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Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Synthesis of a Lariat Ether Having a Phosphinic Acid Functional Group and the Crystal Structure of Its Na^+ Complex: Sodium *sym*-[(Dibenzo-14-crown-4-oxy)methyl]phenylphosphinate Dihydrate Diethanolate

Richard A. Sachleben, John H. Burns,* and George M. Brown

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A dibenzo-14-crown-4 ether with a pendant arm carrying a phosphinic acid moiety was synthesized and the crystal structure of its sodium salt determined by X-ray diffraction methods. The V-shaped macrocycle is almost identical with the unsubstituted version and has its four ether O atoms oriented to one side in a plane. The Na^+ ion is bonded to these atoms and is 1.5 Å above the plane; it is also bonded to the O atom of the oxymethyl side arm and to the O atoms of one water and one ethanol molecule. The phosphinate anion does not coordinate directly to the Na^+ ion but is attached indirectly through an intermediate H_2O molecule. A hydrogen bonding network joins the complex molecules into dimers that interact with each other in the crystal only through van der Waals contacts. The acid and the salt were also characterized by IR and NMR spectroscopy, and the pK_a was determined to be 4.5 in 80% methanol–water. Crystallographic data for $NaPC_{29}H_{42}O_{11}$: monoclinic, $a = 18.439$ (2) Å, $b = 8.680$ (1) Å, $c = 20.606$ (1) Å, $\beta = 102.95$ (1)°, space group $P2_1/n$, $Z = 4$.

Introduction

Lariat ethers having a variety of side arms have been developed to provide ligands that will be cation selective through cooperation of side arm and crown.[1-3] Both neutral and ionizable functional groups have been attached to various crowns, singly and multiply, up to four together. The ionizable side arms are of particular interest as possible phase-transfer agents because they can transport cations from the aqueous to organic phases without accompanying anions. Moreover, the group may participate in bonding to the extracted ion, further enhancing the stability of the complex.

Solvent extraction studies with neutral crown ethers combined in solution with either carboxylic, sulfonic, or organophosphoric acids have shown them to act synergistically and selectively in extracting alkali-metal and alkaline-earth-metal ions from aqueous media.[4] Recently, a number of crown ethers with such functional groups on side arms have been synthesized, and their solvent-extraction behavior[5,6] and kinetic and thermodynamic properties have been studied.[7]

Because these ionizable crowns may involve the functional group in complexing the cation, it is important to know the molecular structure of the complexes. Previously it was found that cations enclosed in crown ethers could also bond directly to sulfonate,[8] phosphate,[9] and carboxylate[10] anions not appended to the crown, but recently several structures of 18-crown-6 derivatives were found in which carboxylates, at least, on pendant arms are also bonded directly to the enclosed cations, viz Ca^{2+}, Sr^{2+}, and Cu^{2+} ions.[11,12] The only 14-crown-4 ether with an ionizable side arm structurally characterized thus far is *sym*-(dibenzo-14-crown-4-oxy)acetate complexed with the Li^+ ion.[13] In it the Li^+ and acetate ions form an ion pair separated by a water molecule. For comparison we have synthesized the same crown with a more acidic side arm, (oxymethyl)phenylphosphinic acid and investigated its complex with the larger Na^+ ion to see how these changes affect the sidearm participation.

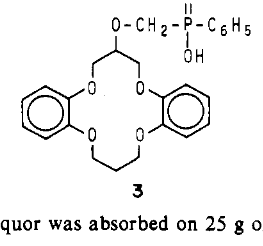
Experimental Section

All commercial reagents were used as obtained unless otherwise noted. THF and *p*-dioxane were distilled from sodium/potassium benzophenone ketyl under Ar. Melting points were obtained with a Hoover Unimelt apparatus. A Digilab FTS-60 was used to obtain IR spectra. The NMR spectra were taken on a Varian EM-360 (^1H) and a Varian FT-80 (^{13}C, ^{31}P) instrument.

