

# Complexation of Metal Salts with Macrocyclic Polyethers in Aprotic Solvents. Crystal Structures of Ionic $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{L}]^{2+}[\text{Zn}_2\text{Cl}_6]^{2-}$ ( $\text{L} = \text{CH}_3\text{CN}$ , THF), $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{L}']_2^{2+}[\text{Zn}_2\text{Cl}_6]^{2-}$ ( $\text{L}' = \text{H}_2\text{O}$ , $\text{CH}_3\text{COCH}_3$ ) and Molecular $\text{ZnCl}_2 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$ Complexes

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## Abstract

Interaction of anhydrous or partially hydrated zinc chloride with the macrocyclic polyether 15-crown-5 in aprotic organic solvents was found to yield intracavity ionic complex salts of two types,  $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{L}]^{2+}[\text{Zn}_2\text{Cl}_6]^{2-}$  and  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{L}']_2^{2+}[\text{Zn}_2\text{Cl}_6]^{2-}$  ( $\text{L} = \text{CH}_3\text{CN}$ , THF;  $\text{L}' = \text{H}_2\text{O}$ ,  $\text{CH}_3\text{COCH}_3$ ). 18-crown-6 in THF and  $\text{CH}_3\text{CN}$  failed to react with anhydrous  $\text{ZnCl}_2$ , the solutions producing here the molecular adducts  $\text{ZnCl}_2 \cdot 2\text{L}$ . Partially hydrated zinc chloride was shown to react with 18-crown-6 to form the molecular complex  $\text{ZnCl}_2 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$ , wherein the zinc atom is linked with one of the oxygen atoms of the macrocycle via donor–acceptor bonds. The formation of the intracavity complexes is proposed to occur only via the ionization of the  $\text{M}-\text{X}$  bond and incorporation of the metal atom into the cavity by the ‘head-to-tail’ mechanism.

## Introduction

Anhydrous or solvated (hydrated) metal halides are extensively used as starting materials in inorganic and organometal syntheses. Reactions with the halides are in general brought about in donor solvents and their interaction with the latter results in solvation of halides or formation of ionic or molecular complexes. The structures of the compounds in the crystal state have been insufficiently studied so far because the  $\text{M} \leftarrow \text{L}$  bonds are not strong; and our basic knowledge of their structures has been acquired

from spectral and electrochemical findings. In some cases, the use of crown ethers (CE) as oxygen-containing ligands enables us to substantially increase the stability of donor–acceptor complexes by their macrocyclic effects (i.e. by incorporation of an atom or ion into the macrocycle cavity) and examine them by X-ray diffraction analysis. No general rules have been yet established to produce the complexes by direct synthesis. For example, in the series of metal-(II) halides, covalent  $\text{BeCl}_2$  in diethyl ether predominantly reacts with 15-crown-5 and 18-crown-6 in a rapid fashion to form the salts  $\text{BeCl}_2 \cdot \text{CE}$ , but it fails to react with them in the presence of THF, from which  $\text{BeCl}_2 \cdot 2\text{THF}$  always crystallizes [1, 2]. More ionic  $\text{MgCl}_2$  in THF and  $\text{HgX}_2$  and  $\text{CdCl}_2$  in methanol react with 18-crown-6 and dibenzo-18-crown-6 ( $\text{MgCl}_2$  also reacts with 15-crown-5) to yield clathrate  $\text{MX}_2 \cdot \text{CE}$  compounds with a linear  $\text{X}-\text{M}-\text{X}$  group [3–6]. Incorporation of a metal atom into the macrocycle cavity seems to proceed via the ionization of the  $\text{M}-\text{X}$  bond [7]. At the same time, fully hydrated  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol and 15-crown-5 form an extracavity molecular complex wherein the components unite by the hydrogen bonds  $\text{O}(\text{H}_2\text{O}) \dots \text{O}(\text{CE})$  [8]. These examples indicate that there are numerous factors that influence the composition and structure of metal salt–CE complexes. Among them, the major ones appear to be the capabilities of the salts to ionize in the chosen solvent, ratios of the solvent and crown-ether basicities and coordination abilities of the metal atoms. To verify these assumptions, X-ray diffraction analysis was used to examine the reaction products of anhydrous or partially hydrated zinc chloride and 15-crown-5 or 18-crown-6 in organic aprotic solvents with various donor numbers ( $DN$ ).

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## Experimental

All the solvents used were dehydrated by conventional procedures. Reactions between the components and preparation of samples for physicochemical studies and analyses were carried out under a dry nitrogen atmosphere.

Anhydrous  $\text{ZnCl}_2$  was prepared by hydrochlorination of metallic zinc in absolute ether [9].

$\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  was produced by dihydrate desiccation *in vacuo* at  $150^\circ\text{C}$  for 1 h.

$3\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  was prepared by dihydrate desiccation at *c.*  $300^\circ\text{C}$  for 5 h.

All the reactions between zinc chloride and CE were performed by identical procedures at equimolar ratios of reagents as described below.

For example, 1.5–2.0 g of the salt were dissolved in 30–40 ml of absolute solvent; the solution was, if necessary, filtered, and equimolar amounts of CE in 10 ml of the same solvent were added. After 5–30 min, spontaneous precipitation (15-crown-5, THF,  $\text{CH}_3\text{CN}$ , acetone) or evaporation-initiated precipitation (18-crown-6, THF,  $\text{CH}_3\text{CN}$ , acetone) gave a crystalline compound that was separated from the mother liquor, washed with ether, and dried *in vacuo* at room temperature. A number of compounds were subject to recrystallization in the same solvent to obtain single crystals suitable for X-ray studies. The reaction between  $\text{ZnCl}_2$  and CE in diethyl ether proceeded with instantaneous precipitation of white microcrystalline compounds.

$[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{THF}][\text{Zn}_2\text{Cl}_6]$  (**I**) was prepared as colorless crystals from dilute anhydrous  $\text{ZnCl}_2$  in the THF–15-crown-5 mixture. The crystalline compound is insoluble in THF. *Anal.* Found: Zn, 25.2; Cl, 27.2. Calc. for  $\text{C}_{18}\text{H}_{36}\text{O}_7\text{Zn}_3\text{Cl}_6$ : Zn, 25.35; Cl, 27.56%. (640, 670, 725, 840, 865, 925, 960, 1020, 1045, 1080, 1145, 1250, 1300  $\text{cm}^{-1}$ .)

