Coordination Chemistry of Alkali and Alkaline Earth Cations: Synthesis and Crystal Structure of Potassium(Benzo-15-crown-5)$_2$ [3,5-Dinitrobenzoate(3,5-dinitrobenzoic acid)$_2$]

WEIXIN XU, K. CLINGER, and M. L. HACKERT★
Chemistry Department and Clayton Foundation Biochemical Institute, University of Texas, Austin TX 78712 U.S.A.

N. S. POONIA
Chemistry Department, Devi Ahilya University, Indore 452 001, India

Abstract. The interaction of K(35-Dnb)(35-Dnb = 3,5-dinitrobenzoate) with benzo-15-crown-5 (B15C5) in ethanol yields a charge-separated sandwich structured complex $[K(B15C5)_2]^+[35\text{-Dnb}(35\text{-DnbH})_2]^-$ even when equimolar amounts of reactants were used and no external 35-DnbH was added to the reaction mixture. The complex $(KC_{49}H_{51}O_{28}N_6$, FW = 1211.1), is monoclinic, $P2_1/c$, $a = 11.063(2)$, $b = 10.680(1)$, $c = 46.548(8)$ Å, $\beta = 91.629(2)°$, $Z = 4$, $D_0 = 1.485$ g/cm^3, $D_c = 1.468$ g/cm^3, CuKα $\lambda = 1.5418$ Å, $\mu = 17.01$ cm^{-1}, $2\theta < 130°$, $F(000) = 2520$, $T = 298$ K. Final R for the 6618 observed reflections was 0.071. In the sandwich moiety, the K$^+$ is 10-coordinated through all the oxygens of the crown molecules (K$^+$—O, 2.76–3.11 Å). The 35-Dnb anion lies 5.3 Å below the lower crown mean plane and is charge separated with respect to K$^+$ (K$^+$—O$^-$ > 7 Å) but undergoes strong hydrogen bonding (2.59 and 2.49 Å) through each carboxylate oxygen with the carboxylic protons of two separate 35-DnbH molecules.

Key words: Potassium, 3,5-dinitrobenzoate, benzo-15-crown-5, X-ray diffraction analysis, charge-separated sandwich.

1. Introduction

With the ultimate aim of understanding the chemical principles responsible for the intriguing discriminatory roles of alkali (M$^+$) and alkaline earth (M^{2+}) cations (general abbreviation M^{Z+}) in biological systems [1], we have undertaken the examination of interactive differences between different M^{Z+} under similar conditions. We are attempting to understand the anion versus crown preferences for different M^{Z+} through X-ray diffraction analysis of M^{Z+}(anion)(B15C5) systems where anion (L) is 2,4,6-trinitrophenolate (Pic) or 3,5-dinitrobenzoate (35-Dnb) and B15C5 is benzo-15-crown-5.

Under the counteracting effect of Pic, M^{Z+} ions have exhibited a gradation in their affinity for B15C5. Lithium [2], like calcium [3], prefers to be contained within an exclusively anionic

---

★ Author for correspondence.

environment (of Pic and water molecules) in the complex $Li(Pic)(B15C5)(H_2O)_2$. Sodium in the complex $Na(Pic)(B15C5)$ [4] undergoes a thorough chelation with the crown on one side while remaining paired with the Pic anion on the other. Potassium in the complex $[K(B15C5)_2]Pic$ [5] becomes completely charge-separated from Pic in favor of 1 : 2 sandwich formation, as has also been noted for iodide as the counteranion [6].

For 35-Dnb, sodium in the complex $Na(35-Dnb)(B15C5)(H_2O)$ [7] again undergoes 1 : 1 chelation with B15C5 while remaining paired with the anion. Even the larger barium in the complex $Ba(35-Dnb)_2(B15C5)$ [8], constitutes a 1 : 1 metal-crown complex whose anion pairs are in turn dimerized in the crystal lattice to form a 2 : 2 complex due to bridging via the carboxylate oxygens of the neighboring complex molecules. In view of potassium being comparable in size with barium and 35-Dnb being more cation-pairing than Pic, we were interested in the structural analysis of the $[K(B15C5)_2]^+[35-Dnb(35-DnbH)_2]^-$ which is unique also in that it contains a conjugate acid-conjugate base pair within the crystalline lattice.

2. Experimental

2.1. PREPARATION OF THE COMPLEX

A mixture containing only K(35-Dnb) and B15C5 in a 1 : 1 ratio in ethanol (0.4 mol in 5 ml) yields greenish yellow crystals of $[K(B15C5)_2][35-Dnb(35-DnbH)_2]$ by partial evaporation. However, to obtain the pure product in a higher yield (over 80%) a reaction mixture containing K(35-Dnb), 35-DnbH, and B15C5 (1 : 2 : 2, 0.4 mol with regard to the salt) in ethanol (5 ml) was used. The complex was characterized through infrared spectroscopy (4000–400 cm^{-1}) and elemental analysis (Calculated: C, 48.60%; H, 4.21%; N, 6.94%; Found: C, 48.40%; H, 4.29%; N, 7.01%).

