^{1}H NMR (CDCl$_3$) δ 6.20 (1 H, dd, J = 12.0, 1.0 Hz), 5.38 (1 H, dd, J = 16.2, 4.7 Hz), 5.40–5.18 (1 H, m), 4.93 (1 H, dd, J = 12.0, 7.9 Hz), 2.76–2.62 (1 H, m), 1.64 (3 H, d, J = 3.7 Hz), 1.03 (3 H, d, J = 6.9 Hz), 0.91 (9 H, s), 0.12 (6 H, s). (1E,4Z)-**2m** 300-MHz ^{1}H NMR (CDCl$_3$) δ 6.22 (1 H, dd, J = 12.0, 1.2 Hz), 5.40–5.18 (2 H, m), 4.95 (1 H, dd, J = 12.0, 7.1 Hz), 3.15–3.03 (1 H, m), 1.61 (3 H, dd, J = 6.7, 1.6 Hz), 1.02 (3 H, d, J = 6.8 Hz), 0.91 (9 H, s), 0.12 (6 H, s). (1E,4E)-**2m** 75-MHz ^{13}C (CDCl$_3$) δ 139.4, 136.4, 122.8, 116.6, 35.1, 25.7, 21.5, 18.3, 17.8, −5.2. (1E,4Z)-**2m** 75-MHz ^{13}C (CDCl) δ 139.3, 135.4, 122.1, 116.5, 30.1, 25.6, 22.0, 15.3, 12.8, −5.2 HRMS calcd for C$_{13}$H$_{26}$OSi, 226.1753; found, 226.1748.

One-Pot Procedure for the Conjugate Addition of Ethenyltributyltin to 2-Propenal with in situ Generated Ni(COD)$_2$. Preparation of *tert*-Butyldimethyl[((E)-1,4-pentadienyl)oxy]silane (2a). In a 25-mL Schlenk flask, equipped with a magnetic stir bar and pressure-equalizing dropping funnel, a slurry of Ni(acac)$_2$ (260 mg, 1.01 mmol), 1,5-cyclooctadiene (500 μL, 4.08 mmol), and 1.00 mL of THF was cooled to −40 °C. Through the addition funnel, diisobutylaluminum hydride (2.50 mL of a 1 M solution in THF) was added dropwise over 10 min. The temperature was maintained at −40 °C for an additional 15 min and then was allowed to increase to 0 °C. After the mixture was stirred at 0 °C for 30 min, 10 mL of Et$_2$O was added to assist precipitation of the Ni(COD)$_2$ and the flask was cooled to −78 °C for 12 h. The supernatent was then removed at −78 °C via a filter-tipped cannula, and the Ni(COD)$_2$ was washed with Et$_2$O (2 × 2.50 mL) at −78 °C. The dirty yellow or gray-green Ni(COD)$_2$ was allowed to warm to 25 °C under vacuum (0.01 mmHg) and then treated with a solution of 2-propenal (370 μL, 5.54 mmol), *t*-BuMe$_2$SiCl (830 mg, 5.51 mmol), ethenyltributyltin (1.50 mL, 5.13 mmol), and CH$_2$Cl$_2$ (7.50 mL), added via cannula. After being stirred at 25 °C for 70 h, the mixture was worked up as per the typical procedure to afford, after chromatography (SiO$_2$, 100 g, gradient neat hexane (500 mL) to 98:2 hexane/Et$_2$O) pure **2a** as a clear, colorless oil (629 mg, 62%, E:Z 10:1 by ^{1}H NMR analysis).

E. Mechanistic Studies. Kinetic Studies of the Ni(COD)$_2$-Catalyzed Reaction of Ethenyltributyltin with (E)-2-Butenal in DMF-*d*$_7$ To Give 2c. (a) Standard Conditions. 2-Butenal (19.5 μL, 0.235 mmol), *t*-BuMe$_2$SiCl (36 mg, 0.24 mmol), ethenyltributyltin (68.5 μL, 0.234 mmol), and Ni(COD)$_2$ (14 mg, 0.051 mmol) in DMF-*d*$_7$ (0.70 mL) were combined as per the typical procedure in a 5-mm NMR tube at time t = 0. ^{1}H NMR spectra (400-MHz) were acquired at 1, 2, 3, 5, and 6 h, and showed the fraction of product, defined as [**2c**]/{[**2c**] + [ethenyltributyltin]} and determined by cutting and weighing, to be 0.22, 0.33, 0.42, 0.56, and 0.63, respectively (each point representing the average of three experiments).

(b) Reaction with 2 equiv of *t*-BuMe$_2$SiCl. Reaction as per the standard conditions but with twice as much *t*-BuMe$_2$SiCl (72 mg, 0.48 mmol) gave 0.20, 0.40, and 0.61 fraction product at 1, 3, and 6 h, respectively.

(c) Reaction with 2 equiv of 2-Butenal. Reaction as per the standard conditions but with twice as much 2-butenal (39.0 μL, 0.470 mmol) gave 0.23, 0.48, and 0.65 fraction product of 1, 3, and 6 h, respectively.

(d) Reaction with 2 equiv of Ethenyltributyltin. Reaction as per the standard conditions but with twice as much ethenyltributyltin (137 μL,

0.468 mmol) gave 0.40, 0.48, 0.66, 0.81, and 0.92 fraction product at 1, 2, 3, 5, and 6 h, respectively, the fraction product in this case being defined as [**2c**]/{[**2c**] + [2-butenal]}.

(e) Reaction with Double the Standard Catalyst Concentration. Reaction as per the standard conditions but with twice as much Ni(COD)$_2$ (28 mg, 0.10 mmol) gave 0.38, 0.66, 0.85, and 0.87 fraction product at 1, 3, 5, and 6 h, respectively.