$[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{CH}_3\text{CN}][\text{Zn}_2\text{Cl}_6] \cdot \text{CH}_3\text{CN}$  (**II**) was prepared as colourless transparent crystals from anhydrous  $\text{ZnCl}_2$  solution in acetonitrile in the presence of 15-crown-5. The crystalline compound is insoluble in acetonitrile. *Anal.* Found: Zn, 25.9; Cl, 28.1. Calc. for  $\text{C}_{16}\text{H}_{29}\text{O}_5\text{Zn}_3\text{Cl}_6$ : Zn, 26.08; Cl, 28.31%. (240, 270, 300, 335, 370, 635, 730, 835, 940, 965, 1035, 1050, 1080, 1250, 1280  $\text{cm}^{-1}$ .)

$[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{H}_2\text{O}]_2[\text{Zn}_2\text{Cl}_6]$  (**III**) was prepared as light-yellow crystals from dilute  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  in acetone in the presence of 15-crown-5 and as a white powder from ether. The compound can be recrystallized from acetone. *Anal.* Found: Zn, 25.2; Cl, 27.4. Calc. for  $\text{C}_{10}\text{H}_{22}\text{O}_6\text{Zn}_2\text{Cl}_4$ : Zn, 25.60; Cl, 27.79%. (765, 785, 845, 950, 1045, 1095, 1250, 1270, 1277, 1630  $\text{cm}^{-1}$ .)

$[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{CH}_3\text{COCH}_3]_2[\text{Zn}_2\text{Cl}_6]$  (**IV**) was prepared in the mixture with **III** as colourless readily hydrolysable crystals from  $3\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  and 15-crown-5 solution in acetone or as an individual

compound from anhydrous  $\text{ZnCl}_2$  and 15-crown-5 in acetone. The compound can be recrystallized from this solvent. *Anal.* Found: Zn, 23.4; Cl, 25.5. Calc. for  $\text{C}_{13}\text{H}_{26}\text{O}_6\text{Zn}_2\text{Cl}_4$ : Zn, 23.74; Cl, 25.77%. (460, 725, 820, 840, 965, 1040, 1090, 1720  $\text{cm}^{-1}$ .)

$\text{ZnCl}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$  (**V**) was prepared as colourless readily weathering crystals on slow evaporation of dilute anhydrous  $\text{ZnCl}_2$  in THF or in the THF–18-crown-6 mixture. *Anal.* Found: Zn, 23.1; Cl, 25.5. Calc. for  $\text{C}_8\text{H}_{16}\text{O}_2\text{ZnCl}_2$ : Zn, 23.32; Cl, 25.32%.

$\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$  (**VI**) was prepared as colourless accreted weathering crystals by dissolving anhydrous  $\text{ZnCl}_2$  in  $\text{CH}_3\text{CN}$  or in the  $\text{CH}_3\text{CN}$ –18-crown-6 mixture. *Anal.* Found: Zn, 29.9; Cl, 32.5. Calc. for  $\text{C}_4\text{H}_6\text{N}_2\text{ZnCl}_2$ : Zn, 29.81; Cl, 32.56%. (240, 275, 290, 385, 530, 640, 735, 890, 925, 965, 1030, 1110, 1250, 1280  $\text{cm}^{-1}$ .)

$\text{ZnCl}_2 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$  (**VII**) was prepared as colourless crystals from  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  and 18-crown-6 solution in THF. The complex was recrystallized from the same solvent. *Anal.* Found: Zn, 15.2; Cl, 16.6. Calc. for  $\text{C}_{12}\text{H}_{26}\text{O}_7\text{ZnCl}_2$ : Zn, 15.63; Cl, 16.97%. (510, 520, 560, 725, 765, 812, 825, 838, 862, 895, 922, 953, 1032, 1040, 1055, 1100, 1140, 1255, 1270, 1310, 1630  $\text{cm}^{-1}$ .)

The same reaction involving ether instantly yielded a white precipitate whose composition corresponded to the formula  $2\text{ZnCl}_2 \cdot 18\text{-crown-6}$  (**VIII**); the precipitate contained no water as shown by IR spectra.

*Anal.* Found: Zn, 24.1; Cl, 26.5. Calc. for  $\text{C}_{12}\text{H}_{24}\text{O}_6\text{Zn}_2\text{Cl}_4$ : Zn, 24.39; Cl, 26.4%. A complex that has a similar composition is formed through the reaction in acetone, from which **VIII** crystallized as accreted druses after a major portion of the solvent has been evaporated (722, 840, 955, 970, 1040, 1060, 1090, 1130, 1235, 1250, 1290  $\text{cm}^{-1}$ .)

IR spectra of the complexes as suspensions in vaseline oil were recorded on a Specord UR-75 spectrometer in the region from 400 to 2000  $\text{cm}^{-1}$ . X-ray studies of the single crystals sealed in glass capillaries were performed on automatic Nicolet P 3 (**III**, **VII**) and Syntex P1 (**I**, **II**, **IV**, **V**) diffractometers (Mo  $\text{K}\alpha$  radiation, a graphite monochromator,  $\theta/2\theta$ -scanning up to  $2\theta \leq 48^\circ$ ). The main crystallographic characteristics of the complexes and conditions for their recording are given in Table 1. The structures of the complexes were identified by a direct method and were elucidated by the full-matrix least-squares method as an anisotropic approximation for non-hydrogen atoms. Corrections for absorption were not applied. Coordinates for the **II**, **IV** and **V** atoms are listed in Tables 2 to 4, basic bond lengths and bond angles are shown in Tables 5 to 7, geometrical parameters of macrocycles in the **II** and **IV** complexes are given in Tables 8 and 9. The study of **I** was restricted only to the determination of coordinates for its heavy metals for its low-quality