2.2. STRUCTURAL ANALYSIS

A crystal of dimensions $0.3 \times 0.3 \times 0.35$ mm with an approximate volume 0.031 mm^3 was used for data collection. Reflections were measured at room temperature (25°) using a Syntex four circle goniostat equipped with a Picker X-ray generator and KRISEL CONTROL automation package. Unit-cell parameters were determined by a least-squares analysis of 19 reflections measured at room temperature with 2θ values ranging from 40 to 63° using CuKα ($\lambda = 1.54184$ Å) radiation. The space group deduced from systematic absences ($0k0$ absent with k odd, $h0l$ absent with l odd) is $P2_1/c$. The density measured at room temperature by the flotation technique in a mixture of xylene and bromobenzene is 1.485 g/cm^3 compared to a calculated value for $Z = 4$ of 1.468 g/cm^3.

Intensity data were obtained using a profile-fitting procedure based on a modified ω-scan mode. The profile of each peak was scanned for 13 steps over a range of 0.36° in ω. Backgrounds were counted for 12 sec on each side of the peak ($\omega \pm 0.60°$). Some 8399 independent reflections in the $-h-kl$ and $h-kl$ quadrant were collected with CuKα radiation between 2θ values of 3.0–120°, of which 6618 reflections were considered observed ($I > 3\sigma(I)$). Three standard reflections were used to determine the crystal and instrument stability and their intensities were measured every 2 h. An absorption correction was done by the empirical psi scan method [9] (max = 1.25, min = 1.23). The intensities also were corrected for decay and Lorentz-polarization effects.

The positions of most non-hydrogen atoms were determined from an E-map computed by the direct methods program MULTAN [10]. The potassium position was confirmed in the Patterson map. The remaining non-hydrogen atoms were located with a difference Fourier synthesis. Refinement was done by block diagonal least-squares. Isotropic refinement converged at 0.149 for $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. Hydrogen atoms which form the H-bonding among the 35-DnbH were found in a difference Fourier synthesis. Other hydrogen atom positions were calculated with respect to the atoms to which they are bonded. Final anisotropic refinement of all non-hydrogen atoms converged at $R = 0.071$.

3. Results and Discussion

The crystallographic parameters are listed in Table I. The coordinates for all atoms are given in Table II. The identification of the atoms, bond distances, and bond angles are shown in

Table I. Crystallographic parameters for K(B15C5)$_2$[3,5-Dini-trobenzoate(3,5-Dinitrobenzoic acid)$_2$]

a	= 11.063(2) Å
b	= 10.680(1) Å
c	= 46.548(8) Å
β	= 91.629(2)°
V	= 5457(1) Å^3
$D_o = 1.485$ g/cm^3	$D_c = 1.468$ g/cm^3
Space group $P2_1/c$	
$Z = 4$ $F(000) = 2520$	FW = 1211.1
Cu$K\alpha$ $\lambda = 1.54184$ Å	
$\mu(\text{Cu}K\alpha) = 17.01$ cm^{-1}	

Fig. 1. Diagram of crown moiety 1 showing the atom designations, the bond distances (Å) and angles (°) with the estimated standard deviations of the last digit in parentheses.
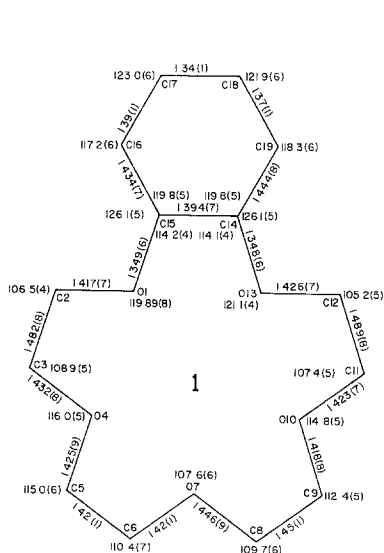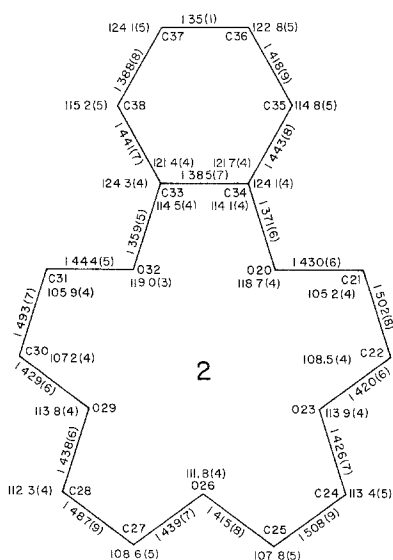

Fig. 2. Diagram of crown moiety 2 showing the atom designations, the bond distances (Å) and angles (°) with the estimated standard deviations of the last digit in parentheses.

