**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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**To cite this Article** Rogers, Robin D. , Huggins, Stephen E. , Henry, Rodger F. and Bond, Andrew H.(1992) 'Arene-substituent effects in benzo-15-crown-5 complexes. The crystal structures of 4-aminobenzo-15-crown-5 and $[KI(OH_2)(4\text{-nitrobenzo-15-crown-5})]_2$', Supramolecular Chemistry, 1: 1, 59 — 63

**To link to this Article: DOI:** 10.1080/10610279208027441

**URL:** http://dx.doi.org/10.1080/10610279208027441

*SUPRAMOLECULAR CHEMISTRY*, Vol. 1, pp. 59–63
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# Arene-substituent effects in benzo-15-crown-5 complexes. The crystal structures of 4-aminobenzo-15-crown-5 and $[KI(OH_2)(4\text{-nitrobenzo-15-crown-5})]_2$

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**The crystal structures of two arene substituted benzo-15-crown-5 moieties have been determined. Aminobenzo-15-crown-5 crystallizes as a hydrogen bonded polymer. The interaction between the amino group and the macrocylic oxygen atoms influences the observed conformation. The structure of $[KI(OH_2)((NO_2)benzo\text{-}15\text{-}crown\text{-}5)]_2$ reveals dimer formation via a donor interaction between the nitro group of one crown ether and the $K^+$ ion coordinated to a second ether. In both structures the arene substituent has a dramatic effect on the observed solid state structure.**

## INTRODUCTION

We recently published the crystal structures of $(NO_2)$benzo-15-crown-5, $(NO_2)_2$benzo-15-crown-5, and $(NO_2)_2$dibenzo-18-crown-6·$2CH_3CN$.[1] The structures revealed that the nitro substituents had very little if any effect on the crown ether conformation in the solid state. Each molecule exhibited the same conformation as found for the unsubstituted ether.

We are continuing our investigations in this area by looking at substituents that can themselves interact with the macrocycle and by beginning our study of the complexation chemistry of these substituted benzo crown ethers. The two structures reported here, $(NH_2)$benzo-15-crown-5 and $[KI(OH_2)((NO_2)$benzo-15-crown-5$)]_2$ reveal that the benzo substituent can in fact have a pronounced effect on the observed structures.

## EXPERIMENTAL

### Synthesis

4-Aminobenzo-15-crown-5 was prepared by modification of the literature preparation for 4,5-diaminobenzo-15-crown-5 to the 4-aminobenzo-15-crown-5 derivative.[3] Crystals suitable for the diffraction analysis were obtained by recrystallization from acetone.

4-Nitrobenzo-15-crown-5 was prepared according to the literature.[3] KI (1 mmol) and nitrobenzo-15-crown-5 (1 mmol) were dissolved in 3:1 $CH_3CN$:$CH_3OH$ and stirred at 60 °C for 1 h. Slow evaporation at ambient temperature afforded crystals of the potassium complex.

### X-ray data collection, structure determination, and refinement

Single crystals of the title compounds were mounted in thin-walled glass capillaries, flushed with Ar, and transferred to the goniometer. The space groups were determined to be the centric $P2_1/n$ from the systematic absences. A summary of data collection parameters is given in Table 1. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with $B$ fixed at 5.5 Å$^2$. The amino hydrogen atoms were located from a difference Fourier map and included with fixed contributions ($B$ = 5.5 Å$^2$). The aquo hydrogen atoms were not included in the final refinement. All nonhydrogen atoms were refined with anisotropic temperature factors. The final values of the positional parameters are given in Tables 2 and 3.