TABLE 1. Crystallographic parameters of zinc chloride complexes with macrocyclic polyethers

| Compound                                                                                               | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\gamma$ (°) | Space group                        | <i>Z</i> | $\mu$ (cm <sup>-1</sup> ) | <i>R</i> | <i>R<sub>w</sub></i> | No. reflections   |
|--------------------------------------------------------------------------------------------------------|--------------|--------------|--------------|--------------|------------------------------------|----------|---------------------------|----------|----------------------|-------------------|
| [Zn·15-crown-5·2THF] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ] (I)                               | 9.823(2)     | 9.761(2)     | 9.600(2)     | <sup>a</sup> | <i>P</i> <i>I</i>                  | 2        |                           |          |                      |                   |
| [Zn·15-crown-5·2CH <sub>3</sub> CN][Zn <sub>2</sub> Cl <sub>6</sub> ] (II)                             | 15.268(5)    | 16.505(6)    | 11.632(5)    | 90           | <i>A</i> 2 <sub>1</sub> <i>am</i>  | 4        | 31.6                      | 0.037    | 0.038                | 1006 <sup>b</sup> |
| [Zn·15-crown-5·H <sub>2</sub> O] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ] (III)                 | 9.548(4)     | 18.210(8)    | 11.705(4)    | 99.10(3)     | <i>P</i> 2 <sub>1</sub> / <i>b</i> | 2        | 15.4                      | 0.045    | 0.044                | 1397 <sup>c</sup> |
| [ZnCl·15-crown-5·C <sub>3</sub> H <sub>6</sub> O] <sub>2</sub> [Zn <sub>2</sub> Cl <sub>6</sub> ] (IV) | 21.150(6)    | 10.263(2)    | 10.149(2)    | 94.53(2)     | <i>P</i> 2 <sub>1</sub> / <i>a</i> | 4        | 27.5                      | 0.071    | 0.072                | 1093 <sup>b</sup> |
| ZnCl <sub>2</sub> ·2CH <sub>3</sub> CN (V)                                                             | 10.077(1)    | 6.663(1)     | 12.848(1)    | 90           | <i>Pm</i> <i>cn</i>                | 4        | 34.6                      | 0.027    | 0.029                | 540 <sup>b</sup>  |
| ZnCl <sub>2</sub> ·18-crown-6·H <sub>2</sub> O (VII)                                                   | 8.802(2)     | 13.198(3)    | 16.596(4)    | 104.48(2)    | <i>P</i> 2 <sub>1</sub> / <i>n</i> | 4        | 16.6                      | 0.035    | 0.035                | 932 <sup>b</sup>  |

<sup>a</sup>*a*<sub>2</sub> = 89.35(2),  $\beta$  = 105.10(2),  $\gamma$  = 118.64(2)°.<sup>b</sup>*I* ≥ 3 $\sigma$ (*I*).<sup>c</sup>*I* ≥ 2 $\sigma$ (*I*).TABLE 2. Coordinates of non-hydrogen atoms ( $\times 10^4$ ) and their equivalent thermal factors ( $\text{\AA}^2 \times 10^4$ ) in the complex [Zn·15-crown-5·2CH<sub>3</sub>CN][Zn<sub>2</sub>Cl<sub>6</sub>]·CH<sub>3</sub>CN (II)

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U<sub>eq</sub></i> |
|------|----------|----------|----------|-----------------------|
| Zn1  | 4948(1)  | 5356(1)  | 1385(1)  | 508(4)                |
| Zn2  | 2500     | 1518     | 0        | 399(4)                |
| Cl1  | 3847(3)  | 5601(3)  | 0        | 612(14)               |
| Cl2  | 6018(2)  | 5007(3)  | 0        | 561(12)               |
| Cl3  | 4602(2)  | 4289(2)  | 2444(2)  | 659(9)                |
| Cl4  | 5366(3)  | 6473(2)  | 2271(3)  | 786(13)               |
| O1   | 2204(6)  | 191(5)   | 0        | 484(32)               |
| C2   | 2488(9)  | -222(6)  | 1047(9)  | 553(34)               |
| C3   | 2179(8)  | 325(7)   | 2000(10) | 638(39)               |
| O4   | 2527(6)  | 1088(5)  | 1793(6)  | 623(25)               |
| C5   | 2293(15) | 1693(9)  | 2623(13) | 895(74)               |
| C6   | 2724(12) | 2439(13) | 2272(13) | 975(72)               |
| O7   | 2651(8)  | 2564(5)  | 1087(7)  | 850(36)               |
| C8   | 2703(18) | 3322(8)  | 629(15)  | 1040(71)              |
| C9   | 443(10)  | 1892(9)  | 0        | 498(52)               |
| C10  | -478(10) | 2077(9)  | 0        | 581(52)               |
| C11  | 4449(11) | 867(8)   | 0        | 491(48)               |
| C12  | 5307(11) | 470(11)  | 0        | 589(63)               |
| C13  | 6269(17) | 7490(11) | 5000     | 737(81)               |
| C14  | 5378(16) | 7864(12) | 5000     | 1025(90)              |
| N1   | 1147(9)  | 1721(7)  | 0        | 540(45)               |
| N2   | 3814(8)  | 1211(8)  | 0        | 501(40)               |
| N3   | 6919(15) | 7235(12) | 5000     | 917(78)               |

TABLE 3. Coordinates of non-hydrogen atoms ( $\times 10^4$ ) and their equivalent thermal parameters ( $\text{\AA}^2 \times 10^4$ ) in the complex [ZnCl·15-crown-5·C<sub>3</sub>H<sub>6</sub>O]<sub>2</sub>[Zn<sub>2</sub>Cl<sub>6</sub>] (IV)

