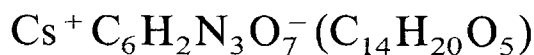


Coordination Chemistry of Alkali and Alkaline Earth Cations: Synthesis and X-ray Crystal Structure of Cesium (picrate) (benzo-15-crown-5)



K. VENKATASUBRAMANIAN, K. JOSHI, and N. S. POONIA
Chemistry Department, Devi Ahilya University, Indore 452001, India

W. R. MONTFORT, S. R. ERNST, and M. L. HACKERT★
Chemistry Department and Clayton Foundation Biochemical Institute, University of Texas, Austin, TX 78712, U.S.A.

(Received: 11 February 1985)

Abstract. Crystals of the $\text{Cs}^+ \text{Pic}^-$ (B15C5) complex (Pic = picrate; B15C5 = benzo-15-crown-5) ($M_r = 629.3$) are yellow prisms which belong to the triclinic space group $P\bar{1}$ with $a = 7.377(4)$, $b = 11.372(2)$, $c = 14.806(2)$ Å, $\alpha = 90.31(1)$, $\beta = 91.06(2)$, $\gamma = 108.32(2)^\circ$, $Z = 2$, $D_x = 1.77$, and $D_m = 1.77 \text{ g cm}^{-3}$. Final $R = 0.055$ for 3575 observed reflections out of a total of 4004 measured reflections. Cesium forms a 1:1 anion paired complex with B15C5 like sodium rather than a charge separated sandwich structure as found for potassium and expected for cesium in view of the ion-cavity radius concept. The Cs cation is 9-coordinate involving the five crown oxygens ($\text{Cs}\cdots\text{O}$, 3.00(1) to 3.24(1) Å), the phenoxide ($\text{Cs}\cdots\text{O}^-$, 3.03(1) Å) and an *ortho* nitro group oxygen ($\text{Cs}\cdots\text{O}$, 3.01(1) Å) of the picrate counteranion and, uniquely, with two additional oxygens ($\text{Cs}\cdots\text{O}$, 3.17(1) and 3.40(1) Å) from a *para* nitro group of the picrate belonging to the adjacent molecule in the lattice. The Cs^+ ion lies 2.07 Å out of the mean plane formed by the crown oxygens. This system provides the first structural evidence that the interaction stoichiometry of an alkali cation with a cyclic multidentate ligand is not a function of the ion and cavity size alone but also of its Lewis acid strength as modified by the charge neutralizing anion.

Key words: cesium ion, picrate ion, benzo-15-crown-5, X-ray structural analysis.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82027.

1. Introduction

Sandwich encapsulation of an alkali (M^+) or alkaline earth (M^{2+}) cation (general abbr. M^{Z+}) with a cyclic multidentate ligand can be likened to the *in vivo* process of cation transport across a cell membrane. Both processes ensure effective cation concealment and charge separation from its charge neutralizer. We have, therefore, studied [1,2] the chemical principles aiding sandwich encapsulation of M^{Z+} with crown ethers to better understand the chemical processes by which seemingly similar pairs of cations (Na^+ and K^+ ; Mg^{2+} and Ca^{2+}) can be discriminated from one another under the conditions commonly found in cation transporting biological membranes. The best known theory in this area is the Ion-Cavity Radius Concept [3] according to which a 1:2 sandwich encapsulate is formed when cation size exceeds the cavity size of the complexing macrocycle. One of us (N.S.P.), however, argued [4] that it is the charge density of the cation together with the nature of the anion which determines its macrocycle versus anion preference. To understand in depth the principles

★ Author for correspondence.

related to these anion versus ligand preferences of M^{Z+} , we have undertaken systematic X-ray diffraction analyses of related M^{Z+} -B15C5 (B15C5 = benzo-15-crown-5) crystalline systems, each carrying either 2,4,6-trinitrophenolate(Pic) or 3,5-dinitrobenzoate(35-Dnb) as the charge neutralizer. Solid state examination has been preferred to obviate the obscuring effects of solvent on the M^{Z+} -ligand and M^{Z+} -anion interactions. This communication describes the results of the X-ray structure determination of the Cs(Pic)(B15C5) compound.

