Crystal Structure of a Solvent-extraction Complex: Bis(dibutylphosphato)aquabarium-18-crown-6

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Received October 2, 1984

Abstract

A complex of barium with dibutylphosphoric acid (HDBP) and 18-crown-6 ether has been prepared and its crystal structure determined. Molecules of the complex contain an 18-crown-6 ring which has a Ba^{2+} ion near its center and is capped on one side by a DBP^- ion and on the other by a DBP^- ion and a H_2O molecule. Five of the O atoms of the crown are very nearly planar, while the sixth O atom and the Ba atom are 0.68 Å and 0.61 Å to one side, respectively. The H_2O molecule makes an intramolecular hydrogen bond to one phosphate group and an intermolecular hydrogen bond to another, by which it links the molecules into continuous chains. The shape of the crown as it adapts to the Ba^{2+} ion is compared to the conformation it has in other complexes. Crystals of $Ba[(C_4H_9O)_2PO_2]_2 \cdot H_2O \cdot (C_{12}O_6H_{24})$ are triclinc, $P\bar{1}$, with a = 13.79(1), b = 17.19(1), c = 9.488(6) Å, α = 105.78(5)°, β = 83.00(6)°, γ = 107.45(6)°, Z = 2.

Introduction

The extraction of alkali and alkaline-earth metal ions by organophosphoric and long-chain neocarboxylic acids has been shown to be enhanced by the presence of certain crown ethers in the organic phase [1, 2]. This synergism is attributed to the formation of an extraction complex in which the metal ion is held in the cavity of the ether ring and for which the anions are provided by the organophilic acid. The extraction was found to be greatest when there is a correspondence between the size of the cation and the ring opening. Thus it is of interest to study such a complex to see what role each of the extractants plays in binding the metal ion, especially as regards its possible encapsulation by the crown. Also the possible inclusion of water in the extraction complex should be examined, because hydrogen bonding has been shown to be significant in both the crystal and molecular structures of many crown-ether complexes [3–12].

In order to answer some of these questions the title compound was prepared, and its crystal structure was determined by X-ray diffraction analysis. Although the extraction of the Ba^{2+} ion by dibutylphosphoric acid (HDBP) and 18-crown-6(1,4,7,10,13,16-hexaoxacyclooctadecane) has not been studied, the extraction of the Ba^{2+} ion by bis(2-ethylhexyl)phosphoric acid and dicyclohexano-18-crown-6 has been [1]; and because the functional groups are essentially the same in the two systems, the mode of bonding to the ion should be similar. The former mixture was chosen to facilitate crystallization and to simplify the structural analysis. And, of course, this compound only typifies the alkaline-earth complexes; the alkali metals must produce different stoichiometries and structures. Structures in which the Ba^{2+} ion is bonded to macrocyclic ethers have been reported before [13–16] but none with a large anion such as studied here.

Experimental

Preparation of $Ba(DBP)_2 \cdot H_2O \cdot (18\text{-crown-}6)$

Di-*n*-butylphosphoric acid was separated from a mixture of mono- and dibutylphosphoric acids (Mobil Chemical Co., Richmond, Va.) by dissolving the mixture in benzene and extracting out the mono acid with water. A 1:1:2 mixture of reagent grade $Ba(OH)_2 \cdot 8H_2O$, 18-crown-6 ether (Aldrich Chemical Co.), and the HDBP were mixed and allowed to react using no solvent. From this mixture grew colorless, mm-sized, thick platelets of $Ba(DBP)_2 \cdot H_2O \cdot (18\text{-crown-}6)$. Free water produced in the reaction was pumped off in a desiccator.

X-ray Data Collection and Reduction

Precession photographs indicated the triclinic symmetry of the crystal and provided preliminary values for the unit-cell dimensions. More precise values were obtained by least-squares refinement

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using twelve reflections in the range $2\theta = 30-38°$, which had been carefully oriented on an automated Picker four-circle diffractometer employing MoK_α radiation. From a crystal sealed in a glass capillary some 3160 intensities, of which 2132 were greater than three standard deviations, were also measured with this device. The refined unit-cell dimensions and various experimental conditions and crystal data are listed in Table I.