| Atom | <i>x</i> | <i>y</i> | <i>z</i>  | <i>U<sub>eq</sub></i> |
|------|----------|----------|-----------|-----------------------|
| Zn1  | 617(1)   | 4158(3)  | -10(3)    | 45(1)                 |
| Cl1  | 497(4)   | 2045(6)  | 453(7)    | 62(3)                 |
| Cl2  | 1566(4)  | 5041(7)  | -495(7)   | 67(3)                 |
| Cl3  | 131(3)   | 5355(6)  | 1645(6)   | 56(3)                 |
| 2    | 6478(1)  | 8530(3)  | 500(3)    | 39(1)                 |
| Cl4  | 6603(3)  | 10738(6) | 347(6)    | 51(3)                 |
| O1   | 7083(7)  | 8527(15) | 2350(15)  | 45(7)                 |
| O4   | 5860(7)  | 8334(15) | 2177(15)  | 45(7)                 |
| O7   | 5493(8)  | 8430(14) | -261(16)  | 58(8)                 |
| O10  | 6484(9)  | 8014(18) | -1632(17) | 69(9)                 |
| O13  | 7413(8)  | 8117(17) | -54(15)   | 63(7)                 |
| C2   | 6738(19) | 8110(38) | 3474(28)  | 65(15)                |
| C3   | 6128(14) | 8738(27) | 3411(24)  | 58(12)                |
| C5   | 5277(14) | 8782(25) | 1967(24)  | 60(12)                |
| C6   | 4965(13) | 8125(26) | 756(28)   | 81(13)                |
| C8   | 5409(14) | 7729(25) | -1512(25) | 81(13)                |
| C9   | 5930(16) | 8119(29) | -2357(28) | 78(14)                |
| C11  | 7073(17) | 8052(31) | -2262(30) | 81(16)                |
| C12  | 7558(15) | 8130(38) | -1367(44) | 107(19)               |
| C14  | 7902(15) | 8349(26) | 874(31)   | 82(15)                |
| C15  | 7633(12) | 7914(24) | 2159(25)  | 58(12)                |
| O6   | 6385(9)  | 6343(14) | 780(16)   | 75(8)                 |
| C16  | 6432(13) | 5168(22) | 599(27)   | 59(11)                |
| C17  | 6377(19) | 4605(27) | -773(29)  | 102(19)               |
| C18  | 6575(16) | 4235(27) | 1634(27)  | 78(15)                |

TABLE 4. Coordinates of non-hydrogen atoms ( $\times 10^4$ ) and their equivalent thermal factors ( $\text{\AA}^2 \times 10^4$ ) in the complex  $\text{ZnCl}_2 \cdot \text{CH}_3\text{CN}$  (V)

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> <sub>eq</sub> |
|------|----------|----------|----------|------------------------|
| Zn1  | 2500     | 317(1)   | 65(1)    | 402(2)                 |
| Cl1  | 2500     | -2716(2) | 738(1)   | 618(5)                 |
| Cl2  | 2500     | 749(2)   | -1632(1) | 568(5)                 |
| N    | 1000(3)  | 1964(5)  | 715(2)   | 518(11)                |
| C1   | 317(4)   | 3013(6)  | 1134(3)  | 458(12)                |
| C2   | -545(6)  | 4385(8)  | 1687(4)  | 690(19)                |

crystals. Preliminary data on the structures of **III** and **VII** were discussed elsewhere [10, 11], and they are used in the present study to compare structural characteristics of all the resultant compounds of this type.

TABLE 5. Main bond lengths and bond angles in the complex  $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{CH}_3\text{CN}][\text{Zn}_2\text{Cl}_6]$  (II)

| Bond     | <i>d</i> (Å) | Angle       | $\omega$ (°) | Angle        | $\omega$ (°) |
|----------|--------------|-------------|--------------|--------------|--------------|
| Zn2–O1   | 2.235(9)     | O1–Zn2–O4   | 71.9(2)      | O1–Zn2–O7    | 143.8(2)     |
| Zn2–O4   | 2.204(7)     | O1–Zn2–N1   | 87.6(4)      | O1–Zn2–N2    | 87.5(4)      |
| Zn2–O7   | 2.153(8)     | O1–Zn2–O4'  | 71.9(2)      | O1–Zn2–O7'   | 143.8(2)     |
| Zn2–O4'  | 2.204(7)     | O4–Zn2–O7   | 72.6(3)      | O4–Zn2–N1    | 94.0(3)      |
| Zn2–O7   | 2.153(8)     | O4–Zn2–N2   | 84.4(3)      | O4–Zn2–O4'   | 142.4(4)     |
| Zn2–N1   | 2.093(13)    | O4–Zn2–O7'  | 144.3(3)     | O7–Zn2–N1    | 88.7(4)      |
| Zn2–N2   | 2.069(12)    | O7–Zn2–N2   | 95.3(4)      | O7–Zn2–O4'   | 144.3(3)     |
| Zn1–Cl1  | 2.364(4)     | O7–Zn2–O7'  | 71.9(4)      | N1–Zn2–N2    | 175.1(5)     |
| Zn1–Cl2  | 2.366(3)     | N1–Zn2–O4'  | 94.0(3)      | N1–Zn2–O7'   | 88.7(4)      |
| Zn1–Cl3  | 2.212(3)     | N2–Zn2–O4'  | 84.4(3)      | N2–Zn2–O7'   | 95.3(4)      |
| Zn1–Cl4  | 2.206(4)     | O4–Zn2–O7'  | 72.6(3)      | Cl1–Zn1–Cl2  | 93.9(1)      |
| Zn1'–Cl1 | 2.364(4)     | Cl1–Zn1–Cl3 | 110.2(2)     | Cl1–Zn1–Cl4  | 112.4(2)     |
| Zn1'–Cl2 | 2.366(3)     | Cl2–Zn1–Cl3 | 110.5(1)     | Cl2–Zn1–Cl4  | 108.8(2)     |
|          |              | Cl3–Zn1–Cl4 | 118.3(1)     | Cl1–Zn1'–Cl2 | 93.9(1)      |

TABLE 6. Main bond lengths and bond angles in the complex  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{C}_3\text{H}_6\text{O}]_2[\text{Zn}_2\text{Cl}_6]$  (IV)

