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Metal- vs Hydrogen-Bonding Complexation in Zinc Complexes of 18-Crown-6

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Interdiffusion of solutions of zinc chloride in diethyl ether and 18-crown-6 in 1,2-dichloroethane affords a crystalline complex, $[18\text{-crown-6}\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$. Single-crystal X-ray diffraction analysis ($C_{24}H_{52}Cl_8O_{14}Zn_4$; triclinic; $P\bar{1}$; $a = 7.659(3)$ Å, $b = 11.696(6)$ Å, $c = 13.190(4)$ Å, $\alpha = 105.23(3)°$, $\beta = 106.52(3)°$, $\gamma = 91.07(3)°$; $Z = 1$) reveals the $ZnCl(H_2O)^+$ cation to be coordinated to three crown ether oxygens, providing a five-coordinate distorted trigonal bipyramidal zinc. The crown ether displays a near-D_{3d} symmetric conformation in this complex. Recrystallization from carbon tetrachloride/acetone affords an extensively hydrolyzed product, $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$, in which both the octahedral $[Zn(H_2O)_6]^{2+}$ cation and the tetrahedral $[ZnCl_3(H_2O)]^-$ anion are bound to the 18-crown-6 through an extensive three-dimensional network of hydrogen bonds. The crown ether in this complex ($C_{27}H_{70}Cl_6O_{21}Zn_3$; orthorhombic; $P2_12_12$; $a = 14.735(7)$ Å, $b = 16.800(3)$ Å, $c = 10.194(2)$ Å; $Z = 2$) displays a severely distorted, asymmetric conformation, giving rise to solid-state chirality.

Introduction

Pedersen's original report in 1967 of the synthesis of macrocyclic polyethers ("crown ethers") and their ability to form complexes with inorganic salts[1] has led to a virtual explosion of solution and solid-state investigations of these complexes. Although the vast majority of these studies have focused on the complexation of alkali metal salts, a rapidly growing body of work has demonstrated the ability of the crown polyethers to complex a wide array of other metal ions as well, including the alkaline earth metal ions and a number of other main-group and transition-metal ions.[2,3] Single-crystal X-ray diffraction analysis remains the single most powerful technique for the characterization of these complexes, and numerous solid-state structural studies have appeared through the years.[4] Not only have these studies allowed for the unambiguous determination of structure, but also the structural data base afforded through such studies promises to aid in the rational design of ion-specific crown ethers and derivatives, in which favored coordination geometries may be designed into the complexation agent. Longer-range goals of such studies include both the development of an understanding of the interactions of metal ions with biological molecules[5] and the generation of precursors for the preparation of solid-state materials.[6]

Bulychev and co-workers have reported the preparation and single-crystal structural analysis of several zinc complexes of crown polyethers.[7] These structures were discussed, in part, in light of their provision of "snapshots" of the process of desolvation of metal cations by crown ethers, in that the various complexes characterized displayed varying degrees of encapsulation of the zinc ion by the crown ether. In the course of our investigations of the crown ether-mediated solubilization of non-alkali metal salts in organic solvents,[8] we have prepared and structurally characterized two new complexes from the interaction of 18-crown-6 with zinc chloride. One of these contains a partially-encapsulated zinc species, with direct zinc-to-crown ether coordination, while the other represents a "complex of complexes", in which hydrated zinc species are complexed to the crown ether via hydrogen-bonding interactions with aquo ligands. Herein is presented the preparation and structural characterization of these complexes, providing two additional "snapshots" of zinc "caught in the act" of complexation.

Experimental Section

Preparation of $[18\text{-crown-6}\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (1). In a 12 mm × 75 mm test tube was placed 3.0 mL of a 0.0200 M solution of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) in 1,2-dichloroethane. Using a pipet, 3.0 mL of a 0.0200 M solution of zinc chloride in diethyl ether was carefully layered onto this solution. The tube was capped and allowed to stand. Long, clear, colorless prisms (ca. 1 mm × 1 mm × 8 mm) formed in a matter of hours at the interface between the two solutions. After a total of 3 days, the crystalline material, mp 147–153 °C, was isolated by decantation in 40% yield (20.0 mg from three parallel preparations). IR (KBr): 3592 (s), 3000–3500 (s, br), 2896 (s), 1645 (ms), 1609 (s), 1476 (m), 1356 (s), 1286 (m), 1251 (ms), 1110 (s, br), 963 (s), 872 (w), 836 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{52}Cl_8O_{14}Zn_4$: C, 25.97; H, 4.72; Zn, 23.56. Found: C, 25.80; H, 4.78; Zn, 23.51.

X-ray Analysis of $[18\text{-crown-6}\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (1). A large crystal of complex 1 was transferred directly from the mother liquor into a pool of hydrocarbon grease. A fragment of dimensions 0.18 × 0.29 × 0.55 mm was cleaved from this crystal and mounted in a glass capillary. The orientation matrix and cell dimensions were calculated from the setting angles of an Enraf-Nonius CAD4 diffractometer for 25 centered reflections in the range $26° \leq 2\theta \leq 28°$. Crystal parameters and the final residuals are summarized in Table 1. The supplementary material contains further details of data collection and structure refinement. The positions of the zinc atoms were obtained from the Patterson function. A single cycle of DIRDIF[9] showed the chlorine and crown ether carbon and oxygen atoms. After these were all refined isotropically, a difference synthesis revealed a water ligand [O(7)] and demonstrated that Zn(1), coordinated

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[1] Pedersen, C. J. *J. Am. Chem. Soc.* **1967,** *89,* 7017–7036.

[2] See, e.g.: Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, England, 1989.

[3] Recent examples of zinc complexes with nitrogen or nitrogen- and oxygen-containing macrocyclic chelating agents: Adams, H.; Bailey, N. A.; Fenton, D. E.; Ford, I. G.; Kitchen, S. J.; Williams, M. G.; Tasker, P. A.; Leong, A. J.; Lindoy, L. F. *J. Chem. Soc., Dalton Trans.* **1991,** 1665–1674. Alcock, N. W.; Berry, A.; Moore, P. *Acta Crystallogr., Sect. C* **1992,** *48,* 16–19.