2. Experimental

Yellow prisms of the complex were obtained by a slow evaporation of an ethanolic reaction mixture of CsPic and B15C5 (1:1; 0.4 mmol). The chemical composition of complexes obtained from solutions containing CsPic and B15C5 was always Cs(Pic)·(B15C5) [5]. A

Table I. Positional parameters¹ of nonhydrogen atoms

Atom	x	y	z	$U_{eq} (\times 10^3)$
Cs	0.08526(8)	0.47305(5)	0.24687(4)	4.49
O(1)	-0.2685(9)	0.2791(5)	0.1375(4)	4.53
C(2)	-0.243(2)	0.3100(8)	0.0448(6)	5.33
C(3)	-0.286(1)	0.4298(9)	0.0340(6)	5.38
O(4)	-0.1480(9)	0.5253(5)	0.0852(4)	4.88
C(5)	-0.214(1)	0.6287(8)	0.1055(7)	5.54
C(6)	-0.339(1)	0.6067(9)	0.1861(7)	4.93
O(7)	-0.2254(9)	0.6105(6)	0.2643(4)	5.09
C(8)	-0.333(2)	0.589(1)	0.3445(8)	5.80
C(9)	-0.207(2)	0.575(1)	0.4211(7)	6.17
O(10)	-0.1469(9)	0.4686(6)	0.4121(4)	5.01
C(11)	-0.286(2)	0.358(1)	0.4404(6)	5.45
C(12)	-0.241(1)	0.2479(9)	0.4030(6)	4.80
O(13)	-0.2662(8)	0.2503(5)	0.3076(4)	4.10
C(14)	-0.248(1)	0.1528(8)	0.2578(6)	4.19
C(15)	-0.251(1)	0.1688(7)	0.1654(6)	4.77
C(16)	-0.238(1)	0.0750(9)	0.1083(7)	5.78
C(17)	-0.221(2)	-0.0347(9)	0.1446(8)	6.13
C(18)	-0.219(1)	-0.0495(9)	0.2360(8)	5.49
C(19)	-0.230(1)	0.0452(8)	0.2925(6)	3.93
C(20)	0.253(1)	0.1750(8)	0.3048(6)	3.97
C(21)	0.255(1)	0.0856(8)	0.3751(5)	4.00
C(22)	0.267(1)	-0.0292(8)	0.3600(6)	4.19
C(23)	0.274(1)	-0.0681(7)	0.2713(6)	4.12
C(24)	0.276(1)	0.0090(8)	0.1991(6)	3.97
C(25)	0.268(1)	0.1271(7)	0.2160(6)	4.10
O(26)	0.249(9)	0.2810(5)	0.3249(4)	4.74
N(27)	0.236(1)	0.1207(7)	0.4676(5)	4.88
O(28)	0.097(1)	0.1481(9)	0.4893(5)	7.67
O(29)	0.362(1)	0.1162(9)	0.5213(5)	8.55
N(30)	0.282(1)	-0.1908(6)	0.2547(6)	4.75
O(31)	0.293(1)	-0.2549(6)	0.3201(5)	6.00
O(32)	0.277(1)	-0.2285(6)	0.1756(5)	6.02
N(33)	0.271(1)	0.2003(7)	0.1365(5)	4.87
O(34)	0.295(1)	0.1587(7)	0.0628(5)	6.98
O(35)	0.254(1)	0.3045(7)	0.1443(5)	6.45

¹ Numbers in parentheses are estimated standard deviations in the least significant figure.

each reflection was then given as $Lp * A_{\text{emp}} * A_{\text{sph}} * D_r * D_{2\theta}$. The structure was solved by the heavy atom method where successive difference Fourier syntheses alternated with least-squares refinement led to the placement of all atoms. Full-matrix anisotropic refinement of the nonhydrogen atoms plus isotropic treatment of hydrogens resulted in a final $R = 0.055$ for the 3575 reflections considered observed ($I > 2\sigma(I)$).

