mm mounted at the end of a glass fiber. The procedures used have been described previously.[14] Crystal data, including lattice dimensions and data-collection parameters, are summarized in Table II. The lattice dimensions and Laue group were verified by axial photography.

Three check reflections, which were rescanned at regular intervals during intensity data collection, did not show any appreciable change in intensity over the 140 h of X-ray exposure time.

The data were reduced by standard procedures. Calculations were done by a PDP-11/60 computer with programs from the package SDP-PLUS. An empirical absorption correction[15] was based on azimuthal scans of nine reflections with diffractometer angle χ near 90°.

Systematic absences uniquely identified the space group as $P2_1/n$. The position of the unique Pt atom was derived from a Patterson map. The full structure was developed in a series of alternating least-squares refinements and difference Fourier maps. For the final refinement all 59 unique atoms were treated with anisotropic displacement parameters. In all, 532 variable parameters were fitted to 4101 data, giving a data-to-parameter ratio of 7.7. The final residuals are defined and summarized in Table II.

Acknowledgment. We thank the U.S. National Science Foundation and the CAYCIT (Spain) for financial support.

Supplementary Material Available: For the crystal structure of $(C_4H_8S)(C_6F_5)_3PtAgPPh_3$, full lists of bond distances, bond angles, and anisotropic displacement parameters (6 pages); a list of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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[14] Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

[15] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

[16] Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive.

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Structural and Molecular Mechanics Studies of Bis(dibutyl phosphato)aquastrontium–18-Crown-6 and Analogous Alkaline-Earth-Metal Complexes

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The stability of bis(dibutyl phosphato)aquastrontium–18-crown-6 (**1**) has been compared with analogous real and hypothetical alkaline-earth-metal complexes by use of molecular mechanics calculations. Trial molecular structures from which energy minimization proceeded were obtained by crystal structure analysis of **1** and from its previously analyzed Ba analogue. Existence of these molecules in solution was also verified by IR and NMR spectra. Crystals of **1** are monoclinic, $P2_1/c$, with $a = 9.23$ (1) Å, $b = 27.24$ (3) Å, $c = 31.55$ (3) Å, $\beta = 94.95$ (6)°, and $Z = 8$. In the two independent molecules of the crystal each Sr^{2+} ion is coordinated by six O atoms of a crown ether, by two monodentate dibutyl phosphato ions, and by one H_2O molecule. The differences in calculated total energies among these complexes are due primarily to the Coulombic contributions, the strain in the crown molecules being relatively unimportant within wide geometrical limits. An estimate of the selectivity of the crown/dibutyl phosphate combination among the hydrated alkaline-earth-metal ions suggests that they are selected in the order Ba > Sr > Ca > Ra > Mg.

Introduction

The stabilities of crown ether complexes with various cations have been the subject of study by many methods.[1] Early estimates of the relative stabilities were made by using solvent extraction of alkali-metal complexes with picrate as the counterion.[2] Subsequently extraction equilibria for crown ether picrates of all the alkali-metal and alkaline-earth-metal ions have been determined.[3] Enhanced extractability has been achieved by using mixtures of crown ethers and organophilic acids as cation exchangers, and several systems of this type have been investigated.[4] The distribution of the various complexes to the organic phase has been found generally to parallel the thermodynamic stabilities found in the aqueous phase. Because the latter have been correlated with the match between macrocycle size and cation radius, it has been suggested that these synergistic mixtures can provide a means of separation of ions on the basis of size.

The work to be described here was undertaken to examine the stabilities of model systems containing a crown ether, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), an organophilic acid, HDBP (di-*n*-butyl phosphoric acid), and the Sr^{2+} and Ba^{2+} ions. The first step was to obtain the crystal structures of the complexes which these components produce, the second step was to correlate these with their NMR and IR spectra in solution, and the final step was to calculate the molecular energies and minimize them by the methods of molecular mechanics. To examine further the effect on the energy of the size of the extracted ion, hypothetical complexes containing Mg^{2+}, Ca^{2+}, and Ra^{2+} ions were treated by the same calculational methods. Previously, molecular mechanics was used by Wipff, Wiener, and Kollman (WWK)[5] to evaluate the energies of crown ether and cryptand complexes of the alkali metals, and the energies of the 18-crown-6 molecule, in various configurations, were minimized by Bovill, Chadwick, Sutherland, and Watkin (BCSW).[6] We have used procedures similar to WWK to facilitate comparison. The crystal structure of $Ba(DBP)_2(H_2O)\cdot$18-crown-6 was already available.[7]

Experimental Section

Preparation of $Sr(DBP)_2(H_2O)\cdot$18-crown-6. Di-*n*-butyl phosphoric acid was separated from a mixture of mono- and dibutyl phosphoric acids (Mobil Chem. Co., Richmond, VA) by dissolving the mixture in benzene and extracting out the mono acid with water. A 1:1:2 mixture of $Sr(OH)_2\cdot 8H_2O$, 18-crown-6 (Aldrich Chem. Co.), and HDBP were mixed neat and allowed to react. The resulting colorless thin platelets of $Sr(DBP)_2(H_2O)\cdot$18-crown-6 were removed from the wet mixture. These crystals lost water under conditions of low humidity and recrystallized when the humidity rose.

NMR and IR Measurements. Samples were prepared by dissolving crystals of $Sr(DBP)_2(H_2O)\cdot$18-crown-6 and $Ba(DBP)_2(H_2O)\cdot$18-crown-6, made earlier,[7] in $CHCl_3$ for IR and in $CDCl_3$ (1% Me_4Si) for NMR measurements. ^1H NMR spectroscopy was performed by use of a Varian EM360L instrument and Fourier-transform IR spectroscopy by use of

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[1] Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

[2] Pederson, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 391.

