Crystal Structure of Potassium 2,2′-(2,5-Cyclohexadiene-1,4-diylidene)-bis[propanedinitrile]-1,4,7,10,13,16-hexaoxacyclooctadecane, [K⁺("18-Crown-6")]TCNQ⁻

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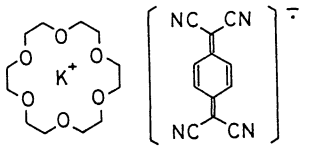
Synopsis. The crystal structure of the title complex was determined by an X-ray diffraction method. The potassium ion is coordinated by six oxygens of a crown ether and two cyano-nitrogens of two TCNQ anion radicals. Both the crown ether dimer and the TCNQ dimer are arranged alternately in the solid.

Macrocyclic polyethers called "crown ether" are known to accommodate metal cations in their cavities.[1] The chemistry of crown ether has been greatly developed within about three decades from many sides, such as analytical chemistry, phase-transfer reactions, and host-guest chemistry.[2] As an extension of crown ether complexes to solid-state chemistry, we have synthesized over 100 kinds of cation-TCNQ-crown ether complexes in the hope of developing highly conducting organic materials.[3-8] Their electrical conductivities and electronic reflection spectra were measured; we found that these two physical properties are correlated very closely to each other. Crown ether-TCNQ complexes are interesting from the viewpoint of solid-state chemistry, since an electronic interaction between TCNQ molecules in a solid can be modified by choosing an appropriate pair comprising a crown ether and a metal-TCNQ salt.[9] In order to discuss the physical properties in more detail, knowledge concerning the crystal structures of crown ether-TCNQ complexes is important. We have thus determined the crystal structure of a complex of [K⁺("18-crown-6")]TCNQ⁻[10] by an X-ray diffraction method. The preliminary results of the crystal structures of [NH_4⁺("18-crown-6")]TCNQ⁻ and [Cs⁺("15-crown-5")$_2$](TCNQ)$_2$⁻ are also reported.[10]

Experimental

Crystal Data. [K⁺("18-crown-6")]TCNQ⁻: K($C_{12}H_{24}O_6$)($C_{12}H_4N_4$), M=507.61, monoclinic, $A2/a$, a=26.613(5), b=8.221(2), c=24.307(5) Å, β=98.70(9)°, V=5256(3) Å^3, Z=8, D_c=1.283 g cm^{-3}, μ(MoK_α)=2.41 cm^{-1}. The black crystal has a parallel-piped shape with an approximate size of 0.52×0.13×0.06 mm^3. Reflection data were collected at room temperature by a θ-2θ scan technique up to 2θ=42° on a Rigaku AFC-3 four-circle diffractometer, using graphite monochromatized MoK_α radiation (λ=0.71069 Å). The data were corrected for Lorentz and polarization factors, but not for absorption.



[K⁺("18-crown-6")]TCNQ⁻

X-Ray Weissenberg photographs showed Laue symmetry of 2/m and systematic absences of the reflections, $k+l$=$2n$+1 for general reflections and h=$2n$+1 (l=$2n$+1) for $h0l$ reflections. This is consistent with a possible space group Aa or $A2/a$. The space group $A2/a$ was assumed; the structure could be solved by a direct method (MULTAN 78).[11] It was refined with anisotropic temperature factors by a block-diagonal least squares procedure (HBLS V),[12] by using 2108 reflections with $|F_o|>3\sigma(|F_o|)$ from 2824 measured reflections. The minimized function was $\sum w(\Delta F)^2$. The weighting function used at the final stage of the refinement was $w=[\sigma^2(F_o)+0.3946|F_o|-0.00131|F_o|^2]^{-1}$. Not all of the hydrogen atoms could be refined reasonably. They were thus relocated at the calculated positions with isotropic temperature factors equal to those of the bonded carbon atoms. They were included in the calculations but were not refined. The atomic scattering factors for neutral atoms were taken from International Tables for X-Ray Crystallography.[13] The atomic coordinates and equivalent isotropic temperature factors[14] are given in Table 1.[15] The final R and R_w indices were 0.086 and 0.051, respectively. The refinement, by assuming the space group Aa, did not give a satisfactory result.

