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Crystallographic Study of the Barium(II) Complex of a Lariat Ether with Long Pendent Arms

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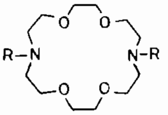
Abstract

The crystal structure of the Ba(II) complex of the ligand L (L = 7,16-bis(2-*o*-hydroxyethyl-2-oxyethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) is reported. The complex $[Ba(L)]I_2 \cdot 3H_2O$ crystallizes in the monoclinic space group $C2/c$ with $a = 11.378(1)$, $b = 15.682(2)$, $c = 18.222(2)$ Å, $\beta = 96.28(8)°$; $Z = 4$, $V = 3231.87$ Å^3, $D_m = 1.80$ g cm^{-3}, $D_c = 1.82$ g cm^{-3}. The final conventional R factor was 0.032. The barium is eleven coordinate in the complex, with a water molecule occupying an apical position. The Ba–O oxygen bond lengths average 2.874(3) Å, and the Ba–N bond lengths 3.079(3) Å. The structure is used to rationalize the higher stability of the Ba^{II} complex of L than is found for other metal ions in terms of the ability of barium to coordinate all the donor atoms of the ligand.

Introduction

In a previous publication [1] the formation constants of the lariat ether BHEE-18-aneN_2O_4 (Scheme 1) were determined with a variety of metal ions. The long pendent 'arms' o the ligand led to a strong decrease in complex stability for all metal ions except for the large Pb(II) and Ba(II) ions, relative to their complexing ability with the shorter armed BHE-18-aneN_2O_4.



Scheme 1. BHEE-18-aneN_2O_4, R = $CH_2CH_2OCH_2CH_2OH$; BHE-18-aneN_2O_4, R = CH_2CH_2OH.

	Cu^{2+}	Cd^{2+}	Ca^{2+}	Pb^{2+}	Ba^{2+}
Ionic radius [2] (Å)	0.59	0.95	1.00	1.18	1.36
log K_1, R = CH_2CH_2OH	6.6	8.0	4.1	9.2	5.3
R = $CH_2CH_2OCH_2CH_2OH$	NEC[a]	3.3	NEC	7.2	4.9

[a]NEC = no evidence of complex formation.

It has been found generally [1] that decreases in complex stability on adding neutral oxygen donors to existing ligands are size related, and that the small drop observed in log K_1 in Scheme 1 was because the large Ba^{II} ion could achieve the ten coordination required by the ligand BHEE-18-ane-N_2O_4. The K^+ ion has an ionic radius [2] of 1.37 Å in octahedral coordination, similar to that of Ba^{2+} at 1.36 Å, suggesting that the two metal ions are generally similar in size. It was thus surprising that the crystal structure of the K^+ complex of BHEE-18-aneN_2O_4 showed the metal ion was only eight or nine coordinate, with one donor atom on one or both pendent arms left uncoordinated. The disordered structure had two types of complex present, occupying the same site: one with nine-coordinate K^+, and one with eight-coordinate K^+. It had been assumed that the long pendent arms of BHEE-18-aneN_2O_4 would greatly destabilize the complex with Ba^{2+} if they were not coordinated. A crystal structure of the Ba(II) complex of BHEE-18-ane-N_2O_4 should indicate whether Ba^{2+} achieves the coordination number of ten required to account for its thermodynamic stability.

A further point is the reason for any difference in coordination number between K^+ and Ba^{2+}, when they apparently have the same ionic radii [2]. Kollman *et al.* [3] have developed a molecular mechanics (MM) parametrization of alkali metal ions and crown ethers, which should be suitable for analyzing the differences in structure between the Ba(II) and K(I) complexes of BHEE-18-aneN_2O_4, and an MM analysis of these complexes is reported here.

Experimental

Preparation of Crystals

A pale yellow solid was obtained by evaporating a 1:1 mixture of $BaI_2 \cdot 2H_2O$ and BHEE-18-aneN_2O_4

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(prepared as described previously [1]). Recrystallization from isopropanol gave twinned crystals, but a second attempt at recrystallization from absolute ethanol gave non-twinned crystals, which were used for the crystallographic study. *Anal.* Calc. for $C_{20}H_{42}N_2O_6 \cdot BaI_2 \cdot 3H_2O$: C, 27.18; H, 5.54; N, 3.16. Found: C, 27.22; H, 5.44; N, 2.93%. Melting point (m.p.) > 220 °C (d).