(Chloromethyl)phenylphosphinyl Chloride (1). To 100 mL (0.737 mol) of dichlorophenylphosphine was added, in one portion, 40 g (1 mol) of paraformaldehyde. An exothermic reaction ensued as the paraformaldehyde dissolved, gas was evolved, and the mixture began to reflux. The resulting solution was heated overnight at 150–160 °C under Ar. Distillation yielded 100 g of material [bp 114–130 °C (25 mm)] containing about 75% **1**. This was dissolved in 200 mL of CCl_4 and cooled to −12 °C to induce crystallization. Filtration under Ar gave 48 g of hygroscopic powder containing ca. 85% **1** (32% yield). (Complete IR and NMR spectra for this and the following compounds are presented in the supplementary material.)

(Chloromethyl)phenylphosphinic Acid (2). To a solution of 40 g (0.16 mol) of **1** (85%) in 200 mL of THF was added dropwise with stirring 4.0 mL (0.22 mol) of H_2O. After 10 min the solution was evaporated in vacuo and the residue crystallized from 200 mL of ether to obtain 22.4 g (72%) of **2** (mp 77.5–79.5 °C).

***sym*-[(Dibenzo-14-crown-4-oxy)methyl]phenylphosphinic Acid (3).** To a stirred suspension of 4.51 g (188 mmol) of NaH (97% dry powder) in 50 mL of THF under Ar was added by cannula 15.0 g (47.4 mmol) of *sym*-hydroxydibenzo-14-crown-4[13] in 200 mL of THF. After 30 min a solution of 13.0 g (68.2 mmol) of **2** in 80 mL of THF was added by cannula, and the mixture was refluxed under Ar for 20 h. Then an additional 5.0 g of **2** in 50 mL of THF was added and refluxing continued for 16 h. Five milliliters of H_2O was added and the mixture refluxed for 1 h, and then the solvent was evaporated in vacuo. The residue was dissolved in 200 mL of H_2O plus 200 mL of $CHCl_3$. The aqueous phase was extracted with 50 mL of $CHCl_3$, and the combined organic phases were extracted with 50 mL of 1 N NaOH. The combined aqueous phases were acidified with concentrated HNO_3 (pH <3) and extracted twice with 100 mL of $CHCl_3$. The $CHCl_3$ extracts were washed twice with 1 M H_2SO_4 and evaporated. Dissolution in 100 mL of CH_3OH resulted in precipitation of 11.4 g of solid, which was recrystallized from 100 mL of 10% CH_3OH in toluene to give 5.24 g of **3** (mp 170.5–171.0 °C). The mother liquor was absorbed on 25 g of silica gel and eluted



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(1) Czech, B. P.; Czech, A.; Son, B.; Lee, H. K.; Bartsch, R. A. *J. Heterocycl. Chem.* **1986**, *23*, 465.

(2) Schultz, R. A.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659.

(3) Gatto, V. J.; Arnold, K. A.; Viscariello, A. M.; Miller, S. R.; Morgan, C. R.; Gokel, G. W. *J. Org. Chem.* **1986**, *51*, 5373.

(4) McDowell, W. J.; Moyer, B. A.; Case, G. N.; Case, F. I. *Solvent Extr. Ion Exch.* **1986**, *4*, 217.

(5) Pugia, M. J.; Ndip, G.; Lee, H. K.; Yang, I.-W.; Bartsch, R. A. *Anal. Chem.* **1986**, *58*, 2723.

(6) Charewicz, W. A.; Walkowiak, W.; Bartsch, R. A. *Anal. Chem.* **1987**, *59*, 494.

(7) Adamic, R. J.; Lloyd, B. A.; Eyring, E. M.; Petrucci, S.; Bartsch, R. A.; Pugia, M. J.; Knudsen, B. E.; Liu, Y.; Desai, D. H. *J. Phys. Chem.* **1986**, *90*, 6571.

(8) Groth, P. *Acta Chem. Scand.* **1971**, *25*, 3189.

(9) Burns, J. H. *Inorg. Chim. Acta* **1985**, *102*, 15.

(10) Ward, D. L.; Popov, A. I.; Poonia, N. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1183.