[3] Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 4684. Danesi, P. R.; Meider-Gorican, H.; Chiarizia, R.; Scibona, G. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1479. Takeda, Y.; Kato, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1027; Takeda, Y.; Goto, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1920.

[4] Kinard, W. F.; McDowell, W. J.; Shoun, R. R. *Sep. Sci. Technol.* **1980**, *15*, 1013. Kinard, W. F.; McDowell, W. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2947. Clark, G. A.; Izatt, R. M.; Christensen, J. J. *Sep. Sci. Technol.* **1983**, *18*, 1473. Moyer, B. A.; McDowell, W. J.; Ontko, R. J.; Bryan, S. A.; Case, G. N. *Solvent Extr. Ion Exch.* **1986**, *4*, 83.

[5] Wipff, G.; Weiner, P.; Kollman, P. *J. Am. Chem. Soc.* **1982**, *104*, 3249. Wipff, G.; Kollman, P. *Nouv. J. Chim.* **1985**, *9*, 457.

[6] Bovill, M. J.; Chadwick, D. J.; Sutherland, I. O.; Watkin, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1529.

[7] Burns, J. H. *Inorg. Chim. Acta* **1985**, *102*, 15.

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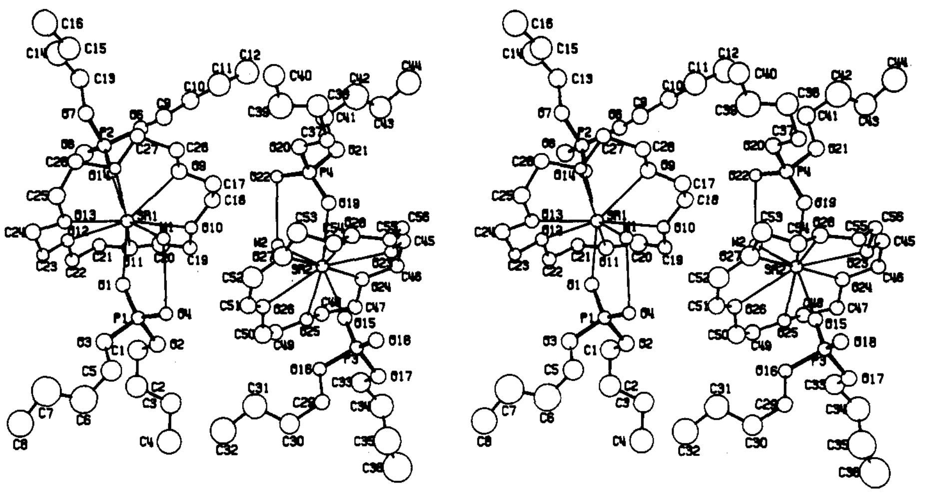

Figure 1. Stereoscopic view of the two molecules of $Sr(DBP)_2(H_2O)\cdot 18$-crown-6 that form the asymmetric unit of structure. Spheres are at 20% probability level.

a Digilab FTS-60 instrument employing NaCl plates.

X-ray Diffraction. Crystals of $Sr(DBP)_2(H_2O)\cdot 18$-crown-6 are very thin and fragile (analogous Ba-containing crystals are more robust), and it was with difficulty that specimens of adequate quality for X-ray study were found. These were sealed in glass capillaries to prevent loss of water. X-ray precession photographs indicated monoclinic symmetry, and systematic absences of $h0l$ with l odd and $0k0$ with k odd indicated space group $P2_1/c$. Data for refinement of the unit cell dimensions, 12 reflections near $2\theta = 25°$, and a set of intensity data were obtained with a computer-controlled Picker X-ray diffractometer. Crystal data and experimental conditions for data collection are summarized in Table I. At increasing 2θ angles the intensities decreased rapidly and were virtually nil beyond 32°. During the measurement of intensities a reference reflection was monitored hourly and its intensity was found to diminish gradually over 2 weeks to 86% of its original value. The observed intensities were corrected[8] for this decline, for absorption, and for Lorentz and polarization effects to convert them to relative structure factor squares, F_o^2. The variance of F_o^2 was taken to be $\sigma_c^2 + (0.05F_o^2)^2$, where σ_c^2 was the variance attributable to the counting statistics alone.

Structure Determination and Refinement. A Patterson map was used to locate the Sr and P atoms, and phases based on these atomic positions were used to calculate electron density maps in which the O and C atoms could be found. While the atoms of the crown ethers were easily recognized, the C atoms of the four butyl groups were not, especially toward the free ends. There are two independent $Sr(DBP)_2(H_2O)\cdot 18$-crown-6 molecules in the asymmetric unit, consisting of 92 non-hydrogen atoms.

This approximate structure was adjusted by the method of least squares by employing the 1308 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Weights were taken to be $1/\sigma^2(F_o^2)$. Because of the large number of variables required to describe this structure, the relatively few observations available, and the large thermal motions of the butyl groups, some constraints were imposed on the refinement. The α-carbons of the butyl groups were allowed to move freely and the O–C–C angle to vary, but the other C atoms were required to have C–C bond lengths of 1.47 Å and C–C–C angles of 112.6°. With these restrictions the torsion angles about the C–C bonds in the butyl groups were varied. The 124 independent H atoms were omitted. A total of 329 parameters were refined, including a single scale factor and an isotropic thermal parameter for each atom. Measures of agreement for the refined structure are given in Table I. The final parameters are given in Table II, and selected interatomic distances are listed in Table III.