Crossover Experiment To Determine the Rate Constant for the Stoichiometric Coupling of 1b with Ethenyltributyltin under Catalytic Reaction Conditions. Conjugate Addition of Ethenyltributyltin to 2-Methyl-2-butenal Using 1b as the Catalyst Precursor. 2-Methyl-2-butenal (22.6 μL, 0.234 mmol), *t*-BuMe$_2$SiCl (28 mg, 0.19 mmol), ethenyltributyltin (68.5 μL, 0.234 mmol), and **1b** (14 mg, 0.050 mmol) in DMF-*d*$_7$ (0.70 mL) were combined as per the typical procedure in a 5-mm ^{1}H NMR tube. ^{1}H NMR spectra (400-MHz) were acquired at 20, 31, 45, 60, and 75 min and showed the fraction of product, defined as [**1d**]/{[**1d**] + [**1b**]}, as determined by cutting and weighing, to be 0.06, 0.18, 0.30, 0.36, and 0.46, respectively. (Calculations were based on upfield half of the upfield peak of the **1b** 3-methyl doublet at δ 0.48 ppm, which partially overlaps with the 3-methyl signal of **1d** at δ 0.46 ppm. The fraction of product at time t = 0 was set equal to zero and included in the data set.) A graph of −ln (1 − f) as a function of time gave a straight line satisfying the equation −ln (1 − f) = −0.0085 + −0.049 with R = 0.99, from which the rate constant k_{sto}, defined by the expression −d[**1b**]/dt = k_{sto}[**1b**][ethenyltributyltin], can be approximately calculated, using an average value of 0.289 M for the ethenyltributyltin concentration (which actually decreased to ca. 75% of its initial value over the interval studied), to be 0.029 min^{-1}. Although **1b** has been previously characterized, its ^{1}H NMR spectrum in DMF-*d*$_7$ had not been reported and is given below. (Poorer resolution, relative to the catalytic reaction solutions, was observed so that the couplings are not resolved.) **1b** 400-MHz ^{1}H NMR (DMF-*d*$_7$) δ 5.08 (2 H, bs), 1.85 (1 H, bs), 0.80 (9 H, s), 0.48 (3 H, br s), 0.17 (3 H, s), 0.08 (3 H, s).

Attempted Conjugate Addition in the Presence of Triphenylphosphine. 2-Butenal (19.5 μL, 0.235 mmol), *t*-BuMe$_2$SiCl (36 mg, 0.24 mmol), ethenyltributyltin (68.5 μL, 0.234 mmol), triphenylphosphine (65 mg, 0.25 mmol), and Ni(COD)$_2$ (14 mg, 0.051 mmol) in DMF-*d*$_7$ (0.70 mL) were combined in an NMR tube. An ^{1}H NMR spectrum taken after 2 days showed no conjugate addition product.

Electron Spin Resonance Spectroscopy. 2-Butenal (19.5 μL, 0.235 mmol), *t*-BuMe$_2$SiCl (36 mg, 0.24 mmol), ethenyltributyltin (68.5 mL, 0.234 mmol), and Ni(COD)$_2$ (14 mg, 0.051 mmol) in DMF (0.80 mL) were combined in a 10-mL flask as per **2a** and an aliquot was removed and placed in a 3-mm quartz tube and sealed under N$_2$. The tube and its contents were frozen in liquid nitrogen at 77 K and a 2000-G scan spectrum, centered at g = 2.00, was obtained on a Varian E-4 spectrometer operating at 9.2 GHz. No signal was detected. Workup of the remaining solution after 72 h showed the catalytic reaction to have proceeded as usual to give **2c**.

Unusual Coordination Number and Geometry in a Potassium 18-Crown-6 Complex

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Abstract: Crystallization of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) from CHCl$_3$/CH$_2$Cl$_2$ solution in the presence of dipotassium tartrate affords a nine-coordinate potassium complex incorporating chloride rather than tartrate as the counteranion. This complex, [(18-crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$, displays an unusual asymmetrical conformation of the crown ether ring. The structure of the complex is discussed and compared with other reported 18-crown-6 complexes of potassium, in which the 18-crown-6 moiety always adopts a much more symmetrical conformation.

Since Pedersen's first report of the synthesis of macrocyclic polyethers and their ability to complex simple inorganic cations,[1] thousands of such "crown ether" complexes have been prepared, and hundreds have been characterized structurally by X-ray

Table I. Crystallographic Data for Complex **1**

empirical formula	$C_{12}H_{35}Cl_2KO_{11}$
formula weight	465.41
temperature (K)	293
crystal system	orthorhombic
space group	$Pca2_1$
a (Å)	28.105 (5)
b (Å)	7.820 (5)
c (Å)	10.101 (4)
V (Å^3)	2220 (3)
Z	4
ρ_{calcd} (g·cm^{-3})	1.392
μ (cm^{-1})	5.24
no. of obsd reflctns [$I > 3\sigma(I)$]	1160
$R(F_o)$	0.075
$R_w(F_o)$	0.084

diffraction crystallography.[2] Perhaps the simplest, prototypical crown ether is 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), a stable, commercially available crown ether noted for its efficient complexation of potassium ion. Indeed, 18-crown-6 is frequently used as an example of the importance of "size matching" in complexation chemistry; the ionic radius of potassium ion matches nicely with the diameter of the "hole" in 18-crown-6, while ions displaying a poorer match of ionic radius with hole size are bound less efficiently.[3]

Solution,[4,5] calculational,[6,7] and solid-state studies[7-16] have repeatedly demonstrated that in its potassium complexes, the 18-crown-6 moiety adopts a conformation of roughly to exactly D_{3d} symmetry. This symmetry appears to be maintained regardless of the number, identity, or arrangement of any additional ligands on potassium. In the course of our studies of the "complexation-mediated crystallization" of organic salts,[17] we have isolated a most unusual 18-crown-6 complex of potassium. In this complex, potassium adopts a rare coordination number of 9, forcing the 18-crown-6 ligand into a conformation of considerably lower symmetry. Herein we report the isolation of this complex and the details of its crystal and molecular structure.

Experimental Section

Preparation of [(18-Crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$ (1). A solution of 18-crown-6 (ca. 3.5 mg, 0.013 mmol) in a minimum of CH$_2$Cl$_2$ was added to a suspension of dipotassium tartrate hemihydrate in 1.5 mL of CHCl$_3$. The mixture was shaken vigorously for 20 min and then filtered through glass wool. The filtrate was placed in a loosely-capped tube and allowed to evaporate slowly. After 3 weeks, the needle-shaped crystals of complex **1** which had formed were separated and dried: yield of complex **1** ca. 3.2 mg (52%); mp 123–126 °C dec. Anal. Calcd for C$_{12}$H$_{35}$Cl$_2$KO$_{11}$: K, 8.40; Cl, 15.24. Found: K, 8.35; Cl, 14.68. (Calcd for C$_{12}$H$_{35}$Cl$_2$KO$_{11}$·H$_2$O: K, 8.09; Cl, 14.67.) These crystals proved suitable for single-crystal X-ray diffraction analysis.

(1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.