(11) Behr, J. P.; Lehn, J. M.; Moras, D.; Thierry, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 701.

(12) Uechi, T.; Ueda, I.; Tazaki, M.; Takagi, M.; Ueno, K. *Acta Crystallogr., Sect. B* **1982**, *B38*, 433.

(13) Shoham, G.; Christianson, D. W.; Bartsch, R. A.; Heo, G. S.; Olsher, U.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1984**, *106*, 1280.

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Table I. Crystal Data and Experimental Conditions

formula	$NaPC_{29}H_{42}O_{11}$
fw	620.61
space group	$P2_1/n$
a, Å	18.439 (2)
b, Å	8.680 (1)
c, Å	20.606 (1)
β, deg	102.95 (1)
V, Å^3	3214.09
Z	4
d_{calcd}, g cm^{-3}	1.28
d_{measd}, g cm^{-3}	1.3
cryst size, mm	0.32 × 0.45 × .45
μ(Mo Kα), cm^{-1}	1.242
instrument	Huber with PDP/11 control
radiation, Å	Mo Kα (λ = 0.709 26)
monochromator	graphite
range of transmissn factors	0.95–0.97
temp, °C	20.0
scan type	ω–2θ
2θ range for intens, deg	2–45
octants	$+h,+k,\pm l$
tot. no. of reflcns measd	4529
no. of indep refl used in refinement (>3σ)	2552
internal R (119 reflcns)	0.021
no. of params	379
$R = \sum \lVert F_o\rvert - \lvert F_c\rVert / \sum \lvert F_o\rvert$	0.049
R_w	0.114
σ_1	1.61
largest peak in difference Fourier, e/Å^3	0.54

with 5% CH_3OH in toluene to obtain 3.21 g of additional **3**; total yield 8.45 g (40.5%).

The pK_a of **3** was obtained by titration with n-Bu_4NOH in 80% CH_3OH/H_2O. An average of three measurements gave a value of 4.5.

Sodium Salt of *sym*-[(Dibenzo-14-crown-4-oxy)methyl]phenylphosphinic Acid. A solution of 28 mg (0.68 mmol) of NaOH in 1 mL of H_2O was added to 300 mg (0.68 mmol) of **3** in 2 mL of *p*-dioxane. Air evaporation of the solvent left a glassy film, which, on repeated dissolution in ethanol and evaporation, gave crystals for X-ray diffraction.

X-ray Diffraction. Crystals obtained by evaporation of an ethanol–water solution of $NaC_{25}H_{26}O_5PO_2$ were colorless multifaceted prisms. Precession photographs were used to identify the monoclinic symmetry and to determine the systematic absences, $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, which are indicative of space group $P2_1/n$. Intensity data were collected with a Huber 4-circle diffractometer controlled by a PDP-11 computer using a program (ORDIF) written by Busing. Thirty reflections in the 2θ range 39–43° were centered and their orientation angles used to refine the lattice parameters by least squares. The refined values are listed in Table I along with other conditions of the experiment and refinement.

A reference reflection, measured hourly, varied by 5% with a net decline of 1.3% over the data collection period. The observed intensities were corrected[14] for this variation, for absorption with measured bounding planes, 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 equal to $\sigma_c^2 + (0.05F_o^2)^2$, where σ_c^2 is the variance attributable to counting statistics alone.

Structure Determination and Refinement. The crystal structure of the title compound was determined by direct methods employing MULTAN 78.[15] The E map contained peaks for each of the 42 non-hydrogen atoms among its 50 highest maxima. The positions and anisotropic thermal parameters for the nonhydrogen atoms were refined by the method of least squares to $R(F) = 0.072$. Hydrogen atoms were then added to the model in positions calculated from normal hydrocarbon and water geometries; this was aided by the examination of O···O contacts to determine H bonding and by use of Fourier peaks in establishing the methyl group orientations. The H atoms were assigned isotropic thermal parameters equivalent to those of the atom to which they are attached.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters[a] and Their Standard Deviations