[4] See, e.g.: Cram, D. J.; Trueblood, K. N. *Top. Curr. Chem.* **1981,** *98,* 43–106.

[5] For a recent example of such studies pertaining to zinc, see: Quiros, M.; Salas, J. M.; Sanchez, M. P.; Alabart, J. R.; Faure, R. *Inorg. Chem.* **1991,** *30,* 2916–2921.

[6] For a recent example of such studies pertaining to zinc, see: Hursthouse, M. B.; Malik, M. A.; Motevalli, M.; Obrien, P. *Polyhedron* **1992,** *11,* 45–48.

[7] Bel'sky, V. K.; Streltsova, N. R.; Bulychev, B. M.; Storozhenko, P. A.; Ivankina, L. V.; Gorbunov, A. I. *Inorg. Chim. Acta* **1989,** *164,* 211–220.

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Table 1. Crystallographic Data for $[18\text{-crown-6}\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (**1**)

$C_{24}H_{52}Cl_8O_{14}Zn_4$	fw 1109.8
$a = 7.659(3)$ Å	space group $P\bar{1}$ (No. 2)
$b = 11.696(6)$ Å	$T = 23$ °C
$c = 13.190(4)$ Å	$\lambda = 0.710\,69$ Å
$\alpha = 105.23(3)°$	$\rho_{calcd} = 1.695$ g cm^{-3}
$\beta = 106.52(3)°$	$\mu = 27.85$ cm^{-1}
$\gamma = 91.07(3)°$	$R(F_o)^a = 0.058$
$V = 1087(2)$ Å^3	$R_w(F_o)^a = 0.065$
$Z = 1$	

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) $[B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j]$ for $[18\text{-crown-6}\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (**1**)[a]

atom	x	y	z	B_{eq}
Zn(1A)	941(2)	2615(2)	6568(1)	6.00(7)
Zn(1B)	−215(6)	2908(5)	7171(4)	8.5(2)
Zn(2)	4443.7(14)	1225.1(8)	691.6(8)	4.39(4)
Cl(1)	−1678(3)	2555(2)	5367(2)	6.2(1)
Cl(2)	4117(3)	2771(2)	−2(2)	5.9(1)
Cl(3)	4117(3)	1526(2)	2341(2)	5.6(1)
Cl(4)	7250(3)	514(2)	571.7(18)	5.23(9)
O(1)	3070(9)	3792(7)	6075(6)	6.7(3)
O(2)	2632(9)	1474(6)	5992(5)	6.3(3)
O(3)	683(9)	1015(5)	7249(5)	5.9(3)
O(4)	−1601(9)	2502(6)	8083(5)	6.6(3)
O(5)	−916(12)	4932(7)	8334(6)	8.3(4)
O(6)	775(10)	5481(5)	6882(5)	6.1(3)
O(7)	2025(8)	3656(5)	7998(5)	5.2(2)
C(1)	3358(16)	2935(12)	5202(10)	7.8(6)
C(2)	4045(16)	1897(12)	5630(10)	8.4(6)
C(3)	3090(15)	561(9)	6510(9)	6.9(5)
C(4)	1433(16)	65(9)	6640(8)	6.7(5)
C(5)	−902(15)	588(11)	7440(10)	7.5(5)
C(6)	−1191(14)	1420(11)	8370(10)	7.4(5)
C(7)	−1934(21)	3363(13)	8926(11)	9.7(7)
C(8)	−2438(18)	4376(13)	8558(11)	9.5(7)
C(9)	−1317(24)	5867(14)	7887(12)	11.1(8)
C(10)	285(21)	6358(9)	7707(10)	8.6(6)
C(11)	2475(18)	5798(10)	6779(10)	7.6(5)
C(12)	2771(15)	4901(11)	5822(10)	7.5(5)

[a] B_{eq} defined by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Table 3. Crystallographic Data for $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$ (**2**)

$C_{27}H_{70}Cl_6O_{21}Zn_3$	space group $P2_12_12$ (No. 18)
$a = 14.735(7)$ Å	$T = 22$ °C
$b = 16.800(3)$ Å	$\lambda = 0.710\,69$ Å
$c = 10.194(2)$ Å	$\rho_{calcd} = 1.500$ g cm^{-3}
$V = 2523(2)$ Å^3	$\mu = 18.3$ cm^{-1}
$Z = 2$	$R(F_o)^a = 0.045$
fw 1139.7	$R_w(F_o)^a = 0.049$

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

to the crown ether, was disordered over two sites ca. 1.2 Å apart. Further refinement provided site occupancy factors of 0.71 and 0.29 for Zn(1A) and Zn(1B). An empirical absorption correction (DIFABS[10]) based on the isotropically-refined structure was applied. The non-hydrogen atoms were subsequently refined with anisotropic thermal parameters, and the crown ether hydrogen atoms were included at calculated "riding" positions. No clear indication of the positions of the hydrogen atoms of the water ligand [O(7)] could be found. The TEXSAN program suite,[11] incorporating standard atomic form factors,[12] was used in all calculations. Coordinates for all heavy atoms are presented in Table 2. Relevant bond lengths, bond angles, and torsion angles are presented and discussed below, and complete tables of these parameters are provided in the supplementary material.

Preparation of $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$ (2). A 50-mg sample of complex **1** was dissolved in 25 mL of boiling 2:1 CCl_4/acetone in a test tube. The solution was cooled to room temperature; then the tube was left partially open to the atmosphere, allowing slow evaporation to occur. After 10 days, the small, clear, colorless multifaceted prisms which had formed were isolated by decantation in 58% yield (mp 178–182 °C). IR (KBr): 3487 (s, br), 2896 (ms), 1639 (m), 1476 (m), 1356 (s), 1251 (m), 1110 (vs), 963 (s), 836 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{70}Cl_6O_{21}Zn_3$: C, 28.45; H, 6.19; Zn, 17.21. Found: C, 28.41; H, 6.28; Zn, 17.09.