The intensity of a reference reflection, measured hourly, gradually declined by a total of about 20% over the two weeks of data collection; this was probably due to decomposition caused by loss of water from the crystal since other specimens not sealed in glass deteriorated even more rapidly. The data were normalized by interpolation between measurements of the reference reflection. A calculated correction for absorption was also made based on measured dimensions of the sample; transmission factors ranged from 0.81 to 0.88. The variance of the observed structure factor, F_o, was set at $\sigma^2(F_o^2) = \sigma_c^2 + (0.05\ F_o^2)^2$, where σ_c^2 is the variance attributable to counting statistics alone.

Structure Determination and Refinement

The barium atoms were found from a Patterson map to occupy twofold general positions of $P\bar{1}$. Subsequent Fourier syntheses allowed the locating of all the other nonhydrogen atoms, also in general positions. Hydrogen atoms were not located. Among the four butyl groups of the asymmetric unit, the carbon atoms were more difficult to find the farther they were from the point of attachment of the chain to the phosphate group. The butyl chains appear to be quite thermally agitated or disordered. Our earlier studies of the dibutylphosphate moiety found the same kind of behavior in other crystals [17, 18].

TABLE I. Crystal Data and Experimental Variables.

Formula	$Ba(C_8H_{18}PO_4)_2 \cdot H_2O \cdot C_{12}H_{24}O_6$
Formula weight	838.07
a, Å	13.79(1)
b, Å	17.19(1)
c, Å	9.488(6)
α, deg.	105.78(5)
β, deg.	83.00(6)
γ, deg.	107.45(6)
V, $Å^3$	2062.7
Z	2
$d_{calc.}$, g cm^{-3}	1.34
$d_{meas.}$, g cm^{-3}	1.3
space group	$P\bar{1}$
crystal dimensions, (mm)	0.12 × 0.15 × 0.06
radiation	MoK_α (0.7107 Å)
μ, cm^{-1} (MoK_α)	10.0
scan type	$\theta - 2\theta$
scan limits, deg. 2θ	3 – 40°
no. refl. > $3\sigma(F^2)$	2132
no. parameters	335
$\Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma \lvert F_o\rvert$	0.067
R_w	0.111
σ_1	2.01

The 415 parameters describing the positions and anisotropic thermal motion of all 46 independent atoms plus one scale factor were adjusted by least squares to the 2132 values of $F_o^2 > 3\sigma(F_o^2)$. This refinement yielded a residual, $R(F)$, of 0.057 and a standard deviation of an observation of unit weight, σ_1, of 1.61. However, in this model many of the bond lengths and angles in the butyl groups had unrealistic values, and the thermal parameters were very large. In view of this and of the fact that the butyl groups are of little interest to the chemical questions being explored, it was decided to treat them as having a constrained geometry. In each C_4 chain the C atom attached to the PO_4 group was refined as before, but the rest of the chain was required to have C–C distances of 1.47 Å and C–C–C angles of 112.6° as found in previous work [17, 18]. Torsion angles of each chain (including the O atoms to which the butyl groups are attached) were varied, and each constrained atom was given an independent isotropic thermal parameter. This description of the structure required 335 variables and refined to the agreement indices in Table I. The thermal parameters of the butyl chains remained large, but the conformations became much more reasonable. The effect of this treatment of the butyl groups was not to change the positions of the other atoms by more than one or two standard deviations from their positions in the earlier 415-parameter refinement.

Results and Discussion

The refined positional and thermal parameters are given in Table II, and the observed and calculated structure amplitudes are available from the author. Selected bond lengths and angles are listed in Tables III and IV, and the torsion angles of the ether molecule are shown in Fig. 1.