Results and Discussion

Crystal Structure of [K⁺("18-crown-6")]TCNQ⁻. Figure 1 shows the molecular arrangement viewed along the b-axis. Two molecules of the TCNQ anion radicals form a dimer. A potassium ion is included into the cavity of "18-crown-6", as expected.[16] No conformational disorder was found at the ethylene portions of "18-crown-6". Figure 2 shows the overlap of the TCNQ dimers projected normal to the molecular plane. The two TCNQ molecules overlap almost completely. The mode of this molecular overlap is unusual, however, because most of the TCNQ complexes show "ring-external bond type overlaps" of TCNQ molecules in the

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Table 1. Fractional Coordinates and Their Equivalent Isotropic Temperature Factors[14] of the Nonhydrogen Atoms of [K$^+$("18-crown-6")]TCNQ$^-$

Atom	x	y	z	B_{eq} / Å^2
K and "18-crown-6"				
K	0.3324(2)	0.0880(4)	0.1772(2)	4.3
O(1)	0.3482(3)	−0.068(2)	0.2855(4)	5.4
O(2)	0.4067(4)	0.199(2)	0.2649(4)	6.0
O(3)	0.3655(3)	0.427(2)	0.1866(4)	6.1
O(4)	0.2830(3)	0.335(2)	0.1063(4)	5.5
O(5)	0.2236(3)	0.067(2)	0.1279(3)	5.0
O(6)	0.2692(3)	−0.168(2)	0.2015(4)	5.4
C(1)	0.4015(5)	−0.053(2)	0.3100(6)	5.6
C(2)	0.4117(6)	0.127(2)	0.3187(6)	6.1
C(3)	0.4235(6)	0.365(2)	0.2670(6)	6.8
C(4)	0.4184(5)	0.427(3)	0.2077(6)	6.8
C(5)	0.3572(6)	0.494(2)	0.1303(6)	6.5
C(6)	0.2997(5)	0.498(2)	0.1135(6)	6.4
C(7)	0.2297(5)	0.328(2)	0.0860(6)	6.2
C(8)	0.2166(5)	0.149(2)	0.0753(6)	5.5
C(9)	0.2102(5)	−0.101(2)	0.1216(5)	5.5
C(10)	0.2161(5)	−0.177(2)	0.1787(6)	5.8
C(11)	0.2786(5)	−0.246(2)	0.2563(5)	6.1
C(12)	0.3352(5)	−0.235(2)	0.2762(6)	5.7
TCNQ				
N(1)	−0.0215(5)	0.539(2)	0.0887(5)	6.1
N(2)	−0.0728(4)	0.105(2)	0.1696(5)	6.8
N(3)	0.1704(4)	−0.053(2)	−0.0704(5)	7.2
N(4)	0.1249(5)	−0.469(2)	0.0197(5)	7.2
C(21)	0.0151(4)	0.130(2)	0.0761(5)	3.9
C(22)	0.0470(4)	0.202(2)	0.0402(5)	4.1
C(23)	0.0788(4)	0.106(2)	0.0150(5)	3.9
C(24)	0.0802(4)	−0.070(2)	0.0215(5)	3.9
C(25)	0.0474(5)	−0.137(2)	0.0569(5)	3.8
C(26)	0.0163(4)	−0.043(2)	0.0834(5)	4.1
C(27)	−0.0172(5)	0.228(2)	0.1027(5)	4.0
C(28)	−0.0204(5)	0.399(2)	0.0949(5)	4.4
C(29)	−0.0484(5)	0.163(2)	0.1397(5)	4.7
C(30)	0.1117(4)	−0.168(2)	−0.0052(5)	4.3
C(31)	0.1438(5)	−0.105(2)	−0.0410(5)	4.7
C(32)	0.1182(5)	−0.338(2)	0.0079(5)	4.6

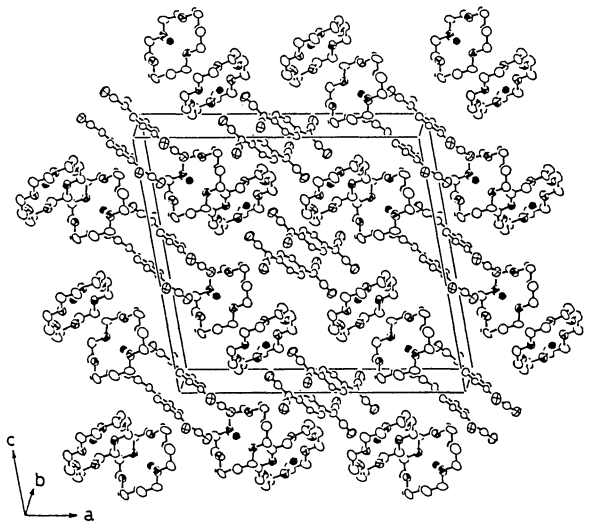

Fig. 1. Molecular arrangement of [K$^+$("18-crown-6")] TCNQ$^-$ complex along the b-axis.[22]