Table I. Crystal Data and Experimental Conditions

formula	$SrP_2O_{15}C_{28}H_{62}$
fw	788.36
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	9.23 (1)
b, Å	27.24 (3)
c, Å	31.55 (3)
β, deg	94.95 (6)
V, Å^3	7903 (14)
Z	8
$F(000)$, e	3344
d_{calcd}, g cm^{-3}	1.325
d_{measd}, g cm^{-3}	1.39
cryst dimens, mm	0.06 × 0.25 × 0.88
μ(Mo Kα), cm^{-1}	14.5
transmiss factors	0.71–0.91
radiation	Mo Kα (λ = 0.71073 Å)
filter	Nb
temp, °C	20
scan mode	ω–2θ
bkgd	10 s at ends
collcn range (2θ), deg	≤32
octants	$+h,+k,\pm l$
tot. no. of reflcns collcd	2328
no. of unique data with $F_o^2 \geq 3\sigma(F_o^2)$	1308
no. params refined	329
$R(F)$	0.087
$R(I)$, internal	0.069
$wR(F)$	0.129
σ_1	2.03

Results and Discussion

Crystal Structure of $Sr(DBP)_2(H_2O)\cdot 18$-crown-6. There are two independent molecules in the asymmetric unit of the crystal; they are shown in Figure 1. They have qualitatively the same structure, exhibiting the same connectivity, but differ somewhat in the ether conformations. Each Sr^{2+} ion is nine-coordinate: there are two phosphate O atoms at 2.41–2.50 Å, a water O atom at 2.61–2.62 Å, and six ether O atoms at 2.67–2.81 Å. The Sr–O bonds to phosphate and water O atoms are about 0.18 Å shorter than the Ba–O bonds in the analogous complex[7] in accord with the differences in radii of nine-coordinate Sr^{2+} and Ba^{2+} ions. The average Sr–O bond to an ether O atom is only 0.09 Å shorter than the average Ba–O bond. The reason for this is that the greater ring strain opposes the formation of Sr–O bonds. These Sr–O(ether) bonds are a little longer (2.75 Å) than those in $Sr(ClO_4)_2(H_2O)_3\cdot$(benzo-18-crown-6) (2.68 Å),[9] in which the three additional ligands are all H_2O molecules, and greater than those in $Sr(ClO_4)_2$(4′-acetobenzo-18-crown-6) (2.68 Å),[10] in which the Sr^{2+} ion is eight-coordinated.

The DBP ligands have slightly irregular tetrahedral PO_4 groups with the P–O bonds for O atoms linked to the butyl groups at an average of 1.62 Å, distinctly longer than the P–O bonds to the other two O atoms (1.48 Å). Although the dimensions of the butyl groups were fixed at assumed values, the torsion angles about the C–C bonds in the 1,2- and 2,3-positions as well as those about

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(8) The calculations in this structure analysis employed the following Oak Ridge computer programs: data reduction and absorption corrections with ORDATLIB (Ellison et al.); Fourier maps with ORFFP (Levy); least squares with ORXFLS-4 (Busing et al.); bond distances and angles with ORFFE-4 (Busing et al.); drawings with ORTEP-II (Johnson).

(9) Hughes, D. L.; Mortimer, C. L.; Truter, M. R. *Inorg. Chim. Acta* **1978**, *29*, 43.

(10) Fenton, D. E.; Parkin, D.; Newton, R. F.; Nowell, I. W.; Walker, P. E. *J. Chem. Soc., Dalton Trans.* **1982**, 327.

Table II. Atomic Positional Parameters ($\times 10^3$) and Isotropic Thermal Parameters[a] ($\times 10^2$) with Estimated Standard Deviations