Each molecule of the title complex consists of a Ba^{2+} atom 'inside' a crown ether ring which is capped on one side by the O atom of a DBP^- ion and on the other side by the O atoms of a DBP^- ion and a water molecule. In turn, the H_2O makes an intramolecular hydrogen bond to a phosphate group and another hydrogen bond to a phosphate group

TABLE II. Fractional Coordinates and Thermal Parameters[a] (Å^2) and Their Standard Deviations.

Atom	10^3x	10^3y	10^3z	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
Ba	261.6(1)	14.9(1)	335.4(1)	5.5(1)	8.4(1)	4.8(1)	2.8(1)	0.1(1)	2.1(1)
P(1)	192.9(5)	−200.2(5)	445.5(7)	7.2(5)	8.5(6)	6.6(5)	2.7(5)	0.2(4)	2.0(5)
P(2)	293.1(5)	154.2(5)	41.0(7)	9(1)	8.3(6)	5.7(5)	3.6(5)	0.2(4)	2.3(5)
O(1)	241(1)	−142(1)	350(1)	10(1)	8(1)	6(1)	3(1)	1(1)	3(1)
O(2)	175(1)	−164(1)	603(2)	11(1)	9(1)	7(1)	2(1)	−1(1)	3(1)
O(3)	86(1)	−262(1)	388(2)	8(1)	11(1)	10(1)	1(1)	1(1)	3(1)
O(4)	263(1)	−263(1)	426(2)	10(1)	10(1)	10(1)	4(1)	1(1)	4(1)
O(5)	301(1)	115(1)	159(1)	14(1)	10(1)	8(1)	5(1)	1(1)	5(1)
O(6)	256(1)	101(1)	−103(2)	13(1)	12(1)	6(1)	4(1)	−1(1)	1(1)
O(7)	227(1)	218(1)	114(1)	12(1)	13(1)	7(1)	7(1)	1(1)	4(1)
O(8)	403(1)	218(1)	11(2)	10(1)	11(1)	13(2)	4(1)	4(1)	7(1)
O(9)	470(1)	26(1)	332(2)	9(1)	11(1)	9(1)	3(1)	−1(1)	6(1)
O(10)	400(1)	161(1)	498(2)	10(1)	9(1)	8(1)	1(1)	1(1)	4(1)
O(11)	190(1)	156(1)	507(2)	10(1)	11(2)	9(1)	5(1)	2(1)	4(1)
O(12)	66(1)	25(1)	306(2)	7(1)	15(2)	13(2)	5(1)	−1(1)	3(1)
O(13)	144(1)	−92(1)	89(2)	9(1)	10(1)	7(1)	3(1)	−1(1)	3(1)
O(14)	356(1)	−70(1)	85(2)	6(1)	10(1)	6(1)	3(1)	0(1)	2(1)
OW	242(1)	4(1)	626(1)	9(1)	11(1)	4(1)	3(1)	1(1)	4(1)
C(1)	84(2)	−300(2)	224(3)	13(3)	21(3)	10(3)	−3(2)	−1(2)	3(2)
C(2)	−19	−357	202	30(3)[b]					
C(3)	−32	−434	250	34(3)[b]					
C(4)	−139	−482	257	53(6)[b]					
C(5)	232(2)	−319(2)	521(3)	13(3)	21(3)	22(3)	6(2)	1(2)	18(3)
C(6)	319	−348	537	24(2)[b]					
C(7)	351	−399	399	29(2)[b]					
C(8)	422	−443	420	35(3)[b]					
C(9)	209(2)	267(2)	20(3)	14(3)	20(3)	12(2)	10(2)	1(2)	9(2)
C(10)	119	293	91	33(3)[b]					
C(11)	141	355	231	28(2)[b]					
C(12)	51	380	302	46(4)[b]					
C(13)	456(3)	267(2)	145(4)	35(5)	35(4)	19(3)	5(3)	−17(3)	−2(3)
C(14)	502	355	139	47(7)[b]					
C(15)	574	364	14	29(3)[b]					
C(16)	629	451	19	46(5)[b]					
C(17)	539(2)	104(2)	415(3)	9(2)	11(2)	12(2)	3(2)	0(2)	3(2)
C(18)	482(2)	140(2)	552(3)	8(2)	12(2)	12(2)	4(2)	−3(2)	3(2)
C(19)	354(2)	210(2)	620(3)	11(2)	15(3)	9(2)	3(2)	−2(2)	4(2)
C(20)	272(2)	232(2)	554(3)	11(2)	8(2)	11(2)	1(2)	2(2)	3(2)
C(21)	112(3)	173(2)	442(3)	12(3)	13(3)	14(3)	8(2)	−3(2)	1(2)
C(22)	30(2)	95(2)	398(3)	10(2)	12(3)	16(3)	9(2)	0(2)	1(2)
C(23)	1(2)	−42(2)	211(2)	5(2)	19(3)	11(3)	2(2)	0(2)	4(2)
C(24)	62(2)	−61(2)	61(2)	8(2)	14(3)	9(2)	4(2)	−1(1)	6(2)
C(25)	203(2)	−113(2)	−46(2)	8(2)	13(2)	5(2)	3(2)	2(1)	4(2)
C(26)	289(2)	−141(2)	−1(3)	8(2)	12(2)	8(2)	5(2)	0(2)	0(2)
C(27)	437(2)	−94(2)	125(3)	9(2)	11(2)	10(2)	5(2)	0(2)	3(2)
C(28)	515(2)	−16(2)	192(3)	8(2)	15(3)	9(2)	6(2)	3(2)	5(2)

