

Coordination Chemistry of Alkali and Alkaline Earth Cations. X-ray Structural Analysis of bis(Benzo-15-crown-5)Potassium Nitrate Monohydrate

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Abstract. The 1:2 charge separated KNO_3 complex with benzo-15-crown-5 (B15C5) has been crystallized from a 50% water-methanol solution. $\text{K}(\text{B15C5})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ is monoclinic, $P2_1/c$, $a = 12.717(2)$, $b = 19.569(2)$, $c = 13.025(3)$ Å, $\beta = 100.79(1)^\circ$, $Z = 4$, $D_c = 1.37 \text{ g} \cdot \text{cm}^{-3}$. The X-ray structure was refined to $R = 0.052$ for 3049 independent reflections with $F_0^2 \geq 2.0\sigma(F_0^2)$, collected with $\text{MoK}\alpha$ radiation for a 2θ -range of $4\text{--}44^\circ$. The K^+ ion is coordinated tenfold in a crown sandwich through all five oxygen atoms of the macrocyclic ligand. Nitrate and water oxygens are not involved in the cation coordination sphere.

Key words: Potassium, benzo-15-crown-5, sandwich complex, counteracting anion effect, X-ray structural analysis.

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1. Introduction

During the course of our pursuits directed at investigating the interactive differences between seemingly alike pairs of alkali or alkaline earth cations (M^{z+}), we have found that chemical distinction of K^+ from Rb^+ and of Sr^{2+} from Ca^{2+} or Ba^{2+} is least in contrast to other pairs [1]. The chemical similarity between K^+ and Rb^+ is, in fact, so pronounced that Rb^+ has been recommended as a possible probe for K^+ in biological studies [2]. Close examination of the chemistries of these two cations [3] has led us to the conclusion that the similarity is indeed striking but that some differences do exist. In order to achieve a deeper understanding, we have undertaken X-ray structural analyses of analogous systems of K^+ and Rb^+ . Herein, we report the structure of $\text{K}(\text{B15C5})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ (B15C5 = benzo-15-crown-5), which enables a comparison with the known structure of the analogous Rb complex [4]. Of particular interest is the conformation of the macrocyclic B15C5 ligands in the two complexes.

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2. Experimental

2.1. SYNTHESIS OF $K(B15C5)_2NO_3 \cdot H_2O$

Single crystals of the complex were grown by slow evaporation of a 1:2 KNO_3 :B15C5 reaction mixture in 50% aqueous methanol.

2.2. X-RAY STRUCTURAL ANALYSIS

A prismatic crystal with the dimensions $0.32 \times 0.22 \times 0.46$ mm was used for the data collection. Crystallographic parameters are summarised in Table I. Cell parameters were determined by a least-squares fitting of the settings for 25 reflections measured on an Enraf-Nonius CAD4 diffractometer. Intensities were collected with graphite-monochromated $MoK\alpha$ ($\lambda = 0.71073$ Å) radiation. Measurements were carried out in the ω -mode at variable speed for a scan range of $0.75 + 0.35 \tan \theta^\circ$. 3888 reflections were collected for one quadrant of reciprocal space for a 2θ range of $4-44^\circ$. Three control reflections were recorded every hour in order to monitor crystal and instrument stability. No significant alteration of their intensities was observed during data collection.

Table I. Crystallographic Parameters for $K(B15C5)_2NO_3 \cdot H_2O$ at $20^\circ C$

| | |
|---------------------------|-------------------------------|
| $a = 12.717(2)$ Å | $Z = 4$ |
| $b = 19.569(2)$ Å | $D_c = 1.37$ g cm $^{-3}$ |
| $c = 13.025(3)$ Å | $M = 655.7$ |
| $\beta = 100.79(1)^\circ$ | Space group $P2_1/c$ (No. 14) |
| $V = 3184(2)$ Å 3 | |

