Coordination Chemistry of Alkali and Alkaline Earth Cations. Barium-Crown Encapsulation Studies: The Synthesis and Crystal Structure of Barium(picrate)₂(benzo-15-crown-5) Monohydrate

K. VENKATASUBRAMANIAN and NARINDER S. POONIA
Chemistry Department, University of Indore, Indore 452 001, India

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

Abstract. The interaction of barium with benzo-15-crown-5 (B15C5) has been followed under the competitive effect of various chelating organic anions (L), nitrophenolates and nitrobenzoates, in ethanol and ethanol-water (9 : 1). The rather heavily hydrated BaL₂ salts yield novel 1 : 1 stoichiometric products in monohydrated or anhydrous states. Use of excess crown does not under any condition lead to the formation of 1 : 2 charge separated complexes, expected in view of the cavity and the cation sizes. The 1 : 1 Ba—B15C5 interaction is counteracted by L in accordance with its nucleophilicity, i.e., the pK_a value of its parent acid, HL. The complex Ba(picrate)₂(B15C5)·H₂O (BaC₂₆H₂₆N₆O₂₀, FW = 879.0), is monoclinic, $P2_1/c$, $a = 11.43(1)$, $b = 16.31(3)$, $c = 17.38(2)$ Å, $\beta = 92.265(3)°$, $Z = 4$, $D_c = 1.77$ g/cm³, $D_0 = 1.73$ g/cm³, MoKα, $\lambda = 0.71069$ Å, 2θ (4.0–50°), $\mu = 13.5$ cm⁻¹, $F(000) = 1752$, $T = -32°$C. Final R for the 5926 reflections was 0.049. The structure reveals barium to be 10-coordinated through all the five crown oxygens (Ba—O, 2.800 to 3.002 Å), the two bidentate picrates (Ba—O, 2.642 and 2.666 Å; Ba—ONO, 2.825 and 2.994 Å), and the water molecule (2.711 Å) so that the cation constitutes a pseudo-sandwich of the crown on one side and the anionic species on the other.

Key words: Barium, benzo-15-crown-5, chelating organic anion, counteracting anion effect, X-ray diffraction analysis.

1. Introduction

Since Pedersen [1] first demonstrated the complexation of crown ethers with alkali (M^+) and alkaline earth (M^{2+}) cations (general abbr. M^{z+}), M^{z+}-crown systems have formed an interesting subject [2] for investigations in solution and the solid state. These systems promise chemical information which may aid in understanding the different roles of sodium, potassium, magnesium and calcium in biological systems [3]. We believe [2] that interactive principles of the biologically important cations can be rationalized more confidently if the trends of all the M^{z+} ions interacting with potential neutral nucleophiles are investigated with regard to the effect of varying the inorganic as well as the organic counterions.

Most available M^{z+} crown ligand complexation results are for the 18-crown-6(18C6) or

★ Author for correspondence.

smaller cavities. However for the 15-crown-5(15C5) cavity and the smaller crowns, the only available results with the large M^{2+} ions (Sr and Ba) are from aqueous solutions with chloride as the counteranion. Under these conditions, 15C5 undergoes complexation with strontium and barium [4]. Naturally, it is of interest to know whether the less basic analog, benzo-15-crown-5(B15C5), can also succeed in encapsulating these cations, especially under a rather strong counteracting effect of the chelating organic anions. Such complexes are also possible models for interactions of the proteinaceous anionic species with metal cations in the somewhat alkaline biological fluids.

This led us to study the trends of the Ba—B15C5 reaction in ethanol and ethanol-water (9 : 1) using nitrophenolates: 2,4,6-trinitrophenolate (Pic), 2,4-dinitrophenolate (Dnp), and 2-nitrophenolate (Onp), and the nitrobenzoates: 2-nitrobenzoate (Onb), 3,4-dinitrobenzoate (34-Dnb), and 3,5-dinitrobenzoate (35-Dnb) as chelating organic charge neutralizers (L). Precise information with regard to the Ba—B15C5 interaction was obtained through X-ray structural analysis of $Ba(Pic)_2(B15C5) \cdot H_2O$ which contains the least nucleophilic L of all those listed. Work on the $Ba(35\text{-}Dnb)_2$—B15C5 complex, which contains the most nucleophilic L, is in progress.