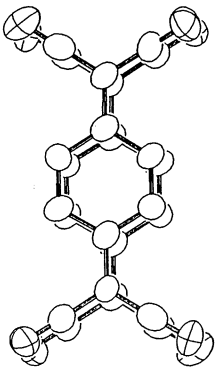

Fig. 2. Overlap of TCNQ$^-$ dimers projected normal to the molecular plane in [K$^+$("18-crown-6")] TCNQ$^-$ crystal.[22]

solid.[17] Two molecules of "18-crown-6" also showed the dimeric structure. The TCNQ dimer and crown ether dimer are located alternately. Since the TCNQ dimer is isolated from the other TCNQ dimers by the presence of neighboring crown ether dimers, a low electrical conductivity and the appearance of a charge-transfer absorption band between the dimeric TCNQ anion radicals are expected from this figure. In fact, this complex showed low electrical conductivity (1.5×10^{-10} S cm^{-1}) at 21 °C for a compressed pellet sample, and a charge-transfer absorption band which peaked at 11.7×10^3 cm^{-1}.[4] The six oxygens of the crown ether lie almost on the same plane. The potassium ion is surrounded by the six oxygens of the crown ether, since the ionic size of the potassium ion fits the cavity of "18-crown-6".[2] The planar arrangement of oxygen atoms and the inclusion of a metal cation into the cavity of the crown ether, as in the present study, have generally been found for a number of crown-ether complexes.[2,18] The distances from K$^+$ to O(1), O(3), and O(5) are slightly longer than those from K$^+$ to O(2), O(4), and O(6) [2.902(8) Å for K$^+$-O(1), 2.837(8) Å for K$^+$-O(2), 2.925(8) Å for K$^+$-O(3), 2.855(8) Å for K$^+$-O(4), 2.969(8) Å for K$^+$-O(5), and 2.819(8) Å for K$^+$-O(6)]. The potassium ion is also coordinated to two cyano-nitrogens (N(2) and N(3)) of two TCNQ anion radicals [3.01(2) Å for K$^+$-N(2), and 2.83(2) Å for K$^+$-N(3)]. The other two cyano groups containing N(1) and N(4) are stretched out toward the b-axis.

The diffraction patterns of Weissenberg photographs of [NH$_4^+$("18-crown-6")]TCNQ$^-$ complex were almost identical to those of [K$^+$("18-crown-6")]TCNQ$^-$. Thus, these two complexes are assumed to be isomorphous. This can be understood in terms of the similar ionic sizes of the two cations (ionic sizes: K$^+$=2.66 Å; NH$_4^+$=2.86 Å).[19] We have also tried to determine the crystal structure of the complex [Cs$^+$("15-crown-5")$_2$](TCNQ)$_2^-$.[20] Because of the distorted structure of "15-crown-5", the atomic positions of the crown ethers could not be determined precisely. The structure is strongly characterized by two-dimensional stacks of the TCNQ molecules along the a-and c-axes.[21]

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10) The following abbreviations of the materials are used in this paper: "TCNQ" for 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bis[propanedinitrile], "18-crown-6" for 1,4,7,10,13,16-hexaoxacyclooctadecane, and "15-crown-5" for 1,4,7,10,13-pentaoxacyclopentadecane. Thus, the names of the complexes are abbreviated to $[K^+$("18-crown-6")$]TCNQ^-$, $[NH_4^+$("18-crown-6")$]TCNQ^-$, and $[Cs^+$("15-crown-5"$)_2](TCNQ)_2^-$.

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20) $[Cs^+$("15-crown-5"$)_2](TCNQ)_2^-$: $Cs(C_{10}H_{20}O_5)_2(C_{12}H_4N_4)_2$, M=981.82, triclinic $P1$ or $P\bar{1}$, a=8.230(2), b=34.307(6), c=8.234(1) Å, α=96.23(1), β=92.73(1), γ=96.18(2)°, V=2293(1) Å^3, Z=2, D_c=1.422 g cm^{-3}, μ(Mo K_α)=8.61 cm^{-1}, R=0.093. Reflection data were collected up to 2θ=48° by the same method described in the experimental section. Of the 7577 reflection measured, 3034 ($|F_o|>5\sigma(|F_o|)$) were used for the refinement. Space group could not be determined conclusively due to the distorted structure of "15-crown-5".

21) One dimensional TCNQ column structure has been found for a number of TCNQ-complexes.[17] Two-dimensional TCNQ-column structure found here will be the first example of the TCNQ-complexes to our knowledge. Cesium ion is sandwiched by two crown ether molecules. This is explained by the fact that cesium ion is too big to be accommodated in the cavity of "15-crown-5". A figure of the molecular arrangement and a Table of fractional coordinates of nonhydrogen atoms are kept as Document No. 8932 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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