| Bond     | <i>d</i> (Å) | Angle        | $\omega$ (°) | Angle        | $\omega$ (°) |
|----------|--------------|--------------|--------------|--------------|--------------|
| Zn1–Cl1  | 2.213(7)     | Cl1–Zn1–Cl2  | 118.8(3)     | Cl1–Zn1–Cl3  | 109.7(3)     |
| Zn1–Cl2  | 2.193(8)     | Cl1–Zn1–Cl3' | 109.2(3)     | Cl2–Zn1–Cl3  | 111.5(3)     |
| Zn1–Cl3  | 2.364(7)     | Cl2–Zn1–Cl3' | 111.1(3)     | Cl3–Zn1–Cl3' | 93.6(2)      |
| Zn1–Cl3' | 2.372(7)     | Cl4–Zn2–O1   | 92.1(4)      | Cl4–Zn2–O4   | 99.8(4)      |
| Zn2–Cl4  | 2.266(6)     | Cl4–Zn2–O7   | 93.3(4)      | Cl4–Zn2–O10  | 99.7(5)      |
| Zn2–O1   | 2.273(16)    | Cl4–Zn2–O13  | 98.3(5)      | Cl4–Zn2–O6   | 176.3(5)     |
| Zn2–O4   | 2.146(16)    | O1–Zn2–O4    | 71.6(4)      | O1–Zn2–O7    | 144.6(5)     |
| Zn2–O7   | 2.217(16)    | O1–Zn2–O10   | 142.0(5)     | O1–Zn2–O13   | 71.7(6)      |
| Zn2–O10  | 2.228(16)    | O1–Zn2–O6    | 84.2(6)      | O4–Zn2–O7    | 73.0(6)      |
| Zn2–O13  | 2.131(16)    | O4–Zn2–O10   | 139.7(5)     | O4–Zn2–O13   | 139.4(6)     |
| Zn2–O6   | 2.255(16)    | O7–Zn2–O6    | 78.6(5)      | O7–Zn2–O10   | 71.0(4)      |
|          |              | O7–Zn2–O13   | 141.5(5)     | O7–Zn2–O6    | 89.4(6)      |
|          |              | O10–Zn2–O13  | 71.0(6)      | O10–Zn2–O6   | 83.6(4)      |
|          |              | O13–Zn2–O6   | 81.1(4)      |              |              |

## Results and Discussion

As indicated above, the reaction of  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  with 15-crown-5 in methanol gives rise to a polymer with the zinc atom that is outside the macrocyclic cavity [8]. At the same time, anhydrous or partially hydrated zinc chloride in aprotic organic solvents reacts with 15-crown-5 to form ionic compounds of two formulas  $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{L}]^{2+}[\text{Zn}_2\text{Cl}_6]^{2-}$  ( $\text{L} = \text{THF}, \text{CH}_3\text{CN}$ ) and  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{L}']_2^+[\text{Zn}_2\text{Cl}_6]^{2-}$  ( $\text{L}' = \text{H}_2\text{O}, \text{CH}_3\text{COCH}_3$ ). In cations of the two complexes that are closely related structurally, the zinc atom is located in the cavity of the macrocyclic ligand and coordinated by 5 atoms of oxygen and 2 ligands in terms of apical positions of the pentagonal bipyramid. It should be noted here that the first publications [12] reporting the existence of such a polyhedron in metal atoms were striking, at present there have been a large number of structurally characterized complexes of metal

TABLE 7. Main bond lengths and bond angles in the complex  $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$  (V)

| Bond    | $\alpha$ (Å) | Angle       | $\omega$ (°) |
|---------|--------------|-------------|--------------|
| Zn1—Cl1 | 2.198(2)     | Cl1—Zn1—Cl2 | 120.7(1)     |
| Zn1—Cl2 | 2.199(1)     | Cl1—Zn1—N   | 109.4(1)     |
| Zn1—N   | 2.046(3)     | Cl1—Zn1—N'  | 109.4(1)     |
| Zn1—N'  | 2.046(3)     | Cl2—Zn1—N   | 109.5(1)     |
| N—C1    | 1.119(5)     | Cl2—Zn1—N'  | 109.5(1)     |
| C1—C2   | 1.448(7)     | N—Zn1—N'    | 95.2(2)      |
|         |              | Zn1—N—C1    | 170.3(3)     |
|         |              | N—C1—C2     | 178.9(5)     |

chlorides (Al [13,14]; Cu [12]; Mg [3]; Fe(III) [15]; Co [16]; Zr(IV) [17]; Sn(IV) [18]) and crown-ethers, in which the same coordination number equal to 7 occurs. In our opinion these examples provide convincing support for the assumption that the coordination of the metal atom is forced by a rather rigid structure of the macrocyclic ligand. All the salts that have a metal atom capable of coordinating octahedrally, as a minimum, are probably expected to form complexes that have a polyhedron as a penta-

gonal bipyramid. Really, beryllium salts which are largely characterized by their tetrahedral surroundings interact with CE, following the other pattern [2].

The zinc atom is fully deprived of chloride ligands in the cations of **I** and **II**. The geometrical parameters of the coordination polyhedron in **II** are close to the ideal values (Fig. 1, Table 5) (the structure of **I** has not been clearly understood and, hence, is not discussed here). The angle N1—Zn—N2 is 175.1°, the angles O—Zn—O(av) and O—Zn—N(av) are 72.2° and 89.9°, respectively. The Zn atom is displaced from the cavity center towards the O7 and O7' atoms. As a consequence, the Zn—O1 bond is maximally enlarged to 2.24 Å, while the Zn—O7 bond is shortened to 2.15 Å ( $r(\text{Zn—O})_{\text{av}} = 2.19$  Å) and close to the sum of the ionic radii of these atoms (2.14 Å). Inequivalence of the M ← O bond lengths seems to be a characteristic feature of intracavity complexes with 15-crown-5, wherein the macrocycle has the conformation that corresponds to the  $C_s$  symmetry. This conformation is characterized by a mirror symmetry plane passing through just the oxygen atom

TABLE 8. Geometrical parameters of the macrocycle in the complex  $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{CH}_3\text{CN}]_2[\text{Zn}_2\text{Cl}_6]$  (II)

| Group of atoms<br>1—2—3—4 | Bond length<br>(Å) 1—2 | Bond angle<br>(°) 1—2—3 | Torsion angle<br>(°) 1—2—3—4 |
|---------------------------|------------------------|-------------------------|------------------------------|
| C2'—O1—C2—C3              | 1.461(12)              | 112.9(1.0)              | 176.6                        |
| O1—C2—C3—O4               | 1.461(12)              | 104.0(8)                | −55.4                        |
| C2—C3—O4—O5               | 1.506(16)              | 107.2(9)                | 179.7                        |
| C3—O4—C5—C6               | 1.387(14)              | 114.8(1.0)              | 179.2                        |
| O4—C5—C6—O7               | 1.434(17)              | 106.7(1.4)              | 43.5                         |
| C5—C6—O7—C8               | 1.456(26)              | 111.4(1.4)              | 155.5                        |
| C6—O7—C8—C8'              | 1.398(17)              | 121.0(1.3)              | 174.0                        |
| O7—C8—C8'—O7'             | 1.362(16)              | 113.0(8)                | 0.0                          |
| C8—C8'—O7'—C6'            | 1.465(35)              | 113.0(8)                | −174.0                       |