The intensities were corrected for Lorentz, polarisation and absorption (ψ -scan, $\mu(Mo-K\alpha) = 2.29$ cm $^{-1}$, transmission factors 0.736 (min)–0.847 (max)). After data reduction, 3049 independent reflections with $F_o^2 \geq 2\sigma(F_o^2)$ were retained for use in the subsequent refinement. The structure was solved by direct methods using MULTAN-82 [5] and refined by full-matrix least squares, $\Sigma w\Delta^2$ being minimised. With the exception of the water protons, positions for the hydrogen atoms were calculated geometrically and included as fixed parameters in the final cycles of refinement. Anisotropic temperature factors were introduced for all other atoms. The terminal R -factor was 0.052 with a weighted value $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.047$. Weights were given by the expression $w = k[\sigma^2(F_o) + p^2F_o^2]^{-1}$, $p = 0.005$. A final difference synthesis was effectively contourless (± 0.32 e Å $^{-3}$); the maximum value of Δ/σ in the final cycle of refinement was 0.16. Table II lists the final coordinates for the nonhydrogen atoms with equivalent isotropic temperature factors. Tables of hydrogen atom positions and anisotropic temperature factor components, and a list of observed and calculated structure factors, have been deposited as supplementary material.

3. Results

3.1. CRYSTAL STRUCTURE

The numbering scheme, bond distances and bond angles are given in Figures 1 and 2. Figure 3 is an ORTEP drawing displaying the K^+ coordination.

Table II. Atom coordinates with equivalent isotropic temperature factors (\AA^2)

| Atom | x/a | y/b | z/c | B_{eq} |
|--------|------------|------------|-----------|-----------------|
| K | 0.2784(1) | 0.0716(1) | 0.7074(1) | 3.4(1) |
| O(1) | 0.1735(3) | -0.2355(2) | 0.5164(3) | 11.3(1) |
| O(2) | 0.2103(3) | -0.1850(2) | 0.3866(3) | 8.4(1) |
| O(3) | 0.6779(3) | 0.2467(3) | 1.0297(4) | 15.9(2) |
| O(4) | 0.2048(3) | -0.3424(2) | 0.6678(3) | 7.5(1) |
| O(11) | 0.1181(2) | -0.0244(1) | 0.6100(2) | 4.0(1) |
| O(12) | 0.2442(2) | 0.0375(1) | 0.4867(2) | 4.1(1) |
| O(13) | 0.1962(2) | 0.1710(1) | 0.5602(2) | 4.2(1) |
| O(14) | 0.1557(2) | 0.1767(1) | 0.7720(2) | 3.8(1) |
| O(15) | 0.0697(2) | 0.0471(1) | 0.7559(2) | 3.9(1) |
| O(21) | 0.3779(2) | -0.0070(1) | 0.9012(2) | 4.1(1) |
| O(22) | 0.3798(2) | -0.0607(1) | 0.7065(2) | 3.9(1) |
| O(23) | 0.4816(2) | 0.0594(1) | 0.6404(2) | 4.3(1) |
| O(24) | 0.4319(2) | 0.1868(1) | 0.7353(2) | 4.6(1) |
| O(25) | 0.4020(2) | 0.1209(1) | 0.9138(2) | 4.1(1) |
| N(1) | -0.2418(3) | 0.2244(2) | 0.5408(3) | 6.8(1) |
| C(11) | 0.1490(3) | -0.0612(2) | 0.5252(3) | 4.2(1) |
| C(12) | 0.1604(3) | -0.0090(2) | 0.4440(3) | 4.7(1) |
| C(13) | 0.2443(4) | 0.0996(2) | 0.4292(3) | 5.1(1) |
| C(14) | 0.1663(4) | 0.1511(2) | 0.4540(3) | 5.3(1) |
| C(15) | 0.1217(3) | 0.2170(2) | 0.5915(3) | 4.1(1) |
| C(16) | 0.1588(3) | 0.2341(2) | 0.7050(3) | 3.8(1) |
| C(17) | 0.0507(3) | 0.1623(2) | 0.7928(3) | 3.9(1) |
| C(18) | 0.0501(3) | 0.0920(2) | 0.8374(3) | 3.7(1) |
| C(21) | 0.3642(3) | -0.0787(2) | 0.8841(3) | 3.8(1) |
| C(22) | 0.4250(3) | -0.0964(2) | 0.7996(3) | 4.4(1) |
| C(23) | 0.4480(3) | -0.0601(2) | 0.6313(3) | 4.7(1) |
| C(24) | 0.5318(3) | -0.0053(2) | 0.6520(3) | 4.9(1) |
| C(25) | 0.5574(3) | 0.1129(2) | 0.6668(3) | 5.2(1) |
| C(26) | 0.4997(4) | 0.1798(2) | 0.6598(3) | 5.4(1) |
| C(27) | 0.4905(3) | 0.2056(2) | 0.8358(3) | 5.0(1) |
| C(28) | 0.4206(3) | 0.1933(2) | 0.9148(3) | 4.5(1) |
| C(191) | 0.0727(3) | -0.0219(2) | 0.7752(3) | 3.4(1) |
| C(192) | 0.0530(3) | -0.0528(2) | 0.8642(3) | 3.8(1) |
| C(193) | 0.0622(3) | -0.1238(2) | 0.8746(3) | 4.7(1) |
| C(194) | 0.0901(3) | -0.1623(2) | 0.7955(4) | 4.7(1) |
| C(195) | 0.1093(3) | -0.1313(2) | 0.7044(3) | 4.0(1) |
| C(196) | 0.1010(3) | -0.0616(2) | 0.6944(3) | 3.4(1) |
| C(291) | 0.3542(3) | 0.0942(2) | 0.9834(3) | 3.4(1) |
| C(292) | 0.3004(3) | 0.1313(2) | 1.0553(3) | 4.2(1) |
| C(293) | 0.2451(4) | 0.0968(2) | 1.1217(3) | 5.1(1) |
| C(294) | 0.2355(3) | 0.0270(2) | 1.1177(3) | 4.8(1) |
| C(295) | 0.2802(3) | -0.0114(2) | 1.0459(3) | 4.0(1) |
| C(296) | 0.3332(3) | 0.0230(2) | 0.9782(3) | 3.3(1) |