Our earlier crystallographic work on M^{z+}—B15C5 systems containing Pic has revealed that the low charge density potassium can be charge-separated by the crown to obtain a 1 : 2 sandwich [5] as occurs for KI [6]. The higher charge density cations which are found in the systems $Li(Pic)(B15C5) \cdot 2H_2O$ [7], $Ca(Pic)_2(B15C5) \cdot 3H_2O$ [8], as well as $Ca(35\text{-}Dnb)_2(B15C5)_2 \cdot 3H_2O$ [9], escape chelation with the neutral ligand (B15C5) in favor of the anionic and solvent environments. In such cases, the non-chelated crown molecule remains stabilized in the lattice merely through bonding with proton(s) of the water molecules. Thus it was of interest to study the complexation of barium, an intermediate acidity cation, by B15C5 in the complex, $Ba(Pic)_2(B15C5) \cdot H_2O$.

Whereas workers with a crystallographic bias (e.g., [10]) focus more attention on features such as conformation and the symmetry of the crown molecule(s), we as chemists examine essentially the crown vis-à-vis anion (and solvent) preferences of the cation. Our ultimate aim is to examine differences between the interactions of different M^{z+} under common or similar conditions.

2. Experimental

2.1. SYNTHESIS OF BaL₂ SALTS

Each BaL_2 was synthesized by a 1 : 2 reaction of $Ba(OH)_2$ (0.5 Mol) with the appropriate organic acid (HL, 1 Mol) in water. The reactants were heated on a water bath (1–2 h) until consumed and the solution was set aside overnight in a refrigerator. The crude BaL_2 was filtered and crystallized twice from water. The rather water-insoluble $Ba(35\text{-}Dnb)_2$, however, could be leached only slightly even with 100 ml aliquots of boiling water. Each salt was characterized by hot stage microscopy, infrared spectral studies (in nujol), and elemental analysis.

2.2. BaL₂-SOLVATION AND COMPLEXATION STUDIES

Each BaL_2 (1 mMol) was warmed gradually with stirring in ethanol (5 ml) or ethanol-water (9 : 1) and the dissolution trends were followed. Each experiment was repeated in the presence of an equivalent amount of B15C5. For the rather non-solvating and non-complexing $Ba(34\text{-}Dnb)_2$, and in particular $Ba(35\text{-}Dnb)_2$, the suspension was refluxed for an hour using

excess (10 equivalents) B15C5. The filtrate of each BaL_2—B15C5 reaction was allowed to evaporate slowly at room temperature. The resulting crystalline complex was characterized as the BaL_2 species.

2.3. CRYSTALLOGRAPHIC STUDIES

A crystal measuring approximately $0.195 \times 0.185 \times 0.160$ mm with an approximate volume of 0.006 mm^3 was used in data collection. Reflections were measured using a Syntex P2$_1$ automated 4-circle diffractometer equipped with the Syntex LT-1 low temperature flow system and a graphite monochromator. Temperatures were maintained at approximately $-32\,°$C.

Lattice constants (Table I) were determined by a least-squares refinement of 15 reflections at approximately $-32\,°$C using graphite monochromated $MoK\alpha$ ($\lambda = 0.71069$ Å) radiation.

Table I. Crystallographic Parameters for $Ba(Pic)_2(B15C5)\cdot H_2O$ at $-32\,°$C

$a = 11.426$ Å	$\sigma = 0.010$ Å
$b = 16.313$ Å	$\sigma = 0.028$ Å
$c = 17.377$ Å	$\sigma = 0.021$ Å
$\beta = 92.265°$	$\sigma = 0.003°$
$V = 3236$ Å^3	
$D_c = 1.77$ g/cm^3 $(-32°)$	
$D_0 = 1.73$ g/cm^3 $(\approx 25°)$	
Space group $P2_1/c$	
$Z = 4$, $F(000) = 1752$, F.W. $= 879.0$	
$MoK\alpha$ $\lambda = 0.71069$ Å	
$\mu(MoK\alpha) = 13.5$ cm^{-1}	

The computed density for $Z = 4$ at the reduced temperature is 1.77 g/cm^3. The observed density at room temperature, measured by the flotation technique in a mixture of carbon tetrachloride and ethyl iodide, is 1.73 g/cm^3.