X-ray Analysis of $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$ (2). Data were collected on an Enraf-Nonius CAD4 diffractometer from a fiber-mounted crystal of approximate dimensions 0.20 × 0.22 × 0.25 mm, after determination of the orientation matrix and cell dimensions from the setting angles of 25 centered reflections in the range $12.0° \leq 2\theta \leq 20.5°$. Table 3 lists the final residuals and a summary of the crystal data; a fuller version, including details of data collection and structure refinement, is provided in the supplementary material. The PHASE Patterson interpretation routine of DIRDIF gave the positions of the zinc atoms, and a further cycle of DIRDIF revealed all remaining non-hydrogen atoms except those of the acetone solvate, which appeared later in a difference synthesis. The non-hydrogen atoms, except for those of the solvate, were refined anisotropically. The water hydrogen atoms were located in a difference synthesis and were included in the model without refinement; other hydrogen atoms were included at calculated "riding" positions. Refinement of the opposite enantiomer gave significantly higher residuals ($R = 0.052$, $R_w = 0.059$) and a higher goodness-of-fit index (2.04 vs 1.70). The TEXSAN program suite, incorporating standard atomic scattering factors, was used in all calculations. Coordinates for all heavy atoms are presented in Table 4. Relevant bond lengths, bond angles, and torsion angles are presented and discussed below, and complete tables of these parameters are provided in the supplementary material.

Results

Interdiffusion of an ethereal solution of zinc chloride and a solution of 18-crown-6 in 1,2-dichloroethane resulted in formation of large, colorless prisms at the interface between the two solutions. Single-crystal X-ray diffraction analysis revealed the molecular structure of this complex (**1**), of composition $[18\text{-crown-6}\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$, as presented in Figure 1 and discussed in detail below.

Recrystallization of complex **1** from 2:1 CCl_4/acetone, taking no precautions to exclude adventitious moisture, afforded a new complex (**2**) as clear, colorless prismatic crystals which, in contrast to those of complex **1**, were indefinitely stable after removal from the mother liquor. Infrared spectral analysis of this complex, as well as of complex **1**, suggested the presence of aquo ligands, and this was confirmed by single-crystal X-ray diffraction analysis, which revealed complex **2** to represent a rather extensively hydrolyzed material, of composition $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$ (Figure 2). The preparations of complexes **1** and **2** have been reproduced a number of times, with identical results, on a variety of scales.

Discussion

Complex **1** (Figure 1) contains two symmetry-equivalent $[18\text{-crown-6}\cdot ZnCl(H_2O)]^+$ units, with charge balance provided by a $[Zn_2Cl_6]^{2-}$ counteranion. The crown ether-associated zinc ion is disordered over two sites [denoted as Zn(1A) and Zn(1B)]. Rather curiously, although the zinc ion is disordered, its associated aquo and chloro ligands are not; the structure refined nicely with only a single position for each of these two groups. The crown ether is coordinated through three ether oxygens to the $ZnCl(H_2O)$

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å^2) [$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$] for $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2 \cdot 2(18\text{-crown-6}) \cdot (CH_3)_2C{=}O$ (**2**)[a]

atom	*x*	*y*	*z*	B_{eq}
Zn(1)	6472.6(8)	2256.7(7)	8407.9(11)	4.28(5)
Zn(2)	5000.0	5000.0	4936.2(16)	4.07(8)
Cl(1)	6924(2)	2153(2)	10472(3)	6.0(2)
Cl(2)	6534(3)	3523(2)	7647(3)	8.1(2)
Cl(3)	5176(2)	1655(3)	7903(4)	9.1(2)
O(1)	0233(6)	7695(5)	6703(11)	8.0(5)
O(2)	1516(6)	7977(5)	4581(9)	7.1(5)
O(3)	2966(5)	9048(6)	5060(9)	6.7(5)
O(4)	2668(5)	10365(5)	6752(11)	7.1(5)
O(5)	1266(6)	10056(5)	8692(7)	6.6(4)
O(6)	0999(5)	8442(5)	8906(8)	6.0(4)
O(7)	5405(4)	5800(5)	6399(7)	5.8(4)
O(8)	3760(5)	5624(5)	4942(8)	6.4(4)
O(9)	5577(5)	5700(4)	3506(7)	5.2(4)
O(10)	7452(4)	1659(4)	7473(6)	4.8(4)
O(11)	10000	5000	7322(17)	11.1(4)[b]
C(1)	0291(13)	7274(10)	5500(20)	11(1)
C(2)	1184(10)	7231(9)	4896(18)	9(1)
C(3)	2414(10)	7941(9)	3992(14)	7.6(9)
C(4)	2784(10)	8743(11)	3828(13)	8(1)
C(5)	3467(9)	9769(9)	5041(19)	9(1)
C(6)	3525(10)	10101(9)	6424(18)	9(1)
C(7)	2664(12)	10672(9)	8051(14)	8(1)
C(8)	1734(11)	10772(8)	8540(17)	9(1)
C(9)	1479(10)	9620(8)	9874(13)	7.2(8)
C(10)	0873(9)	8925(10)	9975(13)	7.9(9)
C(11)	0458(10)	7738(11)	9037(17)	9(1)
C(12)	0539(12)	7274(8)	7787(20)	9(1)
C(13)	10000	5000	8485(22)	7.5(4)[b]
C(14)	9123(12)	4875(12)	9127(17)	11.7(5)[b]

[a] B_{eq} defined by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609–610. Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter. [b] Refined with isotropic thermal parameter.

moiety, with Zn(1A) coordinated to oxygens O(1), O(2), and O(3), while Zn(1B) is coordinated to oxygens O(3), O(4), and O(5), providing overall five-coordination at zinc.