atom	x	y	z	U_{eq}, Å^2
P	0.45406 (7)	0.2332 (2)	0.87545 (6)	0.0569 (7)
Na	0.61975 (9)	0.0052 (2)	0.80099 (8)	0.0514 (8)
O(1)	0.5524 (2)	−0.2186 (3)	0.7517 (1)	0.054 (2)
O(2)	0.6588 (2)	−0.1056 (3)	0.7060 (1)	0.051 (2)
O(3)	0.7481 (2)	−0.0988 (3)	0.8392 (1)	0.052 (2)
O(4)	0.6356 (2)	−0.2029 (3)	0.8808 (2)	0.058 (2)
O(5)	0.5027 (2)	−0.0419 (3)	0.8433 (1)	0.052 (2)
O(6)	0.4995 (2)	0.3060 (4)	0.8318 (2)	0.072 (2)
O(7)	0.4506 (2)	0.3129 (4)	0.9391 (2)	0.077 (2)
Oa(1)	0.5421 (2)	0.1828 (5)	0.7253 (2)	0.092 (3)
Oa(2)	0.6972 (3)	0.2480 (6)	1.0066 (3)	0.141 (4)
Ow(1)	0.6497 (2)	0.2234 (4)	0.8680 (2)	0.079 (2)
Ow(2)	0.4219 (2)	0.6158 (4)	0.9643 (2)	0.087 (2)
C(1)	0.5506 (2)	−0.2538 (5)	0.6869 (2)	0.046 (2)
C(2)	0.4965 (3)	−0.3435 (6)	0.6466 (2)	0.064 (3)
C(3)	0.5010 (3)	−0.3722 (6)	0.5808 (3)	0.077 (4)
C(4)	0.5585 (4)	−0.3118 (6)	0.5569 (2)	0.079 (4)
C(5)	0.6131 (3)	−0.2222 (5)	0.5969 (2)	0.064 (3)
C(6)	0.6089 (2)	−0.1930 (5)	0.6617 (2)	0.048 (3)
C(7)	0.7270 (3)	−0.0639 (5)	0.6865 (2)	0.055 (3)
C(8)	0.7756 (2)	0.0239 (5)	0.7435 (2)	0.058 (3)
C(9)	0.8073 (2)	−0.0676 (5)	0.8056 (2)	0.054 (3)
C(10)	0.7649 (2)	−0.1937 (5)	0.8940 (2)	0.046 (2)
C(11)	0.8360 (2)	−0.2328 (6)	0.9271 (3)	0.062 (3)
C(12)	0.8467 (3)	−0.3337 (6)	0.9809 (3)	0.076 (3)
C(13)	0.7869 (3)	−0.3922 (6)	1.0016 (3)	0.077 (4)
C(14)	0.7152 (3)	−0.3513 (6)	0.9691 (2)	0.066 (3)
C(15)	0.7037 (2)	−0.2518 (5)	0.9160 (2)	0.052 (3)
C(16)	0.5706 (2)	−0.2655 (5)	0.8987 (2)	0.060 (3)
C(17)	0.5028 (2)	−0.2063 (5)	0.8490 (2)	0.052 (3)
C(18)	0.4920 (2)	−0.2703 (5)	0.7798 (2)	0.058 (3)
C(19)	0.4901 (3)	0.0421 (5)	0.8998 (2)	0.061 (3)
C(20)	0.3610 (3)	0.2021 (6)	0.8278 (3)	0.069 (3)
C(21)	0.3008 (3)	0.2313 (9)	0.8530 (3)	0.122 (5)
C(22)	0.2283 (4)	0.2016 (14)	0.8147 (6)	0.177 (8)
C(23)	0.2175 (5)	0.1459 (13)	0.7522 (6)	0.179 (8)
C(24)	0.2749 (5)	0.1106 (14)	0.7306 (5)	0.202 (9)
C(25)	0.3467 (4	0.1392 (11)	0.7659 (4)	0.143 (7)
C(26)	0.4960 (5)	0.2198 (11)	0.6626 (4)	0.143 (7)
C(27)	0.4637 (6)	0.1044 (11)	0.6247 (5)	0.187 (8)
C(28)	0.7163 (5)	0.1215 (11)	0.0449 (5)	0.161 (7)
C(29)	0.7896 (5)	0.0725 (11)	0.0453 (5)	0.174 (7)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$.

