Coordination Chemistry of Alkali and Alkaline Earth Cations: Crystal Structure of Rubidium (Benzo-15-crown-5)$_2$NO$_3$ · H$_2$O

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Abstract. The complex Rb(B15C5)$_2$NO$_3$ · H$_2$O is monoclinic, $P2_1/c$, $a = 12.695(3)$, $b = 19.471(3)$, $c = 12.991(2)$ Å, $\beta = 99.60(2)°$, $V = 3166$ Å^3, $D_c = 1.473$ g/cm^3 (163 K), $D_c = 1.434$ g/cm^3 (298 K), $D_o = 1.44$ g/cm^3 (298 K), $T = 163$ K, $Z = 4$, MoKα $\lambda = 0.71069$ Å, $2\theta(4°-53°)$, $\mu = 16.43$ cm^{-1}, $F(000) = 1424$. Final R for the 4588 observed reflections ($F > 3\sigma$) is 0.062. All ten oxygens of the two benzo-crowns are shown to coordinate to the rubidium ion (Rb···O, 2.92 to 3.07 Å) forming a charge-separated sandwich. The nearest nitrate oxygen is displaced 6.51 Å from the rubidium ion and is hydrogen bonded to a water molecule.

Key words: Benzo-15-crown-5, charge-separated sandwich, rubidium, X-ray diffraction analysis.

1. Introduction

The alkali (M$^+$) and alkaline earth (M^{2+}) cations (general abbreviation M^{z+}) and their interactions with ligands and counterions have far-reaching implications in the fields of inorganic, synthetic, and biological chemistry. In the field of biochemistry alone, an understanding of their interactions with macromolecular ligands may ultimately lead to useful models of ion transport in cells and can be further extended into the study of M^{z+} antibiotic systems [1]. To reach reliable conclusions about the chemistry of M^{z+}, one must examine the effects of various ligands and counterions on them.

A previous study of rubidium with benzo-18-crown-6 (B18C6) and thiocyanate ions showed that the rubidium ion is coordinated on one side with the crown and on the other side through the nitrogen of the thiocyanate [2]. A single molecule of the large cavity crown, dibenzo-30-crown-10, was found to encapsulate rubidium displacing the thiocyanate completely [3]. No studies on rubidium have been done using smaller ligands and different anions with rubidium. Here, we examine the complex formed between this cation and the smaller benzo-15-crown-5 (B15C5) with nitrate as counteranion.

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2. Experimental

Data collection was conducted on a Syntex $P2_1$ diffractometer equipped with a graphite monochromator (Mo$K\alpha$, $\lambda = 0.71069$ Å) and a LT–1 inert gas (N_2) low-temperature delivery system maintained at 163 K. A variable speed ω scan mode (3.0–6.0 deg/min) was used over a range of 1° in ω about the $K\alpha$ maxima with backgrounds counted at 1.0° on each side of a peak for an amount of time equal to the scan time.

A crystal of dimensions 0.86 mm × 1.56 mm × 2.00 mm and volume 2.23 mm³ was used in data collection. Lattice constants (Table I) were determined by a least-squares refinement of the angular settings of 15 reflections. Independent reflections (6562) were collected between 2θ values of 4° and 53°; of these, 4588 were considered observed ($F > 3\sigma(F)$). Four standard reflections were checked every 96 reflections to monitor crystal and instrumental stability. Intensities were corrected for decay by applying a multiplicative correction factor of $1/(1.0-0.00184x + 0.000019x^2)$ where x is exposure time in hours with coefficients determined from a least-squares analysis of the standard reflections. Absorption corrections were applied with a linear absorption coefficient of $\mu = 16.43$ cm^{-1}. The minimum and maximum transmission factors were 0.617 and 0.807, respectively. Intensities were also corrected for Lorentz-polarization effects.