[a] The anisotropic temperature factor has the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$. [b] Isotropic temperature factor.

in an adjacent molecule. Figure 2 shows two molecules of a continuous chain which is linked in this manner.

TABLE III. Bond Lengths (Å).

Ba–O(5)	2.62(1)	ether ring	
Ba–O(1)	2.67(1)		
Ba–Ow	2.79(1)	O(9)–C(17)	1.47(3)
Ba–O(12)	2.81(2)	C(17)–C(18)	1.50(3)
Ba–O(14)	2.82(1)	C(18)–O(10)	1.47(2)
Ba–O(9)	2.83(2)	O(10)–C(19)	1.44(3)
Ba–O(10)	2.84(2)	C(19)–C(20)	1.54(3)
Ba–O(13)	2.87(1)	C(20)–O(11)	1.45(3)
Ba–O(11)	2.90(2)	O(11)–C(21)	1.43(3)
		C(21)–C(22)	1.48(3)
P(1)–O(2)	1.48(1)	C(22)–O(12)	1.45(3)
P(1)–O(1)	1.48(1)		
P(1)–O(3)	1.59(2)	O(12)–C(23)	1.41(3)
P(1)–O(4)	1.61(1)	C(23)–C(24)	1.58(3)
		C(24)–O(13)	1.45(2)
P(2)–O(5)	1.48(1)	O(13)–C(25)	1.45(2)
P(2)–O(6)	1.48(1)	C(25)–C(26)	1.54(3)
P(2)–O(7)	1.60(1)	C(26)–O(14)	1.41(3)
P(2)–O(8)	1.62(2)	O(14)–C(27)	1.43(3)
		C(27)–C(28)	1.48(3)
O(3)–C(1)	1.51(3)	C(28)–O(9)	1.48(3)
O(4)–C(5)	1.43(2)		
O(7)–C(9)	1.46(2)		
O(8)–C(13)	1.46(3)		