(2) See, e.g.: Hilgenfeld, R.; Saenger, W. *Top. Curr. Chem.* **1982**, *101*, 1–82.

(3) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271–339.

(4) Dale, J.; Kristiansen, P. O. *Acta Chem. Scand.* **1972**, *26*, 1471–1478.

(5) Takeuchi, H.; Arai, T.; Harada, I. *J. Mol. Struct.* **1986**, *146*, 197–212. Miyazawa, M.; Fukushima, K.; Oe, S. *J. Mol. Struct.* **1989**, *195*, 271–281.

(6) Bovill, M. J.; Chadwick, D. J.; Sutherland, I. O.; Watkin, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1529–1543.

(7) Maverick, E.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Acta Crystallogr.* **1980**, *B36*, 615–620.

(8) Seiler, P.; Dobler, M.; Dunitz, J. *Acta Crystallogr.* **1974**, *B30*, 2744–2745.

(9) Riche, C.; Pascard-Billy, C.; Cambillau, C.; Bram, G. *J. Chem. Soc., Chem. Commun.* **1977**, 183–184.

(10) Groth, P. *Acta Chem. Scand.* **1971**, *25*, 3189–3191.

(11) Nagano, O. *Acta Crystallogr.* **1979**, *B35*, 465–467.

(12) Nagano, O.; Sasaki, Y. *Acta Crystallogr.* **1979**, *B35*, 2387–2389.

(13) Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1985**, *24*, 2680–2683.

(14) Drew, M. G. B.; Lee, K. C.; Mok, K. F. *Inorg. Chim. Acta* **1989**, *155*, 39–43.

(15) Byrn, M. P.; Strouse, C. E. *J. Am. Chem. Soc.* **1981**, *103*, 2633–2635.

(16) Rath, N. P.; Holt, E. M. *J. Chem. Soc., Chem. Commun.* **1986**, 311–312.

(17) Doxsee, K. M.; Stevens, R. C. *J. Inclusion Phenom.* **1990**, *9*, 327–336.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) for Complex **1**[a]

atom	x	y	z	B_{eq}
K(1)	3882.6 (9)	7796 (4)	4975[b]	2.9 (1)
Cl(1)	5316.7	4959	5958	5.6 (2)
Cl(2)	2611.8 (12)	1049 (6)	2044 (5)	4.8 (2)
O(1)	4508 (3)	9761 (15)	5984 (11)	4.8 (2)
O(2)	4241 (4)	10 308 (18)	3522 (12)	6.8 (3)
O(3)	3650 (3)	8018 (16)	2529 (10)	4.9 (2)
O(4)	3473 (3)	5237 (17)	3956 (12)	5.8 (3)
O(5)	3254 (3)	6196 (14)	6427 (9)	4.0 (2)
O(6)	3666 (3)	9105 (15)	7278 (10)	4.4 (2)
O(7)	3158 (3)	9560 (14)	4756 (11)	4.7 (2)
O(8)	4573 (3)	6578 (15)	3880 (11)	4.8 (2)
O(9)	4249 (3)	5859 (15)	6553 (11)	5.2 (2)
O(10)	6086 (4)	5806 (16)	3774 (12)	5.8 (3)
O(11)	6975 (4)	7285 (17)	4404 (12)	6.6 (3)
C(1)	4820 (5)	10 594 (24)	5083 (20)	5.8 (4)
C(2)	4564 (6)	11 552 (27)	4040 (19)	6.2 (4)
C(3)	3982 (6)	10 841 (27)	2399 (19)	6.2 (4)
C(4)	3833 (5)	9240 (23)	1641 (17)	5.0 (4)
C(5)	3450 (5)	6521 (24)	1870 (18)	5.2 (4)
C(6)	3238 (8)	5425 (35)	2791 (26)	9.7 (7)
C(7)	3234 (6)	4069 (28)	4811 (22)	7.1 (5)
C(8)	2965 (5)	4969 (24)	5827 (18)	5.2 (4)
C(9)	3020 (5)	7129 (23)	7442 (15)	4.6 (3)
C(10)	3383 (5)	8080 (23)	8195 (16)	4.9 (4)
C(11)	4051 (5)	9932 (24)	7963 (17)	4.9 (4)
C(12)	4332 (5)	10 867 (27)	6983 (19)	5.6 (4)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. [b] Fixed to define origin of cell.

Table III. Bond Lengths (Å) Involving Nonhydrogen Atoms for Complex **1**[a]

K(1)	O(1)	2.55 (1)	O(3)	C(5)	1.46 (2)
K(1)	O(2)	2.65 (1)	O(4)	C(6)	1.36 (3)
K(1)	O(3)	2.56 (1)	O(4)	C(7)	1.42 (2)
K(1)	O(4)	2.53 (1)	O(5)	C(8)	1.39 (2)
K(1)	O(5)	2.62 (1)	O(5)	C(9)	1.42 (2)
K(1)	O(6)	2.61 (1)	O(6)	C(10)	1.46 (2)
K(1)	O(7)	2.47 (1)	O(6)	C(11)	1.44 (2)
K(1)	O(8)	2.43 (1)	C(1)	C(2)	1.48 (2)
K(1)	O(9)	2.43 (1)	C(3)	C(4)	1.53 (2)
O(1)	C(1)	1.42 (2)	C(5)	C(6)	1.40 (3)
O(1)	C(12)	1.42 (2)	C(7)	C(8)	1.46 (2)
O(2)	C(2)	1.43 (2)	C(9)	C(10)	1.47 (2)
O(2)	C(3)	1.41 (2)	C(11)	C(12)	1.46 (2)
O(3)	C(4)	1.41 (2)			

[a] Esd values given in parentheses, in units of the least significant digit of the corresponding value.

X-ray Crystallographic Analysis of [(18-Crown-6)K-(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$ (1). Fragments cleaved from colorless elongated prismatic crystals under Apiezon grease were sealed in Lindemann capillaries. A specimen of approximate dimensions 0.10 × 0.10 × 0.45 mm was mounted on a Rigaku AFC6R diffractometer and was found to give narrow and symmetrical peak profiles. Unit cell dimensions and orientation matrix were determined from the setting angles for 25 centered reflections in the range $10.9° \le 2\theta \le 15.8°$. A summary of crystallographic information is given in Table I. A more comprehensive table, including details of data collection and structure refinement, is included in the supplementary material.