Table I.   Crystallographic parameters for Rb(B15C5)$_2$NO$_3 \cdot$ H$_2$O at 163 K

a	= 12.695(3) Å
b	= 19.471(3) Å
c	= 12.991(2) Å
β	= 99.60(2)°
V	= 3166 Å³
D_c	= 1.473 g/cm³ (163 K)
D_c	= 1.434 g/cm³ (298 K)
D_o	= 1.44 g/cm³ (298 K)*

Space group $P2_1/c$

$Z = 4$ $F(000) = 1424$ $FW = 702.11$

Mo$K\alpha$ $\lambda = 0.71069$ Å

μ(Mo$K\alpha$) = 16.43 cm^{-1}

* Unit cell parameters taken from precession photographs at 298 K are $a = 12.92$ Å, $b = 19.56$ Å, c = 13.05 Å, $\beta = 99.58°$, and $V = 3251$ Å³.

The Rb position was obtained from a Patterson map and subsequent phases were determined by the heavy-atom method. The remaining non-hydrogen atoms were located in difference electron density maps. Isotropic refinement converged at $R = 0.101$. Anisotropic refinement converged at $R = 0.078$. The hydrogen atoms associated with the water molecule were located in a difference electron density map. The remaining hydrogen positions were calculated by assigning C—H = 0.95 Å and C—C—H = 120° for hydrogens attached to trigonal carbons and C—C—H = 109° for hydrogens attached to tetrahedral carbons. Addition of the hydrogen positions yielded a final R factor of 0.062 for $R = \Sigma |F_0-F_c|/\Sigma |F_0|$. Atomic positional parameters were refined as well as the temperature factors for non-hydrogens. Atomic positions of the hydrogens were refined one cycle. Isotropic temperature factors of the bonded non-hydrogen atom were assigned to each of the hydrogens and not refined.

The density measured at room temperature by the floatation technique in a gradient of 1-bromopentane and 1,4-dibromobutane was 1.44 g/cm³ compared to a value of 1.434 g/cm³

calculated from unit cell parameters obtained from precession photographs for $Z = 4$. The calculated density at 163 K was 1.473 g/cm^3.

3. Results

Crystallographic parameters are listed in Table I. The positional parameters, with standard deviations, for all non-hydrogen atoms are given in Table II. The numbering scheme, bond distances, bond angles, and standard deviations for the rubidium, nitrate, B15C5, and water molecules are shown in Figures 1 and 2. Figure 3 is a stereo ORTEP drawing of one asymmetric unit while Figure 4 is a stereo ORTEP drawing illustrating the packing in the $P2_1/c$ unit cell.

Table II. Atomic coordinates in fractions of cell edges

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Rb$^+$	0.28735(5)	0.07138(3)	0.21282(5)	C(22)	0.4969(6)	0.2060(4)	0.3379(6)
O(1)	0.0610(4)	0.0491(2)	0.2577(4)	O(23)	0.4411(4)	0.1869(3)	0.2371(4)
C(2)	0.0458(5)	0.0939(3)	0.3407(5)	C(24)	0.5106(7)	0.1777(4)	0.1627(6)
C(3)	0.0456(5)	0.1659(4)	0.2989(5)	C(25)	0.5663(6)	0.1097(4)	0.1698(6)
O(4)	0.1501(4)	0.1799(3)	0.2778(4)	O(26)	0.4895(4)	0.0567(3)	0.1398(4)
C(5)	0.1546(6)	0.2377(4)	0.2093(5)	C(27)	0.5363(6)	− 0.0090(4)	0.1489(6)
C(6)	0.1180(6)	0.2210(4)	0.0951(6)	C(28)	0.4512(6)	− 0.0634(4)	0.1296(6)
O(7)	0.1929(4)	0.1745(3)	0.0619(4)	O(29)	0.3819(4)	− 0.0650(3)	0.2059(4)
C(8)	0.1611(7)	0.1538(4)	− 0.0433(6)	C(30)	0.4259(6)	− 0.1017(4)	0.2993(6)
C(9)	0.2410(7)	0.1035(4)	− 0.0717(6)	C(31)	0.3680(6)	− 0.0819(3)	0.3850(6)
O(10)	0.2422(4)	0.0399(3)	− 0.0140(4)	O(32)	0.3894(4)	− 0.0102(2)	0.4065(4)
C(11)	0.1611(6)	− 0.0066(4)	− 0.0561(5)	C(33)	0.3398(5)	0.0205(4)	0.4801(5)
C(12)	0.1481(5)	− 0.0597(4)	− 0.0250(6)	C(34)	0.3507(5)	0.0923(3)	0.4860(5)
O(13)	0.1103(4)	− 0.0228(2)	0.1079(4)	C(35)	0.3012(6)	0.1302(4)	0.5548(5)
C(14)	0.0981(5)	− 0.0602(4)	0.1938(5)	C(36)	0.2419(6)	0.0953(4)	0.6198(6)
C(15)	0.0691(5)	− 0.0199(3)	0.2765(5)	C(37)	0.2334(6)	0.0251(4)	0.6168(6)
C(16)	0.0528(6)	− 0.0523(4)	0.3679(5)	C(38)	0.2815(6)	− 0.0129(4)	0.5474(6)
C(17)	0.0658(6)	− 0.1231(4)	0.3788(6)	N(39)	0.2315(5)	− 0.2220(3)	− 0.0413(5)
C(18)	0.0942(6)	− 0.1618(4)	0.2986(7)	O(40)	0.3194(6)	− 0.2494(6)	− 0.0284(8)
C(19)	0.1097(6)	− 0.1306(4)	0.2063(6)	O(41)	0.2034(5)	− 0.1825(3)	− 0.1166(4)
O(20)	0.4120(4)	0.1198(2)	0.4185(4)	O(42)	0.1652(5)	− 0.2358(3)	0.0176(5)
C(21)	0.4264(7)	0.1923(4)	0.4171(6)	O(43)	0.2092(5)	− 0.1547(3)	− 0.3357(5)