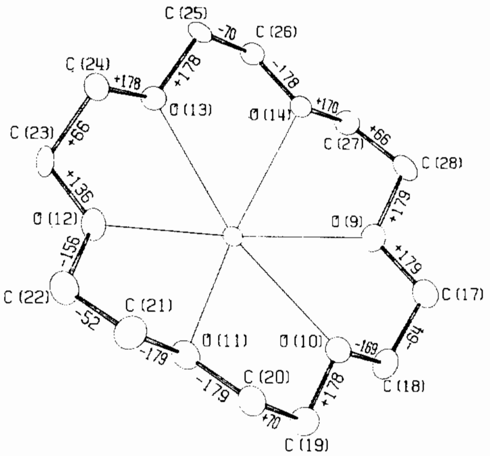

Fig. 1. Torsion angles of the 18-crown-6 ring.

From the molecular structure (Fig. 2) it can be seen that both components of the extractant mixture are included in the complex, that the Ba^{2+} ion is inside a shell of organic ligands and that one H_2O molecule is attached to the Ba^{2+} ion. Whether this crystalline molecule is the same one as exists in solution and is responsible for the phase transfer is a question to be answered by other means, but it certainly represents a likely possibility for fulfilling this role.

TABLE IV. Bond Angles and Torsion Angles (deg).

phosphate		ether	
O(1)–P(1)–O(2)	118.2(9)	C(17)–O(9)–C(28)	116(2)
O(1)–P(1)–O(3)	111.8(9)	O(9)–C(17)–C(18)	109(2)
O(1)–P(1)–O(4)	106.8(8)	C(17)–C(18)–O(10)	105(2)
O(2)–P(1)–O(3)	106.0(9)	C(18)–O(10)–C(19)	109(2)
O(2)–P(1)–O(4)	109.8(8)	O(10)–C(19)–C(20)	106(2)
O(3)–P(1)–O(4)	103.3(9)	C(19)–C(20)–O(11)	109(2)
		C(20)–O(11)–C(21)	111(2)
O(5)–P(2)–O(6)	120.2(9)	O(11)–C(21)–C(22)	109(2)
O(5)–P(2)–O(7)	105.0(8)	C(21)–C(22)–O(12)	113(2)
O(5)–P(2)–O(8)	110(1)		
O(6)–P(2)–O(7)	111.6(9)	C(22)–O(12)–C(23)	121(2)
O(6)–P(2)–O(8)	107(1)	O(12)–C(23)–C(24)	107(2)
O(7)–P(2)–O(8)	101.7(9)	C(23)–C(24)–O(13)	107(2)
		C(24)–O(13)–C(25)	110(2)
phosphate-butyl		O(13)–C(25)–C(26)	105(2)
O(3)–C(1)–C(2)	104(2)	C(25)–C(26)–O(14)	108(2)
O(4)–C(5)–C(6)	109(2)	C(26)–O(14)–C(27)	109(2)
O(7)–C(9)–C(10)	103(2)	O(14)–C(27)–C(28)	108(2)
O(8)–C(13)–C(14)	111(2)	C(27)–C(28)–O(9)	108(2)
butyl torsion angles			
O(3)–C(1)–C(2)–C(3)	-75(2)	C(1)–C(2)–C(3)–C(4)	168(2)
O(4)–C(5)–C(6)–C(7)	-65(2)	C(5)–C(6)–C(7)–C(8)	-168(2)
O(7)–C(9)–C(10)–C(11)	70(2)	C(9)–C(10)–C(11)–C(12)	-180(2)
O(8)–C(13)–C(14)–C(15)	-59(3)	C(13)–C(14)–C(15)–C(16)	-172(2)