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
Sr(1)	85.1 (7)	197.7 (2)	260.8 (2)	5.8 (3)	Sr(2)	418.7 (7)	456.5 (2)	230.2 (2)	5.5 (2)
P(1)	262 (2)	192.6 (8)	158.9 (6)	6.0 (7)	P(3)	743 (2)	445.1 (7)	160.0 (6)	5.9 (7)
O(1)	145 (4)	186 (1)	188 (1)	7 (1)	O(15)	616 (4)	453 (1)	184 (1)	8 (1)
O(2)	230 (5)	234 (1)	123 (1)	9 (2)	O(16)	706 (4)	395 (1)	133 (1)	6 (1)
O(3)	268 (4)	143 (2)	133 (1)	9 (2)	O(17)	754 (4)	485 (1)	124 (1)	7 (1)
O(4)	413 (4)	204 (1)	177 (1)	6 (1)	O(18)	889 (4)	436 (1)	183 (1)	7 (2)
C(1)	88 (8)	234 (2)	100 (2)	11 (3)	C(29)	822 (6)	374 (2)	106 (2)	9 (2)
C(2)	82	239	54	17 (3)	C(30)	739	345	73	15 (3)
C(3)	172	280	41	16 (3)	C(31)	674	301	90	18 (3)
C(4)	197	278	−5	16 (4)	C(32)	606	269	57	22 (4)
C(5)	398 (8)	129 (2)	110 (2)	14 (3)	C(33)	606 (8)	496 (2)	102 (2)	14 (3)
C(6)	335	103	72	25 (5)	C(34)	624	536	71	22 (4)
C(7)	316	50	80	29 (5)	C(35)	722	523	39	27 (5)
C(8)	272	23	40	22 (4)	C(36)	703	556	2	32 (6)
P(2)	−239 (3)	215.7 (7)	332.0 (7)	7.1 (7)	P(4)	248 (3)	461.2 (8)	335.0 (7)	7.3 (8)
O(5)	−113 (4)	203 (1)	308 (1)	7 (2)	O(19)	354 (4)	472 (1)	304 (1)	8 (1)
O(6)	−225 (4)	271 (1)	356 (1)	8 (1)	O(20)	312 (5)	423 (1)	371 (1)	8 (1)
O(7)	−221 (4)	178 (1)	372 (1)	9 (2)	O(21)	236 (4)	509 (2)	364 (1)	10 (2)
O(8)	−387 (5)	212 (2)	313 (1)	12 (2)	O(22)	101 (4)	441 (1)	319 (1)	5 (1)
C(9)	−92 (6)	281 (2)	380 (2)	9 (2)	C(37)	467 (7)	430 (2)	389 (2)	9 (2)
C(10)	−113	329	399	11 (3)	C(38)	475	403	429	15 (3)
C(11)	15	345	426	19 (3)	C(39)	441	351	424	21 (4)
C(12)	−2	395	443	20 (4)	C(40)	495	322	462	15 (3)
C(13)	−321 (5)	181 (2)	408 (2)	9 (3)	C(41)	121 (7)	514 (2)	398 (2)	13 (3)
C(14)	−299	145	443	21 (4)	C(42)	202	547	428	24 (4)
C(15)	−149	127	449	17 (3)	C(43)	183	599	417	19 (4)
C(16)	−130	87	480	22 (4)	C(44)	207	632	454	21 (4)
Ow(1)	369 (3)	198 (1)	263 (1)	6 (1)	Ow(2)	139 (3)	446 (1)	234 (1)	6 (1)
O(9)	203 (4)	251 (2)	332 (1)	9 (1)	O(23)	587 (4)	533 (1)	263 (1)	6 (1)
C(17)	257 (6)	297 (2)	318 (2)	8 (2)	C(45)	492 (6)	577 (2)	266 (2)	7 (2)
C(18)	152 (7)	323 (2)	292 (2)	8 (2)	C(46)	435 (7)	592 (2)	228 (2)	7 (2)
O(10)	118 (4)	298 (1)	255 (1)	7 (1)	O(24)	350 (4)	551 (1)	206 (1)	7 (1)
C(19)	28 (6)	318 (2)	219 (2)	6 (2)	C(47)	291 (6)	560 (2)	163 (2)	7 (2)
C(20)	−121 (7)	301 (3)	219 (2)	11 (3)	C(48)	192 (6)	523 (2)	149 (2)	7 (2)
O(11)	−121 (4)	247 (2)	211 (1)	9 (2)	O(25)	275 (4)	475 (1)	149 (1)	6 (1)
C(21)	−262 (6)	223 (2)	204 (2)	6 (2)	C(49)	197 (6)	436 (2)	127 (2)	8 (2)
C(22)	−228 (5)	175 (2)	185 (2)	6 (2)	C(50)	295 (6)	396 (2)	133 (2)	7 (2)
O(12)	−143 (3)	149 (1)	219 (1)	6 (1)	O(26)	343 (4)	379 (2)	174 (1)	7 (1)
C(23)	−90 (5)	102 (2)	205 (2)	3 (2)	C(51)	418 (7)	335 (2)	182 (2)	9 (3)
C(24)	−47 (7)	72 (2)	238 (2)	8 (2)	C(52)	467 (8)	322 (3)	224 (3)	14 (3)
O(13)	79 (5)	100 (1)	260 (1)	6 (1)	O(27)	513 (5)	362 (2)	252 (2)	12 (2)
C(25)	146 (6)	71 (2)	296 (2)	8 (2)	C(53)	606 (8)	360 (3)	292 (2)	12 (3)
C(26)	121 (5)	100 (2)	337 (2)	6 (2)	C(54)	721 (6)	391 (2)	282 (2)	7 (2)
O(14)	198 (3)	148 (1)	333 (1)	4 (1)	O(28)	652 (4)	439 (2)	287 (1)	9 (1)
C(27)	203 (5)	175 (2)	373 (2)	6 (2)	C(55)	760 (6)	478 (2)	290 (2)	5 (2)
C(28)	282 (7)	224 (2)	363 (2)	7 (2)	C(56)	680 (6)	521 (2)	301 (2)	7 (2)

[a] Temperature factor: $\exp(-8\pi^2 U((\sin\theta)/\lambda)^2)$.

the O–C bonds were varied in the least-squares refinement. The resulting torsion angles are listed in the supplementary material. While all eight butyl groups are in the anti conformation, they have a variety of torsion angles about the C–C bonds in the 1,2-position. The average O–C(butyl) bond length is 1.50 ± 0.04 Å (average deviation). For dimensions of the crown molecules the following average values were obtained: C–O bonds, 1.46 ± 0.03 Å; C–C bonds, 1.43 ± 0.05 Å, C–O–C angles, 117 ± 5°; C–C–O angles, 109 ± 5°.

Hydrogen bonds are inferred from the short O···O distances between water molecules and phosphate groups and from O···O···O angles. Water molecule W1 makes an intramolecular H bond to O(4) and an intermolecular H bond to O(8), connecting molecules of one type in a H-bonded chain. A similar arrangement of H bonds in O(22)···W2···O(18) links the other molecules. In the Ba analogue to this complex, similarly constituted molecules exist in the crystal, but they are all equivalent.[7]

Because of the reputed enhanced stability of complexes with a good match between cation radius and ring opening, the structural features of most interest are the conformations of the ether molecules, as these determine the size of the rings of O atoms. The 18 torsion angles describing each macrocycle are listed in Table IV along with those in the Ba complex for comparison. The symmetry of the crown in the Ba complex is approximately D_{3d}, and the crown molecule bonded to Sr(2) has the same distribution of torsion angles, $(\mathrm{ag^+a, ag^-a})_3$, where a = anti and g = gauche, but is somewhat less symmetrical than the Ba analogue. This conformation has been found in the majority of known complexes of 18-crown-6.[11] The other ether molecule, bonded to Sr(1), is also asymmetric and has a less common conformation, $\mathrm{g^+g^+a}$, $\mathrm{ag^-a}$, $\mathrm{ag^+a}$, $\mathrm{g^+g^+a}$, $\mathrm{ag^-a}$, $\mathrm{ag^+a}$; this is found in complexes with uranium,[12] neodymium,[13] and lanthanum[14] nitrates.