Intensity data were collected by a variable speed ω scan technique using the Syntex recentering ω program. Each peak was scanned symmetrically over a range of $1°$ in ω. Backgrounds were counted at one-half degree on each side of the peak for an amount of time equal to the scan time. 6430 reflections in the hkl and $-hkl$ quadrant were collected with $MoK\alpha$ radiation between 2θ values of 4–$50°$. All the reflections were used in the solution and refinement of the structure. Four standard reflections were used to determine crystal and instrument stability and their intensities were collected after every 96 reflections. The 66 standard sets were used in applying a multiplicative correction factor of $1/(1.0 + (-0.000\,179(x)) + 0.000\,001(x)^2)$ where x is the exposure time in hours. This correction was negligible. The intensities were also corrected for absorption, Lorentz and polarization effects.

The barium positions were determined via a Patterson map. The phases from these positions allowed the determination of all non-hydrogen atoms. Isotropic refinement converged at 0.074 for $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. After anisotropic refinement, all the hydrogen atoms were directly observable in the difference electron density map. Further refinement converged at $R = 0.049$.

3. Results

3.1. CHEMICAL ASPECTS OF BaL$_2$ SYSTEMS

The BaL$_2$—B15C5 reaction is largely insensitive to reaction conditions. Ba(Pic)$_2$(B15C5) · H$_2$O, for instance, can be synthesized irrespective of whether the reaction medium is ethanol, methanol, or 50% aq-methanol or whether B15C5 is present at molar ratios of 1 : 1 or 1 : 3. Therefore the 1 : 2 charge-separated sandwich, expected in view of the cation-cavity radius concept [1,11], is not formed and a thorough dehydration of the cation does not take place even when the most charge-delocalized counteranion (Pic) is involved. Each BaL$_2$—B15C5 product has a definite composition, melting without decomposition at a temperature below that for BaL$_2$ (paper in preparation) and showing an infrared spectrum devoid of the C—O (stretch) peak at 980 cm^{-1} which is attributed to the presence of B15C5 in the uncomplexed conformation [12]. The hydrated 1 : 1 complexes, obtained from the rather more heavily hydrated BaL$_2$, displayed the characteristics of the cation-coordinated water molecule, i.e., the OH (stretch) peak(s) were sharp and above 3500 cm^{-1}.

3.2. CRYSTALLOGRAPHIC ASPECTS

The crystallographic parameters are listed in Table I. The positions for all atoms are shown in Table II. The numbering scheme, bond distances and bond angles are shown in Figures 1 and 2. Figure 3 is an ORTEP drawing demonstrating the Ba^{2+} coordination while Table III gives the corresponding Ba—O distances. Figure 4 shows the packing of the molecules in the unit cell.