The crystal diffracted weakly. The fraction of observed reflections [$I \ge 3\sigma(I)$] fell from ca. 85% at low angles to ca. 20% near $2\theta = 50°$, although the standard reflections showed no significant variation in intensity during data collection. Altogether, 1160 out of 1934 independent reflections were considered observed. The distribution of intensities was acentric, and the systematic absences indicated that the space group was $Pca2_1$. The structure was successfully solved and refined in this space group, and the final coordinates were not consistent with an overlooked crystallographic mirror plane normal to c. Direct method calculations (SIR88,[18] MITHRIL,[19] and SHELXS[20]) and the PHASE Patterson interpretation

(18) Burla, M. C.; Camalli, M.; Cascareno, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389–393.

(19) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42–46.

Table IV. Selected Bond Angles (deg) Involving Nonhydrogen Atoms for Complex 1[a]

O(1)	K(1)	O(2)	60.8 (4)	C(6)	O(4)	C(7)	111 (2)
O(1)	K(1)	O(6)	64.4 (3)	K(1)	O(5)	C(8)	118.6 (9)
O(2)	K(1)	O(3)	60.8 (4)	K(1)	O(5)	C(9)	118.2 (9)
O(3)	K(1)	O(4)	62.9 (4)	C(8)	O(5)	C(9)	113 (1)
O(4)	K(1)	O(5)	62.7 (3)	K(1)	O(6)	C(10)	118.4 (9)
O(5)	K(1)	O(6)	62.0 (3)	K(1)	O(6)	C(11)	115.5 (8)
O(7)	K(1)	O(8)	146.9 (4)	C(10)	O(6)	C(11)	111 (1)
O(7)	K(1)	O(9)	139.2 (4)	O(1)	C(1)	C(2)	113 (1)
O(8)	K(1)	O(9)	73.5 (3)	O(2)	C(2)	C(1)	103 (2)
K(1)	O(1)	C(1)	116 (1)	O(2)	C(3)	C(4)	108 (2)
K(1)	O(1)	C(12)	114.3 (8)	O(3)	C(4)	C(3)	110 (1)
C(1)	O(1)	C(12)	113 (1)	O(3)	C(5)	C(6)	111 (2)
K(1)	O(2)	C(2)	123 (1)	O(4)	C(6)	C(5)	116 (2)
K(1)	O(2)	C(3)	118 (1)	O(4)	C(7)	C(8)	111 (2)
C(2)	O(2)	C(3)	115 (2)	O(5)	C(8)	C(7)	110 (1)
K(1)	O(3)	C(4)	124.5 (9)	O(5)	C(9)	C(10)	108 (2)
K(1)	O(3)	C(5)	118.9 (9)	O(6)	C(10)	C(9)	109 (1)
C(4)	O(3)	C(5)	113 (1)	O(6)	C(11)	C(12)	108 (1)
K(1)	O(4)	C(6)	119 (1)	O(1)	C(12)	C(11)	111 (2)
K(1)	O(4)	C(7)	118 (1)				

[a] Esd values given in parentheses, in units of the least significant digit of the corresponding value.

Table V. Selected Dihedral Angles (deg) for Complex 1[a,b]

O(5)	C(9)	C(10)	O(6)	54 (2)
O(1)	C(1)	C(2)	O(2)	-52 (2)
O(1)	C(12)	C(11)	O(6)	-58 (2)
O(2)	C(3)	C(4)	O(3)	46 (2)
O(3)	C(5)	C(6)	O(4)	-39 (3)
O(4)	C(7)	C(8)	O(5)	-49 (2)
C(1)	O(1)	C(12)	C(11)	-174 (1)
C(1)	C(2)	O(2)	C(3)	-174 (1)
C(2)	O(2)	C(3)	C(4)	156 (1)
C(2)	C(1)	O(1)	C(12)	-82 (2)
C(3)	C(4)	O(3)	C(5)	174 (1)
C(4)	O(3)	C(5)	C(6)	-175 (2)
C(5)	C(6)	O(4)	C(7)	-179 (2)
C(6)	O(4)	C(7)	C(8)	-102 (2)
C(7)	C(8)	O(5)	C(9)	-180 (1)
C(8)	O(5)	C(9)	C(10)	167 (1)
C(9)	C(10)	O(6)	C(11)	-175 (1)
C(10)	O(6)	C(11)	C(12)	177 (1)

[a] Esd values given in parentheses, in units of the least significant digit of the corresponding value. [b] Sign is positive if, when viewed from atom 2 to atom 3, a clockwise motion of atom 1 would superimpose it on atom 4.

subprogram of DIRDIF[21] all gave the same set of coordinates for the potassium and the two independent chlorine atoms. The oxygen and carbon atoms were all located by a single cycle of DIRDIF. No hydrogen atoms could be definitively located by difference synthesis. The crown ether hydrogen atoms were included at "riding" positions, with U(H) equal to $1.2U_{eq}$(C) in the later stages of refinement, but no attempt was made to include the other hydrogen atoms in the calculation as the interpretation of the probable hydrogen-bond network was not clear-cut. Refinement with anisotropic thermal parameters for the potassium and chlorine atoms converged at R = 0.075, R_w = 0.084, and W = 2.64. The TEXSAN 5.0 program suite[22] was used in all calculations. Final atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, and dihedral angles are provided in Tables II-V. Other crystallographic data, including anisotropic thermal parameters and observed and calculated structure factors, are provided as supplementary material.

Refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at R = 0.060, R_w = 0.068, and S = 2.25. The C(6) atom still refined with comparatively high positional parameters and B_{eq} and with bond lengths appreciably different from those of chemically-equivalent bonds elsewhere. The elongation of the thermal ellipsoid for

(20) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175-189.

(21) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van Den Hark, T. E. M.; Prick, P. A. J.; Noordik, K. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C.; Strumpel, M.; Smits, J. M. M. DIRDIF: Direct Methods for Difference Structures. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, Netherlands, 1984.