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**Table 1** Crystal data and summary of intensity data collection and structure refinement

| Cmpd | $(NH_2)$benzo-15-crown-5 | $[KI(OH_2)((NO_2)$benzo-15-crown-5$)]_2$ |
|---|---|---|
| For. wt. | 283.33 | 994.66 |
| Space group | $P2_1/n$ | $P2_1/n$ |
| Temp., °C | 18 | 18 |
| Cell Constants[a] | | |
| a, Å | 8.433(6) | 7.956(3) |
| b, Å | 18.961(5) | 13.435(4) |
| c, Å | 9.135(6) | 17.998(7) |
| $\beta$, deg | 94.35(6) | 94.44(3) |
| Cell vol, Å$^3$ | 1456 | 1918 |
| Formula units/unit cell | 4 | 2 |
| Radiation, graphite monochromator | MoK$\alpha$($\lambda$ = 0.71073) | MoK$\alpha$($\lambda$ = 0.71073) |
| $D_{calc}$, g cm$^{-3}$ | 1.29 | 1.72 |
| $\mu_{calc}$, cm$^{-1}$ | 1.05 | 19.5 |
| $R$ | 0.051 | 0.056 |
| $R_w$ | 0.052 | 0.062 |

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 23 reflections $\theta > 16°$.

## RESULTS AND DISCUSSION

An ORTEP illustration of aminobenzo-15-crown-5 is provided in Fig. 1. The amino nitrogen atom is pyramidal and resides 1.41(1) Å from C(12) and 0.05 Å out of the plane defined by the arene ring. These values are nearly identical to those found for the Ph-$NH_2$ bond in 4,4'-diamino-3,3'-dichlorobiphenyl[4] and 2-amino-5-bromotoluene.[5] It is hydrogen bonded to a neighboring crown ether such that polymeric hydrogen bonded chains are formed.

The N···O contacts range from 3.12(1) Å (O(4)) to 3.36(1) Å (O(2)), but neither O(4) nor O(2) participate in the hydrogen bonding. Instead, as depicted in Fig. 2, there is a single hydrogen bond to the alkyl ether O(3) (N···O = 3.18(1) Å) and a bifurcated interaction with the two aryl ethers, O(1) (N···O = 3.18(1) Å) and O(5)(N···O = 3.222(9) Å). In the sandwich cation found in $[(NH_4)$(benzo-15-crown-5$)_2]_2[UO_2Cl_4]\cdot 4CH_3CN$[6] the ammonium ion donates two hydrogen bonds to each crown ether. Here too a single hydrogen bond and a bifurcated

**Table 2** Final fractional coordinates for $(NH_2)$benzo-15-crown-5

| *Atom* | *x/a* | *y/b* | *z/c* | *B(eqv)*[a] |
|---|---|---|---|---|
| O(1) | 0.1261(6) | 0.3072(3) | 0.2243(7) | 3.04 |
| O(2) | 0.0987(7) | 0.4557(3) | 0.2048(7) | 2.98 |
| O(3) | −0.2225(8) | 0.5009(4) | 0.2407(8) | 3.98 |
| O(4) | −0.3076(7) | 0.3580(4) | 0.1327(7) | 3.51 |
| O(5) | −0.1246(7) | 0.2246(3) | 0.2520(6) | 2.96 |
| N | 0.3807(9) | 0.1313(4) | −0.0605(8) | 3.13 |
| C(1) | 0.260(1) | 0.3525(5) | 0.214(1) | 3.24 |
| C(2) | 0.224(1) | 0.4207(5) | 0.287(1) | 3.16 |
| C(3) | 0.056(1) | 0.5205(5) | 0.270(1) | 3.28 |
| C(4) | −0.097(1) | 0.5452(5) | 0.197(1) | 3.72 |
| C(5) | −0.335(1) | 0.4825(6) | 0.125(1) | 4.42 |
| C(6) | −0.291(1) | 0.4173(6) | 0.043(1) | 4.48 |
| C(7) | −0.278(1) | 0.2952(5) | 0.062(1) | 3.56 |
| C(8) | −0.274(1) | 0.2335(5) | 0.167(1) | 3.37 |
| C(9) | −0.003(1) | 0.2002(5) | 0.171(1) | 2.56 |
| C(10) | 0.129(1) | 0.2437(5) | 0.1552(9) | 2.44 |
| C(11) | 0.253(1) | 0.2196(5) | 0.077(1) | 2.84 |
| C(12) | 0.248(1) | 0.1534(5) | 0.014(1) | 2.53 |
| C(13) | 0.118(1) | 0.1097(5) | 0.028(1) | 2.70 |
| C(14) | −0.004(1) | 0.1337(5) | 0.111(1) | 2.85 |

