Cl(1)–C(37)	0.1979(13)	O(1)–C(16)	0.1444(8)	O(10)–C(27)	0.1414(9)
Na(1)–O(1)	0.2663(6)	O(2)–C(6)	0.1380(8)	O(11)–C(28)	0.1396(10)
Na(1)–O(2)	0.2595(5)	O(2)–C(7)	0.1420(7)	O(11)–C(29)	0.1449(9)
Na(1)–O(3)	0.2626(5)	O(3)–C(8)	0.1416(7)	O(12)–C(30)	0.1404(9)
Na(1)–O(4)	0.2544(6)	O(3)–C(9)	0.1447(8)	O(12)–C(31)	0.1467(8)
Na(1)–O(5)	0.3000(5)	O(4)–C(10)	0.1420(8)		
S(1)–Pt(1)–S(2)	86.71(7)	N(1)–C(33)–S(1)	171.9(7)		
S(1)–Pt(1)–S(3)	176.41(9)	N(2)–C(34)–S(2)	175.9(7)		
S(1)–Pt(1)–S(4)	91.98(8)	N(3)–C(35)–S(3)	169.3(8)		
S(2)–Pt(1)–S(3)	93.37(8)	N(4)–C(36)–S(4)	173.7(10)		
S(2)–Pt(1)–S(4)	176.08(9)	C(33)–S(1)–Pt(1)	108.2(3)		
S(3)–Pt(1)–S(4)	87.72(9)	C(34)–S(2)–Pt(1)	102.4(2)		
Na(1)–O(5)–Na(1)#1	97.46(16)	C(35)–S(3)–Pt(1)	106.2(3)		
Na(2)–O(10)–Na(2)#2	100.51(18)	C(36)–S(4)–Pt(1)	104.0(3)		

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

## References

- C.J. Pedersen: *J. Am. Chem. Soc.* **89**, 7019 (1967).
- S.R. Cooper: *Crown Ether Compounds: Toward Future Applications*, VCH, New York (1992).
- N. Komia, T. Naota, and S.-I. Murahashi: *Tetrahedron Lett.* **37**, 1633 (1996).
- D.L. Clark, D.W. Keogh, and C.L. Palmer: *Angew. Chem. Int. Ed.* **37**, 164 (1998).
- T. Nakamura, T. Akutagawa, K. Honda, A.E. Underhill, A.T. Coomber, and R.H. Friend: *Nature* **394**, 159 (1998).
- R.M. Izatt, K. Pawlak, and J.S. Bradshaw: *Chem. Rev.* **91**, 1721 (1991).
- J.W. Steed: *Coord. Chem. Rev.* **215**, 171 (2001).
- D.L. Hughes, C.L. Mortimer, and M.R. Truter: *Inorg. Chim. Acta* **29**, 43 (1978).
- D.S. Shephard, B.F.G. Johnson, J. Matters, and S. Parsons: *J. Chem. Soc. Dalton Trans.* 2289 (1998).
- J. Lipkowski, M.S. Fonari, V.C. Kravtsov, Y.A. Simonov, E.V. Ganin, and V.O. Gelmboldt: *J. Chem. Crystallogr.* **26**, 823 (1996).
- K.-F. Tebbe and I.Z. Dombrowski: *Anorg. Allg. Chem.* **625**, 167 (1999).
- J. Pickardt and D. Dechert: *Anorg. Allg. Chem.* **625**, 153 (1999).
- H. Haser and K. Huml: *Acta Cryst.* **B34**, 1812 (1978).
- J. Pickardt and P. Wischlinski: *Anorg. Allg. Chem.* **625**, 1527 (1999).
- J. Pickardt and P.Z. Wischlinski: *Naturforsch.* **54B**, 747 (1999).
- A.B. Charette, J.-F. Marcoux, and B.-J. Francine: *J. Am. Chem. Soc.* **118**, 6793 (1996).
- Y. Liu, J.M. Dou, L.Y. Zhu, D.Z. Sun, and P.J. Zheng: *Indian J. Chem.* **39A**, 983 (2000).
- J.M. Dou, X.M. Song, Y. Liu, X. Li, P.J. Zheng, C.X. Du, and Y. Zhu: *Acta Chim. Sinica* **59**, 729 (2001) (in Chinese).
- Z.X. Li, Z.H. Zhong, T. Wang, D.C. Li, D.Q. Wang, J.M. Dou, and P.J. Zheng: *Acta Chim. Sinica* **60**, 1465 (2002) (in Chinese).
- J.M. Dou, Y. Liu, D.Z. Sun, X. Li, P.J. Zheng, C.X. Du, and Y. Zhu: *Acta Chim. Sinica* **59**, 918 (2001) (in Chinese).
- J.M. Dou, D.C. Li, Q.J. Yu, Y. Liu, L.Q. Xu, W.H. Bi, W. Yong, and P.J. Zheng: *Acta Chim. Sinica* **59**, 2162 (2001) (in Chinese).
- D.Q. Wang, Q.J. Yu, and J.M. Dou: *Chin. J. Chem.* **20**, 189 (2002).
- D.Z. Zhu, X.M. Song, J.M. Dou, Y. Liu, and D.Q. Wang: *Chin. J. Chem.* **20**, 424 (2002).
- D.Z. Zhu, T. Wang, X.M. Song, J.M. Dou, D.C. Li, D.Q. Wang, M.M. Wu, and Y.Q. Gao: *Acta Chim. Sinica* **60**, 910 (2002) (in Chinese).
- D.Z. Zhu, X.M. Song, J.M. Dou, Y. Liu, D.Q. Wang, W. Yong, and P.J. Zheng: *J. Chin. Inorg. Chem.* **18**, 697 (2002) (in Chinese).
- Z.H. Zhang, J.M. Dou, Y. Liu, D.Q. Wang, W. Yong, and P.J. Zheng, C.X. Du, and Y. Zhu: *Acta Chim. Sinica* **60**, 1645 (2002) (in Chinese).