The maximum deviation for the mean plane containing the basal crown-oxygens is merely 0.36 Å. The Pic anions displace barium from the mean plane of the crown cavity by 1.76 Å. The interacting atoms of the Pic anions (O26, O28, O42, O44) and the water molecule are situated more than 2.8 Å above this plane so that barium is encapsulated within a pseudo-
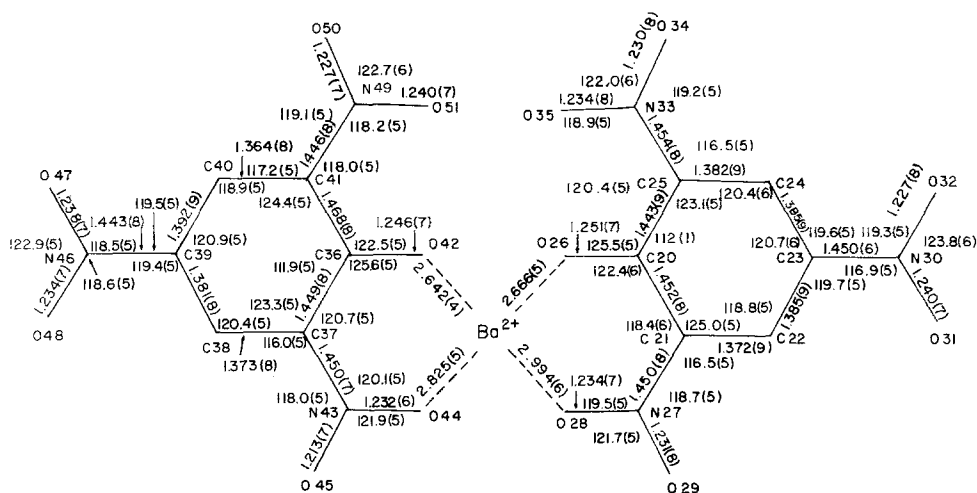

Fig. 1. Diagram of the barium and two picrate moieties showing the atom designations, the bond distances (Å) and angles with the estimated standard deviations of the last digit in parentheses.

Table II. Atomic coordinates in fractions of cell edges and their estimated standard deviations

