

[Na (DB18-C-6) (H₂O)₂] [Na (DB18-C-6) (SCN)₂]: Two-Dimensional Network Complex Assembled by π - π Stacking Interactions, Hydrogen Bonds and Electrostatic Interactions

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A novel two-dimensional network dibenzo-18-crown-6 (DB18-C-6) complex: [Na (DB18-C-6) (H₂O)₂] [Na (DB18-C-6) (SCN)₂] has been isolated and characterized by elemental, IR and X-ray diffraction analysis. The crystal structure belongs to monoclinic, space group $P2_1/c$ with cell dimensions $a = 1.06178(7)$, $b = 1.40243(8)$, $c = 3.03496(19)$ nm, $\beta = 90.4220(10)^\circ$, $V = 4.5292(5)$ nm³, $Z = 4$, $D_{\text{calcd}} = 1.351$ g/cm³, $F(000) = 1936$, $R_1 = 0.0369$, $wR_2 = 0.0821$. The most interesting feature in this structure is that complex cation and complex anion form a two-dimensional network via π - π stacking interactions, hydrogen bonds and electrostatic interactions.

Keywords π - π stacking interactions, hydrogen bonds, crown ether, DB18-crown-6, crystal structure

Introduction

It has been widely agreed that weak interactions could play vital roles in the conformational stability of a wide variety of chemical systems, with applications ranging from materials science to molecular biology. In particular, π - π stacking and hydrogen bonding interactions have been shown to influence the binding properties of nucleic acids, the stability of proteins, the binding affinities in host-guest and supramolecular chemistry. π - π stacking interactions are well characterized by X-ray single structure analysis in complexes of para-X-substituted *L*-phenylalanine (*L*-X-phe; X = H, NO₂, OH, NH₂) with 2,2'-bipyridine or 1,10-phenanthroline,¹ 2,2'-bipyridine,² 1,10-phenanthroline,² phenylmalonate with 2,2'-bipyridine,³ phenylalkanecarboxylate with 2,2'-bipyridine,⁴

pyridinone,⁵ phenazine,⁶ pyrene,⁷ porphyrin,⁸ 2-hydroxyquinoxaline.⁹ In this paper, the synthesis and crystal structure of two-dimensional network complex assembled by phenyl-phenyl stacking interactions, hydrogen bonds and electrostatic interactions: [Na(DB18-C-6)(H₂O)₂]-[Na(DB18-C-6)(SCN)₂] were reported.

Experimental

The synthesis of the title complex was effected by adding aqueous mixture (10 mL) of uranyl acetate (0.025 mol·dm⁻³) and NaSCN (2 mol·dm⁻³) to dibenzo-18-crown-6 (0.1 mol·dm⁻³) in 1,2-dichloroethane (10 mL). The reaction mixture was stirred at room temperature for 2 h and then filtered. The precipitates were dissolved in acetone. The single crystal was obtained from diethyl ether/acetone ($V:V = 4:1$) solution, m. p. 241—243 °C, selected FT-IR ν : 3420, 2928, 2840, 2084, 2056, 1665, 1595, 1508, 1256, 1219, 1126, 953, 750 cm⁻¹; Anal. calcd for C₄₂H₅₂Na₂N₂O₁₄S₂: C 54.89, H 5.66, N 3.05, S 6.96; found C 54.51, H 5.65, N 3.22, S 7.01.

X-ray Crystallography

An orange-yellow crystal (*ca.* 0.6 mm × 0.6 mm × 0.4 mm) was mounted on a glass fiber. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo K α (0.071073 nm) ra-

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diation. The data were collected at temperature of 293(2) K to maximum θ value of 26.43°. The crystal structure belongs to monoclinic, space group $P2_1/c$ with cell dimensions $a = 1.06178(7)$, $b = 1.40243(8)$, $c = 3.03496(19)$ nm, $\beta = 90.4220(10)^\circ$, $V = 4.5292(5)$ nm³, $Z = 4$, $D_{\text{calcd}} = 1.351$ g/cm³, $F(000) = 1936$. The structure was solved by direct methods and expanded using Fourier techniques. All atoms were refined by full-matrix least-squares calculations to $R_1 = 0.0369$ and $wR_2 = 0.0821$ for 4890 unique reflections with $I > 2\sigma(I)$. In the final difference map, the maximum and minimum residuals were 5.15×10^2 e/nm³ and -4.37×10^2 e/nm³, respectively.

Description of the crystal structure and discussion

The crystal structure and packing diagram of unit cell for the complex in crystal are shown in Fig. 1 and Fig. 2, respectively. The title complex consists of a $[\text{Na}(\text{DB18-C-6})(\text{H}_2\text{O})_2]^+$ complex cation and a $[\text{Na}(\text{DB18-C-6})(\text{SCN})_2]^-$ complex anion. In the complex cation $[\text{Na}(\text{DB18-C-6})(\text{H}_2\text{O})_2]^+$, $\text{Na}(1)^+$ ion is coordinated by six O atoms from crown ether molecule. $\text{Na}(1)^+$ ion is 0.00816 nm out of the ether oxygens plane and $\text{Na}(1)-\text{O}$ bond lengths are in the range of 0.26053–0.28117 nm respectively. $\text{Na}(1)^+$ ion is also coordinated by two O atoms from two H_2O molecules. The distances of $\text{Na}(1)-\text{O}(13)$, $\text{Na}(1)-\text{O}(14)$ are 0.22204(19) nm and 0.2333(3) nm, respectively, which are slight shorter than $\text{Na}-\text{O}$ distance (0.2321 nm) in compound $[\text{Na}(\text{18-C-6})\text{H}_2\text{O}](\text{NCS})$.¹⁰ The bond angle of $\text{O}(13)-$

$\text{Na}(1)-\text{O}(14)$ is $166.72(12)^\circ$.