The aqueous speciation chemistry of zinc chloride has been analyzed in detail, with the major species present shown to be $[Zn(H_2O)_6]^{2+}$, $[ZnCl(H_2O)_5]^+$, $[ZnCl_4]^{2-}$, $[ZnCl_4(H_2O)_2]^{2-}$, and $ZnCl_2(H_2O)_4$.[13] Coordination numbers of 4 and 6 appear most commonly found for zinc(II),[14] although a respectable number of examples of five-coordinate zinc complexes have also been structurally characterized.[15] To our knowledge, complexes of the form $[ZnCl(H_2O)_4]^+$ or $[L_3ZnCl(H_2O)]^+$ have not previously been reported in either aqueous or nonaqueous solution or in the solid state. The coordination geometry observed [shown for Zn(1A) in Figure 3] essentially represents a geometry intermediate between the two limiting forms, trigonal bipyramidal and square pyramidal. (As Auf der Heyde has discussed,[16] the structure may be considered to represent a point on the Berry pseudorotation potential surface for the interchange between these two limiting forms.) The zinc–crown ether oxygen bonds, at an average of 2.28 Å, fall well within the range of distances observed for typical zinc–oxygen coordination compounds.[17] The Zn–Cl bond, at an average of 2.20 Å, also appears unremarkable, with other reported terminal Zn–Cl bonds typically falling in the range of 2.2–2.3 Å.[18] The zinc–aquo bond, at an average of 1.85 Å, however, is considerably shorter than seen in other aquozinc(II) complexes, be they four-, five-, or six-coordinate, with more typical values centered around ca. 2.0–2.1 Å.[19] The significant shortening of this bond may reflect a stronger interaction between zinc and the coordinated water, which may in turn reflect a zinc center made comparatively electron-deficient by virtue of the preponderance of relatively poor donor ligands in its coordination shell.

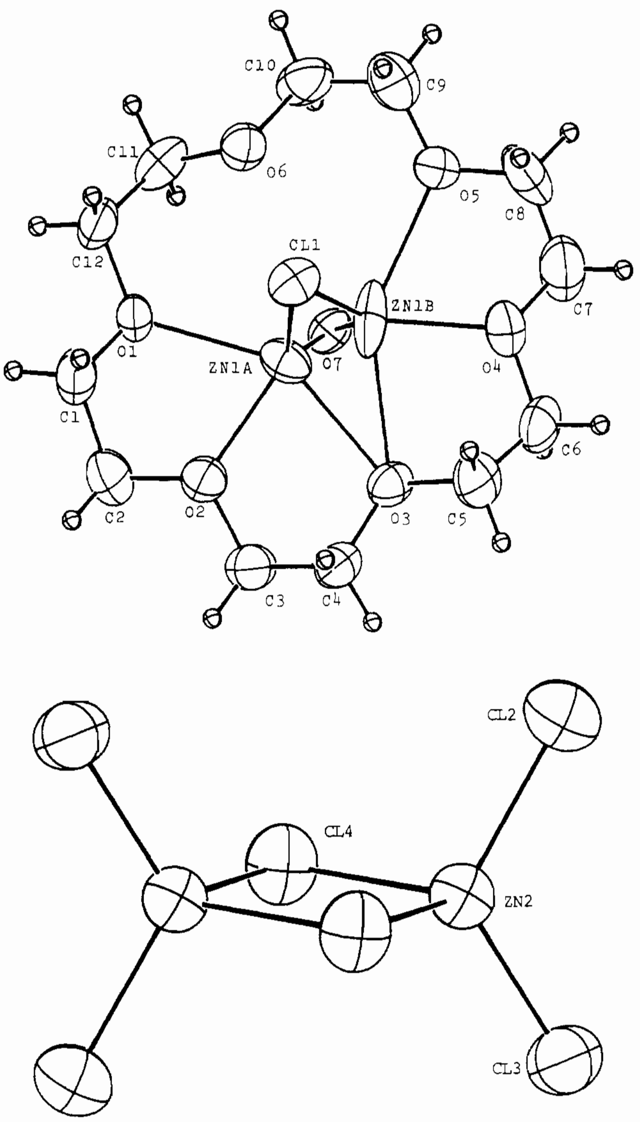

Figure 1. (a) Top: Structural elements of $[18\text{-crown-6} \cdot ZnCl \cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (**1**), including numbering scheme for atoms in the asymmetric unit. Redundant symmetry-equivalent groups and the counteranion are omitted for clarity. (b) Bottom: Structure of $[Zn_2Cl_6]^{2-}$ in complex **1**, including numbering scheme for atoms in the asymmetric unit.

Despite coordination of the zinc ion to only three of the crown ether oxygens, the 18-crown-6 ring conformation approximates the highly symmetric D_{3d} conformation generally seen in its potassium complexes.[20] This symmetry is best monitored by the O–C–C–O torsion angle, which, in the ideal D_{3d} symmetric conformation, should display alternating values of ±60°, and by the C–O–C–C angle, which should be ±180°. The experimental values for these torsion angles (Table 5), 64 ± 4 and 173 ± 6°, respectively, are well within range of those seen in a number of crystallographically-characterized potassium complexes of 18-crown-6 displaying near-ideal D_{3d} symmetry; torsion angles for one of these, the K^+(18-crown-6) salt of $[FeTPP(SR)_2]^-$ (TPP

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(17) See Tables 7 and 8 for leading references.

(18) See Table 8 for leading references.

(19) See Tables 7 and 8 for leading references for four- and six-coordinate complexes. For five-coordinate complexes, see refs 15 and 16 and references therein.

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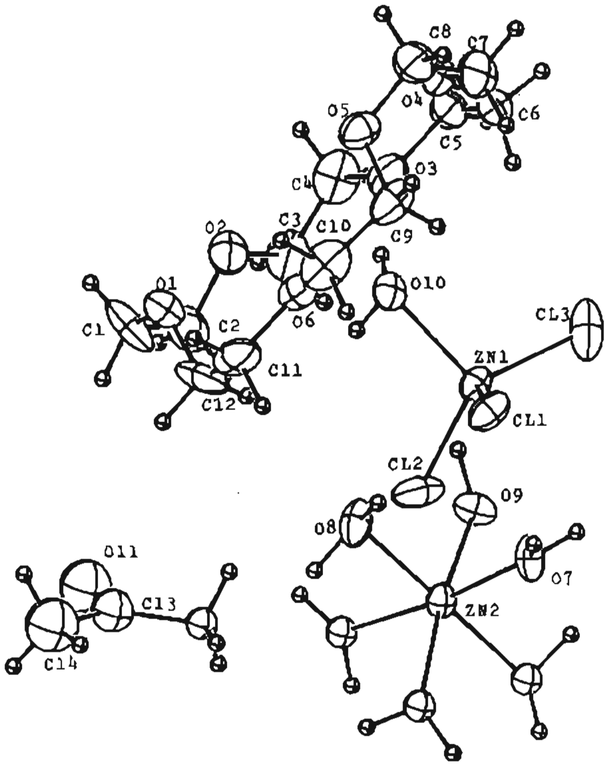

Figure 2. Structural elements of $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-{}_2 \cdot 2(18\text{-crown-}6)\cdot(CH_3)_2C{=}O$ (**2**), including numbering scheme for atoms in the asymmetric unit. Redundant symmetry-equivalent groups are omitted for clarity.