Atom	x/a (σ)	y/b (σ)	z/c (σ)	Atom	x/a (σ)	y/b (σ)	z/c (σ)
Ba^{2+}	0.51953(3)	0.18092(2)	0.20317(2)	C40	0.0886 (5)	0.1354 (4)	− 0.0198 (3)
O1	0.3698 (4)	0.0330 (3)	0.2182 (2)	C41	0.2031 (5)	0.1260 (4)	0.0036 (3)
C2	0.4086 (6)	− 0.0324 (4)	0.1700 (4)	O42	0.3654 (3)	0.1616 (3)	0.0872 (2)
C3	0.5291 (6)	− 0.0539 (4)	0.1996 (4)	N43	0.2345 (4)	0.3008 (3)	0.1458 (3)
O4	0.6012 (4)	0.0171 (2)	0.1925 (2)	O44	0.3210 (4)	0.2837 (3)	0.1873 (2)
C5	0.7154 (6)	0.0093 (4)	0.2299 (4)	O45	0.1832 (4)	0.3654 (3)	0.1515 (3)
C6	0.7121 (6)	0.0329 (4)	0.3140 (4)	N46	− 0.0982 (5)	0.2074 (3)	− 0.0098 (3)
C7	0.6694 (4)	0.1143 (3)	0.3182 (2)	O47	− 0.1550 (4)	0.2614 (3)	0.0220 (3)
C8	0.6656 (6)	0.1422 (4)	0.3962 (4)	O48	− 0.1432 (4)	0.1575 (3)	− 0.0554 (3)
C9	0.6223 (6)	0.2319 (4)	0.3937 (4)	N49	0.2644 (5)	0.0556 (3)	− 0.0255 (3)
O10	0.5079 (3)	0.2375 (3)	0.3566 (2)	O50	0.3709 (4)	0.0592 (4)	− 0.0314 (3)
C11	0.4161 (6)	0.2204 (4)	0.4087 (4)	O51	0.2063 (5)	− 0.0061 (3)	− 0.0436 (3)
C12	0.3029 (5)	0.2139 (4)	0.3624 (4)	O52	0.6740 (5)	0.1532 (3)	0.0916 (3)
O13	0.3213 (4)	0.1489 (3)	0.3074 (2)	H2A	0.398 (5)	− 0.012 (4)	0.117 (4)
C14	0.2263 (5)	0.1197 (4)	0.2643 (3)	H2B	0.363 (5)	− 0.083 (4)	0.168 (4)
C15	0.2528 (5)	0.0555 (4)	0.2144 (3)	H3A	0.557 (5)	− 0.098 (4)	0.175 (4)
C16	0.1664 (6)	0.0215 (4)	0.1668 (4)	H3B	0.533 (5)	− 0.072 (4)	0.254 (4)
C17	0.0515 (6)	0.0502 (4)	0.1694 (4)	H5A	0.745 (5)	− 0.045 (4)	0.224 (4)
C18	0.0257 (6)	0.1132 (4)	0.2192 (4)	H5B	0.771 (5)	0.045 (4)	0.198 (4)
C19	0.1119 (6)	0.1491 (4)	0.2671 (4)	H6A	0.649 (5)	− 0.004 (4)	0.334 (4)
C20	0.7295 (5)	0.3550 (4)	0.1807 (3)	H6B	0.781 (5)	0.029 (4)	0.335 (4)
C21	0.6810 (5)	0.4052 (4)	0.1182 (3)	H8A	0.743 (5)	0.140 (4)	0.422 (4)
C22	0.7394 (6)	0.4673 (4)	0.0828 (3)	H8B	0.609 (5)	0.104 (4)	0.425 (4)
C23	0.8562 (5)	0.4805 (4)	0.1035 (3)	H9A	0.618 (5)	0.249 (4)	0.443 (4)
C24	0.9120 (5)	0.4334 (4)	0.1602 (4)	H9B	0.675 (5)	0.263 (4)	0.364 (4)
C25	0.8514 (6)	0.3732 (4)	0.1979 (4)	H11A	0.430 (5)	0.169 (4)	0.436 (4)
O26	0.6681 (4)	0.3064 (3)	0.2176 (3)	H11B	0.415 (5)	0.264 (4)	0.448 (4)
N27	0.5608 (5)	0.3910 (3)	0.0916 (3)	H12A	0.241 (5)	0.199 (4)	0.396 (4)
O28	0.5211 (4)	0.3206 (3)	0.0915 (3)	H12B	0.283 (5)	0.264 (4)	0.336 (4)
O29	0.5021 (4)	0.4496 (3)	0.0678 (3)	H16	0.183 (5)	− 0.024 (4)	0.131 (4)
N30	0.9203 (5)	0.5449 (3)	0.0661 (3)	H17	− 0.005 (6)	0.030 (4)	0.138 (4)
O31	0.8626 (5)	0.5926 (3)	0.0240 (3)	H18	− 0.050 (6)	0.136 (4)	0.222 (4)
O32	1.0264 (4)	0.5509 (3)	0.0790 (3)	H19	0.099 (5)	0.195 (4)	0.300 (4)
N33	0.9160 (5)	0.3289 (3)	0.2584 (3)	H22	0.701 (5)	0.497 (4)	0.046 (3)
O34	0.8748 (5)	0.2651 (3)	0.2837 (3)	H24	0.983 (5)	0.442 (4)	0.172 (4)
O35	1.0102 (5)	0.3571 (3)	0.2836 (3)	H38	0.033 (5)	0.297 (4)	0.085 (3)
C36	0.2636 (5)	0.1764 (3)	0.0627 (3)	H40	0.055 (5)	0.100 (4)	− 0.059 (4)
C37	0.1903 (5)	0.2426 (3)	0.0887 (3)	H52A	0.600 (6)	0.125 (4)	0.057 (4)
C38	0.0762 (5)	0.2536 (4)	0.0630 (3)	H52B	0.711 (6)	0.180 (4)	0.064 (4)
C39	0.0251 (5)	0.2000 (4)	0.0101 (3)				