Table II. Atomic coordinates in fractions of cell edges and isotropic thermal parameters with e.s.d.'s

Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	U_{eq} or U
K$^+$	0.0045(1)	0.1654(1)	0.40530(2)	0.044
O(1)	0.0592(3)	− 0.0534(4)	0.4409(1)	0.055
C(2)	− 0.0284(5)	− 0.0734(5)	0.4621(1)	0.061
C(3)	− 0.1430(6)	− 0.1040(6)	0.4463(1)	0.075
O(4)	− 0.1818(4)	0.0032(4)	0.4301(1)	0.076
C(5)	− 0.2730(6)	− 0.0186(9)	0.4085(2)	0.110
C(6)	− 0.2297(6)	− 0.0610(9)	0.3816(2)	0.113
O(7)	− 0.1545(4)	0.0308(5)	0.3694(1)	0.088
C(8)	− 0.1083(8)	− 0.0207(8)	0.3432(2)	0.102
C(9)	− 0.0137(7)	0.0593(7)	0.3327(1)	0.087
O(10)	0.0881(4)	0.0649(4)	0.3518(1)	0.064
C(11)	0.1676(6)	− 0.0396(6)	0.3505(1)	0.071
C(12)	0.2614(5)	− 0.0241(5)	0.3738(1)	0.063
O(13)	0.1965(3)	− 0.0239(4)	0.3998(1)	0.064
C(14)	0.2545(4)	− 0.0352(5)	0.4255(1)	0.052
C(15)	0.1778(5)	− 0.0513(5)	0.4485(1)	0.050
C(16)	0.2279(6)	− 0.0641(6)	0.4771(1)	0.073
C(17)	0.3536(7)	− 0.0623(7)	0.4804(2)	0.090
C(18)	0.4274(6)	− 0.0485(7)	0.4582(2)	0.086
C(19)	0.3838(5)	− 0.0343(6)	0.4306(2)	0.077
O(20)	0.1847(3)	0.3333(4)	0.4402(1)	0.053
C(21)	0.1823(5)	0.3102(5)	0.4704(1)	0.058
C(22)	0.0570(5)	0.3452(5)	0.4790(1)	0.059
O(23)	− 0.0262(3)	0.2599(3)	0.4659(1)	0.055
C(24)	− 0.1489(5)	0.3008(6)	0.4661(1)	0.070
C(25)	− 0.1777(5)	0.4013(6)	0.4442(1)	0.069
O(26)	− 0.1699(3)	0.3471(4)	0.4166(1)	0.060
C(27)	− 0.1946(5)	0.4370(6)	0.3942(1)	0.068
C(28)	− 0.1787(5)	0.3749(6)	0.3659(1)	0.067
O(29)	− 0.0565(3)	0.3334(3)	0.3622(1)	0.054
C(30)	0.0227(5)	0.4293(5)	0.3526(1)	0.050
C(31)	0.1488(5)	0.3808(5)	0.3562(1)	0.049
O(32)	0.1689(3)	0.3627(3)	0.3867(1)	0.047
C(33)	0.2809(4)	0.3291(4)	0.3966(1)	0.042
C(34)	0.2910(4)	0.3153(5)	0.4262(1)	0.045
C(35)	0.4051(5)	0.2863(6)	0.4405(1)	0.072
C(36)	0.5034(5)	0.2718(6)	0.4220(2)	0.071
C(37)	0.4913(5)	0.2824(6)	0.3931(2)	0.069
C(38)	0.3834(4)	0.3112(5)	0.3786(1)	0.060
C(39)	0.5673(4)	0.3287(5)	0.2699(1)	0.045
C(40)	0.5067(4)	0.3743(5)	0.2456(1)	0.046
C(41)	0.5390(4)	0.3317(5)	0.2187(1)	0.047
C(42)	0.6290(5)	0.2456(5)	0.2150(1)	0.051
C(43)	0.6847(4)	0.2016(5)	0.2397(1)	0.054
C(44)	0.6576(5)	0.2395(5)	0.2671(1)	0.051
C(45)	0.5391(5)	0.3754(5)	0.2996(1)	0.051
O(46)	0.5879(4)	0.3354(4)	0.3207(1)	0.071
O(47)	0.4547(3)	0.4634(4)	0.2987(1)	0.061
N(48)	0.7851(5)	0.1085(5)	0.2368(1)	0.073
O(49)	0.8361(5)	0.0721(5)	0.2584(1)	0.112
O(50)	0.8136(4)	0.0796(5)	0.2127(1)	0.107
N(51)	0.4764(4)	0.3843(5)	0.1932(1)	0.059