Another means of comparing the crowns is to examine the deviations of the O atoms from the best planes through them. Since there is no unique choice of atoms for this purpose, we chose the four O atoms which lie close to a plane and calculated the deviations from the best plane through them (Table V). From this it is seen that the O rings may be described as boat form with $\mathrm{Sr^{2+}}$ and $\mathrm{Ba^{2+}}$ ions at ~0.6 Å from the base and opposite ends

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(11) Uiterwijk, J. W. H. M.; Harkema, S.; van de Waal, B. W.; Göbel, F.; Nibbeling, H. T. M. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1843.

(12) Uiterwijk, J. W. H. M.; Harkema, S.; Reinhoudt, D. N.; Daasvaten, K.; den Hertog, H. J.; Geevers, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 450.

(13) Bombieri, G.; dePaoli, G.; Benetollo, F.; Cassol, A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1417. Bünzli, J.-C. G.; Klein, B.; Wessner, D. *Inorg. Chim. Acta* **1980**, *44*, L147.

(14) Backer-Dirks, J. D. J.; Cooke, J. E.; Galas, A. M. R.; Ghotra, J. S.; Gray, C. J.; Hart, F. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2191.

Table III. Selected Interatomic Distances (Å) in $Sr(DBP)_2(H_2O)\cdot$18-crown-6

atoms		dist	atoms		dist
Sr(1)	O(1)	2.41 (4)	Sr(2)	O(15)	2.43 (4)
	O(5)	2.47 (4)		O(19)	2.50 (4)
	Ow(1)	2.62 (3)		Ow(2)	2.61 (3)
	O(9)	2.81 (4)		O(23)	2.74 (4)
	O(10)	2.74 (4)		O(24)	2.74 (4)
	O(11)	2.72 (4)		O(25)	2.81 (3)
	O(12)	2.72 (4)		O(26)	2.80 (4)
	O(13)	2.67 (3)		O(27)	2.80 (5)
	O(14)	2.76 (3)		O(28)	2.73 (4)
P(1)	O(1)	1.50 (3)	P(3)	O(15)	1.46 (3)
	O(2)	1.62 (4)		O(16)	1.63 (3)
	O(3)	1.60 (4)		O(17)	1.58 (4)
	O(4)	1.50 (3)		O(18)	1.50 (4)
O(2)	C(1)	1.44 (6)	O(16)	C(29)	1.53 (6)
O(3)	C(5)	1.49 (7)	O(17)	C(33)	1.52 (7)
P(2)	O(5)	1.47 (3)	P(4)	O(19)	1.47 (3)
	O(6)	1.69 (4)		O(20)	1.61 (4)
	O(7)	1.62 (3)		O(21)	1.61 (4)
	O(8)	1.45 (4)		O(22)	1.51 (3)
O(6)	C(9)	1.40 (5)	O(20)	C(37)	1.50 (5)
O(7)	C(13)	1.53 (6)	O(21)	C(41)	1.59 (7)

Table IV. Conformation Angles (deg) in the Two Crown Molecules of $Sr(DBP)_2(H_2O)\cdot$18-crown-6 and in $Ba(DBP)_2(H_2O)\cdot$18-crown-6

Sr complex[a,b]				Ba[c] complex
	angle		angle	angle
O(10)–C(18)–C(17)–O(9)	65	O(23)–C(45)–C(46)–O(24)	57	66
C(19)–O(10)–C(18)–C(17)	171	C(45)–C(46)–O(24)–C(47)	−175	179
	99		−170	179
	67		−62	−64
	173		−166	−169
	−165		−179	178
	−67		58	70
	175		169	−179
	163		177	−179
	64		−33	−52
	177		−160	−156
	115		118	136
	61		79	66
	170		164	178
	179		−172	178
	−63		−70	−70
	−180		−179	−178
	169		165	170

[a] When one sights along the middle bond, the sign of the torsion angle is positive if a clockwise motion of the first atom superimposes it onto the fourth atom. [b] Only the first two angles are identified. Succeeding angles are found by proceeding around the rings in the same direction as the first two. [c] For identity of these atoms see ref 7.

Table V. Deviations (Å) from the Best Planes through Four Oxygen Atoms

atom	dev	atom	dev	atom	dev
O(19)	−0.074	O(25)	−0.002	O(11)	0.000
O(20)	0.076	O(27)	0.002	O(12)	0.000
O(22)	−0.079	O(28)	−0.002	O(13)	0.000
O(23)	0.077	O(30)	0.002	O(14)	0.000
O(21)	0.804	O(26)	0.601	O(9)	0.799
O(24)	0.803	O(29)	0.333	O(10)	0.183
Sr(1)	0.646	Sr(2)	0.579	Ba	0.655

tilted toward the cations to varying degrees. In no case does the cation lie *within* a hole in the ring; the rings are wrapped around one side of the cations.

Solution Studies. Proton NMR and IR spectroscopy show that the Sr and Ba complexes remain intact in chloroform solution. The ^1H NMR spectrum of free 18-crown-6 in $CDCl_3$ has a sharp singlet for the methylene protons at 3.71 ppm. In the complexed species that signal is a broadened singlet at about 3.80 ppm (Table VIa). This downfield shift indicates deshielding, which is expected on complexation of a cation as the electron density shifts from the O atoms of the crown ether to the metal and from the methylenes to the O atoms. Similar downfield shifts have been seen in studies of other crown ether complexes in solution.[10,15-17] Coordination by the dibutyl phosphate ion can also be seen with ^1H NMR. The protons of the α-methylene groups of the free acid in $CDCl_3$ show a quartet at 4.05 ppm that, upon complexation, moves to about 3.80 ppm and merges with the signal from the crown ether. The move upfield of about 0.25 ppm shows an increase in shielding of the protons as the Sr^{2+} or Ba^{2+} ions replace the acidic H^+ ions. This effect is seen also in the ^1H NMR spectrum of $Ba(DBP)_2$ in $CDCl_3$ where the quartet moves upfield by about 0.1 ppm. The coordination of the phosphate does not appear to affect the other protons of the butyl groups.