Refinement, including the H atoms but not varying them, significantly reduced the R to 0.049, and difference Fourier maps then showed that no further atoms were present. Observations, F_o^2, were given weights, w, of $1/\sigma^2(F_o^2)$; the atomic scattering factors were taken from a standard source[16] and the functions minimized was $\sum w(\Delta F^2)^2$. During the final cycle of refinement, no parameter changed by more than 0.25σ and most changed far less. The measures of agreement are listed in Table I. Refined coordinates and equivalent isotropic thermal parameters are given in Table II, and a table of H atom parameters and a listing of observed and calculated structure factor squares are available as supplementary material.

Results

Compound **3**, *sym*-[(dibenzo-14-crown-4-oxy)methyl]phenylphosphinic acid, was synthesized by condensation of *sym*-hydroxydibenzo-14-crown-4 with (chloromethyl)phenylphosphinic acid. Crystals of the complex with sodium ion were grown from ethanol–water, and the structure was determined by X-ray diffraction. The asymmetric unit of structure is shown in Figure 1. It includes one molecule of the complex plus additional molecules of H_2O and ethanol. Relevant bond lengths and angles of the molecule are listed in Table III and torsion angles of the crown are given in Table IV.

The dibenzo-14-crown-4 portion of the molecule is folded along the C(8)–C(17) line to form a "V" with the atoms in each half

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(14) The following Oak Ridge computer programs were employed in this structure analysis: 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).

(15) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, York, England, and University of Louvain, Louvain, Belgium, 1978.

(16) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table III. Selected Bond Lengths (Å) and Angles (deg)

Bond Lengths			
Na–O(1)	2.404 (5)	ether ring	
Na–O(2)	2.430 (4)	O(1)–C(1)	1.364 (6)
Na–O(3)	2.490 (4)	C(1)–C(6)	1.397 (7)
Na–O(4)	2.416 (4)	C(6)–O(2)	1.372 (6)
Na–O(5)	2.535 (4)	O(2)–C(7)	1.448 (6)
Na–Ow(1)	2.336 (5)	C(7)–C(8)	1.513 (8)
Na–Oa(1)	2.420 (5)	C(8)–C(9)	1.509 (7)
P–O(6)	1.499 (4)	C(9)–O(3)	1.442 (6)
P–O(7)	1.497 (4)	O(3)–C(10)	1.377 (6)
P–C(19)	1.816 (7)	C(10)–C(15)	1.401 (7)
P–C(20)	1.797 (7)	C(15)–O(4)	1.369 (6)
		O(4)–C(16)	1.437 (6)
benzo rings		C(16)–C(17)	1.517 (8)
C(1)–C(2)	1.384 (8)	C(17)–C(18)	1.502 (8)
C(2)–C(3)	1.399 (8)	C(18)–O(1)	1.438 (6)
C(3)–C(4)	1.370 (9)		
C(4)–C(5)	1.388 (9)	C(17)–O(5)	1.432 (7)
C(5)–C(6)	1.379 (9)	O(5)–C(19)	1.436 (6)
C(10)–C(11)	1.378 (7)		
C(11)–C(12)	1.391 (8)	phenyl ring	
C(12)–C(13)	1.367 (9)	C(20)–C(21)	1.35 (1)
C(13)–C(14)	1.388 (8)	C(21)–C(22)	1.42 (2)
C(14)–C(15)	1.371 (7)	C(22)–C(23)	1.35 (2)
		C(23)–C(24)	1.27 (1)
C(26)–Oa(1)	1.42 (1)	C(24)–C(25)	1.38 (1)
C(26)–C(27)	1.33 (2)	C(25)–C(20)	1.36 (1)
C(28)–Oa(2)	1.35 (1)		
C(28)–C(29)	1.42 (2)		