Table III. Barium-oxygen distances and estimated standard deviations in Å

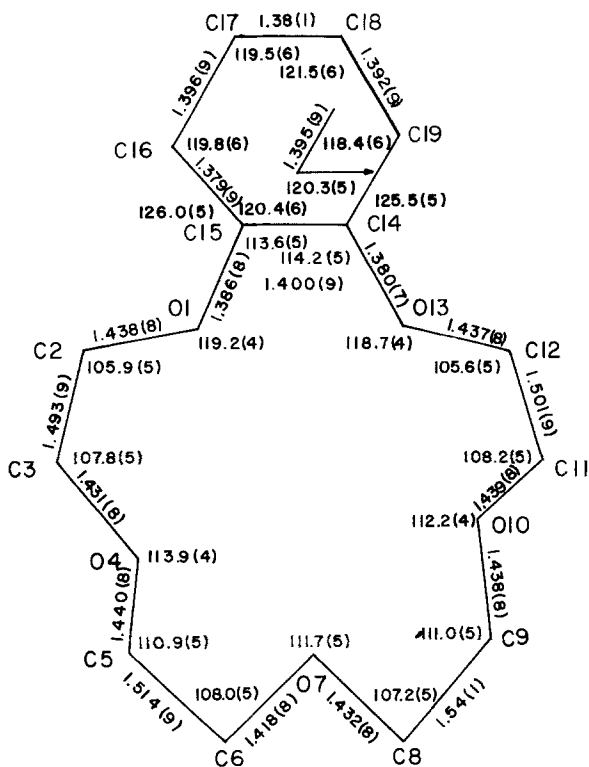| Ba–O1	2.975(5)	Ba–O26	2.666(5)
Ba–O4	2.838(6)	Ba–O28	2.994(6)
Ba–O7	2.800(5)	Ba–O42	2.642(4)
Ba–O10	2.831(5)	Ba–O44	2.825(5)
Ba–O13	3.002(5)	Ba–O52	2.711(6)

Fig. 2. Diagram of one molecule of benzo-15-crown-5 showing the atom designations, the bond distances (Å) and angles with the estimated standard deviations of the last digit in parentheses.
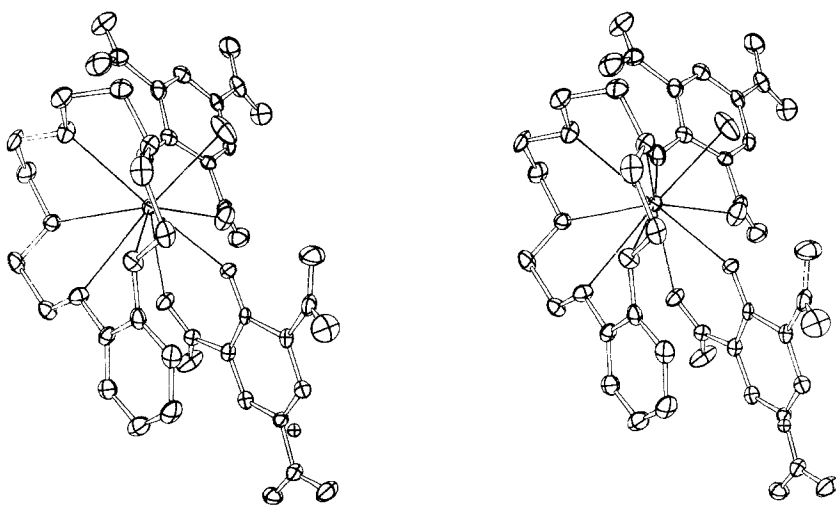

Fig. 3. Stereo ORTEP drawing of one asymmetric unit showing the coordination of the Ba^{2+} ion by the five oxygens of the benzo-15-crown-5 on one side, and by the two phenolic oxygens, two nitro group oxygens, and a water molecule oxygen on the opposite side.
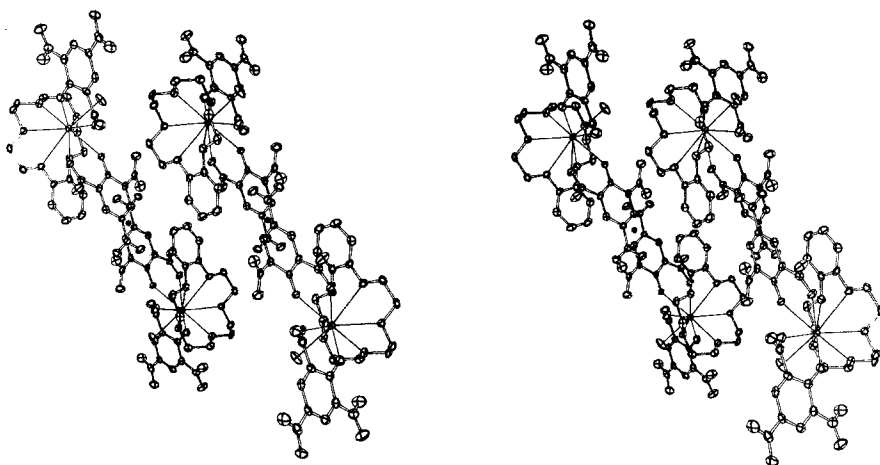
Fig. 4.   Stereo ORTEP drawing showing the packing of barium (picrate)$_2$ benzo-15-crown-5 mono-hydrate in the $P2_1/c$ unit cell.