Crystallographic Studies

The data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (0.71073 cm^{-1}). The cell constants were obtained from least-squares refinement of 25 high theta reflections. An ω–2θ scan mode was used with a scan width of $0.6 + 0.35 \tan\theta$ and a variable scan speed. Three standard reflections were monitored and showed no significant variations over the data collection. Empirical L_p and adsorption corrections were applied to the data according to the method of North *et al.* [4]. The structure was solved by Patterson and Fourier techniques using the program SHELX-76 [5]. Crystal data are given in Table 1, fractional atomic coordinates are given in Table 2, and important bond angles and bond lengths are given in Table 3. See also 'Supplementary Material'.

TABLE 1. Details of the crystallographic analysis of [Ba(BHEE-18-aneN_2O_4)H_2O]$I_2 \cdot 2H_2O$

Formula	$C_{20}H_{42}N_2O_8BaI_2 \cdot 3H_2O$
Molecular weight	883.74
Crystal system	monoclinic
Space group	*C*2/*c*
a (Å)	11.378(1)
b (Å)	15.682(2)
c (Å)	18.222(2)
β (°)	96.28(8)
V (Å^3)	3231.87
Z	4
D_{obs} (g cm^{-3})	1.80
D_{calc} (g cm^{-3})	1.82
F(000)	1728
Crystal colour	colourless
Cystal dimensions (mm)	0.35 × 0.25 × 0.25
Theta range (°)	$2 \leq \theta \leq 30$
Range of *h*, *k*, *l*	±15, +22, +25
Scan speed range (° min^{-1})	1.3–5.5
No. reflections measured	4992
No. unique data	4340
R_{int}	0.0145
No. data used	3494
Cut off criteria	$[F > 4\sigma(F_o)]$
Absorption coefficient, μ (cm^{-3})	29.74
Range of transmission factors (%)	92.9–100.0
Final *R*	0.032
No. parameters	177
Residual denisty (e Å^{-3})	0.98

TABLE 2. Fractional coordinates (×10^4, I × 10^5) and equivalent isotropic temperature factors (Å^2, ×10^3, I and Ba × 10^4) for $C_{20}H_{48}N_2O_{11} \cdot BaI_2$

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
I	12232(3)	7617(2)	39303(2)	532(1)
Ba	5000	10901	7500	289(1)
N	2476(3)	11067(2)	6711(2)	40(1)
O(1)	4566(4)	11685(2)	6103(2)	43(1)
O(2)	6920(3)	11552(2)	6733(2)	44(1)
O(3)	3735(3)	9410(2)	6834(2)	43(1)
O(4)	4052(3)	9808(2)	8534(2)	53(1)
O(5)	5000	12721(4)	7500	65(1)
Hw(1)	4766(70)	12949(44)	7220(36)	137(5)*
C(1)	2489(4)	11779(3)	6174(3)	52(1)
C(2)	3446(4)	11688(4)	5673(3)	51(1)
C(3)	5529(5)	11695(4)	5661(3)	49(1)
C(4)	6574(5)	12080(3)	6098(3)	50(1)
C(5)	7917(5)	11909(4)	7176(3)	56(1)
C(6)	8373(4)	11270(4)	7740(3)	51(1)
C(7)	7936(4)	10282(3)	8695(3)	51(1)
C(8)	2484(4)	9484(3)	6766(3)	53(1)
C(9)	4159(5)	9024(4)	6215(3)	52(1)
C(10)	4486(5)	8958(3)	8618(3)	50(1)
Ow	4076(6)	3644(4)	241(4)	124(2)
Hw(2)	3822(68)	4110(51)	414(43)	137(5)*
Hw(3)	4551(66)	3802(48)	−26(41)	137(5)*

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \cdot \mathbf{a}_j)$. Starred item = isotropic temperature factor.

TABLE 3. Bond lengths (Å) and bond angles (°) for the complex cation [Ba(BHEE-18-aneN_2O_4)H_2O]$^{2+}$ studied in this work[a]

Bond lengths			
Ba–N	3.079(3)	Ba–O(1)	2.822(3)
Ba–O(2)	2.905(3)	Ba–O(3)	2.938(3)
Ba–O(4)	2.846(3)	Ba–O(5)	2.854(5)
C(3)–O(1)	1.428(6)	C(5)–O(2)	1.432(5)
C(9)–O(3)	1.411(6)	C(1)–C(2)	1.502(7)
Bond angles			
N–Ba–O(1)	58.7(1)	N–Ba–O(2)	117.3(1)
O(1)–Ba–O(2)	58.6(1)	N–Ba–O(3)	59.0(1)
O(1)–Ba–O(3)	86.8(1)	O(2)–Ba–O(3)	116.2(1)
N–Ba–O(4)	87.6(1)	O(1)–Ba–O(4)	144.9(1)
O(2)–Ba–O(4)	152.8(1)	O(3)–Ba–O(4)	65.8(1)
N–Ba–O(5)	85.2(1)	O(1)–Ba–O(5)	64.2(1)
O(2)–Ba–O(5)	69.5(1)	O(3)–Ba–O(5)	142.8(1)
O(4)–Ba–O(5)	127.1(1)	Ba–N–C(1)	107.1(1)
Ba–O(1)–C(2)	123.8(3)	Ba–O(1)–C(3)	116.4(3)
C(2)–O(1)–C(3)	112.7(3)	Ba–O(2)–C(4)	115.7(3)
Ba–O(2)–C(5)	117.2(3)	C(4)–O(2)–C(5)	110.9(3)
Ba–O(3)–C(8)	114.4(3)	Ba–O(3)–C(9)	118.4(3)
C(8)–O(3)–C(9)	113.1(4)	Ba–O(4)–C(10)	118.9(3)
N–C(1)–C(2)	112.9(4)	O(1)–C(2)–C(1)	109.3(4)
O(1)–C(3)–C(4)	108.8(4)	O(2)–C(4)–C(3)	109.2(4)