Averaged Bond Angles in Crown			
C–C–C	116.0 ± 0.5	O–C–C (aryl)	115.3 ± 0.4
C–O–C	117.4 ± 0.4	C–C–C (aryl)	119.9 ± 0.8
C–C–O	108.1 ± 0.5		

Table IV. Torsion Angles (deg) in the Ether Ring

O(1)–C(1)–C(6)–O(2)	–0.6 (7)
C(1)–C(6)–O(2)–C(7)	169.1 (5)
C(6)–O(2)–C(7)–C(8)	–176.9 (4)
O(2)–C(7)–C(8)–C(9)	68.7 (6)
C(7)–C(8)–C(9)–O(3)	–73.4 (6)
C(8)–C(9)–O(3)–C(10)	174.2 (4)
C(9)–O(3)–C(10)–C(15)	–165.3 (5)
O(3)–C(10)–C(15)–O(4)	–1.6 (7)
C(10)–C(15)–O(4)–C(16)	176.6 (5)
C(15)–O(4)–C(16)–C(17)	–174.7 (5)
O(4)–C(16)–C(17)–C(18)	69.9 (6)
C(16)–C(17)–C(18)–O(1)	–65.5 (6)
C(17)–C(18)–O(1)–C(1)	–175.0 (5)
C(18)–O(1)–C(1)–C(6)	176.7 (5)

coplanar within 0.17 Å. The four O atoms are coplanar within 0.02 Å and are arrayed in a rectangle 2.57 by 2.81 Å; the shorter sides are adjacent to benzo groups. The Na^+ ion is bonded to the four O atoms at an average distance of 2.44 Å and is 1.52 Å from their plane. It is also bonded to the ether O atom of the sidearm, O(5), and to Ow(1) and Oa(1) of water and ethanol molecules to complete its seven coordination. The nearest phosphoryl O atom is 3.57 Å away, and the Na^+ ion is linked to it indirectly through a water molecule.

The crown ether, exclusive of the side arm, is virtually identical in shape with that in the oxyacetate-substituted[13] and the unsubstituted[17] crowns (Li complex of each). For these three crowns respectively, the following metric comparisons are made: dihedral angle of the "V" (120.7, 118.6, 121°), average C–C bond in the benzo groups (1.384, 1.382 Å, "expected"), average C–C bond in the ether (1.510, 1.510, 1.49 Å), average C–O bond in the ether (1.406, 1.406 Å, "expected"), average C–C–O–C torsion angle in the ether (175.1, 175.3, 178°), and average C–C–C–O torsion angle (69.4, 68.7, 71°). The Li^+ ion to O_4 to plane distances are 0.84 and 0.79 Å, respectively.

In Figure 2 is shown the H-bonding network, which was deduced from the distances and angles in Table V. Some of the bonds are intramolecular while others serve to link pairs of complexes. The dimer that this creates has H_2O, ethanol, and the Na^+ and phosphinate ions in its interior and an exterior that is hydrophobic. Between such dimers there are only C and H contacts.

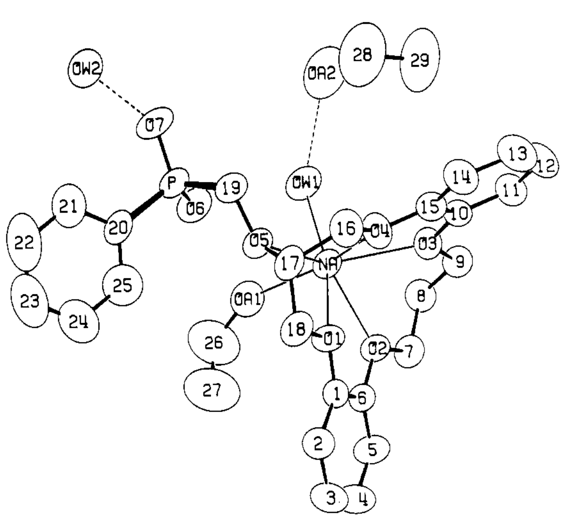

Figure 1. Asymmetric unit of sodium [(dibenzo-14-crown-4)oxy)-methyl]phenylphosphinate dihydrate diethanolate. Atoms are labeled as in Table II; the carbon atoms are designated solely by numbers, while Ow and Oa refer to oxygen atoms in water and ethanol molecules, respectively. Thermal ellipsoids are drawn at the 50% probability level.