(22) *TEXSAN: TEXRAY Program for Structural Analysis*, version 5.0; Molecular Structures Corporation: The Woodlands, TX, 77381, 1989.
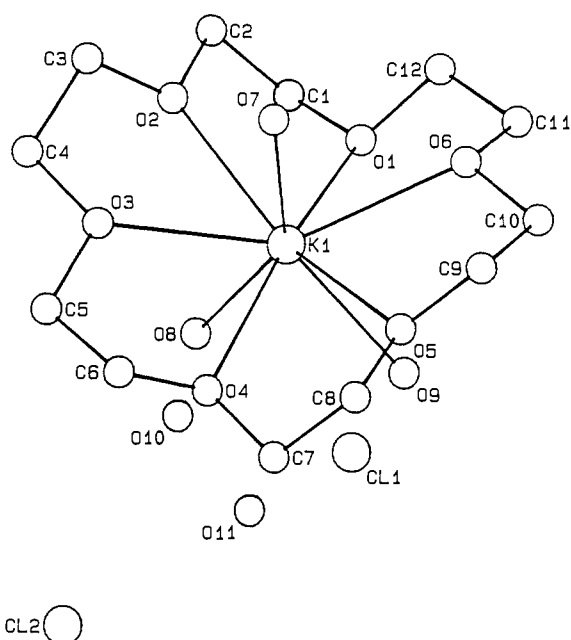
Figure 1. Molecular structure of [(18-crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$ (1), showing associated hydrates and counterions and atom-numbering scheme.
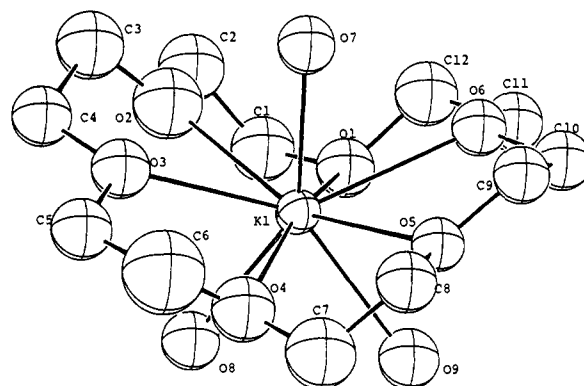

Figure 2. ORTEP plot of molecular structure of [(18-crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$ (1) (omitting chlorides and noncoordinated hydrates).

this carbon suggests that it is disordered over two nonresolvable sites. The all-anisotropic refinement required 234 parameters, with only 1160 observed, independent data, and the reduction in R factors and S appears to be merely cosmetic. Accordingly, the discussion and all tables refer

Table VI. Coordination Numbers, Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 18-Crown-6 Complexes of Potassium[a]

complex	coord no.	K-O$_{crown}$ length (Å)	K-anion length (Å)	K-O$_{solvate}$ length (Å)	O-K-O angle (deg)	O-C-C-O angle (deg)	C-O-C-C angle (deg)	ref
1	9	2.53-2.65	4.71, 7.03	2.428, 2.428, 2.470	62.3 (1.2)	50 (6)	160 (31)	this work
KSCN	6 (8)	2.77-2.83	3.19, 3.19	-	60.4 (0.5)	66.8 (2.2)	176.4 (2.7)	8
potassium ethyl acetoacetate	8	2.83-3.02	2.65, 2.73	-	d	d	d	9
potassium tosylate	8	2.78-2.94	2.69, 2.93	-	58.2 (2.8)	d	d	10
$K(H_2O)_2^+ \cdot K(H_2O)$-MoO$_4$	8	2.78-3.05	-	2.78, 2.82	56.8 (0.8)	63.4 (2.2)	176.8 (2.5)	11
$K(H_2O)_2^+ \cdot K(H_2O)$-MoO$_4$	8	2.76-2.99	2.79	2.81	58.0 (0.5)	65.6 (3.1)	176.2 (3.1)	11
K$_2$(H$_2$O)$_2$-Mo$_6$O$_{19}$	8	2.72-2.88	2.70, 2.72	2.89, 2.93	60.3 (0.7), 60.2 (1.1)	65.5 (3.0), 66.9 (4.0)	176.8 (2.6), 175.8 (3.0)	12
K$_2$Cu(S$_2$C$_2$O$_2$)$_2$-DMF	8 (9)	2.69-3.05	2.76, 2.80	3.16	57.6 (0.7)	63.4 (3.8)	176.2 (3.0)	13
K$_2$(H$_2$O)$_2$-Hg$_2$I$_6$	7 (8)	2.69-2.85	3.77	3.14c	60.2 (1.3)	60.4 (7.8)	163.3 (21.2)	14
KFeTPP(SR)$_2$[b]	6	2.76-2.78	-	-	60.4 (0.6)	64.2 (1.8)	176.1 (4.3)	15
KCuI$_2$	6 (8)	-	3.60, 3.66	-	d	d	d	16

[a] Distance and angle information taken from the indicated references or calculated from atomic positional coordinates provided therein. Standard deviations of averaged values in parentheses. [b] TPP = *meso*-tetraphenylporphyrinate. [c] Contact with oxygen of adjacent crown ether ring. [d] Parameters not available.
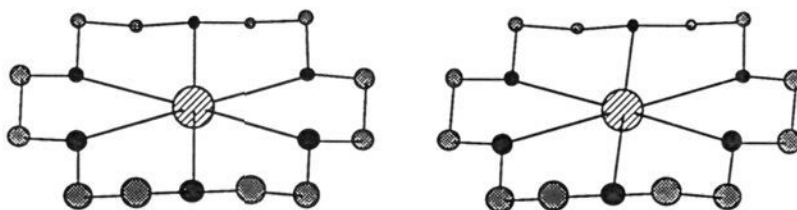
Figure 3. Stereoview of the molecular structure of 18-crown-6·K$^+$ as derived from coordinates presented in ref 15 (view from ca. 30° above best plane of crown ether ring).

to the results of the partial anisotropic refinement ($R = 0.075$).