TABLE 9. Geometrical parameters of the macrocycle in the complex  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{C}_3\text{H}_6\text{O}]_2[\text{Zn}_2\text{Cl}_6]$  (IV)

| Group of atoms<br>1—2—3—4 | Bond length<br>(Å) 1—2 | Bond angle<br>(°) 1—2—3 | Torsion angle<br>(°) 1—2—3—4 |
|---------------------------|------------------------|-------------------------|------------------------------|
| O1—C2—C3—O4               | 1.402(36)              | 106.3(2.5)              | 56.6                         |
| C2—C3—O4—C5               | 1.489(50)              | 104.6(2.1)              | 177.6                        |
| C3—O4—C5—C6               | 1.423(29)              | 112.9(1.9)              | −170.0                       |
| O4—C5—C6—O7               | 1.365(33)              | 110.4(2.1)              | −53.7                        |
| C5—C6—O7—C8               | 1.527(37)              | 99.7(1.9)               | 168.9                        |
| C6—O7—C8—C9               | 1.535(32)              | 115.2(1.8)              | 179.4                        |
| O7—C8—C9—O10              | 1.463(30)              | 108.9(2.2)              | 49.7                         |
| C8—C9—O10—C11             | 1.425(41)              | 107.2(2.3)              | 166.0                        |
| C9—O10—C11—C12            | 1.398(38)              | 120.7(2.2)              | 171.0                        |
| O10—C11—C12—O13           | 1.399(40)              | 111.2(2.6)              | 2.1                          |
| C11—C12—O13—C14           | 1.368(47)              | 118.7(2.8)              | −172.7                       |
| C12—O13—C14—C15           | 1.367(38)              | 119.3(2.2)              | −164.6                       |
| O13—C14—C15—O1            | 1.405(35)              | 106.3(2.3)              | −53.0                        |
| C14—C15—O1—O2             | 1.477(40)              | 107.7(2.1)              | 173.9                        |
| C15—O1—O2—C3              | 1.380(31)              | 114.4(2.2)              | −172.5                       |

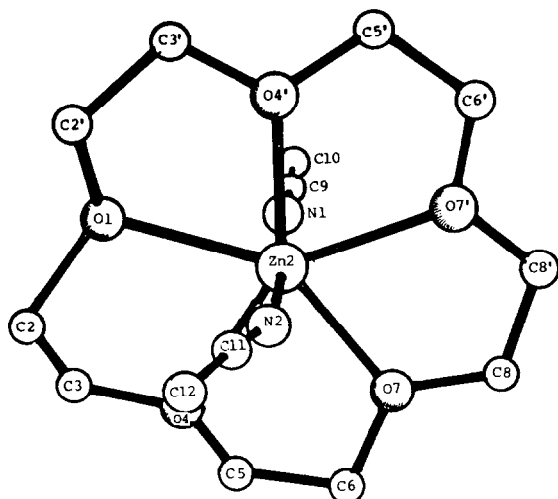


Fig. 1. The structure of the cation  $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{CH}_3\text{CN}]^{2+}$  in the complex  $[\text{Zn} \cdot 15\text{-crown-5} \cdot 2\text{CH}_3\text{CN}]^{2+}[\text{Zn}_2\text{Cl}_6]^{2-} \cdot \text{CH}_3\text{CN}$  (II). (The H atoms of the crown-ether molecules are omitted for clarity in this and all following Figures.)

O1 and the middle point of the C8—C8' bond perpendicularly to the root-mean-square plane of the macrocycle. Accordingly, some torsion angles have values different from standard energetically beneficial ones, producing a more strained cycle as compared to the non-symmetric ( $C_1$ ) conformations observed in **III** (Fig. 2) and **IV** (Table 8) [10].

The arrangement of oxygen atoms in the macrocycle of **IV** is close to a planar one; the maximal deviation from the root-mean-square plane is ob-

served for the atom O1 and accounts for 0.15 Å. The average distances C—C and C—O and angles OCC and COC are 1.41 and 1.48 Å and 108.5 and 116.9°, respectively. These slightly differ from those found in the complexes having the composition  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{L}']_2[\text{Zn}_2\text{Cl}_6]$  and a strainless  $C_1$  conformation (the respective parameters for **II** being 1.35 and 1.51 Å, 109.2 and 115.5°; for **IV**, 1.41 and 1.46 Å, 108.1 and 116.5°). Due to unequal apical ligands and differences in the nature of the M—L bond, the metal atom was found somewhat off the root-mean-square plane of the macrocycle towards an acceptor atom of chlorine. The second apical position in the pentagonal bipyramid is occupied by a water molecule (**III**) or acetone (**IV**). Here, the angles Cl—Zn—O in the two molecules are approximately equal (176°). The Zn—O bond lengths in both complex cations are also nearly equal (**III**, 2.30 Å and **IV**, 2.27 Å), whereas the Zn—O(L') distances substantially differ (**III**, 2.08 Å and **IV**, 2.26 Å), which is most likely to be associated with the steric hindrance arising from the coordination between the metal atom and acetone molecule (Fig. 3). On the whole, the Zn—Cl and Zn—O(L') distances are much greater than those observed in the molecules with tetrahedral coordinations of the Zn atom. For example, these are 2.20 and 2.00 Å, respectively, in the complex  $\text{ZnCl}_2 \cdot 15\text{-crown-5} \cdot 2\text{H}_2\text{O}$  [8]. All the Zn—O(CE) distances in the two complexes are equivalent ( $r(\text{Zn—O(CE)})_{\text{av}} = 2.20$  Å).