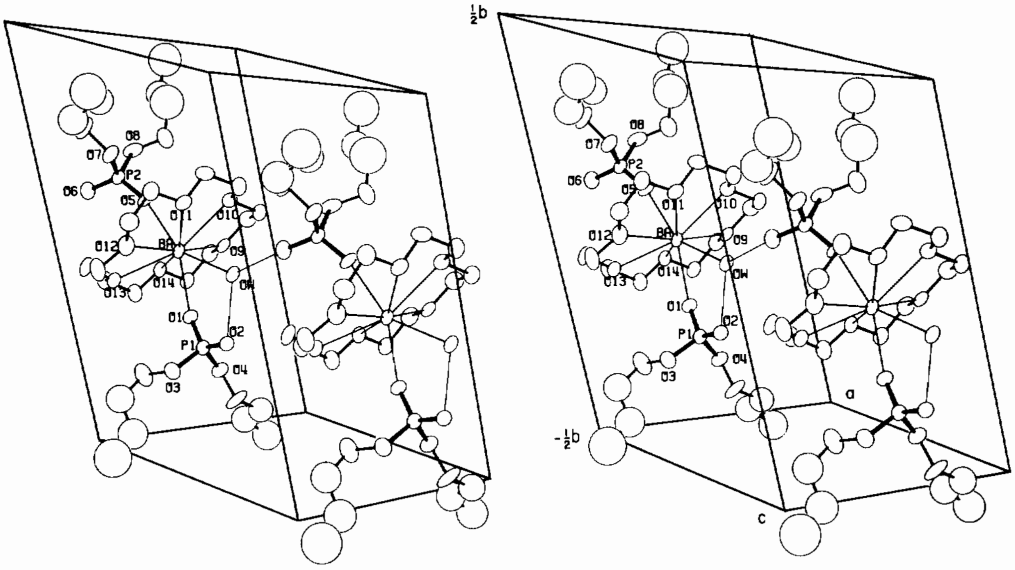

Fig. 2. Stereoscopic view of two molecules of the complex linked by a hydrogen bond. Thermal ellipsoids are at the 20% probability level. The identity of atoms not labelled may be deduced by reference to Tables III and IV.

In this structure the Ba^{2+} ion is nine coordinate: two phosphate O atoms at 2.62 and 2.67 Å, a water O atom at 2.79 Å, and six ether O atoms at distances of 2.81 to 2.90 Å. A similar arrangement exists in $Ba(SCN)_2 \cdot H_2O \cdot$(dicyclohexano-18-crown-6), except that the two SCN ions are on one side of the crown and the H_2O molecule on the other [13]. Ten and eleven coordinate Ba^{2+} ions are found in the cryptate complexes $Ba(SCN)_2 \cdot H_2O \cdot$[222] and $Ba(SCN)_2 \cdot 2H_2O \cdot$[322], respectively [14, 15].

The DBP ligands in $Ba(DBP)_2 \cdot H_2O \cdot$18-crown-6 have nearly tetrahedral phosphate groups in them. The P–O bonds to atoms covalently linked to butyl groups are significantly longer (1.59–1.62 Å) than the other P–O bonds (1.48 Å) from which the O atoms have only electrostatic attractions to other atoms. The existence of the hydrogen bonds is inferred from the close O···O contacts between the O atom of water and the O atoms of two phosphate groups, O(6) at 2.64 and O(2) at 2.70 Å, and the O···O···O angle of 115.8°.

Although the dimensions of the butyl groups were fixed at assumed values, the torsion angles about the C–C bonds of atoms in the 1, 2 and 2, 3 positions as well as about the O–C bonds were refined in the least-squares treatment. Their final values are given in Table IV. All four butyl chains adopt the anti conformation. The angle at which the butyl groups are attached to the phosphate groups are also listed in Table IV.