[a] Numbers in parentheses are uncertainties in last significant figure of reported length or angle.

Molecular Mechanics Calculations

The program used for the calculations was MOLBLD-3 due to Boyd *et al.* [6]. The force field was that of Kollman *et al.* [3], using a unified atom approach. As a test of the reliability of the force field, the latter was used to reproduce the calculated strain energies and geometries obtained by Kollman *et al.* [3] for the crown ether complexes of alkali metal ions, Parameters for Ba^{2+} are not available in this parametrization, and these were taken as being the same as for the similarly sized K^+, but with the charge on the cation increased from 1+ to 2+. This was found to reproduce satisfactorily the structures of Ba^{2+} with BHEE-18-aneN_2O_4. Calculations of the structure and energy of both K^+ and Ba^{2+} in the eight-coordinate K^+ type of BHEE-18-aneN_2O_4 structure and the Ba^{2+} were performed using the observed structures (ref. 1 and this work) as trial structures. The water molecule was removed from the Ba(II) structure so that comparison could be made with the energies of the K(I) type of structure. The energies of the calculated structures are shown in Table 4.

TABLE 4. Total strain energies, ΣU, for the K^+ and Ba^{2+} complexes of BHEE-18-aneN_2O_4 (kcal mol^{-1})

	Coordination number		
	8	9	10
K^+	−16.7[a] −10.6[b]	−18.7	−10.5
Ba^{2+}	c	−350.9	−354.2

[a]Both alcoholic (terminal) oxygens of the pendent arms non-coordinating. [b]Both oxygens of one pendent arm coordinated, with both oxygens of the second pendent arm non-coordinated. [c]Eight-coordinate structure of Ba^{2+} becomes nine coordinate during course of refinement.

Results and Discussion

In Fig. 1 the structure and atomic numbering scheme of the $[Ba(BHEE\text{-}18\text{-}aneN_2O_4)(H_2O)]^{2+}$ complex cation is given. Figure 2 shows the skeletal diagram illustrating the coordination geometry of the complex cation of Ba^{II} compared with the two types of complex found for K^I. The Ba^{II} complex is eleven coordinate with a water molecule occupying the eleventh coordination site, as compared with the K^I which is only eight coordinate. The full coordination of BHEE-18-aneN_2O_4 to Ba^{II} accounts for the fact that its complexes show only slightly decreased complex stability as compared with BHE-18-aneN_2O_4.

The Ba^{II} complex has a *cis* conformation, with the arms on the same side of the macrocyclic ring,

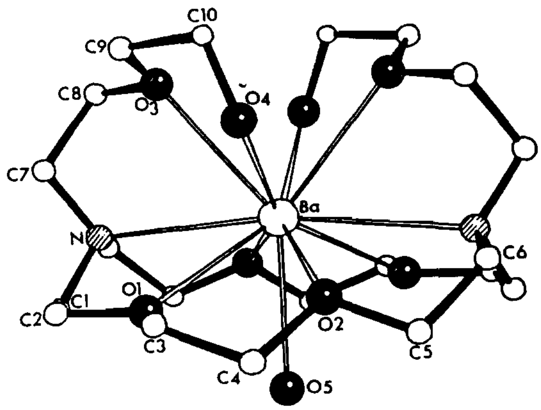

Fig. 1. ORTEP [7] drawing of the $[Ba(BHEE\text{-}18\text{-}aneN_2O_4)\text{-}H_2O]^{2+}$ cation showing the numbering scheme. The oxygen donor atoms are drawn in black to highlight the coordination sphere of the metal ion. The oxygen atom indicated as O(5) is a coordinated water increasing the coordination number to eleven.