3. Results

The positional parameters for all nonhydrogen atoms are given in Table I. Figures 1a and 1b show the numbering schemes, bond distances and bond angles for the crown and the picrate counterion in a state chelated with Cs. Figure 2 displays the coordination around the cation. The Cs⁺ ion is 9-coordinate through the five crown oxygens (Cs \cdots O, 3.00(1) to 3.24(1) Å), the intramolecular picrate via its phenoxide (Cs \cdots O⁻, 3.03(1) Å) and an *ortho* nitro oxygen (Cs \cdots O, 3.01(1) Å), and an intermolecular picrate via its *para* nitro oxygens (Cs \cdots O, 3.17(1) and 3.40(1) Å). Deviations from the crown oxygen and picrate planes are given in Table II. A packing diagram of the compound is depicted in Figure 3. Angles in the Cs coordination sphere of the type O—Cs—O range from 91 to 150°. The plane through the uncoordinated nitro group formed by N(27), O(28), and O(29) is 58.5° out of the plane formed by the picrate ring system while those of the nitro groups formed by N(30), O(31), O(32) and N(33), O(34), O(35) are out by only 5.1° and 4.6°, respectively.

Table II. Least squares plane calculations

A. Deviations of atoms from picrate ring* system					
C(20)*	-0.012	O(26)	0.033	O(31)	0.055
C(21)*	-0.002	N(27)	-0.053	O(32)	-0.133
C(22)*	0.013	O(28)	-0.980	N(33)	0.025
C(23)*	-0.012	O(29)	0.846	O(34)	0.124
C(24)*	-0.002	N(30)	-0.027	O(35)	-0.033
C(25)*	0.014				
B. Deviations of atoms from plane of 5 crown oxygens*					
O(1)*	0.126	O(4)*	-0.339	O(7)*	0.433
O(10)*	-0.336	O(13)*	0.116	Cs	-2.072

* Atoms used in the least squares plane calculation are indicated with an *.

4. Discussion

There are three unique features of this structure. First, in contrast to the well known ion-cavity radius concept [3, 7], Cs yields a 1:1 anion paired complex and not the predicted 1:2 sandwich, even though the Cs cation is larger than the cavity of B15C5. Second, unlike any other nitrophenolate reported thus far [1], the picrate anion is bidentate with respect to Cs ions and acts as a bridge between complexes. It coordinates to Cs intramolecularly through its phenoxide and one *ortho* nitro oxygen and then coordinates intermolecularly to a neighboring complex via the two oxygens of the *para* nitro group. Third, of the three oxygens on the aliphatic part of the crown ring (O(4), O(7), O(10)), the one (O(7)) on the most flexible region is attracted by the Cs rather poorly. These features of the complex should result, at