[a] $B(eqv) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table 3** Final fractional coordinates for $[KI(OH_2)((NO_2)$benzo-15-crown-5$)]_2$

| *Atom* | *x/a* | *y/b* | *z/c* | *B(eqv)* |
|---|---|---|---|---|
| K | 0.4756(3) | 0.7566(2) | 0.5927(1) | 2.30 |
| I | 0.6380(1) | 0.59208(7) | 0.72667(5) | 3.07 |
| O(1) | 0.259(1) | 0.6215(6) | 0.4988(4) | 2.65 |
| O(2) | 0.445(1) | 0.7666(6) | 0.4357(4) | 2.47 |
| O(3) | 0.317(1) | 0.9162(7) | 0.5300(5) | 2.79 |
| O(4) | 0.244(1) | 0.8476(6) | 0.6762(5) | 2.68 |
| O(5) | 0.170(1) | 0.6587(6) | 0.6271(5) | 2.84 |
| O(6) | 0.208(1) | 0.2487(7) | 0.4726(7) | 4.02 |
| O(7) | 0.133(2) | 0.1996(8) | 0.5769(7) | 5.40 |
| O(8) | 0.653(1) | 0.8724(8) | 0.6986(6) | 4.96 |
| N | 0.170(2) | 0.2667(9) | 0.5353(8) | 3.36 |
| C(1) | 0.313(2) | 0.6074(9) | 0.4266(6) | 2.70 |
| C(2) | 0.325(2) | 0.7073(9) | 0.3926(7) | 2.95 |
| C(3) | 0.437(2) | 0.869(1) | 0.4195(7) | 3.06 |
| C(4) | 0.290(2) | 0.922(1) | 0.4504(7) | 3.29 |
| C(5) | 0.172(2) | 0.949(1) | 0.5668(8) | 3.57 |
| C(6) | 0.214(2) | 0.947(1) | 0.6492(8) | 3.39 |
| C(7) | 0.091(2) | 0.798(1) | 0.6945(8) | 3.18 |
| C(8) | 0.122(2) | 0.692(1) | 0.6993(7) | 3.35 |
| C(9) | 0.166(2) | 0.5612(9) | 0.6113(6) | 2.03 |
| C(10) | 0.217(2) | 0.5398(9) | 0.5375(7) | 2.14 |
| C(11) | 0.223(2) | 0.443(1) | 0.5117(7) | 2.61 |
| C(12) | 0.177(2) | 0.368(1) | 0.5614(8) | 2.85 |
| C(13) | 0.130(2) | 0.388(1) | 0.6331(8) | 2.94 |
| C(14) | 0.128(2) | 0.484(1) | 0.6572(7) | 2.84 |