Table II (continued)

Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	U_{eq} or U
O(52)	0.3801(4)	0.4371(5)	0.1969(1)	0.079
O(53)	0.5245(4)	0.3728(4)	0.1701(1)	0.077
C(54)	0.8173(4)	0.7020(4)	0.2856(1)	0.043
C(55)	0.7418(4)	0.6682(5)	0.2629(1)	0.045
C(56)	0.7746(4)	0.7003(5)	0.2353(1)	0.046
C(57)	0.8782(5)	0.7666(5)	0.2297(1)	0.049
C(58)	0.9494(4)	0.7978(5)	0.2531(1)	0.048
C(59)	0.9237(4)	0.7669(5)	0.2811(1)	0.047
C(60)	0.7840(5)	0.6710(5)	0.3161(1)	0.049
O(61)	0.8559(3)	0.6789(4)	0.3357(1)	0.062
O(62)	0.6709(3)	0.6373(4)	0.3175(1)	0.061
N(63)	1.0596(4)	0.8744(4)	0.2480(1)	0.059
O(64)	1.0857(4)	0.8945(5)	0.2232(1)	0.084
O(65)	1.1185(4)	0.9102(4)	0.2690(1)	0.075
N(66)	0.6943(4)	0.6616(4)	0.2109(1)	0.056
O(67)	0.7231(5)	0.6892(6)	0.1871(1)	0.101
O(68)	0.6028(4)	0.6052(4)	0.2161(1)	0.073
C(69)	0.4158(4)	0.6250(4)	0.3951(1)	0.040
C(70)	0.4865(4)	0.6275(5)	0.4200(1)	0.048
C(71)	0.4302(5)	0.6355(5)	0.4461(1)	0.057
C(72)	0.3067(5)	0.6420(5)	0.4482(1)	0.056
C(73)	0.2407(5)	0.6431(4)	0.4233(1)	0.046
C(74)	0.2917(4)	0.6344(4)	0.3967(1)	0.043
C(75)	0.4741(5)	0.6077(5)	0.3661(1)	0.046
O(76)	0.4053(3)	0.5826(3)	0.3454(1)	0.051
O(77)	0.5868(3)	0.6196(4)	0.3664(1)	0.059
N(78)	0.1078(4)	0.6551(4)	0.4250(1)	0.062
O(79)	0.0494(4)	0.6743(5)	0.4029(1)	0.087
O(80)	0.0646(4)	0.6463(4)	0.4490(1)	0.080
N(81)	0.5067(7)	0.6387(6)	0.4727(1)	0.093
O(82)	0.4537(5)	0.6357(6)	0.4955(1)	0.126
O(83)	0.6148(6)	0.6444(7)	0.4704(1)	0.126
H(21)	− 0.039(5)	0.004(1)	0.473(1)	0.060
H(22)	− 0.003(5)	− 0.153(5)	0.474(1)	0.060
H(31)	− 0.209(5)	− 0.130(6)	0.460(1)	0.072
H(32)	− 0.125(5)	− 0.173(6)	0.431(1)	0.072
H(51)	− 0.303(6)	0.076(6)	0.402(1)	0.095
H(52)	− 0.326(6)	− 0.091(7)	0.416(1)	0.095
H(61)	− 0.303(6)	− 0.081(6)	0.366(1)	0.095
H(62)	− 0.178(6)	− 0.149(6)	0.387(1)	0.095
H(81)	− 0.167(6)	− 0.131(6)	0.328(1)	0.091
H(82)	− 0.073(6)	− 0.123(6)	0.346(1)	0.091
H(91)	− 0.057(5)	0.157(6)	0.331(1)	0.080
H(92)	0.014(5)	0.028(6)	0.312(1)	0.080
H(111)	0.206(5)	− 0.041(6)	0.329(1)	0.068
H(112)	0.114(5)	− 0.123(6)	0.354(1)	0.068
H(121)	0.301(5)	0.063(5)	0.370(1)	0.061
H(122)	0.330(5)	− 0.102(5)	0.371(1)	0.061
H(16)	0.163(5)	− 0.086(5)	0.496(1)	0.065
H(17)	0.379(5)	− 0.080(6)	0.499(1)	0.080
H(18)	0.518(5)	− 0.059(6)	0.461(1)	0.082
H(19)	0.445(5)	− 0.027(5)	0.412(1)	0.067
H(211)	0.242(6)	0.369(5)	0.481(1)	0.056

Table II (continued)

Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	U_{eq} or U
H(212)	0.198(6)	0.210(5)	0.475(1)	0.056
H(221)	0.037(5)	0.442(5)	0.471(1)	0.058
H(222)	0.050(5)	0.340(5)	0.499(1)	0.058
H(241)	−0.160(5)	0.332(6)	0.483(1)	0.069
H(242)	−0.207(5)	0.212(6)	0.462(1)	0.069
H(251)	−0.114(5)	0.483(5)	0.447(1)	0.067
H(252)	−0.267(5)	0.440(5)	0.447(1)	0.067
H(271)	−0.138(5)	0.507(5)	0.397(1)	0.065
H(272)	−0.271(5)	0.476(5)	0.396(1)	0.065
H(281)	−0.198(5)	0.434(5)	0.350(1)	0.065
H(282)	−0.228(5)	0.296(5)	0.364(1)	0.065
H(301)	0.009(4)	0.505(5)	0.364(1)	0.051
H(302)	0.002(4)	0.450(5)	0.332(1)	0.051
H(311)	0.210(4)	0.448(5)	0.349(1)	0.048
H(312)	0.155(4)	0.295(5)	0.346(1)	0.048
H(35)	0.326(5)	0.277(5)	0.452(1)	0.060
H(36)	0.578(5)	0.245(5)	0.432(1)	0.067
H(37)	0.562(5)	0.263(5)	0.380(1)	0.067
H(38)	0.298(4)	0.314(5)	0.369(1)	0.053
H(40)	0.447(4)	0.440(5)	0.246(1)	0.045
H(42)	0.653(4)	0.218(5)	0.195(1)	0.052
H(44)	0.700(4)	0.209(5)	0.285(1)	0.052
HA	0.439(0)	0.500(0)	0.318(1)	0.058
H(55)	0.665(4)	0.627(5)	0.266(1)	0.045
H(57)	0.897(4)	0.785(5)	0.209(1)	0.049
H(59)	0.978(4)	0.793(5)	0.298(1)	0.049
HB	0.650(0)	0.625(0)	0.338(1)	0.058
H(70)	0.577(4)	0.620(5)	0.419(1)	0.049
H(72)	0.269(5)	0.647(5)	0.467(1)	0.055
H(74)	0.234(4)	0.631(5)	0.380(1)	0.044

Figures 1–4. Figure 5 is a stereo ORTEP drawing of one asymmetric unit while Table III gives the corresponding K—O distances. Figure 6 is a stereo ORTEP drawing illustrating the packing of the molecules in the unit cell. The analysis reveals (Figure 5) that the K^+ ion is 10-coordinated with the two crown molecules (K—O, 2.76 to 3.11 Å) only and the product is a genuine charge-separated sandwich wherein the cation has no contact with the anion as noted for KI [6] and K(Pic) [5]. The distance between the two mean planes containing the basal crown oxygens is about 3.53 Å and the maximum deviations from the planes are 0.18 and 0.28 Å, respectively. The 35-Dnb moiety lies 5.3 Å below the lower crown mean plane and it is not in contact with potassium ($K^+ — O^- > 7$ Å). Each carboxylate oxygen of 35-Dnb

Table III. Potassium-oxygen distances (Å) and their estimated standard deviations

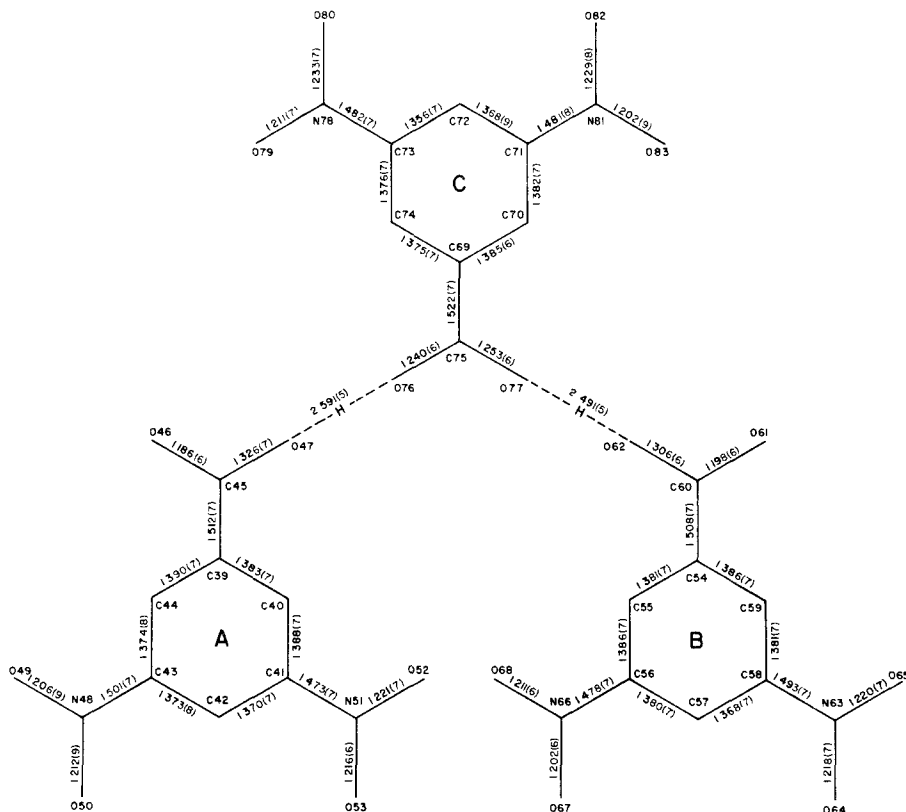|			
K—O(1)	2.919(4)	K—O(4)	2.952(4)
K—O(7)	2.789(5)	K—O(10)	2.885(4)
K—O(13)	2.948(4)	K—O(20)	3.106(3)
K—O(23)	3.027(4)	K—O(26)	2.797(4)
K—O(29)	2.759(4)	K—O(32)	2.931(3)