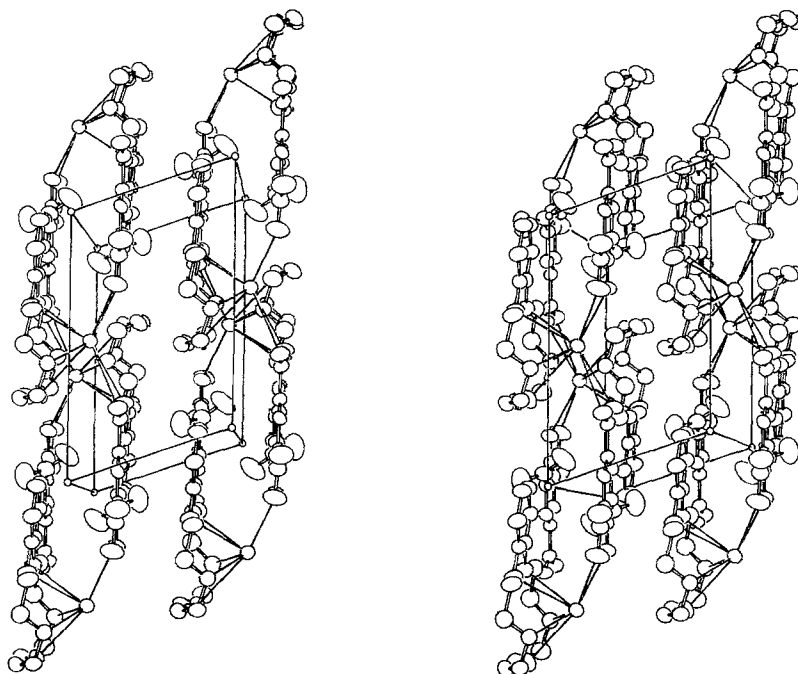


Fig. 3. ORTEP drawing of the crystal packing indicating the relative stacking of the planar groups and the environment of the *ortho* nitro group twisted out of the plane of the ring atoms. The origin is at the upper left with a^* horizontal and y vertical.

least in part, from the modification of the Lewis acid strength of Cs^+ towards the crown by the paired picrate anion.

The structure suggests that the cation within the discrete molecule $\text{Cs}(\text{Pic}) \cdot (\text{B15C5})$ is coordinatively unsaturated. For Cs^+ to achieve its coordinative saturation number, normally 8–12 [1], it does not form the expected sandwich. Instead, coordination is completed via a *para* nitro group of a neighboring Pic^- , a type of chelation which is unique for any nitrophenolate toward M^{Z+} , not noted even for the uncomplexed CsPic itself [8].

Of further interest are the non-equivalent $\text{Cs} \cdots \text{O}$ distances of the *para* nitro group, viz., O(31) and O(32), and the large out-of-plane twist of O(28) and O(29) in the nonchelating *ortho* nitro group. The first of these two features may be linked to the fact that coordination of cesium to the central picrate phenoxide O(26) and O(35) of the *ortho* nitro group creates a nonequivalence between O(31) and O(32). The out-of-plane twist of O(28) and O(29), an unexpected and energetically unfavorable state, most likely results from the steric restrictions imposed by neighboring atoms. The distance from O(29) to a C(19) related by $(-x, -y, 1-z)$ is 3.31 Å. Also, O(28) is wedged between C(12), a C(9) $(-x, 1-y, 1-z)$, and another O(28) $(-x, -y, 1-z)$ at 3.29, 3.26 and 3.24 Å, respectively. These distances are only slightly longer than the expected Van der Waals' distances and twisting the *ortho* nitro group either into or further out of the plane of the picrate ring system would severely shorten these contact distances to unacceptable values. In the related $\text{Na}(\text{pic})(\text{B15C5})$ [9] structure, the coordinating *ortho* nitro group was found to be rotated 20° from the plane of the picrate while the two remaining nitro groups were from 7 to 8° from the plane of the ring.

The structure of the Cs(Pic)(B15C5) complex is of interest in view of structural information already available on the series Li(Pic)(B15C5)2H₂O [10], Na(Pic)(B15C5) [9] and K(Pic)(B15C5)₂ [11] for which the crown preference is noted to increase towards K⁺. In the Li⁺ system, lithium prefers to be contained within the exclusive environment of the picrate and associated water molecules. Na⁺ chelates through all of the crown oxygens in a state that still maintains its pairing with the chelating picrate. For KPic, even a 1 : 1 reaction mixture with B15C5 yields a complete charge separation of K⁺ from picrate in favor of the two sandwiching B15C5 molecules. This situation for K⁺ (ionic diameter, 2.66 Å) has also been noted when iodide [12] or 3,5-Dnb [13] serves as the anion. Furthermore, the rather nucleophilic 3,5-Dnb forces disproportionation with the protic medium (ethanol) to generate free acid (3,5-DnbH) to form an acid-anion (2 : 1 conjugate acid–base pair) within the crystal [13]. In view of this trend, Cs⁺ was also expected to form a charge separated sandwich complex. However, it does not form the sandwich structure with picrate as it does with 15C5 in the presence of iodide [14]. In Cs(Pic)(B15C5), the effects of the acidic benzo substituent on the crown ring plus the chelating strength of pic collectively prevent this from happening. The strength of the pic is also evidenced in that even Rb⁺ yields 1 : 1 Rb(Pic)(B15C5), which is isomorphous [15] with the Cs⁺ complex, rather than a 1 : 2 sandwich like K⁺. Under some conditions Rb⁺ mimics K⁺ [16]. Even the use of excess crown (CsPic : B15C5, 1 : 5) or of ion-pair 'loosening solvents', including water, [2, 4] does not lead to the formation of a 1 : 2 sandwich. It would appear, therefore, that a 1 : 1 interaction of Cs⁺ (ionic diameter, 3.34 Å) [17] with B15C5 (cavity diameter, 1.7–2.2 Å) [18] in a state paired with Pic is a consequence of the Lewis acidity of the metal toward B15C5 (as modified by the paired Pic) and that the larger size of Cs⁺ alone cannot promote sandwich formation. This may be partially due to the poor polarizing ability of Cs⁺ when chelated with picrate anion as demonstrated by its inability to bring O(7), the oxygen on the most flexible part of the crown ring, as close into its coordinating sphere as O(4) and O(10).