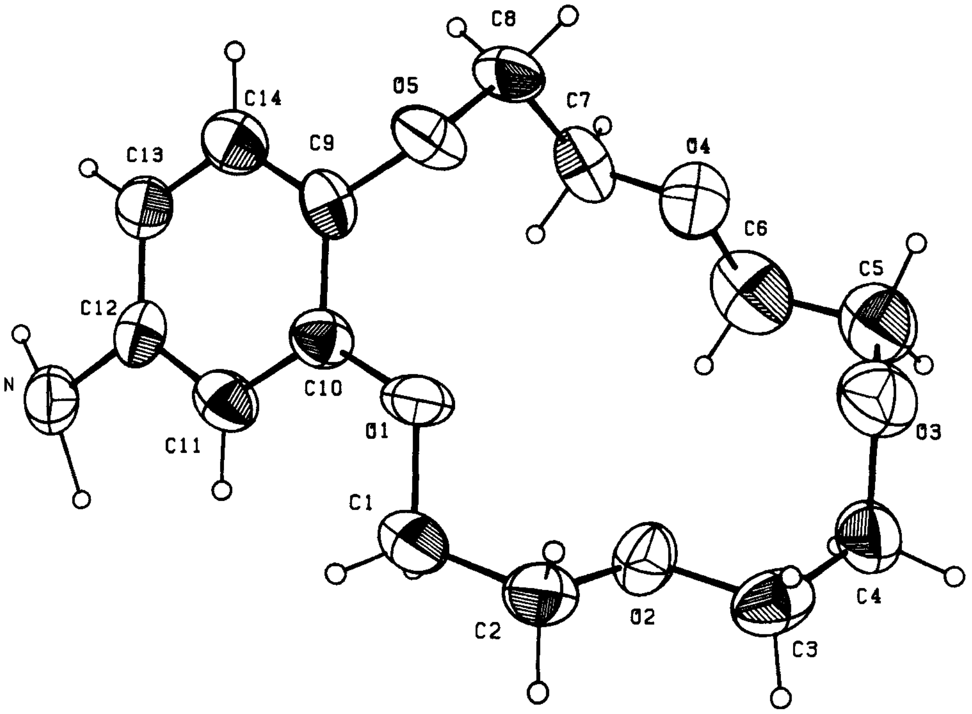

Figure 1 ORTEP illustration of $(NH_2)$benzo-15-crown-5 with 50% probability ellipsoids.

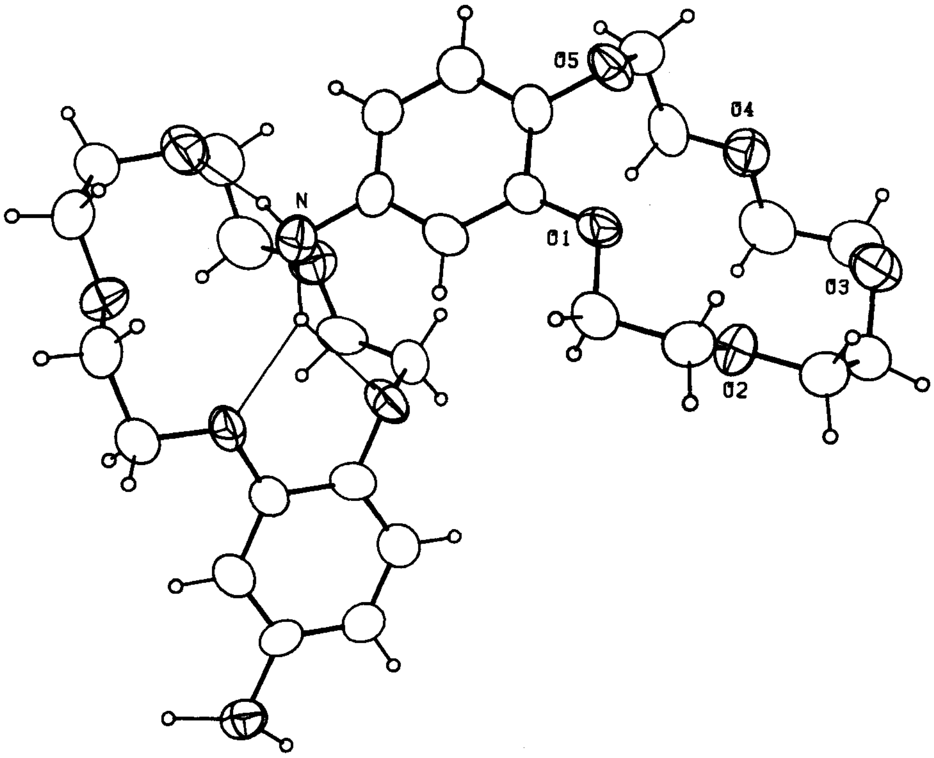

Figure 2 Hydrogen bonding of the amino substituent to the oxygen atoms of a neighboring crown ether.

hydrogen bond are observed, however, the bifurcated hydrogen bond is split between one alkyl and one aryl ether. Two single hydrogen bonds to alkyl ethers are observed in the sandwich cation of $[(H_5O_2)((NO_2)$-benzo-15-crown-$5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$.[7] Hydrogen bonding similar to that in the title compound produced a layer like structure for 4,5′-$(NH_2)_2$dibenzo-18-crown-6.