Fig. 3. Diagram of 3,5-dinitrobenzoate and 3,5-dinitrobenzoic acid moieties showing the atom designations and bond distances (Å) including hydrogen bonds with the estimated standard deviations of the last digit in parentheses.

is strongly hydrogen-bonded (2.59 and 2.49 Å) to a carboxylic proton of separate 35-DnbH molecules constituting a type of asymmetric fork.

The bond lengths in the benzene ring of the first B15C5 (O(1)—C(19)) (Figure 1) range from 1.34 to 1.44 Å, and the bond angles from 117.2 to 123.0°. This nucleus is planar within 0.005 Å and coplanar with O(1) and O(13) within 0.01 Å. The ring in the second B15C5 (O(20)—C(38)) (Figure 2) has bond lengths and angles ranging from 1.35 to 1.44 Å and from 114.8 to 124.1°, respectively. It is planar within 0.008 Å and coplanar with O(20) and O(32) within 0.022 Å. The oxygen atoms adjacent to the benzo ring are influenced by a strong electron-withdrawing effect of the aromatic nuclei and are not as strongly bound to potassium, with an average K—O distance of 2.98 Å vs. 2.87 Å for the remaining oxygens. The distances C(15)—O(1) (1.349 Å), C(14)—O(13) (1.348 Å), C(33)—O(32) (1.359 Å) and C(34)—O(20) (1.371 Å) are distinctly shorter and the angles C(14)—C(15)—O(1) (114.2°), C(15)—C(14)—O(13) (114.1°), C(34)—C(33)—O(32) (114.5°), and C(33)—C(34)—O(20) (114.1°) are larger than those observed for the other crown carbon-oxygen bonds. The angles at O(1), O(13), O(32), and O(20) are widened to values approaching 120° (119.9, 121.1, 119.0, and 118.7°). The widening of the angles may also be seen to arise from the necessity of C(14), C(15), C(33), and C(34) to be coplanar with other carbons of the benzene rings which also affects the coordination characteristics of the cation. The $C(sp^3)$—$C(sp^3)$ distances vary from 1.42 to 1.49 Å within the first crown and from 1.49 to 1.51 Å in the second crown. The mean distances are 1.46 and 1.50 Å, respectively.
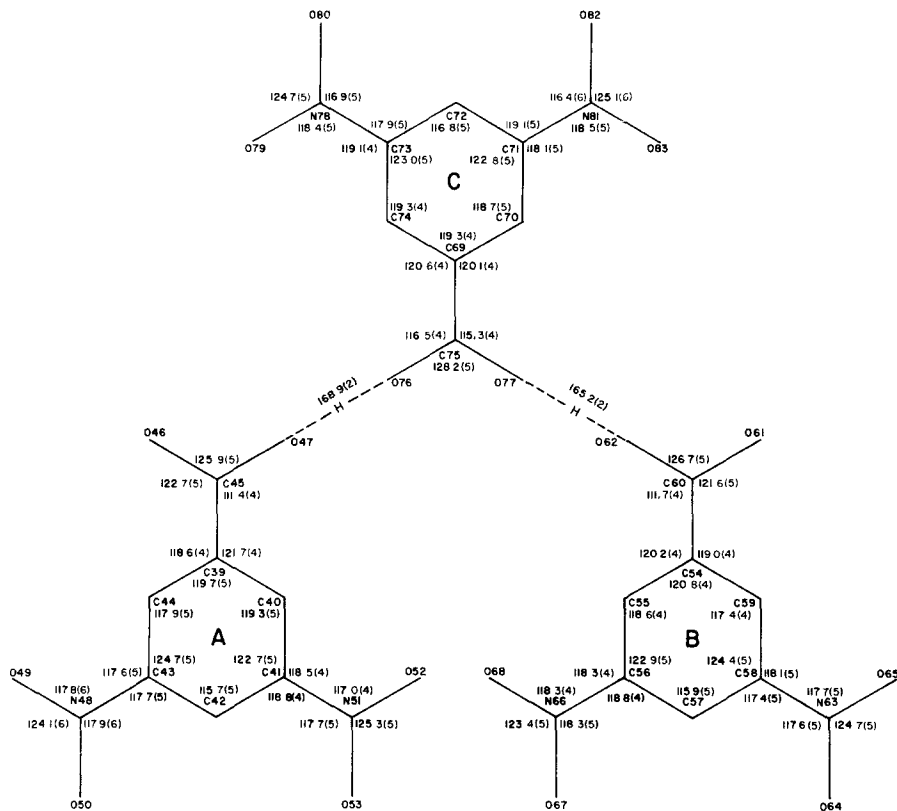
Fig. 4. Bond angles (°) of 3,5-dinitrobenzoate and 3,5-dinitrobenzoic acid moieties with the estimated standard deviations of the last digit in parentheses.
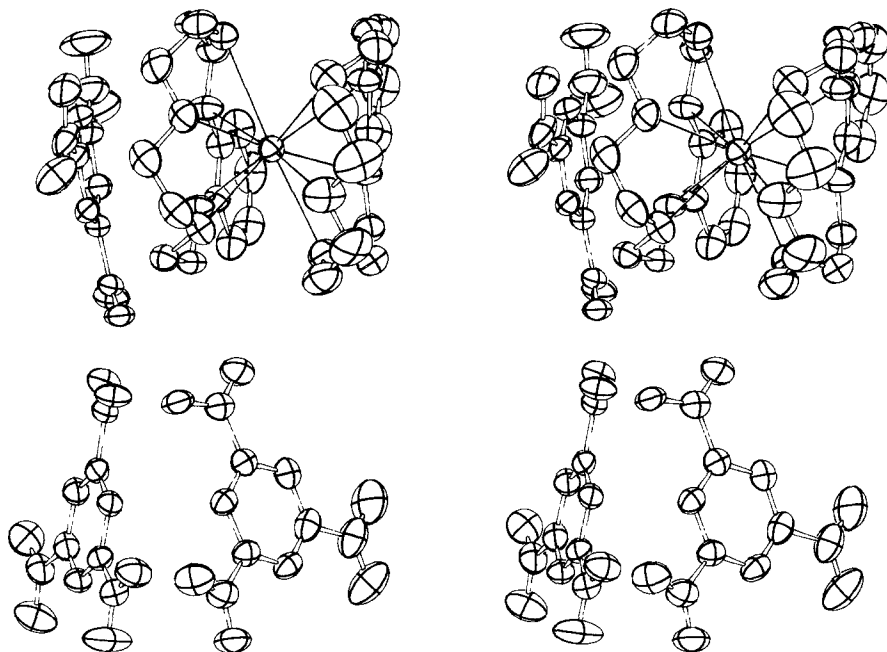