Table V. Hydrogen Bonds

atoms 1, 2, and 3	d_{1-2}, Å	d_{2-3}, Å	angle 1–2–3, deg
O(6)···Ow(1)···Oa(2)	2.796 (6)	2.801 (8)	108.5 (2)
O(7)···Ow(2)···O′(7)	2.754 (6)	2.788 (6)	100.3 (2)
C(26)–Oa(1)···O(6)	1.42 (1)	2.711 (6)	115.2 (7)
C(28)–Oa(2)···Ow(2)	1.35 (2)	2.767 (7)	110.4 (7)

Discussion

The results of this structure analysis have implications for studies on the mechanism of lariat ether complexation, especially with regard to side arm interaction. Among the possible steps in complex formation are ion pairing of the functionalized side arm and the cation, desolvation of the cation, rearrangement of the crown, and insertion of the cation into the ring.[7,18] It is important to know whether the side arm facilitates capture of the cation and/or contributes to the stability of the complex.

Rearrangement of the crown is not expected to be a significant step with this ligand, although the more flexible crown-4 ethers usually undergo conformational changes on complexation, in agreement with the view that the guest organizes the host whenever possible.[19,20] Illustrative of the latter is a comparison of the structures of the free 12-crown-4 ether[21] and Li·SCN·12-crown-4,[22] $NaCl(H_2O)_5$·2(12-crown-4),[23] $NaOH(H_2O)_8$·2(12-crown-4),[24] and $NaClO_4$·2(12-crown-4).[25] Also, the larger 16-crown-4 molecule[26] has O atoms alternately up and down. However when complexed with LiSCN, all the O atoms move to one side into a square array.[27] When the semirigid benzo-13-crown-4 is complexed with

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(17) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Chem. Soc., Chem. Commun.* **1983**, 208.

(18) Echegoyen, L.; Gokel, G. W.; Kim, M. S.; Eyring, E. M; Petrucci, S. *J. Phys. Chem.* **1987**, *91*, 3854.

(19) Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981**, *98*, 43.

(20) Gandour, R. D.; Fronczek, F. R.; Gatto, V. J.; Minganti, C.; Schultz, R. A.; White, B. D.; Arnold, K. A.; Mazzocchi, D.; Miller, S. R.; Gokel, G. W. *J. Am. Chem. Soc.* **1986**, 108, 4078.

(21) Groth, P. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 279.

(22) Groth, P. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 463.

(23) van Remoortere, F. P.; Boer, F. P. *Inorg. Chem.* **1974**, *13*, 2071.

(24) Boer, F. P.; Neuman, M. A.; van Remoortere, F. P.; Steiner, E. C. *Inorg. Chem.* **1974**, *13*, 2826.

(25) Mason, E.; Eick, H. A. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1821.

(26) Groth, P. *Acta Chem. Scand.* **1971**, *25*, 725.