The hydrogen bonding to the macrocycle results in a conformation different from that observed in the free ether. In the title complex the torsion angle sequence starting with O(1)–C(1)–C(2)–O(2) is $\underline{g}^-(-60^\circ)$,a(180°), a,$\underline{g}^+$,a,$g^+$,$\underline{g}^+$,a,a,$\underline{g}^-$,$g^-$,a,$\underline{s}$,a,a. (The O–C–C–O angles are underlined.) In free benzo-15-crown-5[9] and its nitro and dinitro derivatives[1] this sequence is $\underline{g}^-$,a,$g^-$,$\underline{g}^-$,a,a,$\underline{g}^+$,$g^+$,a,$\underline{g}^+$,a,a,$\underline{s}$,a,a. Despite the conformational difference, however, the bonding parameters are not greatly affected. The average parameters within the macrocyclic ring include O–C(aryl) = 1.37(1) Å, O–C(alkyl) = 1.42(2) Å, C–C(alkyl) = 1.50(1) Å, C–C(aryl) = 1.39(1) Å, C–O–C(alkyl) = 113.1(7)°, C–O–C(alkyl,aryl) = 115(2)°, O–C–C(alkyl) = 110(2)°, and O–C–C(aryl) = 117(2)°. The C–C bonds within the arene ring average 1.39(1) Å with internal C–C–C angles which average 120(1)°.

The dimer $[KI(OH_2)((NO_2)$benzo-15-crown-$5)]_2$ (Fig. 3) resides around a crystallographic center of inversion. The most unique feature of this complex is the interaction between O(6) in the nitro group of one crown ether with a $K^+$ ion coordinated to a second ether. (A similar coordination of the nitro-substituent was observed in $[M(SCN)(4$-$(NO_2)$benzo-18-crown-6)] (M = Cs,[13]Rb[14]).) This interaction precludes the formation of a [K(benzo-15-crown-$5)_2]^+$ sandwich cation normally observed for potassium complexes of benzo-15-crown-5 (e.g., [K(benzo-15-crown-$5)_2]I$[10] and [K(benzo-15-crown-$5)_2][NO_3]\cdot H_2O$[11]). The sandwich cation is even retained in the structure of [K((OH)benzo-15-crown-$5)_2]$SCN although it too has an oxygen donor benzo substituent.[12]

The nitro-group does show the effects of coordination to $K^+$. The N atom and O(7) reside 0.094 Å out of the benzene plane, while the coordinated O(6) is 0.124 Å out of this plane. (All deviations are in the same direction.) In free nitrobenzo-15-crown-5 the deviations are much less—0.020 Å for N and 0.011 and 0.017 Å for the two oxygen atoms.

The K–O(6)$^a$ separation (2.86(1) Å, Table 4) and K–$OH_2$ distance (2.76(1) Å) are within the 0.256 Å range of the K–O (crown ether) separations (2.691(9)–2.947(9) Å). The longest K–O contacts are to the two less basic aryl ethers. The shortest K–O distance is to the alkyl position (O(3)) directly opposite the aryl oxygens. This was also observed in [K(benzo-15-crown-$5)_2][NO_3]\cdot H_2O$ where the K–O separations ranged from 2.778–2.996 Å. A similar range of 2.777(7)–2.955(8) Å was observed for [K(benzo-15-crown-$5)_2]$I.

Despite its coordination to $K^+$, the conformation of the crown ether is the same as observed in both benzo-15-crown-5 and $(NO_2)$benzo-15-crown-5. The average bonding parameters within the macrocycle are also similar with O–C(aryl) = 1.34(1) Å, O–C(alkyl) = 1.43(1) Å, C–C(alkyl) = 1.48(2) Å, C–C(aryl) = 1.45(2) Å, C–O–C(alkyl) = 112.7(9)°, C–O–C(alkyl,aryl) = 118(1)°, O–C–C(alkyl) = 109(2)°, and O–C–C(aryl) = 114(1)°.