Results and Discussion

Attempted crystallization of the 18-crown-6 complex of dipotassium tartrate hemihydrate from CHCl$_3$/CH$_2$Cl$_2$ by slow evaporation afforded single crystals of an 18-crown-6 complex (1) which chemically did not appear to contain the tartrate counterion. Single-crystal X-ray diffraction analysis (Figures 1 and 2) demonstrated the unexpected stoichiometry for this complex of [(18-crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$. Formation of this complex is presumably facilitated by slow decomposition of the CHCl$_3$ solvent, affording the "extra" proton and the chloride counterions. This decomposition may be accelerated by the solubilization by the crown ether of tartrate dianion in the organic phase; although only weakly basic in aqueous solution, tartrate may be sufficiently basic as a relatively naked anion in organic solution to deprotonate CHCl$_3$ (or CH$_2$Cl$_2$). Of relevance to this observation, crystallization of dipotassium tartrate from aqueous solution proceeds uneventfully, but crystallization from an aqueous solution in contact with a chloroform solution of 18-crown-6 gives rise to crystallization of potassium hydrogen tartrate at the interface between the two solutions.[23]

In [(18-crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$ (1), the potassium ion is directly coordinated by the six crown ether oxygens and three additional oxygens from water molecules. The chloride counterions and two additional waters (one of which is apparently protonated, balancing the overall charge on the complex) appear to be involved in a rather extensive hydrogen-bonding network, but are not directly associated with the potassium ion. Nine-coordination about potassium in an 18-crown-6 complex is most unusual. Other crystallographically characterized complexes (Table VI) display six- to eight-coordination, with a strong preference for eight-coordination evident. In only one crystal structure has a nine-co-

ordinate geometry been claimed;[13] in this complex, a weakly-associated dimethylformamide ligand, refined at partial occupancy, was identified as the ninth ligand. In all these previously characterized complexes, whether six-, seven-, eight-, or nine-coordinate, the 18-crown-6 adopts a quite symmetrical, near to perfect D_{3d} symmetry conformation (e.g., see Figure 3). A simpler view of this coordination geometry is provided in Figure 4, in which only the coordination shell about potassium is depicted, with the six crown ether oxygens linked directly together; in this depiction, the D_{3d} conformation is readily apparent in the chair-like arrangement of the six ether oxygens about the potassium ion. As Figure 4 clearly shows, this conformation is preferred regardless of the coordination number or the nature or distribution of other ligands on potassium. In contrast, the crown ether in [(18-crown-6)K(H$_2$O)$_3$](H$_3$O)(H$_2$O)Cl$_2$ (1) adopts a much less symmetrical conformation, in which the six ether oxygens are disposed about the potassium in effectively a twist-boat orientation (Figure 5).

This severely distorted crown ether conformation serves to wrap the bound potassium ion more tightly, allowing the three additional water ligands to coordinate, and shrinking all the potassium–oxygen bonds in the complex (both to the crown ether and to the water ligands) appreciably from the values seen in all other potassium crown ether complexes (Tables III and VI). Even the longest potassium–crown ether oxygen bond, at 2.65 (1) Å, is shorter than the shortest previously recorded such contact, and the potassium–water oxygen bonds, at 2.43 (1) and 2.47 (1) Å, are shorter than those in other such hydrates by at least 0.3 Å.

Given these unusually short potassium–oxygen bond lengths, we were led to question whether in fact the central ion was sodium rather than potassium. We repeated the structure determination ab initio with a sodium ion at the center of the crown ether. At the convergence of an all-isotropic refinement (omitting hydrogens and using no absorption correction; counterions and solvates assigned as above; $R = 0.152$, $R_w = 0.174$), the central ion displayed

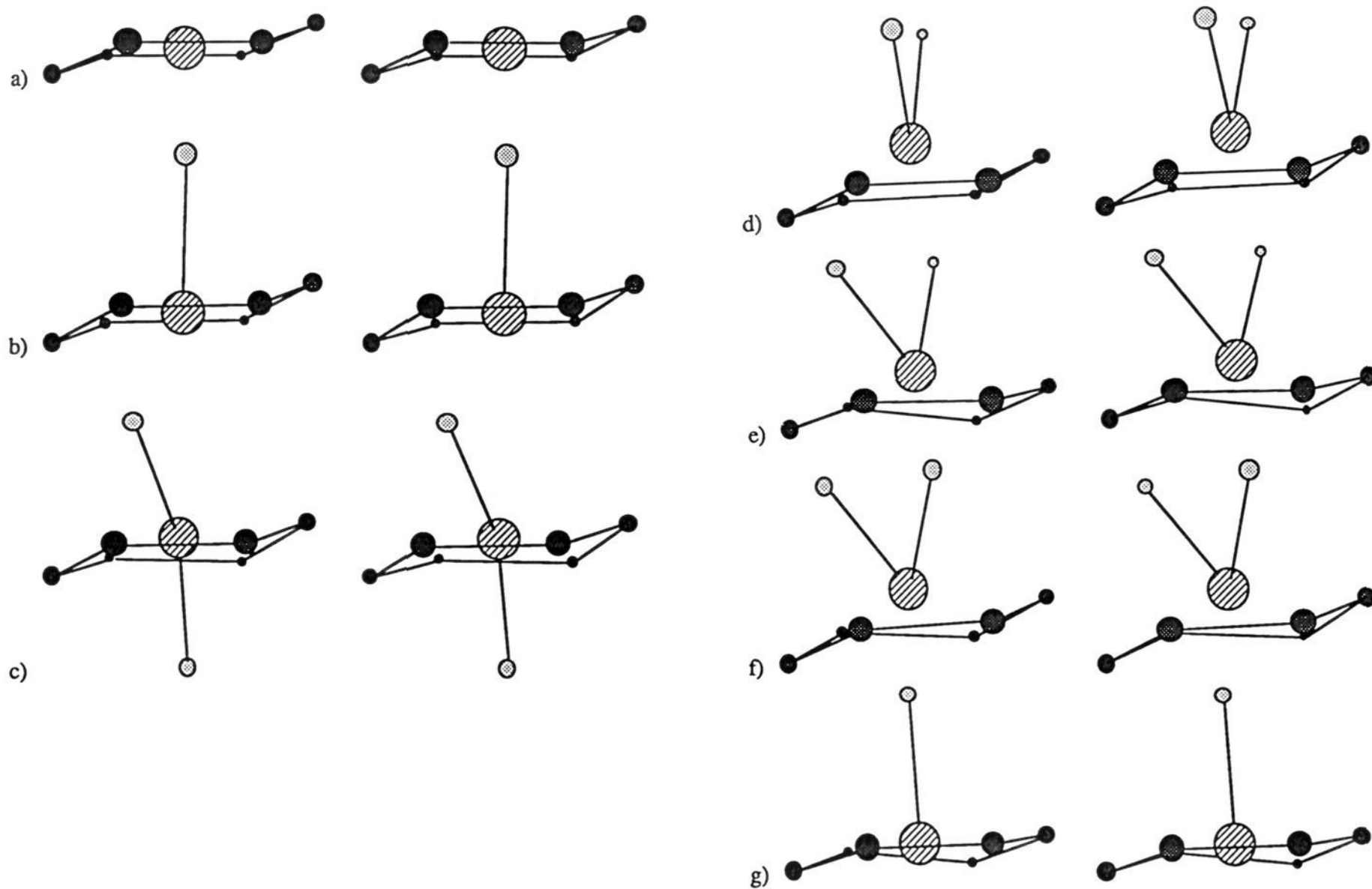(23) Doxsee, K. M.; Wierman, H. Unpublished observations.