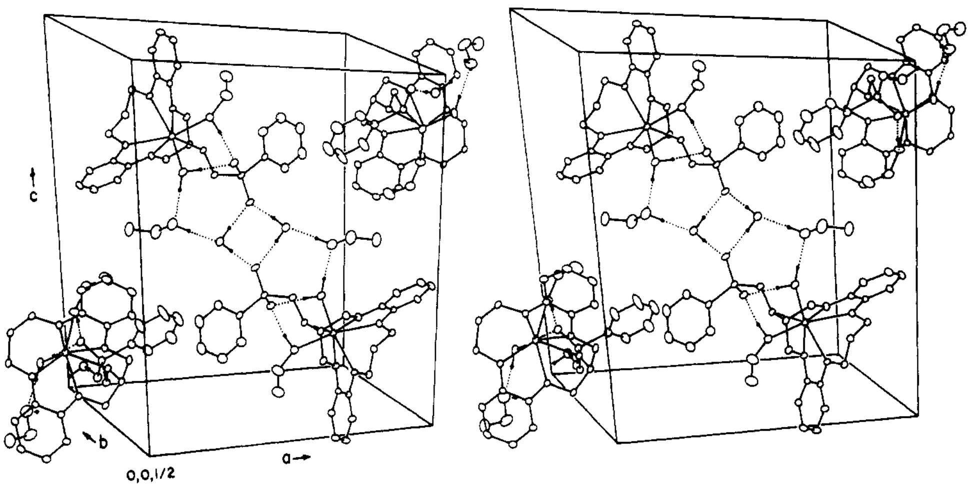

Figure 2. Stereoview of a unit cell and part of its contents to show the hydrogen-bonding network and the contacts between dimeric units of structure.

LiSCN, a rearrangement of the O atoms into a planar array results in conformational changes in the ring on the side opposite to the benzo group.[28] Although the structure of the free *sym*-(dibenzo-14-crown-4-oxo)phenylphosphinic acid is not known, it appears that the O atom arrangement (Figure 1) results from the relative rigidity of the molecular halves rather than their bonding to the Na^+ ion in the complex. The methylene H atoms next to the catecholate groups have the benzo H atoms interleaved with them at about 2.3 Å. Any deviation of the C–O–C–C torsion angle from 0° (see Table IV) brings these H atoms closer together; hence the planarity of that half of the crown is favored. The IR data also support the concept of a rigid crown that changes very little on complexation. The ν(C–C–O) stretching frequency for atoms in the ring is the same (1254 cm^{-1}) for the free acid and the Na complex, while the equivalent ν for atoms in the side arm changes from 1117 to 1128 cm^{-1} as the complex is formed.

As for the interaction of cation and the side arm, Adamic et al.[7] have concluded from kinetic studies of the system *sym*-(dibenzo-16-crown-5-oxy)acetic acid and the Na^+ ion that the mechanism of complex formation involves initial ion pairing of the solvated Na^+ and the acetate ions, followed by incorporation into the crown. The present results, for a system analogous in its main features, support their conclusion; in the title complex the Na^+ ion has part of its solvation sphere intact and forms an outer-sphere ion pair with the phosphinate anion, while the remainder of the solvent has been replaced by the five ether O atoms. The Li^+ complex of *sym*-(dibenzo-14-crown-4-oxy)acetate[13] has a similar arrangement although fewer ligands because of the cation's smaller size. In neither case is the lariat anion bonded directly to the cation.

The attachment of the phosphinic acid to the sidearm was expected to enhance the ligand's extraction capability relative to one with the acetate anion,[13] and preliminary experiments have shown that it will extract Li^+ and Na^+ ions from neutral and weakly acidic solutions. This follows from its pK_a of 4.5, but the low solubility of the ligand in organic solvents makes it impractical for extraction purposes unless the molecule can be modified to make it more lipophilic.

From our results and those of ref 13 we conclude that the presence of the ether O atom in the side arm is more determinative of the cation's coordination than is the nature of the lariat anion. In these molecules the location of the ether O atom on the sidearm is conducive to its coordination to the bound metal ion (directly for Na^+ ion, through H_2O for Li^+ ion). The conformational requirements of this coordination forces the phosphinate (or acetate) anion away from the metal site and produces a solvent-separated ion pair. To further test this conclusion we are pursuing the synthesis of ligands in which a methylene group replaces the ether linkage in the sidearm.

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Supplementary Material Available: Tables SI and SII, giving infrared and NMR data, Table SIII, listing anisotropic thermal parameters, Table SIV, listing bond angles, and Table SV, giving calculated H atom positions (7 pages); Table SVI, containing the observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(27) Groth, P. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 460.

(28) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Am. Chem. Soc.* **1983**, *105*, 1247.