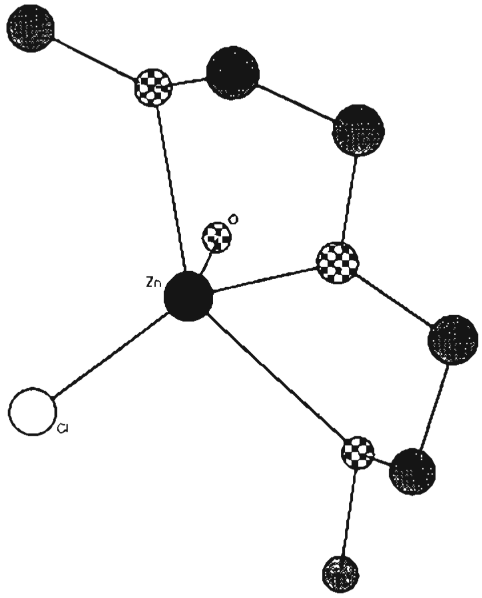

Figure 3. Zinc coordination geometry in $[18\text{-crown-}6\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (**1**).

= *meso*-tetraphenylporphyrinate)[21] are included in Table 5 for comparison. Figure 4, in which only the oxygen atoms of the crown ether are shown, with adjacent oxygens of the ring connected, highlights the spatial relationship of the crown ether oxygens. As we have discussed previously,[20] in the D_{3d} conformation, these oxygens effectively form a chairlike arrangement, and this arrangement is readily apparent in Figure 4.

Several salts containing the $[Zn_2Cl_6]^{2-}$ ion have been crystallographically characterized.[22–25] Key metrical parameters, when available, are compiled for comparison in Table 6. As previously observed, the $[Zn_2Cl_6]^{2-}$ ion is quite symmetrical, with each zinc having effective tetrahedral geometry (Figure 1a).

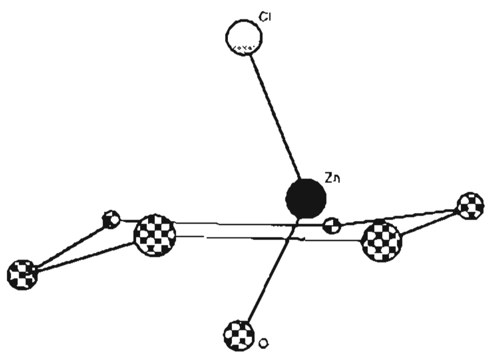

Figure 4. Depiction of the crown ether conformation in $[18\text{-crown-}6\cdot ZnCl\cdot H_2O]^+{}_2[Zn_2Cl_6]^{2-}$ (**1**). Only the zinc ion and its coordinated ligands are shown; the oxygens of the 18-crown-6 ring are joined to each other for clarity.

Table 5. Torsion Angles (deg) for 18-Crown-6 in Complexes **1** and **2** and in the K^+(18-crown-6) Salt of $[FeTPP(SR)_2]^-$ (TPP = *meso*-Tetraphenylporphyrinate)[21]

torsion angle	**1**	**2**	$[K^+(18\text{-crown-}6)]\text{-}[FeTPP(SR)_2]^-$
O(1)–C(1)–C(2)–O(2)	61(1)	–61(2)	63
O(2)–C(3)–C(4)–O(3)	–57(1)	69(2)	–67
O(3)–C(5)–C(6)–O(4)	65(1)	–71(1)	62
O(4)–C(7)–C(8)–O(5)	–66(1)	66(2)	–63
O(5)–C(9)–C(10)–O(6)	66(1)	60(1)	67
O(6)–C(11)–C(12)–O(1)	–70(1)	–61(2)	–62
C(1)–C(2)–O(2)–C(3)	–175(1)	176(1)	–180
C(3)–C(4)–O(3)–C(5)	–178(1)	170(1)	178
C(5)–C(6)–O(4)–C(7)	179(1)	179(1)	–179
C(7)–C(8)–O(5)–C(9)	175(1)	80(2)	180
C(9)–C(10)–O(6)–C(11)	–170(1)	176(1)	–178
C(11)–C(12)–O(1)–C(1)	–180(1)	–179(1)	179
C(12)–O(1)–C(1)–C(2)	168(1)	–78(2)	–173
C(2)–O(2)–C(3)–C(4)	–169(1)	–173(1)	174
C(4)–O(3)–C(5)–C(6)	158(1)	173(1)	–177
C(6)–O(4)–C(7)–C(8)	–176(1)	–166(1)	173
C(8)–O(5)–C(9)–C(10)	179(1)	174(1)	–174
C(10)–O(6)–C(11)–C(12)	–174(1)	174(1)	177

The stoichiometry of complex **1** is the same as that of a 15-crown-5 analog, $[15\text{-crown-}5\cdot ZnCl(H_2O)]^+{}_2[Zn_2Cl_6]^{2-}$ (Figure 5a), reported by Bulychev et al.[26] The latter complex, formed from the interaction of $ZnCl_2\cdot H_2O$ with 15-crown-5 in acetone or ether, differs most notably from complex **1** in that all five crown ether oxygens are coordinated, providing an overall seven-coordinate zinc ion. The zinc–crown ether oxygen bonds are in line with those in complex **1**, at an average of 2.30 Å, while the zinc–aquo bond, at 2.08 Å, is somewhat longer than that in **1**. This is consistent with the above suggestion that this bond length may provide an indication of relative electron deficiency at zinc, with the higher coordination number in the Bulychev complex providing greater electron density at zinc and therefore weakening the interaction with the aquo ligand. 15-Crown-5 appears to favor formation of such seven-coordinate zinc complexes, with essentially complete encapsulation of the zinc ion by the crown ether, a fact which Bulychev attributes to the relatively rigid structure of this smaller ring macrocyclic polyether.