Table VI. Spectroscopic Data

ligand	group	free	Ba complex	Sr complex
	(a) Proton NMR Chemical Shifts (ppm)			
18-crown-6	CH_2	3.71	3.80	3.78
HDBP	OCH_2C	4.05	3.80	3.78
	CH_2CH_2	~1.5	~1.5	~1.5
	CH_3	0.93	0.93	0.93
	(b) Infrared Data (cm^{-1})			
18-crown-6	C–O–C (ν_{as})	1118	1099	1104
HDBP	P–O(H)	1005	1005	1005
	C–O(P)	1038	1033	1032
	P–O(C)	1066	1073	1072

The effects seen by NMR are reflected in the IR spectra of the bound and free crown ethers (Table VIb), in which the C–O–C asymmetric stretching bands are shifted to lower energy by about 20 cm^{-1} on complexation. This decrease in C–O bond strength is due to the inductive effect of the cation in the complex.[14,18,19] Bands of the phosphates that might be associated with coordination all shift by less than 10 cm^{-1} but were also not significantly changed in other dialkyl phosphate complexes.[20-22]

Molecular Mechanics Studies

Because the Sr and Ba complexes are similar in structure, differing mainly in the conformation of the 18-crown-6 rings, it is of interest to compare their energies to see how they reflect the difference in ion size. To make this comparison an energy calculation and minimization computer program by Busing[23] was employed in the molecular mechanics mode. Each complex was treated as an isolated molecule and its energy calculated from the known structural parameters by use of a potential function of the form

$$W = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{\substack{ij \\ \text{non-} \\ \text{bonded}}} -A_{ij} r_{ij}^{-6} + B_{ij} r_{ij}^{-12} + \sum_{\text{bonds}} \frac{k_d}{2}(d - d_0)^2 + \sum_{\text{angles}} \frac{k_\theta}{2}(\theta - \theta_0)^2 + \sum_{\substack{\text{torsion} \\ \text{angles}}} \frac{k_\phi}{2}(1 + \cos 3\phi) \quad (1)$$

In this expression r_{ij} is the distance between atoms of charge q_i and q_j, A_{ij} and B_{ij} are the nonbonded attraction and repulsion coefficients for a pair of atoms i and j, and k_d, k_θ, and k_ϕ are force constants related to stretching, bending, and twisting from

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(15) Lockhart, J. C.; Robson, A. C.; Thompson, M. E.; Tyson, P. D.; Wallace, I. H. M. *J. Chem. Soc., Dalton Trans.* **1978**, 611.

(16) Weber, G.; Sheldrick, G. M.; Burgemeister, T.; Dietl, F.; Mannschreck, A.; Merz, A. *Tetrahedron* **1984**, *40*, 855.

(17) Hubert-Pfalzgraf, L. G.; Tsunoda, M. *Inorg. Chim. Acta* **1980**, *38*, 43.

(18) Bünzli, J.-C. G.; Wessner, D. *Helv. Chim. Acta* **1978**, *61*, 1454.

(19) Cusack, P. A.; Patel, B. N.; Smith, P. J.; Allen, D. W.; Powell, I. W. *J. Chem. Soc., Dalton Trans.* **1984**, 1239.

(20) Kiss, A. B.; Hegedüs, A. J. *Mikrochim. Acta* **1966**, 771.

(21) Thomas, L. C.; Chittenden, R. A. *Spectrochim. Acta, Part A* **1970**, *26A*, 781.

(22) Katzin, L. I.; Mason, G. W.; Peppard, D. F. *Spectrochim. Acta, Part A* **1978**, *34A*, 51.

(23) Busing, W. R. "WMIN, A Computer Program to Model Molecules and Crystals in Terms of Potential Energy Functions", Report ORNL-5747; Oak Ridge National Laboratory: Oak Ridge, TN, 1981.

Table VII. Minimized Energies (kcal mol^{-1})

compd	Coulombic	van der Waals	repulsion	strain	tot.
18-crown-6	46.7	-47.4	34.2	4.2	37.7
$M(DBP)_2(H_2O)\cdot$(18-crown-6)					
M = Ra	-230.3	-110.5	109.5	9.3	-272.1
M = Ba	-267.7	-106.5	106.7	8.5	-259.0
M = Sr	-290.1	-105.7	106.9	10.4	-278.5
M = Ca	-317.6	-109.8	108.2	11.1	-308.1
M = Mg	-391.6	-94.7	108.8	12.9	-364.8

equilibrium values d_0, θ_0 and ϕ_0. Values used for all these parameters are listed in the supplementary material. They were derived from several sources and chosen to be consistent with those of WWK[5] wherever possible. One difference was our inclusion of H atoms individually (in calculated sites) instead of using their "united-atom" approach. The H atoms involved in H bonding were treated by the method of Hagler, Huler, and Lifson.[24]

The model molecule for each energy calculation included the cation, an ether ring, a water molecule, and the phosphate portion of two DBP^- ions (butyl groups were omitted to reduce computing time). Each CH_2 and PO_4 group was treated as a rigid body, and one H-bonded water molecule from an adjacent complex was included to prevent one of the PO_4 groups from rotating. Charges were assigned as follows: O (-0.6), C (0.3), and P (1.4) for the complexes and O (-0.3) and C (0.15) for the free ligand, whose energy was also calculated for comparison with WWK, who assigned these charges to their models.