sandwich constituted by the crown oxygens on one side and an anionic-cum-solvent species on the other. The Ba—OH$_2$ (O52) contact is fairly short (2.711 Å). The hydrogen bond (2.929 Å) that the water molecule establishes with O48 (the nitro-oxygen of Pic moiety II) links the entire structure in three dimensions.

The molecular geometries of the Pic anions (Figure 1) show that the bonds constituting the benzene ring vary from 1.364 to 1.468 Å while the inner angles vary from 111.9 to 125°. Elongation of the C20—C25 and C20—C21 bonds (Pic I) as well as the C36—C37 and C36—C41 bonds (Pic II) and the compression of the angles contained by these bonds is typical of picrates and is indicative of the delocalization of anionic charge [13]. The unusual bond angles made by the phenolic oxygen and the benzene ring carbons (O26—C20—C21, O26—C20—C25, O42—C36—C37, and O42—C36—C41) arise from the steric interactions of the phenoxide oxygen with the ortho nitro groups. The smaller angles (O26—C20—C21 and O42—C36—C41) are associated with the nitro group with the greater deviation (33 and 30°, respectively) from the plane of the benzene ring. These twist angles are within the range of values observed in previously determined picrate complexes [14].

The bond lengths and angles in the benzene nucleus of B15C5 (Figure 2) range from 1.379 to 1.400 Å, and from 118.4 to 121.5°, respectively. This nucleus is planar within 0.01 Å and coplanar with O1 and O13 within 0.016 Å. The distances C15—O1 (1.386 Å) and C14—O13 (1.380 Å) are distinctly shorter and the angles C14—C15—O1 (113.6°) and C15—C14—O13 (114.2°) are distinctly larger than the tetrahedral values. The angles at O1 and O13 are widened to values approaching 120° (119.2 and 118.7°). These values indicate that O1 and O13 are under the strongest acidic effect of the aromatic nucleus and are least strongly bound to barium. The widening of the angles may also be seen to arise from the necessity of C14 and C15 to be coplanar with other carbons of the benzene ring which also affects the coordination characteristics of the cation. The C(sp^3)–C(sp^3) distances within the crown moiety vary from 1.493 to 1.540 Å with a mean of 1.51 Å.

4. Discussion

The barium ion in this complex is in a pseudo-sandwich configuration with the crown molecule on one side and Pic ions in conjunction with the water molecule on the other. The ion-cavity radius concept [1,11] predicts the formation of a 1 : 2 charge separated sandwich for this complex. The potassium ion of approximately the same size consistently yields a 1 : 2 charge-separated sandwich with this crown irrespective of whether the counteranion is iodide [6], picrate [5], or the acid anion [(3,5-dinitrobenzoate)(3,5 dinitrobenzoic acid)$_2$] (work in progress). The complex in question as well as another involving still a larger cation, viz., Cs(Pic)(B15C5) [15] is an anion-paired 1 : 1 ligation species. We, therefore, reaffirm our earlier conclusion [2,12,16] that the stoichiometry is determined by the charge density (charge-radius ratio) of the cation as modified by the anion-effect of the counterion.