The crown/anion preferences shown by Cs in the present complex are in line with our observations [1] in diverse solvating media wherein the neutral ligand preference of the rather poorly polarizing Cs⁺ decreases drastically (compared to K⁺) when more nucleophilic chelating organic anions are involved. That the nature of the anion can alter the neutral ligand preference of the cation is further evidenced by the structural results of the Na-B15C5 complexes. Sodium forms a 1 : 1 complex with picrate [9] (anion paired) or iodide [19] (water coordinated) but can be made to yield a charge separated 1 : 2 sandwich using BPh₄⁻ [20].

Acknowledgement

One of us (NSP) gratefully acknowledges the support of this work from the Department of Science and Technology, New Delhi. We also want to thank the referees for their helpful comments.

References

1. N. S. Poonia and A. V. Bajaj: *Chem. Rev.* **79**, 389 (1979).
2. N. S. Poonia, A. V. Bajaj, A. K. Arora, K. Joshi, A. Banthia: *Indian J. Chem., Sect. A* **19**, 37 (1980).
3. C. J. Pedersen and H. K. Frensdorff: *Angew. Chem., Int. Ed. Engl.* **11**, 16 (1972).
4. N. S. Poonia: *Progr. Macrocyclic. Chem.* **1**, 115 (1979).
5. Elemental analysis, Found: C, 38.01; H, 3.47; N, 6.71; Calc: C, 38.16; H, 3.50; N, 6.68.
6. A. C. T. North, D. C. Phillips, and F. S. Mathews: *Acta Crystallogr.* **A24**, 351 (1968).
7. C. J. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).

8. J. A. Kanters *et al.*: personal communication.
9. D. L. Ward, A. I. Popov, and N. S. Poonia: *Acta Crystallogr.* **C40**, 238 (1984).
10. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **16**, 373 (1980).
11. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **17**, 207 (1981).
12. P. R. Mallinson, and M. R. J. Truter: *J. Chem. Soc., Perkin Trans 2* 1818 (1972).
13. W. X. Xu, K. Clinger, M. L. Hackert, and N. S. Poonia: *J. Incl. Phenom.* **3**, 163–172 (1985).
14. M. Van Meerssche: personal communication.
15. K. Venkatasubramanian, N. S. Poonia, W. H. Watson: to be published.
16. N. S. Poonia: *J. Sci. Ind. Res.* **36**, 268 (1977).
17. R. T. Sanderson: *Inorganic Chemistry*, Van Nostrand Reinhold: New York, p. 136 (1967).
18. N. K. Dalley: *Synthetic Multidentate Macrocyclic Compounds* (Eds. R. M. Izatt and J. J. Christensen), p. 217 Academic Press, New York, (1978).
19. (a) M. A. Bush and M. R. Truter: *J. Chem. Soc. Chem. Commun.* 1439 (1970); (b) *J. Chem. Soc., Perkin Trans. 2* 341 (1972).
20. J. D. Owen: *J. Chem. Soc., Dalton Trans.* 1066 (1980).