$\text{K}(\text{B15C5})_2\text{NO}_3 \cdot \text{H}_2\text{O}$ is a sandwich complex in which the K^+ ion is coordinated by all five oxygen atoms of the B15C5 ligand. Nitrate and water oxygens are not involved in the cation coordination sphere. The K complex is isostructural with the analogous Rb complex [4]. As a result of the smaller size of the K^+ cation, $\text{K} \cdots \text{O}$ distances are between 0.051 and 0.117 \AA shorter than the equivalent $\text{Rb} \cdots \text{O}$ distances, which is in accordance with the difference in the effective ionic radii of the cations [6]. As has been observed in previous studies

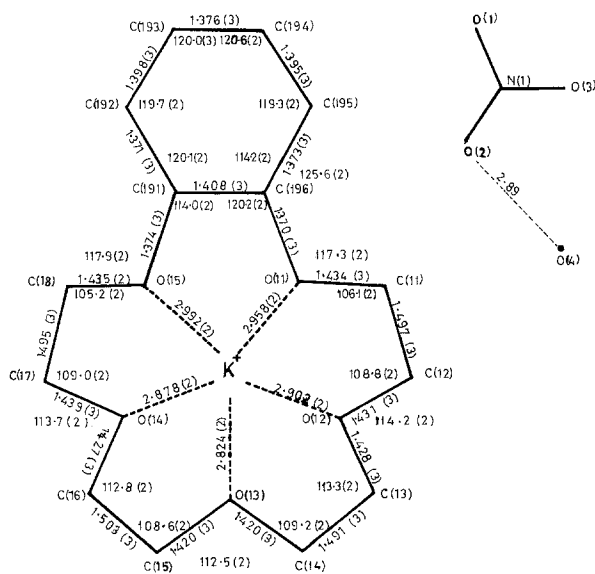


Fig. 1. Bond distances (Å) and angles with estimated standard deviations for the first B15C5 ligand.