In addition to the donor—acceptor bond, the water molecule in the cationic moiety of **III** forms hydrogen bonds to the chlorine atoms of the second

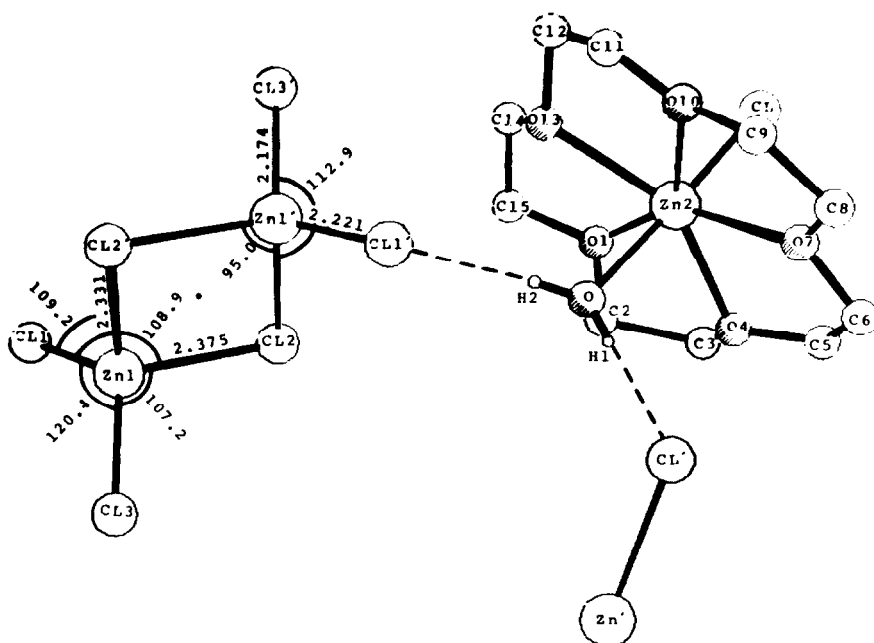


Fig. 2. The structure of the complex salt  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{H}_2\text{O}]_2^{2+}[\text{Zn}_2\text{Cl}_6]^{2-}$  (III).

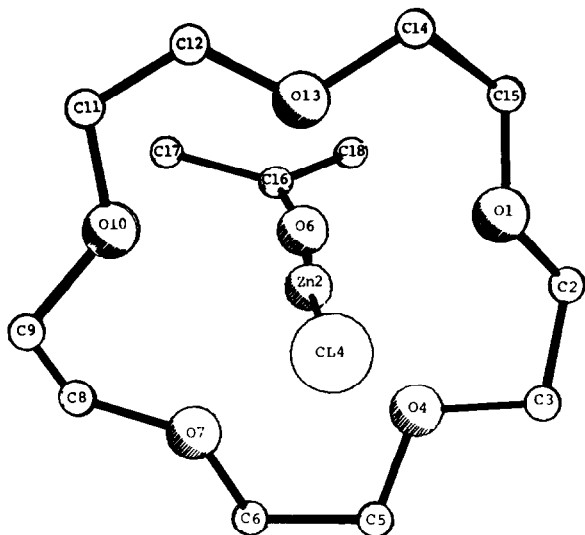


Fig. 3. The structure of the cation  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{CH}_3\text{COCH}_3]^+$  in the complex salt  $[\text{ZnCl} \cdot 15\text{-crown-5} \cdot \text{CH}_3\text{COCH}_3]_2^+[\text{Zn}_2\text{Cl}_6]^{2-}$  (IV).

cation ( $\text{O}-\text{H}(1)-\text{Cl}'$ , 3.13 Å) and anion ( $\text{O}-\text{H}(2)-\text{Cl}(1)'$ , 3.23 Å), the bond angles being 162.4 and 168.1°, respectively.

The complex anions  $[\text{Zn}_2\text{Cl}_6]^{2-}$  do not seem to be common in the chemistry of zinc coordination compounds. In any case, we are aware of only two structures involving the anion, i.e.  $[(\text{C}_5\text{H}_5)_2\text{Ti} \cdot \text{DME}]_2[\text{Zn}_2\text{Cl}_6]$  [19] and  $[\text{V}_2(\mu\text{-Cl})_3 \cdot \text{THF}_6]_2[\text{Zn}_2\text{Cl}_6]$  [20]. The anion  $[\text{Zn}_2\text{Cl}_6]$  represents the centrally symmetric system consisting of two tetrahedral

anions that are linked with two bridging chlorine atoms. The structural parameters of the anions are practically identical in all compounds. The slightly more elongated  $\text{Zn}(1)-\text{Cl}_{\text{term}}$  distance (2.22 Å) in **III**, as compared to the terminal  $\text{Zn}-\text{Cl}$  bonds (c. 2.17 Å) in other complexes, results from the hydrogen bonding  $\text{O}-\text{H}(1)-\text{Cl}(1)'$ .

The situation is basically different when zinc chlorides interact with 18-crown-6 in aprotic solvents. For example, anhydrous zinc chloride fails to react with 18-crown-6 in tetrahydrofuran and acetonitrile; the solutions afford the typical solvates  $\text{ZnCl}_2 \cdot 2\text{L}$ . The structure of the molecular complex  $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$  is shown in Fig. 4. As in all other complexes of metal(II) halides, the Zn atom has tetrahedral surroundings. The bond lengths and bond angles in **V** are common (Table 7). The molecule has a mirror symmetry plane passing through the Zn, Cl(1) and Cl(2) atoms. At the same time partially hydrated zinc chloride  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  in THF reacts with 18-crown-6 to give a molecular, rather than ionic, complex (Fig. 5) [11]. The Zn atom in **VII** is 2.14 Å up to root-mean-square plane passing through the polyether oxygen atoms and linked with one of them via the donor-acceptor  $\text{Zn} \leftarrow \text{O}$  bond (2.08 Å). Another two coordination sites at the Zn atom are occupied by two chlorine atoms ( $r(\text{Zn}-\text{Cl})_{\text{av}} = 2.21$  Å), whereas the fourth site is occupied by the oxygen atom of the water molecule ( $r(\text{Zn}-\text{O}_{\text{w}}) = 1.97$  Å), thus completing the tetrahedral surroundings of the metal atom. In this case the two hydrogen atoms of the water molecule are involved in the hydrogen bonding  $\text{O}(\text{H}_2\text{O})-\text{H} \cdots \text{O}(\text{CE})$  with atoms O7 and