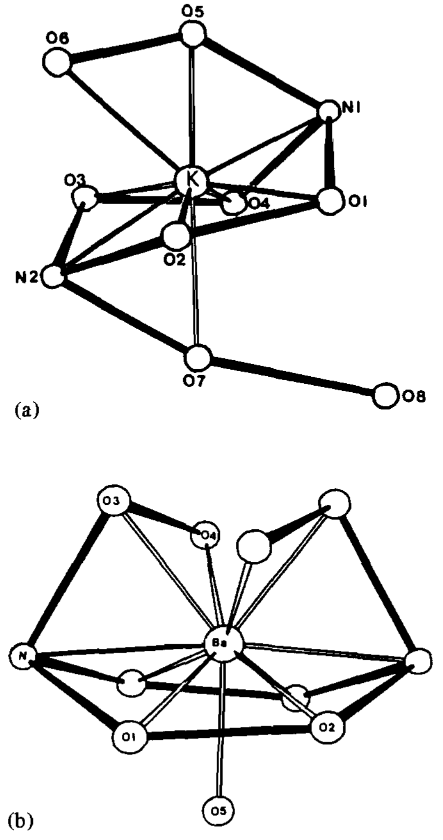

Fig. 2. Skeletal diagram showing the coordination of the donor atoms in (a) the nine-coordinate $[K(BHEE\text{-}18\text{-}aneN_2O_4)]^+$ cation, and (b) the eleven-coordinate $[Ba(BHEE\text{-}18\text{-}aneN_2O_4)H_2O]^{2+}$ cation. The thick filled 'bonds' indicate ethylene bridges forming the organic skeleton of the ligands, and non-filled bonds are metal to ligand bonds.

whereas the K^I complex has the *trans* conformation, with the arms on opposite sides of the macrocyclic ring. It has been suggested [1] that the *trans* conformer is adopted for sterically crowded situations, and the *cis* conformer for less crowded complexes. The MM calculations shed some light on the difference in structure between the K^+ and Ba^{2+} complexes with BHEE-18-aneN_2O_4. In Table 4 the energies of K^+ and Ba^{2+} in the eight- and nine-coordinate *trans* form complex of BHEE-18-aneN_2O_4, derived from the K^+ structure [1], and of the *cis* form of complex, derived from the Ba^{2+} structure reported in this work, are given. It was not possible to generate an eight-coordinate structure for Ba^{2+} with BHEE-18-ane-N_2O_4 starting with the appropriate coordinates for K^+, since the uncoordinated oxygen of one arm became coordinated to Ba^{2+} during the course of refinement. The energies of the K^+ complexes are at a minimum for the nine-coordinate type of structure, in accord with the fact that this is the major conformer found [1] in the crystal structure. The MM calculations in Table 4 also show that the observed eight-coordinate form of the K^+ complex is of lower energy than an alternative conformer where one arm is totally coordinated and the second arm totally non-coordinated. The K^+ ion in a ten-coordinate structure derived from the Ba^{2+} structure is at a higher energy by some 8 kcal mol^{-1}, in accord with the non-observation of a ten-coordinate structure for this metal ion. In contrast, for the Ba^{2+} structure, the ten-coordinate structure is lowest in energy. This illustrates the role of charge on the metal ion in producing higher coordination numbers. The unfavourable factor to be overcome in producing a higher coordination number is electrostatic repulsion between the charges on the coordinating oxygen atoms. The higher charge on the Ba^{2+} in the parametrization used here leads to stronger attraction for the negatively charged oxygens, which helps to counter their mutual repulsion. The effect of charge on ionic radii in comparing K^+ and Ba^{2+} is seen in Table 5, where it is evident that the ionic radii [2] of the K^+ ion increase more rapidly with increasing coordination number than is the case for Ba^{2+}, with the exception of coordination number 12. The more rapid increase in ionic radius of K^+ with increase in coordination number is therefore a sign of the inability of the single positive charge to counter the rapid buildup of electrostatic repulsion between the donor atoms, with resulting increase in M–L bond length.

TABLE 5. Ionic radii [2] of K^+ and Ba^{2+} as a function of coordination number

Coodination number	Ionic radius (Å)	
	K^+	Ba^{2+}
6	1.37	1.36
8	1.51	1.42
9	1.55	1.47
10	1.59	1.52
12	1.60	1.60

This work has shown that the relatively high complex stability of the Ba(II) complex of BHEE-18-aneN_2O_4 relates to the ability of the Ba(II) to accommodate the ten donor atoms of the ligand, even coordinating a water molecule to achieve a coordination number of eleven. In contrast, the K^+ complex is only nine coordinate. Molecular mechanics calculations demonstrate the importance of charge on the metal ion in countering mutual electrostatic repulsion between the donor atoms as a factor in stabilizing complexes of high coordination number.

Supplementary Material

Tables of observed and calculated structure factors are available from the authors on request.

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