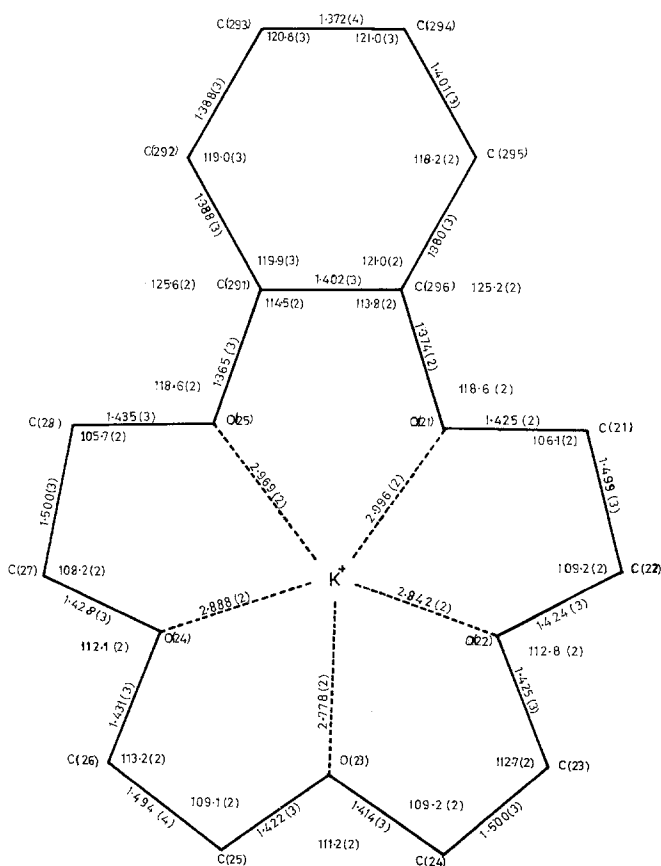


Fig. 2. Bond distances (Å) and angles with estimated standard deviations for the second B15C5 ligand.

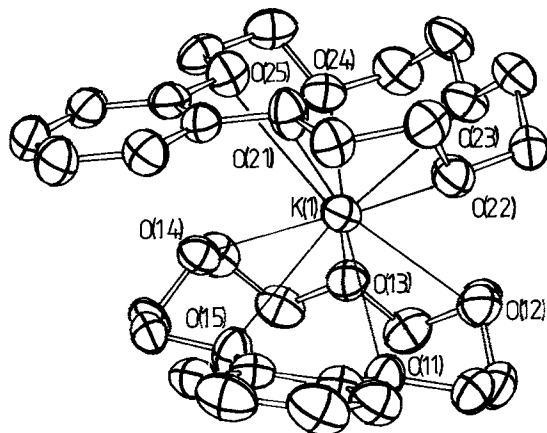


Fig. 3. ORTEP drawing of the $[K(B15C5)_2]^+$ cation.

on B15C5-complexes [7,8], the two oxygens adjacent to the phenyl ring form the longest $K \cdots O$ bonds (2.958–2.996 Å). The distances to atoms O(12)[O(22)] and O(14)[O(24)] are intermediate in length (2.842–2.902 Å), and the $K \cdots O$ bonds to the O atoms opposite to the phenyl ring, O(13)[O(23)], are short (2.824, 2.778 Å).

The K^+ cation is displaced, respectively, +1.738(1) and $-1.707(1)$ Å from the best least-square planes of the coordination O atoms of the two crown ligands of the sandwich (plane 1, $0.799x - 0.213y + 0.561z - 4.587 = 0$; plane 2, $0.904x - 0.137y + 0.404z - 6.194 = 0$). The five O-atoms are coplanar to within $-0.37 \dots + 0.28$ Å for the first ligand and $-0.29 \dots + 0.36$ Å for the second ligand. For the Rb complex the crown ligands are somewhat further apart with cation distances +1.804 and -1.838 Å, respectively, from the coordinating O atom planes. The benzene moieties make angles of 20.6 and 18.1°, respectively, with the O atom planes for $K(B15C5)_2NO_3 \cdot H_2O$, similar to the value of 20° found by Owen in $Na(B15C5)ClO_4$ [9]. An angle of 20.4° is observed between the planes of the individual benzene rings with the closest contacts occurring between C(192) and C(295) (3.471 Å) and C(193) and C(296) (3.495 Å). Bond distances and angles in the crown ligands lie in the typical regions. The nitrate oxygen O(2) builds an $O \cdots H - O$ hydrogen bond of length 2.89 Å with the water oxygen O(4).