In complex anion $[\text{Na}(\text{DB18-C-6})(\text{SCN})_2]^-$, $\text{Na}(2)^+$ ion is coordinated by six O atoms from crown ether molecule with the bond lengths ranging from 0.25699 nm to 0.27576 nm. The $\text{Na}(2)^+$ ion is 0.00039 nm out of ether oxygen plane. The $\text{Na}(2)^+$ ion is also coordinated by one N(2) atom from the SCN group with a bond length of 0.2413(2) nm, which is consistent with $\text{Na}-\text{N}$ distance [0.2472(8) nm] in compound $[\text{Na}(\text{B15C5})]_2[\text{Pd}(\text{SCN})_4]$.¹¹ It is interesting that the remainder of $\text{Na}(2)^+$ coordinating sphere is made up of S(1) atom from another SCN group. The distance of $\text{Na}(2)-\text{S}(1)$ is 0.29164(10) nm and the bond angle of $\text{N}(2)-\text{Na}(2)-\text{S}(1)$ is $166.96(6)^\circ$.

In the title complex, the two phenyl ring planes $[\text{C}(1)-\text{C}(6)$ and $\text{C}(31)-\text{C}(36)]$ are almost parallel to each other and the dihedral angle between the two phenyl ring planes is 1.8° . The shortest distance of $\text{C}(3)$ atom to $\text{C}(31)-\text{C}(36)$ plane is 0.3473 nm and the average distance is 0.35207 nm, which is shorter than that of benzene dimer in theoretical studies (0.38–0.39 nm).¹²⁻¹⁴ It indicate that in this molecule there exists strong face-to-face $\pi-\pi$ stacking interactions between the two phenyl ring planes. Between different molecules of the complex, there are also double hydrogen bonds between $\text{H}_2\text{O}[\text{O}(13)]$ molecule in complex cation and N(1) atom of SCN group and O(8) atom of crown ether in complex anion. The distances of $\text{O}(13)-\text{N}(1)$ and $\text{O}(13)-\text{O}(8)$ are 0.2869(3) nm and 0.2851(2) nm, respectively, and the angles of $\text{O}(13)-\text{H}(25)-\text{N}(1)$ and $\text{O}(13)-\text{H}(26)-\text{O}(8)$ are $160(3)^\circ$ and $176(3)^\circ$, respectively. Thus, the complex cation and the complex anion

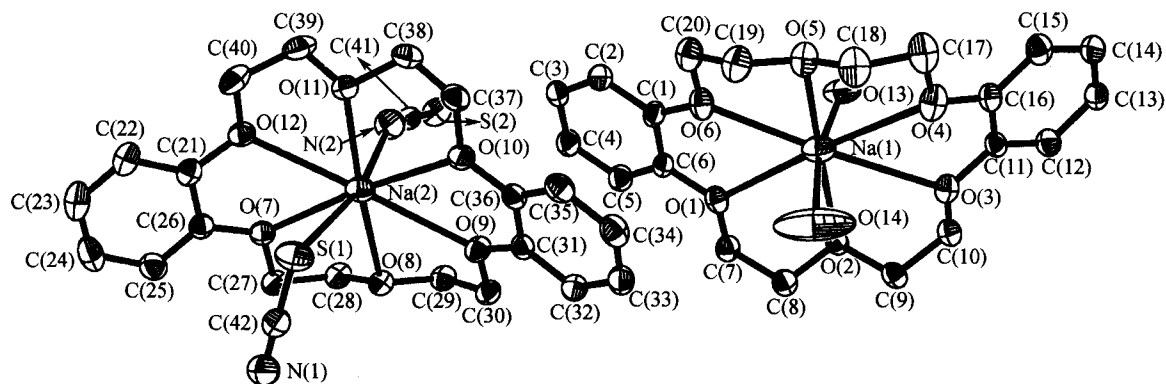


Fig. 1 The structure of title complex.

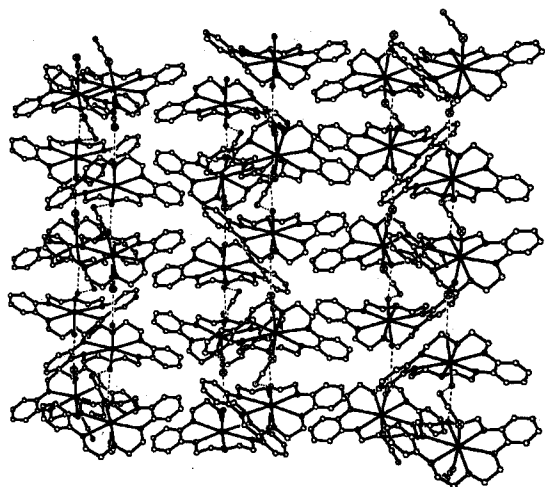


Fig. 2 Packing diagram of title complex.

are packed alternately to form a two-dimensional network via π - π stacking interactions, hydrogen bonds and electrostatic interactions. To our knowledge, there are no such crystallographically characterized complexes in crown ether compounds, and the title complex would be the first example of this type.

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