Analysis of the structure (Figure 3) reveals that all ten crown oxygens of the B15C5 molecules are coordinated with the rubidium (Rb$\cdots$O distances, 2.92 to 3.07 Å). The nearest oxygen from a nitrate anion is displaced 6.5 Å from the rubidium yielding a charge-separated sandwich. Each nitrate is hydrogen bonded to two nearby water molecules O(43)$\cdots$O(41), 2.910(9) Å; O(43)$\cdots$O(42), 2.851(9) Å). This combination presents a chain of alternating nitrate-water *ad infinitum*. Oxygen O(40) is not fixed by hydrogen bonding and can be seen in the ORTEP drawings to have much higher thermal parameters than the other nitrate oxygens.

Overall, each B15C5 crown closely resembles the structure of the uncomplexed crown [4]. The crown 1 and crown 2 oxygen atoms (Figures 1 and 2) deviate from planarity alternately with a maximum deviation of 0.39 Å. The distance between these two planes is approximately
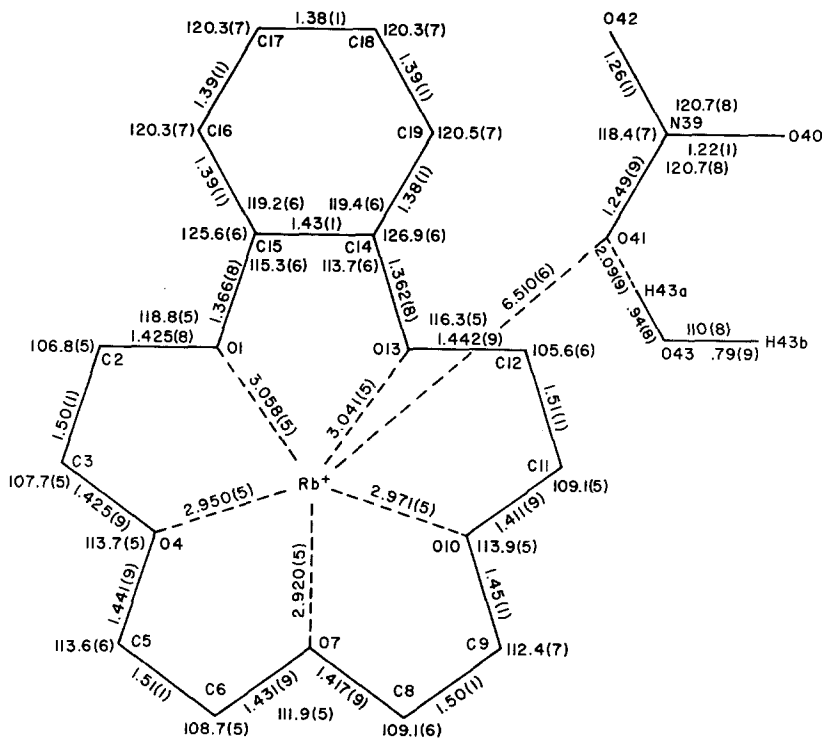
Fig. 1. Diagram of the rubidium, crown moiety 1, and the nitrate–water showing atom designations, the bond distances (Å) and angles (°).
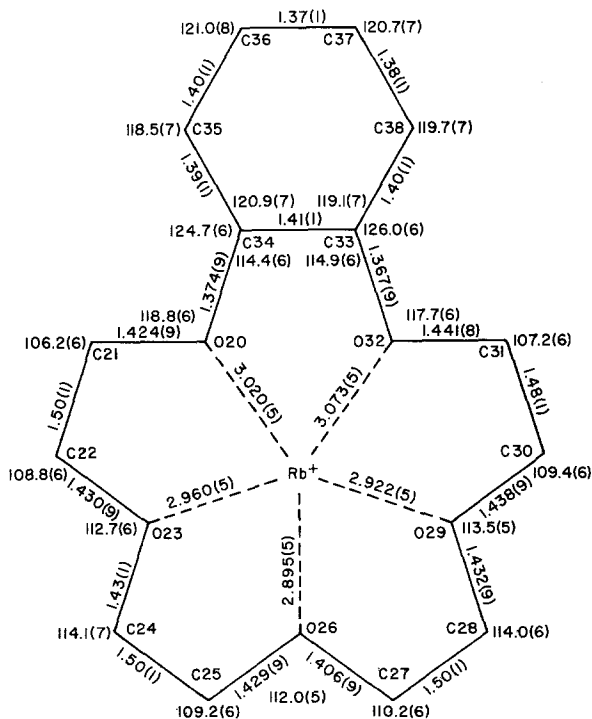

Fig. 2. Diagram of the rubidium and crown moiety 2 showing the atom designations, the bond distances (Å), and angles (°).
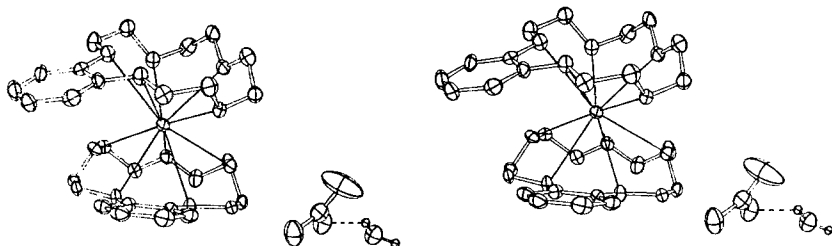
Fig. 3. Stereo ORTEP drawing of one asymmetric unit showing the coordination of the rubidium to the two crowns and the nitrate and water molecules.
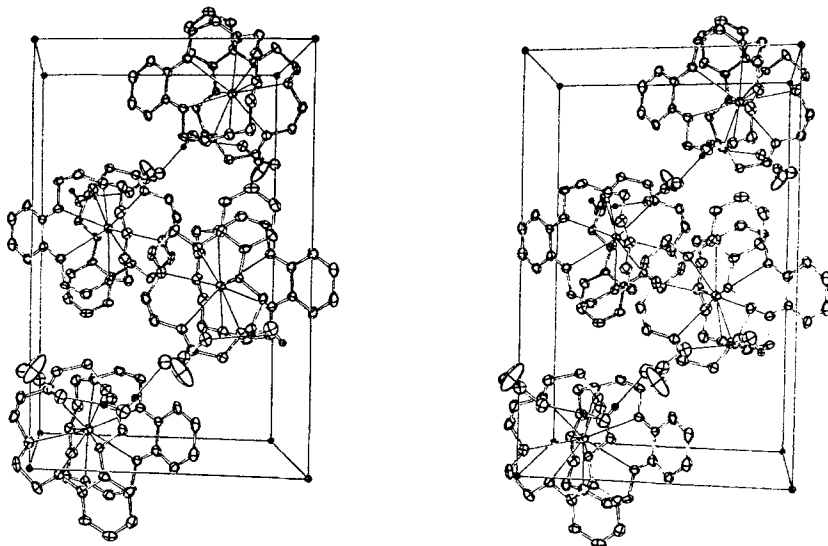

Fig. 4. Stereo ORTEP drawing of a $P2_1/c$ unit cell looking down the a-axis with the b-axis vertical.

