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Cation-π Interactions. Synthesis and Crystal Structure of Palladium Complex: $[K(DB18C6)]_2[Pd(SCN)_4]$

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Abstract: A novel Pd(II)-dibenzo-18-crown-6 (DB18C6) complex $[K(DB18C6)]_2[Pd(SCN)_4]$ has been isolated and characterized by X-ray diffraction analysis. In the solid state, it displays a quasi-one-dimensional infinite chain of two $[K(DB18C6)]^+$ complex cations and a $[Pd(SCN)_4]^{2-}$ anion bridged by K^+-π interactions between adjacent $[K(DB18C6)]^+$ units.

Keywords: Cation-π interactions, crown ether, crystal structure, palladium complex.

Noncovalent interactions play a dominant role in many forefront areas of modern chemistry, from materials design to molecular biology. Recently, the K^+-π interactions have attracted much attention because of the ion selectivity in potassium channels[1]. In other system, Sunner *et al*. showed the first time by mass spectrometry that K^+ binds to benzene in the gas phase[2]. This finding stimulated the study of the K^+-π interactions. Indeed, the K^+-π interactions have also been identified by X-ray single crystal diffraction analysis for several compounds: K^+-benzene or –phenyl[3], K^+-phospholide anions[4], K^+-boratebenzene[5] and K^+-calixarenes[6]. We have synthesized and characterized a series metal complexes with macrocyclic ligands[7,8]. In present paper, we report the synthesis and crystal structure of the novel complex of DB18C6 with $K_2[Pd(SCN)_4]$ which exist cation-π interactions. This is the first example which exist K^+-π interactions in crown ether compounds.

Preparation

$[K(DB18C6)]_2[Pd(SCN)_4]$ was prepared by adding 10 mL aqueous mixture of $PdCl_2$(0.025 $molL^{-1}$) and KSCN (2 $molL^{-1}$) to 10mL 0.1 $molL^{-1}$ dibenzo-18-crown-6 in 1,2-dichloroethane solution. The reaction mixture was stirred for 2 hours at room temperature and then filtered. The participation was dissolved in acetone. Yield, 0.256 g(90%), m.p. 224-225°C. (Found: C: 46.01, H: 4.25, N: 4.72, $C_{22}H_{24}KN_2O_6Pd_{0.5}S_2$, requires, C: 46.45, H: 4.22, N: 4.92.).

Figure 1. The structure of title complex

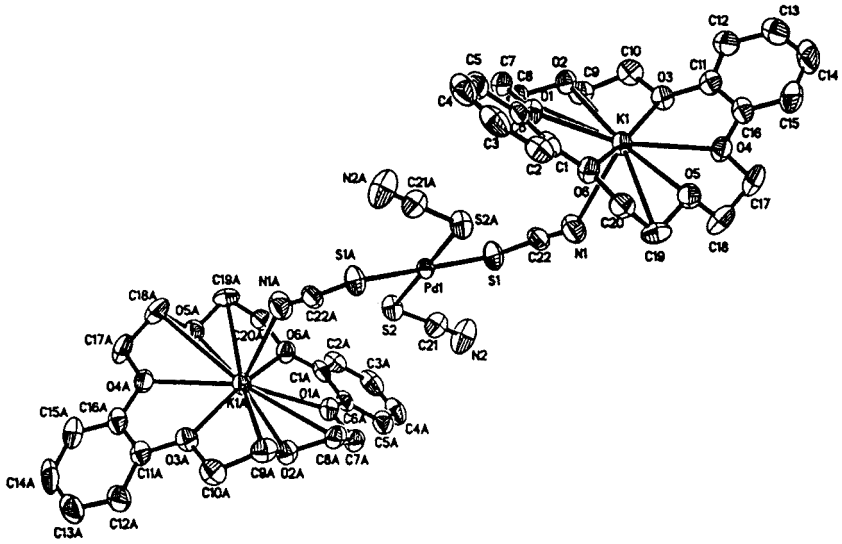
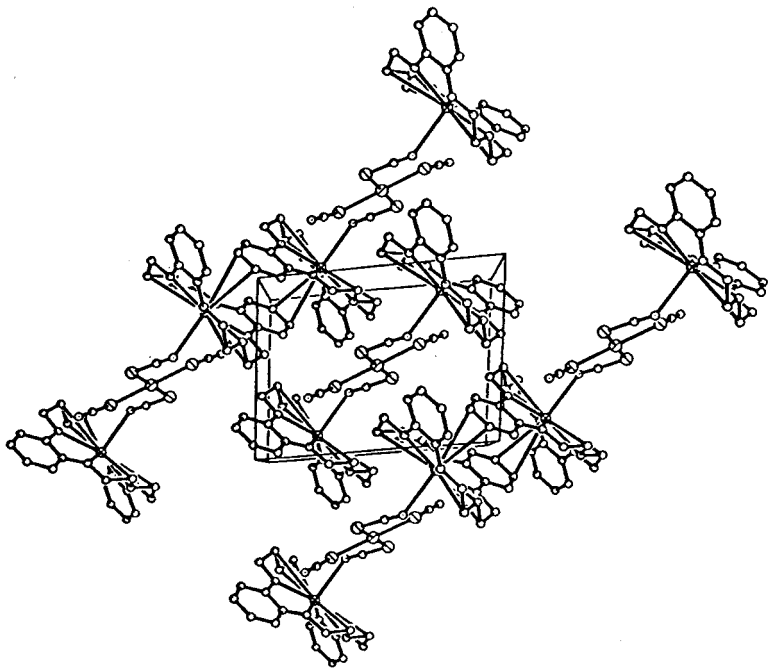