After the energies were calculated for the Sr and Ba complexes having the structures found in the crystals, the structural parameters were systematically changed so as to minimize the energy in each case. Details are given in the program description,[23] but briefly the procedure involved a modified Rosenbrock search followed by adjustment using Newton's method. Refinements were also made on hypothetical complexes having the same structures but with the Ba replaced by Ra and the Sr replaced by Ca and Mg, respectively. While the molecules containing Ca and Ra refined as before, the molecule with Mg changed its bonding pattern and a six-coordinate Mg^{2+} ion resulted; this gave an improbable molecular configuration. Refinement of the uncomplexed 18-crown-6 molecule with our methods gave a relative energy more negative by 10 kcal mol^{-1} than that found by WWK, but the molecular conformation was close to theirs and slightly closer to the crystal structure.[25] The conformation of the free crown was also close to that of BCSW, but comparison of energies is not possible because they only gave relative values for various configurations.

The minimized energies are given in Table VII. Clearly the electrostatic contribution is the dominant contribution and that from ring strain is not large even in the Ca complex (although presumably it would be intolerably large in the Mg complex were all the O atoms of the crown forced to be at the minimal distance to the tiny ion). The crown, therefore, is seen to be flexible within broad limits and is not selective because of its size alone.

The structures of the energy-minimized complexes and the free crown are shown in Figure 2. The complex containing Mg is included only to show the result of minimization and is not intended to represent a realizable molecule. For the other complexes crown O atoms labeled 1–4 lie in planes within 0.07 Å while O(5), O(6), and M^{2+} ions deviate (Å) as follows: Ca complex, -2.1, -2.4, -0.6; Sr, -2.2, -2.3, -0.6; Ba, -1.8, -1.8, -0.3; Ra, -0.6, -0.9, 0.4. The average M–O distances (Å), M–O(P), M–O(W), and M–O(crown), are as follows: Ca, 2.37, 2.53, 2.55; Sr, 2.55, 2.70, 2.67; Ba, 2.67, 2.83, 2.80; Ra, 2.94, 3.12, 3.03. Conformation angles of all the crown ether molecules are given in Table VIII. These can be compared with their structures in crystals of the free crown[25] and the Sr and Ba complexes (Table IV).

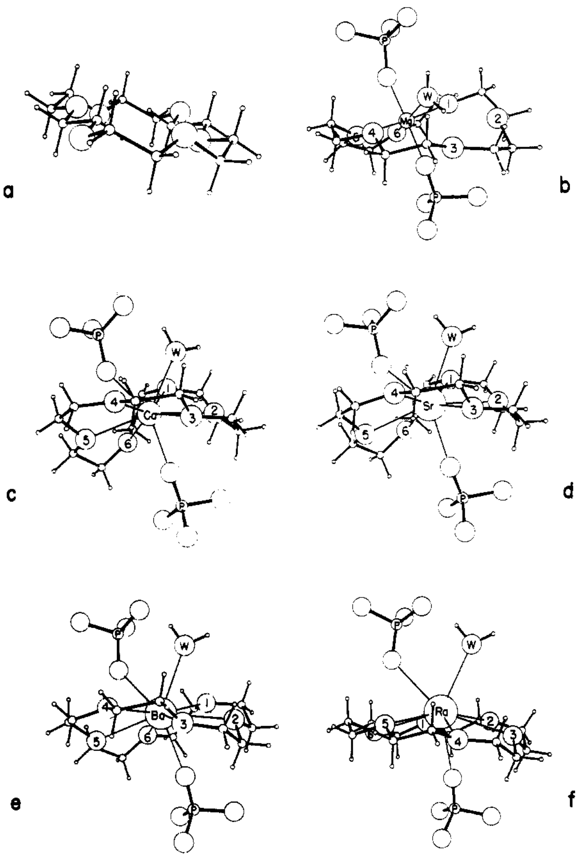

Figure 2. Structures of energy-minimized actual and hypothetical molecules: (a) 18-crown-6 ligand; (b–f) $M(DBP)_2(H_2O)\cdot$18-crown-6, where M = Mg, Ca, Sr, Ba, and Ra, respectively.

Table VIII. Torsion Angles in Energy-Minimized Structures (deg)

angle	crown	Ca	Sr	Ba	Ra
C–C–O–C	-162	-145	-159	171	174
C–O–C–C	165	-114	173	172	176
O–C–C–O	-64	-50	36	-48	-54
C–C–O–C	179	-171	-171	160	162
C–O–C–C	-178	173	173	-168	171
O–C–C–O	-178	30	-55	55	62
C–C–O–C	167	162	100	-173	173
C–O–C–C	69	-178	174	178	178
O–C–C–O	-72	-42	-51	-52	-52
C–C–O–C	162	168	178	130	144
C–O–C–C	-165	-165	-170	118	134
O–C–C–O	64	43	52	54	55
C–C–O–C	-179	-177	-116	-170	-180
C–O–C–C	178	-165	-166	-163	176
O–C–C–O	178	-46	-33	-57	-65
C–C–O–C	167	122	69	-168	177
C–O–C–C	-69	86	179	172	176
O–C–C–O	72	44	-48	50	56

Although these calculated energies of isolated "gas-phase" molecules are most stable for the smallest cation, the relative stabilities in water depend on the hydration energies of the cations. In order to estimate selectivities in these systems the following equation is considered:

$$M_1(\text{crown}) + M_2(H_2O)_m(\text{aq}) = M_2(\text{crown}) + M_1(H_2O)_m(\text{aq}) \quad (2)$$

By combining the calculated total energies of the "gas-phase" crown complexes with the ΔG's of hydration of the gaseous ions,[26] one can estimate the ΔG of reaction 2. The results of such a calculation are given in Table IX. These approximate values suggest that the DBP/18-crown-6 combination selects the alka-

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(24) Hagler, A. T.; Hugler, E.; Lifson, S. *J. Am. Chem. Soc.* **1974**, *96*, 5319.