Fig. 5. Stereo ORTEP drawing of one asymmetric unit showing the coordination of the K$^+$ ion by the ten oxygens of two benzo-15-crown-5 moieties.

1.49 to 1.51 Å in the second crown. The mean distances are 1.46 and 1.50 Å, respectively.

The molecular geometry of the 35-Dnb (moiety C, Figures 3 and 4) shows that the bonds constituting the benzene ring vary from 1.36 to 1.39 Å while the inner angles vary from 116.8 to 122.8°. The compression or widening of the angles is a normal effect of the substituents, which arises from the electron-withdrawing effect of the nitro substituents and the conjunctive effect of the carboxyl group with the benzene ring [11–13]. The twist of the carboxyl group from the plane of the benzene ring is 12.7° which may be due to H-bonding. The nitro groups are displaced from the plane by 6.7° (N(78)—O(89)—O(80)) and 10.4° (N(81)—O(82)—O(83)), respectively. The two 35-DnbH moieties (Figures 3 and 4) possess almost identical geometries. The bond distances and angles in ring A vary from 1.37 to 1.39 Å and from 115.7 to 124.7°, respectively. Comparatively, the bonds constituting ring B vary from 1.37 to 1.39 Å while the inner angles vary from 115.9 to 124.4°. The three substituents deviate slightly from the benzene rings due to the strain of the crystal lattice.