4.9 Å and the acute angle between them is 13.4°. The C—O—C angles of the crowns vary from 112° to 119° with the C—O bond lengths between 1.37 and 1.45 Å. The larger C—O—C angles and shorter O—C bond lengths are associated with the oxygens nearest to the benzo rings (O(1), O(13), O(20), O(32)). The bond lengths between these oxygens and Rb (Rb···O, 3.02 to 3.07 Å) are also longer than the other crown O—Rb distances (Rb···O, 2.90 to 2.97 Å) as expected by the electron-withdrawing effect of the aromatic rings. The C(sp^3)—C(sp^3) distances vary from 1.48 to 1.51 Å with O—C—C angles between 106° and 114°.

Bond lengths in the benzene rings range from 1.38 to 1.43 Å in crown 1 whereas bond lengths in crown 2 vary from 1.37 to 1.41 Å. The longer bond lengths lie between carbon atoms of the benzo ring that are also bound to the crown oxygens (C(14) to C(15) and C(33) to C(34)). The benzene ring in crown 1 is coplanar within 0.004 Å and is coplanar with O(1) and O(13) to within 0.014 Å. The angle between the crown 1 oxygen plane and the benzo group plane is 24°. The benzo group in crown 2 has a maximum planar deviation of 0.01 Å

Table III. Planes through various groups of atoms and the deviations (Å) of individual atoms. The equations refer to orthogonal axes parallel to the crystallographic a, b, and c^* axes.

(i) Crown 1 oxygen atoms
$0.800\,I - 0.230\,J + 0.555\,K = 1.903$
O(1) -0.119 O(4) 0.309   O(7) -0.392 O(10) 0.303   O(13) -0.101

(ii) Crown 2 oxygen atoms
$0.917\,I - 0.149\,J + 0.370\,K = 5.529$
O(20) 0.070   O(23) -0.284 O(26) 0.390   O(29) -0.327 O(32) 0.151

(iii) Crown 1 benzene ring
$0.916\,I + 0.129\,J + 0.380\,K = 1.547$
C(14) 0.001   C(15) 0.003   C(16) -0.004 C(17) 0.001   C(18) 0.003   C(19) -0.004

(iv) Crown 2 benzene ring
$0.718\,I - 0.085\,J + 0.691\,K = 6.577$
C(33) -0.012 C(34) 0.011   C(35) -0.0003 C(36) -0.009 C(37) 0.008   C(38) 0.003

(v) Nitrate
$0.265\,I + 0.768\,J + 0.583\,K = 2.841$
N(39) -0.018 O(40) 0.006   O(41) 0.006   O(42) 0.006

(i):(ii)   13.41°
(i):(iii)   23.97°
(ii):(iv)   22.10°

and is coplanar with O(20) and O(32) to 0.027 Å. The angle between the benzo carbons and the crown 2 oxygen plane is 22°.

4. Discussion

As is predicted from the charge-density theory [1], rubidium forms a 1:2 charge-separated sandwich with the crown ether B15C5. The charge on the displaced nitrate is stabilized by hydrogen bonding with neighboring water molecules to form chains parallel to the c-axis that extend throughout the crystal. The related complex, RbI(B15C5)$_2$, is unstable in the solid state, probably because iodide is not similarly stabilized [5]. While the picrate anion does not permit sandwich formation of cesium (or rubidium) with B15C5 [6], stable 1:2 sandwiches are formed with potassium for any of [(3,5-dinitrobenzoate)(3,5-dinitrobenzoic acid)$_2$] [7], iodide [8], and picrate [9].

Acknowledgements

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