Interestingly, the larger ring crown ether, 18-crown-6, appears to favor formation of lower coordination number complexes. The

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Table 6. Key Structural Parameters of $Zn_2Cl_6^{2-}$

	1	$[V_2Cl_3(THF)_6]_2$-$[Zn_2Cl_6]$	$[V_2Cl_3$-$(THF)_6]_2$-$[Zn_2Cl_6]$	$(Cp_2Ti(DME))_2$-$[Zn_2Cl_6]\cdot C_6H_6$	[Zn(15-crown-5)-$(CH_3CN)_2]$-$[Zn_2Cl_6]$	[ZnCl(15-crown-5)-$(H_2O)]_2$-$[Zn_2Cl_6]$	[ZnCl(15-crown-5)-$(CH_3COCH_3)]_2$-$[Zn_2Cl_6]$
ref	this work	23	24	25	7	26	7
Zn–$Cl_{terminal}$ (Å)	2.198, 2.219	2.215, 2.218	2.211	2.151, 2.199	2.206, 2.212	2.174, 2.221	2.193, 2.213
Zn–$Cl_{bridging}$ (Å)	2.343, 2.351	2.351, 2.363	2.355	2.319, 2.455	2.364, 2.366	2.331, 2.375	2.364, 2.372
Zn—Zn (Å)	3.240	3.257	3.251	3.303	3.222^b	3.176^b	3.242^b
Cl_t–Zn–Cl_t (deg)	116.0	116.51	NR^a	113.0	118.3	120.4	118.8
Cl_t–Zn–Cl_b (deg)	107.3, 112.0, 113.1, 113.3	108.00, 110.46, 111.92, 114.90	NR^a	108.8, 111.1, 113.1, 116.7	108.8, 110.2, 110.5, 112.4	107.2, 108.9, 109.2, 112.9	109.1, 109.7, 111.1, 111.5
Cl_b–Zn–Cl_b (deg)	92.7	92.61	NR^a	92.5	93.9	95.0	93.6
Zn–Cl_b–Zn (deg)	87.3	87.4	NR^a	87.5	85.8^b	84.9^b	86.4^b

^{a} Values not reported. ^{b} Calculated from reported atomic coordinates.

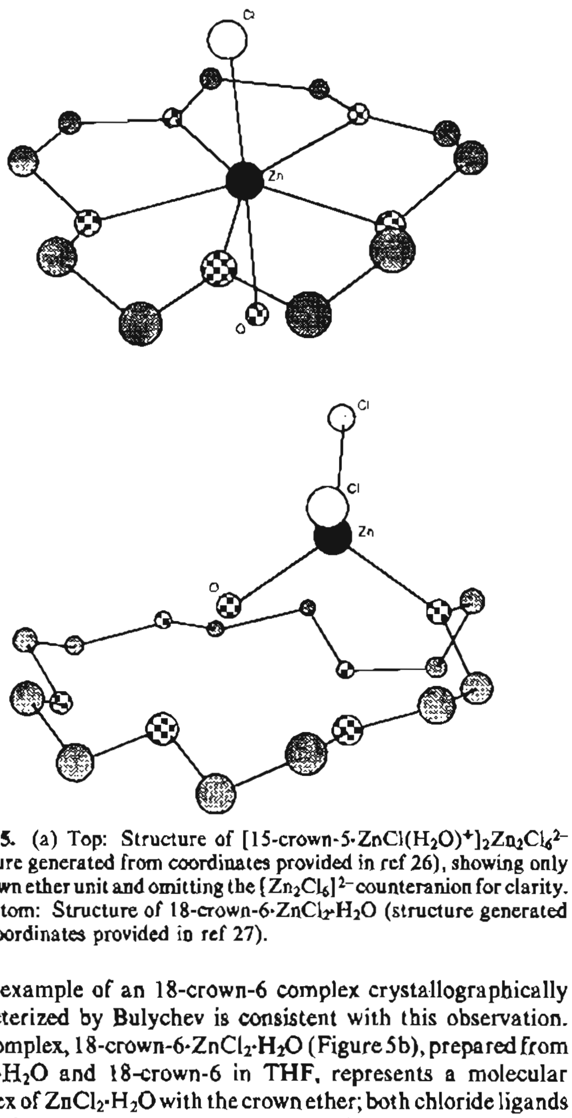

Figure 5. (a) Top: Structure of $[15\text{-crown-}5\cdot ZnCl(H_2O)^+]_2Zn_2Cl_6^{2-}$ (structure generated from coordinates provided in ref 26), showing only one crown ether unit and omitting the $[Zn_2Cl_6]^{2-}$ counteranion for clarity. (b) Bottom: Structure of 18-crown-6·$ZnCl_2\cdot H_2O$ (structure generated from coordinates provided in ref 27).

single example of an 18-crown-6 complex crystallographically characterized by Bulychev is consistent with this observation. This complex, 18-crown-6·$ZnCl_2\cdot H_2O$ (Figure 5b), prepared from $ZnCl_2\cdot H_2O$ and 18-crown-6 in THF, represents a molecular complex of $ZnCl_2\cdot H_2O$ with the crown ether; both chloride ligands are retained in the coordination sphere of zinc, which is overall four-coordinate in this complex. As in complex **1**, the zinc ion in this complex perches well above the plane of the crown ether. The formation of two such structurally distinct complexes from the "simple" reaction between $ZnCl_2$ and 18-crown-6 suggests the potential complexity of this system. Indeed, in addition to the crystallographically characterized complex shown in Figure 5b, Bulychev also reports the formation of a complex in the form of a powder upon admixture of $ZnCl_2\cdot H_2O$ and 18-crown-6 in ether. This complex appears water-free, as indicated by its infrared spectrum, and displays zinc and chlorine analyses consistent with formulation as 18-crown-6·2$ZnCl_2$. The elemental analytical and infrared data reported for this complex suggest it to be distinct from complex **1**; although these data for zinc and chlorine are not fully conclusive in this regard (Calcd: Zn, 24.35 (Bulychev), 23.56 (**1**); Cl, 26.41 (Bulychev), 25.56 (**1**). Found: Zn, 24.1; Cl, 26.5), the presence of aquo ligands appears easily determined by infrared spectroscopy. Interestingly, Bulychev has also reported the formation, in acetone, of a noncrystalline complex to which, on the basis of analytical data, he assigned the stoichiometry of complex **1**.[27]

The Bulychev complex is also clearly distinct from complex **2** (Figure 2), which is formed upon attempted recrystallization of complex **1**. An extensive reorganization of ligands occurs in this crystallization, with zinc in the product complex appearing in the form of two $[ZnCl_3(H_2O)]^-$ units and one $[Zn(H_2O)_6]^{2+}$ dication. The $[Zn(H_2O)_6]^{2+}$ dication displays near-octahedral symmetry, with an average zinc–aquo bond length of 2.08 Å. The metrical parameters for the $[Zn(H_2O)_6]^{2+}$ ion observed in complex **2** appear quite similar to those determined in earlier X-ray diffraction analyses of salts containing this ion, as the examples in Table 7 indicate.