Figure 4. Stereoviews of the coordination geometry in various 18-crown-6·K⁺ complexes. Only coordinated ligands are shown; the oxygens of the 18-crown-6 ring are joined to each other for clarity; other ligands are connected directly to the central potassium. Complex stoichiometries and references are as follows: (a) KFe(tetraphenylporphyrinate)(SPh)₂ (ref 15); (b) KSCN (ref 8); (c) K₂Mo₆O₁₉·H₂O (ref 12); (d) KMoO₄·H₂O (form 1) (ref 11); (e) KMoO₄·H₂O (form 2) (ref 11); (f) KCu(S₂C₂O₂) (ref 13); (g) K₂Hg₂I₆·H₂O (coordination to one I of counteranion not depicted) (ref 14).
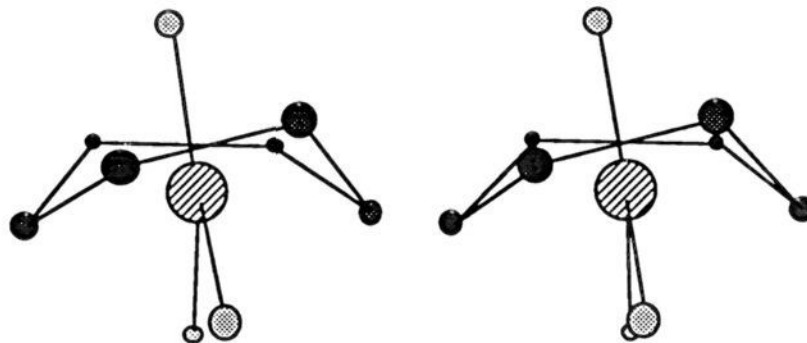
Figure 5. Stereoview of the coordination geometry in $[(18\text{-crown-}6)K(H_2O)_3](H_3O)(H_2O)Cl_2$ (**1**), using the same presentation as in Figure 4.

an isotropic thermal ellipsoid far smaller (B_{iso} = 0.08 Å^2) than those for the other non-hydrogen atoms in the structure (B_{iso} = 5–7 Å^2). Replacement of the sodium ion with a potassium ion in this structure solution gave significantly better refinement (R = 0.127, R_w = 0.144), and the central ion displayed a thermal parameter (B_{iso} = 2.86 Å^2) much more in line with those of the other non-hydrogen atoms (B_{iso} = 5–7 Å^2). These results are consistent with the dependence of X-ray diffraction on electron density, with the remarkably small thermal parameter for the putative sodium ion due to the computational attempt to explain why a sodium gives rise to so much electron density. If, in spite of the clear suggestion from this analysis that the central ion is a potassium, one assumes that it is a sodium, then to account for the presence of 1 equiv of potassium in the complex (shown by elemental analysis), one must assume that one of the lattice waters (presumably the one formulated as H_3O^+) is in fact a potassium. This is problematic on two counts: (1) As discussed above for sodium vs potassium, X-ray diffraction results allow easy distinction between oxygen (8 electrons) and potassium (18 electrons). (2) The coordination numbers for the atoms we have assigned as chlorides and waters are completely consistent with a hydrogen-bonded network (vide infra) and are far too low for any of these atoms to actually be even a sodium, let alone a potassium. Finally, we noted that the longest component of each potassium–water bond is parallel to the shortest cell dimension (the b axis), and therefore we considered whether an error in the determination of the length of b could be responsible for the short potassium–water bond lengths. However, an error in this determination of sufficient magnitude to account for the short bonds observed would be readily apparent. The cell parameters calculated from the setting angles of 25 centered reflections, well-distributed in reciprocal space, had acceptably small standard deviations, and the indices assigned to these reflections (in particular the k indices) were nicely integral. In addition, a poorly-determined orientation matrix would have resulted in the collection of a much poorer data set and a much less sharply resolved structure. Thus, on all these counts, one is led to conclude that this is indeed a most unusual 18-crown-6 complex of potassium, not sodium.

The distortion of the crown ether conformation appears to be reflected in the O–K–O bond angles, which are on average several degrees larger in our complex than in other reported 18-crown-6 complexes (Tables IV and VI), but the differences are sufficiently small to make such an assay for crown ether distortion less than definitive. Analysis of crown ether torsion angles (Tables V and VI), on the other hand, provides a simple indication of the extent of distortion. Whereas simple D_{3d} symmetrical complexes display alternating O–C–C–O torsion angles of ±60° and alternating C–O–C–C torsion angles of ±180°, several bonds in complex **1** display drastically different values for these bond twists. The O–C–C–O torsion angles range from 39° to 58°, with an average of 50°, while two of the C–O–C–C torsion angles display severe distortions from the idealized 180° for D_{3d} symmetry, at 82° and 102°. Two other C–O–C–C angles are considerably altered (156° and 167°), while the others (174–180°) fall within the normal range for other 18-crown-6 complexes.
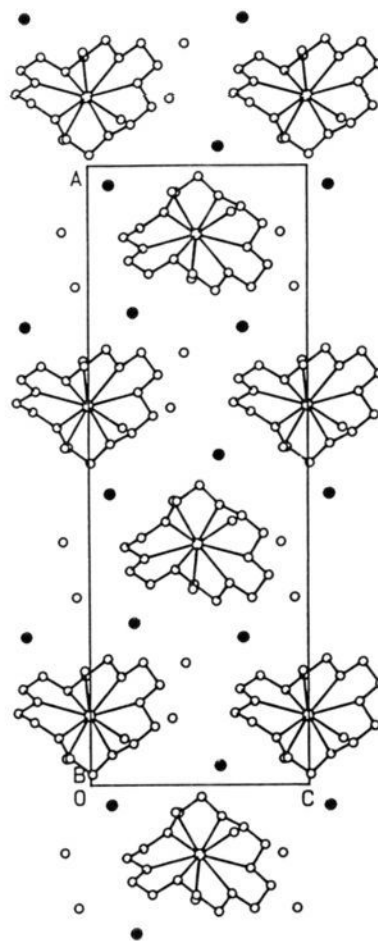

Figure 6. Packing diagram for $[(18\text{-crown-}6)K(H_2O)_3](H_3O)(H_2O)Cl_2$ (**1**). Noncoordinated water molecules are represented by small, open circles; chloride counterions are represented by larger, shaded circles.