3.2. CHEMICAL SIGNIFICANCE

Crown complexes of metal nitrates have not previously been reported in the literature. This is essentially because the relatively high lattice energy of $M(NO_3)_z$ salts prevents the complexation (solubilization) in the organic media required for work on crowns in solution. The KNO_3 and $RbNO_3$ complexes could, however, be obtained because these are salts of comparatively low lattice energy, the synthesis medium (50% water-methanol) is efficiently solubilizing towards the salt as well as the crown, and the crown understandably causes charge separation of both the salts in solution.

In the crystal lattice, potassium has invariably been found to be charge separated by B15C5 ligands irrespective of whether the counter ion is iodide [7], picrate [8], or the acid anion [3,5-dinitrobenzoate(3,5-dinitrobenzoic acid) $_2$] $^-$ [10]. Such complexes are indefinitely stable in the solid state, which also applies to the present complex. The conclusions from these

observations are that (i) potassium is poorly anionophilic and strongly ligandophilic, and (ii) the K—O(crown) bonds are strong enough to resist the effect of the charge separated (electrostatically destabilized) counter ion. This consistent behaviour of potassium distinguishes it from rubidium for which the B15C5/anion preference is strongly anion dependent. For nitrate, which is stabilized in the lattice by a hydrogen bonded molecule of water, Rb also builds a stable sandwich, leading to a crystal lattice isostructural with the analogous K complex reported in this work. For iodide, which crystallises without water in the lattice, the complex — Rb(B15C5)₂I — slowly decomposes, precluding any X-ray structural work (unpublished studies). For picrate, which is chelating in character, the Lewis acidity of Rb is quenched to the extent that a 1 : 2 sandwich is not formed at all and the 1 : 1 product, which is obtained, is similar to the anion-paired Ca(pic)(B15C5) [11].

As for the RbNO₃ complex with B15C5, but unlike other analogous K complexes [7, 8, 10], the benzene moieties of the crown molecules in the present complex approach one another rather closely, which is probably necessary in order to accommodate the chains of solvated nitrate ions. In the close-fit complexes such as (KNCS)₂(DB24C8) [12], the K···O(crown) distances can be as short as 2.7 Å, but for the [K(B15C5)₂]⁺ sandwiches, in which the cation enjoys a greater degree of freedom, distances have been found to range between 2.78 and 2.96 Å [7, 8, 10]. In the present complex the K···O distances to the four benzene based oxygens are on average significantly longer than previously observed [approaching 3.0 Å for K···O(15) and K···O(21)]. These bonds are markedly longer than K···O bonds to the other oxygens in the crown rings, as has been found for M^{z+} complexes with B15C5 in general [7, 8, 10, 13, 14].

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References

1. N. S. Poonia and A. V. Bajaj: *Chem. Rev.* **79**, 389 (1979).
2. R. J. P. Williams: *Quart. Rev.* **24**, 331 (1970).
3. N. S. Poonia: *J. Sci. Ind. Res.* **36**, 288 (1977).
4. C. Momany, K. Clinger, M. L. Hackert, and N. S. Poonia: *J. Incl. Phenom.* **4**, 000 (1986).
5. P. Main: Multan-82, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, York, 1982.
6. R. D. Shanon and C. T. Prewitt: *Acta Crystallogr.* **B25**, 925 (1969).
7. P. R. Mallinson and M. R. Truter: *J. Chem. Soc., Perkin Trans. 2*, 1818 (1972).
8. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **17**, 207 (1981).
9. J. D. Owen: *J. Chem. Soc., Dalton Trans.*, 1066 (1980).
10. W. X. Xu, K. Clinger, M. L. Hackert, and N. S. Poonia: *J. Incl. Phenom.* **3**, 163 (1985).
11. W. Montfort, S. R. Ernst, M. L. Hackert, N. S. Poonia, and K. Venkatasubramanian: *J. Incl. Phenom.* in the press.
12. D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter: *J. Chem. Soc., Chem. Commun.* 66 (1972).
13. K. Venkatasubramanian, N. S. Poonia, M. L. Hackert, C. Clinger, and S. R. Ernst: *J. Incl. Phenom.* **1**, 319 (1984).
14. D. L. Ward, A. I. Popov, and N. S. Poonia: *Acta Crystallogr.* **C40**, 238 (1984).