Although the $[ZnCl_3(H_2O)]^-$ ion appears far less common, the observed metrical parameters again are in accord with those reported earlier, as well as with those of related $[ZnCl_3L]^-$ ions, as demonstrated by the data in Table 8. The $[ZnCl_3(H_2O)]^-$ ion displays pseudotetrahedral symmetry, with a zinc–aquo bond length of 1.999 Å.

Neither the $[ZnCl_3(H_2O)]^-$ ion nor the $[Zn(H_2O)_6]^{2+}$ ion in complex **2** is directly associated with the crown ether moieties via direct zinc–crown ether oxygen ligation. Both ions, however, are involved in an extensive three-dimensional hydrogen-bonding network, in which each aquo ligand of both ions forms hydrogen bonds to a crown ether and/or to a chloride ligand on an adjacent zinc complex (Figure 6). Each crown ether oxygen is engaged in at least one hydrogen bond, and one participates in two hydrogen bonds to aquo ligands. Overall, the hydrogen-bonding arrangement is qualitatively reminiscent of that seen in the solid-state structures of extensively hydrolyzed lanthanide complexes of the crown polyethers.[37] The acetone solvate appears to serve simply as a structural "hole filler" and does not participate in any hydrogen bonds.

The 18-crown-6 moiety adopts a rather asymmetric conformation in complex **2**. Although the O–C–C–O torsion angles, at 64.5 ± 4.4°, do not readily reveal this asymmetry (but note that

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Table 7. Key Structural Parameters of $[Zn(H_2O)_6]^{2+}$

	1	$Zn(NH_4)_2$-$(SO_4)_2(H_2O)_6$	$Zn(O_3SC_6H_5)_2$-$(H_2O)_6$	$Zn(O_3SC_6H_4CH_3$-$p)_2$-$(H_2O)_6$	$Zn(NO_3)_2(H_2O)_6$
ref	this work	28	29	30	31
$Zn-O_{axial}$ (Å)	2.057	2.075	2.08[a,b]	2.08	2.064
$Zn-O_{equatorial}$ (Å)	2.094, 2.106	2.117, 2.129	2.08[a,b]	2.05, 2.14	2.083, 2.104, 2.129, 2.130
O–Zn–O (deg)	85.7, 85.9, 89.2, 89.7, 91.2, 94.0, 94.4	89.1, 89.2, 90.6	NR[b,c]	88, 89, 89	88.7, 89.2, 89.5, 89.7, 89.7, 90.2, 90.5, 92.4

[a] Reported average value for Zn–O bond length. [b] Ambiguities in the presentation of crystallographic data in ref 29 preclude reliable calculation of these values. [c] Values not reported.

Table 8. Key Structural Parameters of $[ZnCl_3(H_2O)]^-$ and Related Species

	1	$K[ZnCl_3(H_2O)]\cdot H_2O$	$[C_6H_9N_2S_3]$-$[ZnCl_3(H_2O)]$	$[TiCl_2(THF)_4]$-$[ZnCl_3(THF)]$	$[VCl_2(THF)_3(H_2O)]$-$[ZnCl_3(THF)]$	$[MoOCl(dppe)_2]$-$[ZnCl_3(acetone)]$
ref	this work	32	33	34	35	36
Zn–O (Å)	1.999	1.98	2.035	2.121	2.025	2.12
Zn–Cl (Å)	2.213, 2.221, 2.266	2.24, 2.26, 2.28	2.220, 2.225, 2.240	2.239, 2.240, 2.242	2.226, 2.247, 2.251	2.23 (mean)
O–Zn–Cl (deg)	101.3, 106.2, 106.4	104, 107, 109[a]	99.4, 104.5, 108.2	102.3, 103.3, 104.3	103.8, 104.1, 105.8	NR[b]
Cl–Zn–Cl (deg)	112.4, 112.8, 116.3	106, 113, 114[a]	112.8, 114.9, 115.0	112.9, 115.8, 115.9	111.9, 114.8, 114.9	NR[b]

[a] Calculated from reported atomic coordinates. [b] Values not reported.

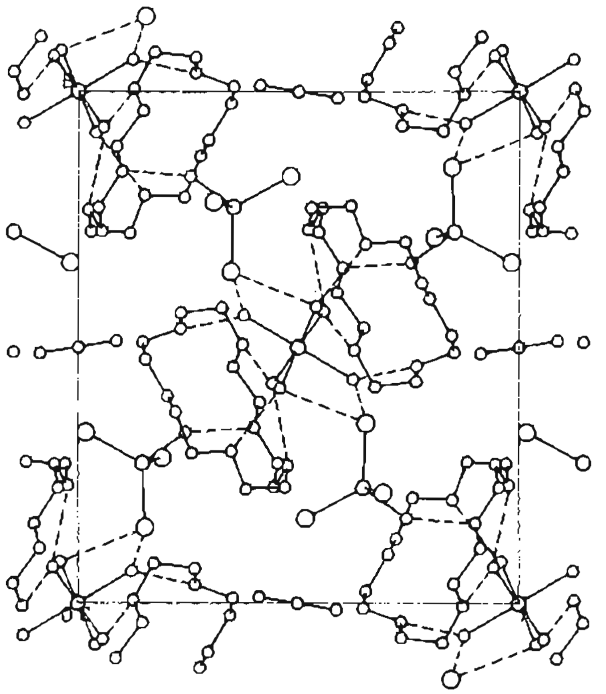

Figure 6. Packing diagram for $[Zn(H_2O)_6]^{2+}[ZnCl_3(H_2O)]^-_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$ (**2**), showing the extensive hydrogen-bonding network.