Some distortion of the crown ether conformation from D_{3d} symmetry was noted in the structure of the $K_2Hg_2I_6$ complex of 18-crown-6.[14] This distortion was noted primarily in the twist of one C–O–C–C torsion angle to 97°, permitting the oxygen to serve as a donor to a second potassium ion. As the coordination diagram (Figure 4g) suggests, this distortion is actually quite subtle by comparison to that seen in complex **1** and, in fact, is very similar to that observed in the molybdate complexes (Figure 4e,f).[11,13] Interestingly, the crown ether ring in the *sodium* thiocyanate complex of 18-crown-6 adopts a conformation in which five of the six ether oxygens form the "normal" D_{3d} array of ligands around sodium while the sixth oxygen occupies a pseudoaxial position.[24]

Table VII. Intermolecular Contacts (Å) Suggesting Hydrogen Bonding for Complex 1[a]

Cl(1)	O(9)	3.14 (1)	Cl(2)	O(11)[d]	3.25 (1)
Cl(1)	O(10)	3.16 (1)	Cl(2)	O(7)[e]	3.35 (1)
Cl(1)	O(8)[b]	3.20 (1)	Cl(2)	O(7)[f]	3.37 (1)
Cl(1)	O(8)	3.22 (1)	O(9)	O(10)[b]	2.76 (2)
Cl(2)	O(11)[c]	3.19 (1)	O(10)	O(11)	2.83 (2)

[a] Symmetry codes are given in footnotes *b–f*. [b] $1 - x$, $1 - y$, $^1/_2 + z$. [c] $1 - x$, $1 - y$, $-^1/_2 + z$. [d] $-^1/_2 + x$, $1 - y$, z. [e] x, $-1 + y$, z. [f] $^1/_2 - x$, $-1 - y$, $-^1/_2 + z$.

A number of important hydrogen bonds would appear to be made between the various water molecules and chloride ions within the crystal lattice (Figure 6); close contacts between heavy atoms which almost certainly are mediated by hydrogen bonds are listed in Table VII. Unfortunately, we were unable to locate the appropriate hydrogens crystallographically, making any detailed discussion of this hydrogen-bonding network inappropriate.

Summary and Conclusions

In the solid state, uncomplexed 18-crown-6 displays an elliptical conformation of C_i symmetry. In solution, although 18-crown-6 is conformationally mobile, some preference for the more symmetrical D_{3d} conformation has been noted. Upon complexation with potassium ion, both solution and solid-state studies have

previously demonstrated that 18-crown-6 adopts a more symmetrical D_{3d} or near-D_{3d} conformation, thus directing all six oxygen donors toward the complexed potassium ion. The unusual complex [(18-crown-6)K(H₂O)₃](H₃O)(H₂O)Cl₂ (1) crystallizes from CHCl₃/CH₂Cl₂ solutions of 18-crown-6 and dipotassium tartrate, perhaps a result of deprotonation of solvent by the solubilized tartrate ion. The crown ether in this complex adopts a quite unsymmetrical conformation, with the oxygens disposed in a twist-boat arrangement around the potassium, rather than the symmetrical D_{3d} conformation, which places the oxygens in a chair arrangement. The potassium ion in this complex is effectively "shrink-wrapped", with all oxygen–potassium bonds appreciably shorter than in other 18-crown-6 complexes of potassium. The question of what factors are responsible for formation of this unusual crown ether geometry and for the contraction of the bonds in this complex remains an open one, but it is clear that even a prototypical crown ether such as 18-crown-6 may continue to provide unusual and unexpected coordination complexes and geometries.

Supplementary Material Available: Details of crystallographic data collection and refinement and tables of intermolecular contacts, anisotropic thermal parameters, torsion angles, and calculated positions of hydrogen atoms of 1 (9 pages); observed and calculated structure factors of 1 (9 pages). Ordering information is given on any current masthead page.

(24) Dobler, M.; Dunitz, J. D.; Seiler, P. *Acta Crystallogr.* **1974**, *B30*, 2741-2743. Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerley, R. P. *Acta Crystallogr.* **1974**, *B30*, 2733-2738.

Silver, Sodium Halosodalites: Class A Sodalites

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Abstract: Class A sodalites of the composition Na₈X₂(SiAlO₄)₆ were synthesized hydrothermally (X = Cl⁻, Br⁻, I⁻). AgNO₃ melt and hydrothermal aqueous exchanges were used to replace Na⁺ ions by Ag⁺ ions. The sodalite precursors and products were studied by chemical analysis, powder XRD, mid- and far-IR, multinuclear MAS- and DOR-NMR and optical reflectance spectroscopy. The structures of selected precursors as well as partially and fully silver exchanged sodalites were determined by Rietveld refinement of high resolution powder X-ray data. The unit cell sizes depended on the type and loading of cation and anion. Combined results from the above techniques indicated that a solid-solution structure of cages with different cation contents was formed. Organized assemblies of Na₄₋ₙAgₙX³⁺ clusters consisting of the components of insulators (NaX) and semiconductors (AgX) were encapsulated by the cubic sodalite framework which forms perfectly periodic arrays of all-space filling 6.6 Å cages. The concentration and identity of cations and nature of the anion controlled the extent of vibrational and electronic coupling between clusters. Vibrational coupling was strongly mediated by the anions. Electronic interaction was possible through the framework (Na, Ag) or directly (Ag). Extended Hückel molecular orbital calculations supported the idea of band formation for an extended Na₄₋ₙAgₙX³⁺ cluster lattice at increasing Ag⁺ loadings. They also aided in the assignment of the optical spectra. The calculations indicated that electronic transitions existed between clusters and the framework.

Introduction

Traditional or previously suggested applications of sodalites have included pigments, gas storage materials, and the use of photochromic and cathodochromic sodalites for information storage,

display, and filter optics.[1] Because sodalites allow one to create organized assemblies of clusters consisting of the components of insulators, semiconductors, or metals, inside a host material composed of single size bcc packed cuboctahedral cavities,[2–4] new

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(1) Stein, A.; Ozin, G. A Sodalite: An Old Material for Advanced Uses. In *Advances in the Synthesis and Reactivity of Solids*; Mallouk, T. E., Ed.; **1991**; Vol. 3, and references cited therein.