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The Novel Benzo-15-Crown-5 with Palladium(II) Complex: $[Na(B15C5)]_2[Pd(SCN)_4]$

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Abstract: A novel Pd(II) Benzo-15-crown-5 complex $[Na(B15C5)]_2[Pd(SCN)_4]$ has been isolated and characterized by IR and X-ray diffraction analysis. The crystal structure belongs to monoclinic, space group $P2_1/n$ with cell dimensions, a = 1.0164(6), b = 1.3743(3), c = 1.4987(7) nm, β = 95.248(6)°, V = 2.0847 nm^3, Z = 2, F(000) = 944, R = 0.053, Rw = 0.072. The compound consists of two $[Na(B15C5)]^+$ complex cations and a $[Pd(SCN)_4]^{2-}$ complex anion. Each sodium ion is coordinated by five crown ether oxygen atoms and one N atom from the SCN group of $[Pd(SCN)_4]^{2-}$ to form stable neutral complex.

Keywords: Benzo-15-crown-5, crown ether, crystal structure, palladium complex.

The extensive pioneering study of Pedersen [1] has led to a virtual explosion of solution and solid-state investigation of crown ethers and metal ions which include alkali metal, alkali earth metal, other main-group and transition-metal ions. It is shown that single-crystal X-ray diffraction analysis is a most powerful technique for the characterization of these complexes and numerous solid-state structural studies have appeared through the years. The reported B15C5 complexes structurally characterized by X-ray diffraction analysis have so far included: $[Na(B15C5)ClO_4]$, $[Na(B15C5)_2]ClO_4$, $[Na(B15C5)_2][BPh_4]$[2], $[Na(B15C5)H_2O]I$[3] $[K(B15C5)_2]pic$[4], $[K(B15C5)_2][InBr_4]$[5], $[K(B15C5)_2][InI_4]$[6] and $[K(B15C5)_2]I$[7], $[K(B15C5)_2][Co(NCS)_4]$[8], most of them have sandwich complex cations. We now report the novel B15C5 complex $[Na(B15C5)]_2[Pd(SCN)_4]$ which was established by X-ray diffraction analysis.

Preparation

The title compound was prepared by adding 10 mL aqueous mixture of $PdCl_2$(0.025 $molL^{-1}$) and NaSCN (2 $molL^{-1}$) to 10mL 0.1 $molL^{-1}$ benzo-15-crown-5 in 1,2-dichloroethane solution. The reaction mixture was stirred for 2 hours at room

temperature and then the organic phase was separated. The single crystal was obtained from 4:1 diethyl ether /1,2-dichloroethane solution. M.p. 151-152°C. (Found: C: 41.97, H: 4.80, N: 5.88, for $C_{32}H_{40}N_4O_{10}PdNa_2S_4$, requires, C: 41.71; H: 4.69, N: 6.08). Selected FT-IR ν/cm^{-1}: 2917, 2879, 2118, 2109, 1594, 1504, 1253, 1210, 1125, 1104, 938, 741.

X-ray Crystallography

A red prismatic crystal having approximate dimensions of 0.30 x 0.30 x 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα(0.07107 nm) radiation. The data were collected at temperature of 291±1 K to maximum 2θ value of 55° for 2996 reflections. The crystal structure belongs to monoclinic, space group $P2_1/n$ with cell dimensions, a = 1.0164(6), b = 1.3743(3), c = 1.4987(7) nm, β = 95.248(6)°, V = 2.08470 nm^3, Dcalc = 1.468 g/cm^3, Z = 2, F(000) = 944. 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 = 0.053 and Rw = 0.072 for 2041 observed reflections with I>3σ(I). In the final difference map, the residuals are 7.10 x 10^2 and – 6.60 x 10^2 e/nm^3 respectively.

Description of the Crystal Structure

The crystal structure and packing in a crystal unite cell of the title complex are shown in **Figure 1** and **Figure 2**. The structure consists of two $[Na(B15C5)]^+$ 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 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 0.23695, 0.1677, 0.1164 nm respectively, which are consistent with the corresponding values in compound $[K(18C6)]_2[Pd(SCN)_4]$-(H_2O)[9] and $[K(DB18C6)]_2[Pd(SCN)_4]$[10].

In the complex cation $[Na(B15C5)]^+$, sodium ion is coordinated by five oxygen atoms of the crown ether rings. Na-O bond lengths are at the range from 0.2427 to 0.2497 nm, which are similar to that found in $[Na(B15C5)ClO_4]$[2] and $[Na(B15C5)H_2O]I$[3]. Na^+ ion is 0.0858 nm out of the ether oxygen plane. The five oxygen atoms in the ether ring are not good least-square plane and the deviations of oxygen atoms from the plane is 0.0473 nm. Na^+ ion is also coordinated by one N atom from the SCN group of $[Pd(SCN)_4]^{2-}$at the distance of 0.2472(8) nm. Thus, two $[Na(B15C5)]^+$ complex cations and a $[Pd(SCN)_4]^{2-}$ complex anion form a stable neutral complex.

Figure 1. The structure of title complex

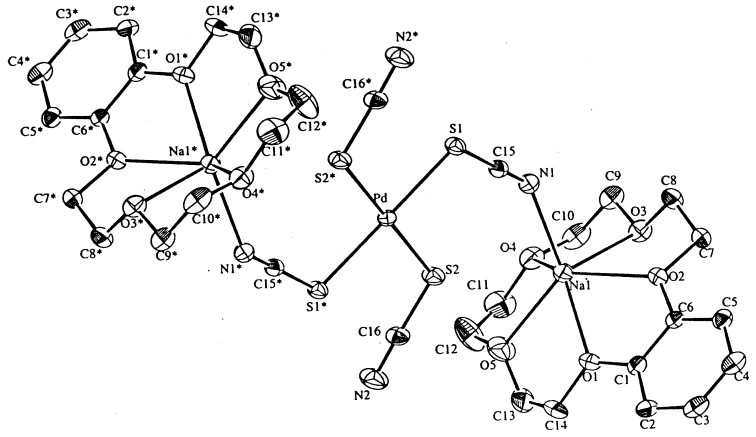
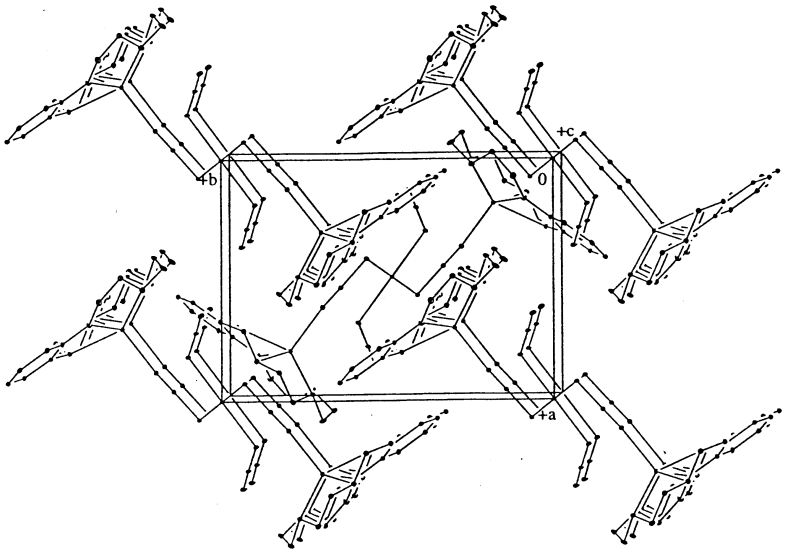


Figure 2. Packing of title complex



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