Dissolution and ion-solvation studies (paper in preparation) of the BaL$_2$ species suggest that the Ba^{2+}L$^-$ pairing becomes increasingly strong with the accumulation of charge on the anionic binding site of L, as evaluated from the pK$_a$ of the parent acid (HL) in water [17]. This can be effected through decreasing the number of the charge delocalizing substituents (for Pic, Dnp, and Onp) or by shifting them to unfavorable positions (for Onp, 34-Dnb, and 35-Dnb).

On the addition of B15C5 (and 15C5, in particular), each BaL$_2$ becomes a loose ion-pair indicated, at least for the rather colorless nitrobenzoates, by the development of a yellow color which is characteristic of an ineffectively paired nitro anion [18]. The anion exercises a recognizable counteraction toward the Ba-crown interaction as indicated by the degree of insolubility of the BaL$_2$ in the presence of B15C5 [cf.19]. This was found to vary in the same manner as described above for ion-solvation. The BaL$_2$ species derived from the high pK$_a$ HL, e.g., Ba(35-Dnb)$_2$, do not solvate freely, even in water, and are insoluble. Their complexation (dispersion) with B15C5 is far more facilitated in water than in ethanol, even though water could deactivate B15C5 much more effectively through HOH$\cdots$O(crown) complexation and could also act hydrolyticly toward the Ba$^{2+}\cdots$O(crown) bonds. This may suggest that Ba-crown encapsulation is favored as anion-stabilization (L$\cdots$HOH bonding) [20] is incorporated.

Barium, although it could not constitute a genuine sandwich involving an exclusive environment of the crown molecules, is obviously within a pseudo-sandwich so that B15C5 successfully dehydrates and encapsulates the cation which has not been found in analogous systems of the smaller cations, Ca(Pic)$_2$(B15C5)$\cdot$3H$_2$O [8] and Li(Pic)(B15C5)$\cdot$2H$_2$O [7].

Acknowledgements

References

1. C. J. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).
2. N. S. Poonia and A. V. Bajaj: *Chem. Rev.* **79**, 389 (1979).
3. R. J. P. Williams: *Quart. Rev.* **24**, 331 (1970).
4. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hanson, N. K. Dalley, A. G. Avondet, and J. J. Christensen: *J. Am. Chem. Soc.* **98**, 7620 (1976).
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. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **16**, 373 (1980).
8. V. W. Bhagwat, H. Manohar, and N. S. Poonia: *Inorg. Nucl. Chem. Lett.* **16**, 289 (1980).
9. P. D. Cradwick and N. S. Poonia: *Acta Crystallogr., Sect. B* **33**, 197 (1977).
10. J. D. Owen: *J. Chem. Soc., Dalton Trans.* 1066 (1980).
11. C. J. Pedersen and H. K. Frensdorff: *Angew. Chem., Int. Ed. Engl.* **11**, 16 (1972).
12. N. S. Poonia, A. V. Bajaj, A. K. Arora, K. Joshi, and A. Banthia: *Indian J. Chem., Sect. A* **19**, 37 (1980).
13. E. Hough: *Acta Crystallogr., Sect. B* **32**, 1154 (1976).
14. B. Braden, J. A. Hamilton, M. N. Sabesan, and L. K. Steinrauf: *J. Am. Chem. Soc.* **102**, 2704 (1980).
15. Paper in Preparation (1984).
16. N. S. Poonia: *Multidentate Macromolecules – Principles of Complexation with Alkali and Alkaline Earth Cations* (Progress in Macrocyclic Chemistry, vol. I, Ed. R. M. Izatt and J. J. Christensen), pp. 15–155, Wiley (1979).
17. R. Weast: *The Handbook of Chemistry and Physics*, 56th edn., pp. D-150–51, Rubber Publishing Co. (1975/76).
18. N. S. Poonia: *J. Indian Chem. Soc.* **56**, 22 (1979).
19. R. J. P. Williams: *Bioinorganic Chemistry*, Am. Chem. Soc. Publ. No. 100 (1971).
20. N. S. Poonia: *J. Am. Chem. Soc.* **96**, 1012 (1974).