the angles do not *alternate* ±60°, as seen for the D_{3d} symmetric conformation), it is readily evidenced by the C–O–C–C torsion angles, two of which are ca. 79° instead of the 180° anticipated for the ideal D_{3d} symmetric conformation. Examination of the spatial arrangement of the oxygen atoms of the crown ether again provides the most graphic visualization of the asymmetry. Figure 7, in which only the crown ether oxygens are displayed, with adjacent oxygens connected, shows that, in contrast to the chairlike arrangement of oxygens found in complex **1**, the oxygens more closely approximate a boat arrangement in complex **2**. In keeping with the asymmetric crown ether conformation, complex **2** crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12$, with the crown ether providing the asymmetric element of the structure. Initial solution of the crystal structure with arbitrary choice of the crown ether's asymmetric conformation provided an *R* factor of 5.2% and goodness-of-fit of 2.04. Refinement of the opposite enantiomer afforded an immediate and significant decrease in these parameters ($R = 4.5\%$, goodness-of-fit = 1.70), confirming the configuration depicted in Figure 2 as the correct one.[38]

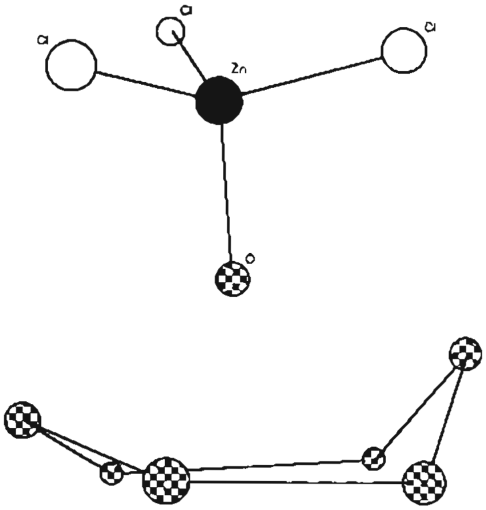

Figure 7. Depiction of the crown ether conformation in $[Zn(H_2O)_6]^{2+}$-$[ZnCl_3(H_2O)]^-_2\cdot 2(18\text{-crown-6})\cdot(CH_3)_2C{=}O$ (**2**). Only the zinc ion and its coordinated ligands are shown; the oxygens of the 18-crown-6 ring are joined to each other for clarity.

Complex **2** represents a "complex of complexes", in which the zinc complex ions are complexed indirectly by the crown ether, via hydrogen bonding to the ligands of the zinc ions. Although this form of supramolecular complexation[39] has perhaps been most extensively studied for the metal ammines,[40] examples of aquo ion complexes have also been reported. Rogers has characterized a number of such supramolecular aquo complexes,[41] including one in which a hydrated dysprosium ion is so-complexed.[37] Interestingly, this complex appears to be formed through hydrolysis of an initially-obtained complex in which the

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(38) As no asymmetry was present in the starting materials, presumably both antipodes of the complex were formed during the crystallization; had another crystal been examined by X-ray diffraction, it could well have displayed the opposite configuration. Note, however, that spontaneous crystallization of a single chiral form of a crystalline solid, $NaClO_3$, has been reported (McBride, J. M.; Carter, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 293–295). In this case, each individual crystallization experiment in general afforded only a single enantiomer of the crystalline product, but which enantiomer was formed varied randomly from experiment to experiment.

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dysprosium ion is directly ligated by the crown ether. The hydrolytic conversion of this complex to the supramolecular complex appears quite analogous to the conversion of complex **1** to **2**.

Conclusions

The $ZnCl_2$/crown ether/H_2O system is clearly complex. Using relatively subtle changes in solvent, reaction conditions, and crown ether, one may "tune" the reaction to provide access to a variety of structurally diverse complexes. In addition to those crystalline complexes structurally characterized by us and others, additional species, with unique stoichiometries, appear to be produced as well.[42] Several general trends are evident: (1) The larger crown ether, 18-crown-6, favors complexes in which not all of its oxygens participate in the coordination of the metal ion, whereas the smaller-ring 15-crown-5 favors coordination by all five oxygens of its ring. (2) The higher the hydration level of the zinc ion, the less likely it is to be directly coordinated to the crown ether, and the more likely it is to be associated with it only via a network of hydrogen bonds. These general trends appear evident in the complexation chemistry of other complex metal ions as well.[37,41]

In addition to the information about the interaction of the zinc ion with crown ethers that these structural studies have provided, structural details of relatively uncommon and/or seldom crystallographically characterized complex zinc ions, including the pseudotetrahedral $[ZnCl_3(H_2O)]^-$ anion and the apparently unprecedented five-coordinate $[ZnCl(H_2O)L_3]^+$ cation (L = crown ether oxygen), have also been obtained. In a sense, these structures, together with those reported by Bulychev et al., represent "snapshot" glimpses of the process of complexation/desolvation. Fully-hydrated $[Zn(H_2O)_6]^{2+}$ interacts with the crown ether only via the mediation of hydrogen bonds, while $ZnCl_2(H_2O)$ is coordinated directly by one crown ether oxygen and one hydrogen bond, and $[ZnCl(H_2O)]^+$ is coordinated directly by three crown ether oxygens. Ultimately, studies of this nature may lead to a clearer picture of the molecular-level details of the very processes of complexation and solubilization.

Acknowledgment. This work was supported by the Office of Naval Research, whose support is gratefully acknowledged. We also express our appreciation to Robin Rogers for his helpful discussions.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, anisotropic thermal parameters, hydrogen atom locations, bond lengths, bond angles, torsion angles, and intermolecular contacts for **1** and **2** (20 pages). Ordering information is given on any current masthead page.

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[42] E.g., Bulychev reports[7] the instant precipitation from ether of a powder of stoichiometry $2ZnCl_2 \cdot 18$-crown-6 which infrared spectroscopy suggests to be water-free.