The $K^+$ ion can be considered to be in either a very distorted dodecahedral geometry or a very distorted

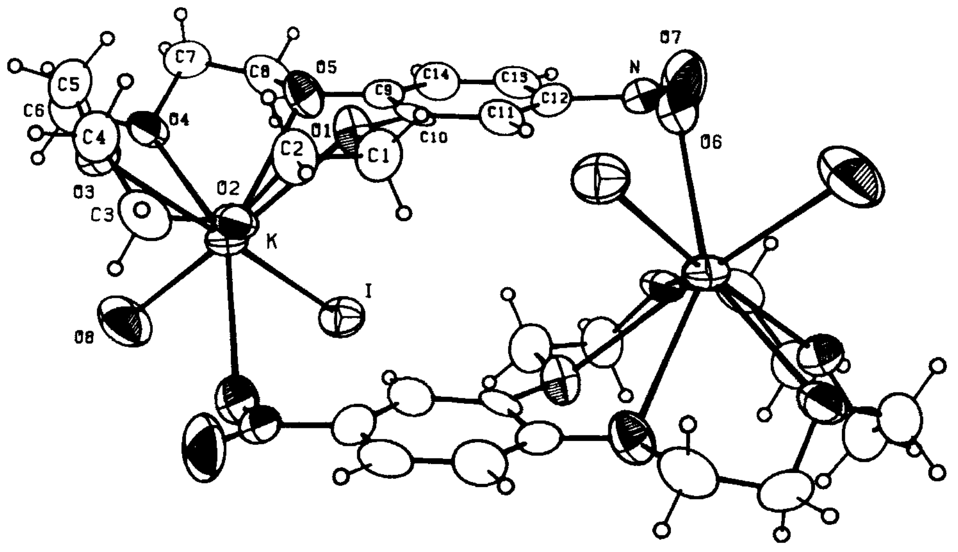

**Figure 3** ORTEP illustration of the $[KI(OH_2)((NO_2)$benzo-15-crown-$5)]_2$ dimer.

**Table 4** Distances (Å) and angles (deg) for the $K^+$ coordination sphere in $[KI(OH_2)((NO_2)benzo\text{-}15\text{-}crown\text{-}5)]_2$

| *Atoms* | *Distance* | *Atoms* | *Distance* |
|---|---|---|---|
| K···I | 3.448(3) | K···O(1) | 2.947(9) |
| K···O(2) | 2.820(8) | K···O(3) | 2.691(9) |
| K···O(4) | 2.753(9) | K···O(5) | 2.877(9) |
| K···O(8) | 2.76(1) | K···O(6)[a] | 2.86(1) |

| *Atoms* | *Angle* | *Atoms* | *Angle* |
|---|---|---|---|
| I···K···O(1) | 100.2(2) | I···K···O(2) | 136.8(2) |
| O(1)···K···O(2) | 56.9(2) | I···K···O(3) | 160.4(2) |
| O(1)···K···O(3) | 90.9(3) | O(2)···K···O(3) | 62.7(3) |
| I···K···O(4) | 97.7(2) | O(1)···K···O(4) | 101.5(3) |
| O(2)···K···O(4) | 121.1(3) | O(3)···K···O(4) | 64.1(3) |
| I···K···O(5) | 80.5(2) | O(1)···K···O(5) | 51.2(2) |
| O(2)···K···O(5) | 103.2(3) | O(3)···K···O(5) | 94.4(3) |
| O(4)···K···O(5) | 58.1(2) | I···K···O(8) | 74.6(2) |
| O(1)···K···O(8) | 171.3(3) | O(2)···K···O(8) | 131.6(3) |
| O(3)···K···O(8) | 92.3(3) | O(4)···K···O(8) | 72.7(3) |
| O(5)···K···O(8) | 120.4(3) | I···K···O(6)[a] | 88.7(2) |
| O(1)···K···O(6)[a] | 104.1(3) | O(2)···K···O(6)[a] | 66.4(3) |
| O(3)···K···O(6)[a] | 104.3(3) | O(4)···K···O(6)[a] | 152.0(3) |
| O(5)···K···O(6)[a] | 149.7(3) | O(8)···K···O(6)[a] | 83.0(3) |

[a] Symmetry code = $(1 - x, 1 - y, 1 - z)$.

bicapped trigonal prismatic geometry with O(1) and O(4) in capping positions. The K-I separation of 3.448(3) Å is shorter than observed in most of the few crown or lariat ether complexes that have direct K-I contacts.[15-18]

The two title structures have shown that the introduction of donor substituents into the arene rings of benzo crown ethers can dramatically alter their complexation chemistry. This should provide a fertile field for crystallographic study which we intend to pursue.

## ACKNOWLEDGEMENT

We wish to thank the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

*(Received January 29, 1992)*

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