(25) Maverick, E.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, B36, 615.

(26) Friedman, H. L.; Krishnan, C. V. In *Water, A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 3, p 55.

Table IX. $\Delta E_{\text{calcd}} - \Delta G_{\text{hyd}}$ (kcal mol^{-1}) for the Reaction M_1(crown) + $M_2(H_2O)_n$(aq) = M_2(crown) + $M_1(H_2O)_n$(aq)

	M_2			
M_1	Ca	Sr	Ba	Ra
Mg	−18	−25	−35	−7
Ca		−7	−17	+11
Sr			−9	+18
Ba				+28

line-earth-metal ions in the sequence Ba > Sr > Ca > Ra ≫ Mg. Actual thermodynamic data[27] for ΔG_f of crown ether complexes of alkaline-earth-metal ions in aqueous chloride solutions give ΔG_f(Ba) = −5.28 kcal mol^{-1}, ΔG_f(Sr) = −3.71 kcal mol^{-1}, and ΔG_f(Ca) = −0.7 kcal mol^{-1}. It is encouraging that our simple estimate is in agreement with this sequence of stabilities.

Summary

It has been shown that the stabilities of some extraction complexes of alkaline-earth metals can be compared by calculating their energies by molecular mechanics. Configurations of these molecules having minimum energies were found by starting with structures determined by X-ray diffraction analysis and adjusting their parameters. The contributions of the various terms to the total energy can be examined to see which are most important to stability, and in particular, the role of the crown ether molecule as a selective extractant can be assessed. In $Sr(DBP)_2(H_2O)\cdot$18-crown-6 and $Ba(DBP)_2(H_2O)\cdot$18-crown-6 it is seen that the differences in electrostatic components are more important than the differences in ring strain induced in the crowns as they adapt to the cations of different size. Energies of analogous hypothetical molecules containing Ca and Ra were also calculated, and the total energies of the alkaline-earth-metal complexes are in the order Ra < Ba < Sr < Ca. However, when hydration energies of these ions are taken into account, the stabilities of the complexes in aqueous solution are Ba > Sr > Ca > Ra. This is in the same order as measured stabilities of the first three of these ions when complexed with 18-crown-6 in aqueous chloride solutions.

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Supplementary Material Available: Table SI listing torsion angles involving butyl groups, Table SII giving nonbonded interaction parameters, and Table SIII giving force-field parameters (3 pages); a table of observed and calculated structure factors for **1** (8 pages). Ordering information is given on any current masthead page.

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[27] Izatt, R. M.; Terry, R. E.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondet, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620.

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Crystal Structures and Magnetic Properties of Dinuclear Copper(II) Complexes of 2,6-Bis(*N*-(2-pyridylmethyl)formimidoyl)-4-methylphenolate with Azido and Cyanato-*O* Exogenous Ligands

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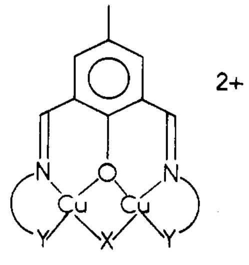
Two complexes of formula $[Cu_2(Famp)(X)](ClO_4)_2$ were synthesized. Famp$^-$ ($=C_{21}H_{19}N_4O^-$) is the binucleating ligand 2,6-bis(*N*-(2-pyridylmethyl)formimidoyl)-4-methylphenolate; X$^-$ is 1,1-N_3^- (**1**) and 1,1-OCN$^-$ (**2**). The crystal structures of **1** and **2** are isomorphous; space group $P2_1$, a = 8.973 (3) and 8.987 (3) Å, b = 14.785 (3) and 14.774 (4) Å, c = 9.650 (1) and 9.664 (1) Å, β = 90.63 (2) and 90.71 (2)°, and Z = 2. The copper(II) ions of the binuclear units are bridged by the phenolic oxygen atom and by the X$^-$ exogenous ligand. Both N_3^- and OCN$^-$ bridge in an end-on fashion and make angles of 18.7 (8) and 18.8 (8)°, respectively, with the plane of the Famp$^-$ ligand. OCN$^-$ bridges by its oxygen atom. The magnetic and EPR properties were investigated: in **1**, the copper(II) ions are antiferromagnetically coupled with a singlet–triplet (S–T) energy gap of −161 cm^{-1}; in contrast, **2** is one of the few copper(II) dinuclear complexes with a triplet ground state. The S–T energy gap is 43 (10) cm^{-1}.

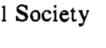
Introduction

We have recently undertaken the study of the magnetic properties of copper(II) dinuclear complexes with two dissimilar bridging ligands.[2,3] More precisely, one of the bridges, a phenolato group, remains constant and the other bridge can be modified. The former bridge may be considered as endogenous and the latter as exogenous. To limit the frame of this study, we have decided to focus on the hydroxo, azido, and cyanato groups as exogenous ligands. Our goal is to investigate several series of compounds of the type



with X$^-$ = OH$^-$, N_3^-, and OCN$^-$ and various lateral chains N⌒Y.

The first paper along this line has already been published.[3] It was devoted to the compounds $[Cu_2(Fdmen)(X)](ClO_4)_2$, in which the lateral chain was



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[1] (a) Université de Paris-Sud. (b) Université Pierre et Marie Curie. (c) University of New Orleans.

[2] Boillot, M. L.; Kahn, O.; O'Connor, C. J.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 178.

[3] Mallah, T.; Boillot, M. L.; Kahn, O.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 3058.

0020-1669/87/1326-1375$01.50/0