This complex is the first crystallographically studied example of an M^{Z+}-complex wherein the charge neutralizer is an acid-anion (conjugate acid-conjugate base). The sandwich formation and conversion of the anion into an acid anion are the consequences of the proper Lewis acidity of potassium [14]. Barium is similar in size to potassium but Ba(35-Dnb)$_2$ yields only a 1 : 1 metal complex with the same crown, as the cation forces a dimerization of the
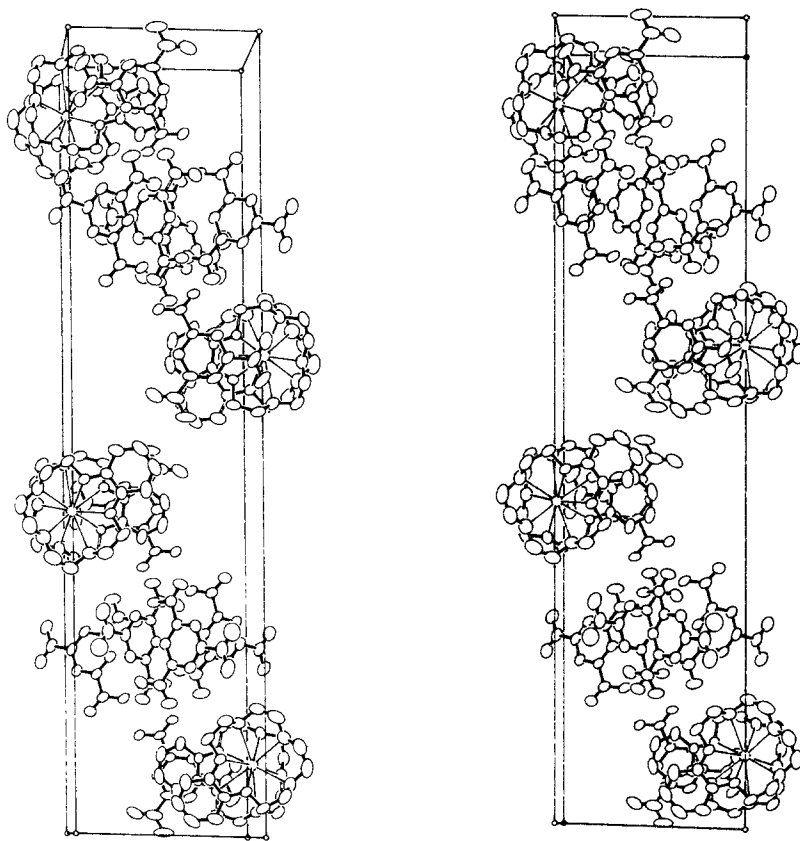

Fig. 6. Stereo ORTEP drawing showing the packing of [K(B15C5)$_2$]$^+$[35-Dnb(35-DnbH)$_2$]$^-$ in the $P2_1/c$ unit cell.

anion-pairs in the system through interaction with neighboring carboxylate oxygens in the lattice [8]. Furthermore, this 1 : 1 complex is formed in spite of the fact that in the synthesis of this complex the rather insoluble $Ba(35\text{-}Dnb)_2$ necessitates the use of a five-fold excess of B15C5 and about 50% water in the reaction solvent (ethanol) in order to decrease ion-pair interactions. That is, the stoichiometry of an M^{Z+}-crown complex is a function of the charge/radius ratio parameter of the cation [15] rather than just its size compatibility with the cavity of the crown, as was believed earlier [16].

Acknowledgements

References

1. M. N. Hughes: *The Inorganic Chemistry of Biological Processes,* Wiley, New York, 2nd eds., pp. 256–295 (1981).
2. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **16**, 373 (1980).
3. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **16**, 289 (1980).
4. D L. Ward, A. I. Popov, and N. S. Poonia: *Acta Crystallogr.* **C40**, 238 (1984).
5. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **17**, 207 (1981).
6. P. R. Mallinson and M. R. Truter: *J. Chem. Soc., Perkin Trans.* 2, 1818 (1972).
7. K. Venkatasubramanian, N. S. Poonia, and S. Chaudhuri: In preparation.
8. D. L. Ward, A. I. Popov, and N. S. Poonia: *Acta Crystallogr.* **C40**, 1183 (1984).
9. A. C. T. North, D. C. Phillips, and F. S. Mathews: *Acta Crystallogr.* **A24**, 351 (1968).
10. G. Germain, P. Main, and M. M. Woolfson: *Acta Crystallogr.* **A27**, 368 (1971).
11. A. J. Dekok and C. Romers: *Acta Crystallogr.* **B31**, 1535 (1975).
12. D. F. Grant: *Acta Crystallogr.* **B25**, 564 (1969).
13. A. Domenicano and A. Vaciago: *Acta Crystallogr.* **B31**, 221 (1975).
14. N. S. Poonia: *J. Am. Chem. Soc.* **96**, 1012 (1974).
15. N. S. Poonia and A. V. Bajaj: *Chem. Rev.* **79**, 389 (1979).
16. C. J. Pedersen and H. K. Frensdorff: *Angew. Chem. Int. Ed. Engl.* **11**, 16 (1972).