Figure 2. Packing of the title complex in a unit cell



Selected FT-IR ν/cm^{-1}: 2920, 2850, 2108, 1698, 1595, 1504, 1251, 1213, 1127, 960, 940, 750. The single crystal was obtained from 4:1 diethyl ether/acetone solution.

X-ray Crystallography

An orange-red crystal having approximate dimensions of 0.40 x 0.32 x 0.28 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV diffractometer with graphite monochromated Mo-Kα(0.71073Å) radiation. The data were collected at temperature of 293(2) K to maximum θ value of 27.56°. The crystal structure belongs to triclinic, space group P-1 with cell dimensions, a = 8.7375(17), b = 11.990(2), c = 13.180(3) Å, α = 73.56(3), β = 79.88(3) γ = 82.34(3)°, V = 1298.6(4) $Å^3$, Z = 2. The structure was solved by direct methods and expanded using Fourrier techniques. The non-hydrogen atoms were refined by full-matrix least-squares calculations to R=0.0752 and wR2 = 0.1660 for 3268 observed reflections with I>2σ(I). In the final difference map, the residuals are 0.471 and -0.882 e $Å^{-3}$ respectively.

Description of the crystal structure and discussion

The crystal structure and stereogram of the complex packing in a crystal unite cell are shown in **Figure 1** and **Figure 2**. The structure consists of two $[K(DB18C6)]^+$ complex cations and a $[Pd(SCN)_4]^{2-}$ complex anion. The Pd atom is located on the twofold axis and does not bond directly to the O atoms of the crown ether. Pd atom is coordinated by four S atoms from four SCN groups. The bond angles of S1-Pd-S1'and S2-Pd-S2' are 180° and the average bond angles of other S-Pd-S are 90°, indicating that $[Pd(SCN)_4]^{2-}$ is square planar configuration. The average bond lengths of Pd-S, S-C, C-N are 2.3520, 1.682, 1.168 Å respectively, which are consistent with the corresponding values in compound $[K(18C6)]_2[Pd(SCN)_4](H_2O)$[7].

In the complex cation $[K(DB18C6)]^+$, K-O bond lengths are at the range from 2.726 to 2.810 Å. K^+ ion is 0.325 Å out of the ether oxygen plane formed by six ether oxygen atoms. K^+ ion is also coordinated by one N atom from the SCN group at the distance of 2.840(6) Å. The remainder of its coordinating sphere is made up of close K-C(3), K-C(4) contacts with the phenyl ring of the DB18-crown-6 in another $[K(DB18C6)]_2[Pd(SCN)_4]$ molecular, thus forming K-C bridging structure of a quasi-one-dimensional infinite chain between neighboring molecules. The distances of K-C(3), K-C(4) are 3.356(6), 3.347(6) Å respectively. The other quasi-one-dimensional infinite chain structures were found in complexes $K[Nd(O\text{-}2,6\text{-}I\text{-}Pr_2C_6H_3)_4]$[8] and $KBPh_4$[9] which also exist K^+-π interactions. The average bond length are 3.30Å in $K[Nd(O\text{-}2,6\text{-}I\text{-}Pr_2C_6H_3)_4]$ and 3.29Å in $KBPh_4$. The same structure is also found in complexes $[K(DB18C6)]_2[Pt(SCN)_4]$ which we have synthesized and characterized by X-ray crystal structure analysis.

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References and notes

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11. Crystallographic parameters of $[K(DB18C6)]_2[Pd(SCN)_4]$ have deposited in the editorial office of CCL.

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