Of considerable interest is the conformation of the 18-crown-6 molecule because it has been studied in the structures of numerous complexes. The most symmetrical form that has been found is one of D_{3d} symmetry with the O atoms at about 0.2 Å on either side of the mean plane and having torsion angles about the C–C bonds close to 65° and 180°. This structure is adopted by the 18-crown-6 ring in complexes with K^+ [19], Rb^+ [19], NH_4^+ [4], Cs^+ [19], and Ca^{++} [20] ions, whose radii range from 1.12 to 1.76 Å (for the particular coordination involved). For K^+ and Ca^{2+} ions, the ion is at the center of the ring, but for the others it is out of the ring's plane by up to 1.44 Å (for Cs^+). Although these complexes have the symmetrical form of the crown, the 18-crown-6 molecule is quite flexible, and the conformation that it adopts in a particular complex is determined by the energy balance among several factors; these include, in addition to the internal strain, the size and charge of the cation, the other coordinating species, and the solvation [21, 22]. Thus, in the known structures of the crown there is a wide variation in shape, from the symmetrical one in the KSCN complex to that in the NaSCN complex [23] in which there is a kink in the ring as one O atom assumes an apical position above the other five. Between these extremes is the skew-boat conformation adopted by the O atoms in La^{3+} [4] and Nd^{3+} [24] nitrate complexes with 18-crown-6. This ring shape is found in $BaSCN \cdot H_2O \cdot$(dicyclohexano-18-crown-6), but the deviations of the six O atoms from planarity are not as great as in the lanthanide complexes. The present structure, $Ba(DBP)_2 \cdot H_2O \cdot$(18-crown-6), is similar to that of the $NaSCN \cdot$(18-crown-6) molecule; five O atoms are nearly planar, and the sixth is 0.68 Å

TABLE V. Deviations (A) of the Crown Oxygen Atoms From the Best Plane Through Them; a Comparison of Structures.

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	M[a]
$La(NO_3)_3$·(18-crown-6) [Ref. 7]	0.53	−0.48	0.06	0.56	−0.53	−0.03	−0.47
$Nd(NO_3)_3$·(18-crown-6) [Ref. 24]	0.57	−0.53	−0.03	0.54	−0.50	−0.06	−0.46
$Ba(SCN)_2$·H_2O·(dicyclohexano-18-crown-6) [Ref. 13]	0.20	−0.16	−0.03	0.20	−0.16	−0.03	0.61
Na(SCN)·H_2O·(18-crown-6) [Ref. 23]	0.06	0.12	−0.30	0.36	−0.24	1.95[b]	−0.27
$Ba(DBP)_2$·H_2O·(18-crown-6)	0.05	−0.06	0.02	0.03	−0.04	0.68[b]	0.61

[a]Distance of the metal ion from the best plane. [b]Best plane fitted to the other five O atoms.

away from the plane. In the two Ba complexes described here the distortions of the 6-ring from planarity are less severe than in the similar La^{3+} and Na^+ complexes because the Ba^{2+} ion is nearer to optimal size for the opening in an undistorted planar ring. In Table V comparisons are made among these structure types.

It has been suggested that the enhanced extraction observed when crown ethers are added to organophilic acid extractants can be correlated with a matching between ion size and the size of the crown opening [1, 2]. Yet several authors have questioned the significance of this size correlation for the stability of the complexes formed [19, 25, 26], and energy contributions from other factors have been calculated to be important [21]. By examination of the structure of $Ba(DBP)_2$·H_2O·(18-crown-6) it may also be inferred that factors other than size matching contribute to the synergism, assuming that this is the molecule extracted. First, it is clear from this and other work that there is no unique 'hole size' for the 18-crown-6 molecule; it distorts within wide limits in achieving bonding of its O atoms to various cations (this is less true in rings made more rigid by substituent groups [27–30]). Secondly, the presence of a H_2O molecule bonded to the Ba^{2+} ion both reduces the degree to which the hydration sphere in the aqueous phase must be removed and provides hydrogen bonding which adds stability to the complex. Finally, the fact that the organic anion is an integral part of the complex means that its organophilic character plays a role in addition to that of the crown in facilitating the transfer of the Ba^{2+} ion to the organic phase.

A complex of the (15% smaller) Sr^{2+} ion with these same extractants has been prepared. Its structure, which is not isomorphous with the complex described here, will be determined to see what changed roles the ligands may have which could lead to selectivity in the extraction of alkaline-earth cations.

Acknowledgements

This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

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