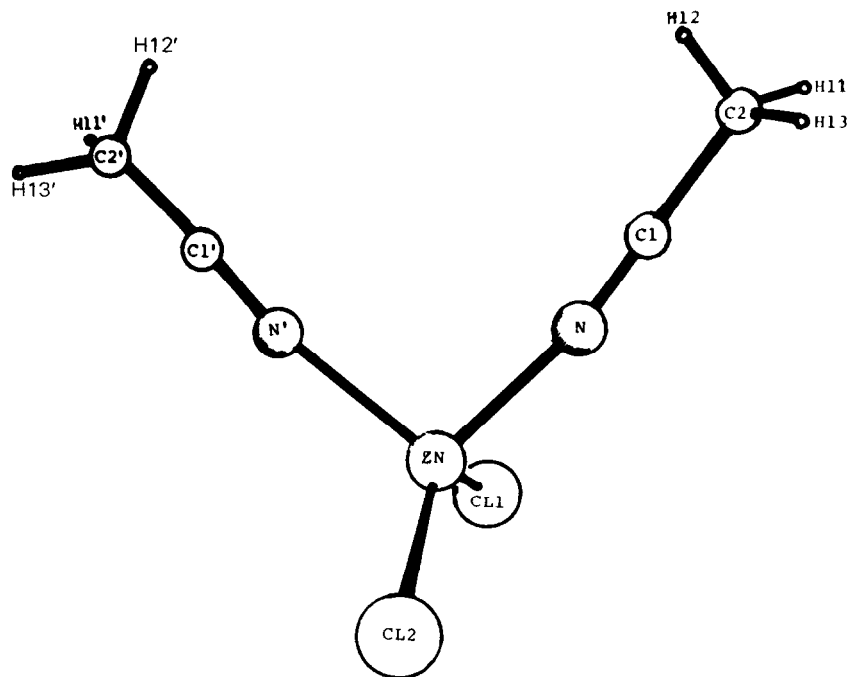


Fig. 4. Molecular structure of the complex  $\text{ZnCl}_2 \cdot 2\text{CH}_3\text{CN}$  (VI).

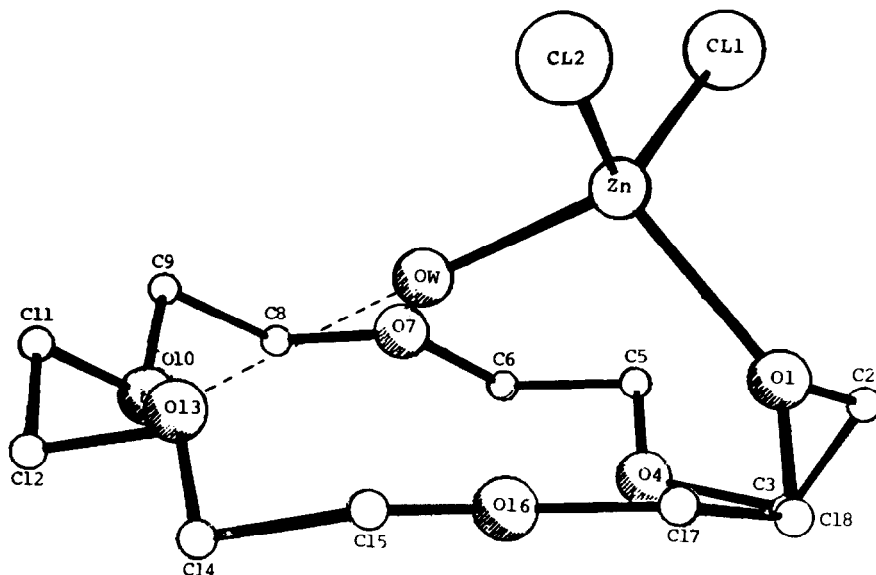


Fig. 5. Molecular structure of the complex  $\text{ZnCl}_2 \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$  (VII).

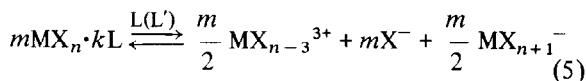
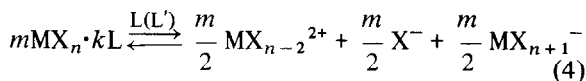
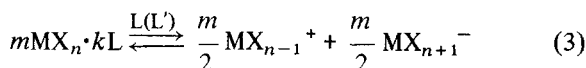
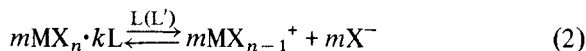
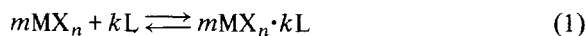
O13. The lengths of these bonds are approximately equal and account for 2.77 Å, i.e. they are identical to those found in the complex  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \cdot 15\text{-crown-5}$  [8]. While the angles  $\text{O}_w\text{—H1—O13}$  and  $\text{O}_w\text{—H2—O7}$  in VII are significantly different and equal to 172 and 145°, respectively, which is well accountable for by a larger size of 18-crown-6 over 15-crown-5 and by a basically different coordination pattern of the Zn atom in VII, as compared to the complex  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \cdot 15\text{-crown-5}$ . In fact, the Zn atom in the latter compound is not involved in the donor–acceptor bonding together with the molecule of crown-ether but is directly related to it.

The conformation of the macrocycle in VII is close to the optimal one, except for the O1–C2–C3–O4 moiety, whose oxygen atom (O1) coordinates the Zn atom. The mean values for the bond lengths C–C (1.48 Å) and C–O (1.42 Å) and for bond angles COC (113.0°) and OCC (116.0°) are practically the same as those found in other complexes of 18-crown-6 with metal halides, (e.g.  $[\text{FeCl}(\text{18-crown-6})_2]^{2+}[\text{FeCl}_4]_2^-$ ) [21].

Thus, the findings on the complexation of 18-crown-6 with anhydrous  $\text{ZnCl}_2$  and hydrate  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  in THF in general support the conclusion [14] that this polyether is a less strong base than 15-crown-5, on the one hand, and THF ( $DN = 20.0$ ;  $\epsilon = 7.6$  [7]) and  $\text{H}_2\text{O}$  ( $DN = 18.0$ ;  $\epsilon = 81.0$  [7]), on the other. Since 18-crown-6 cannot replace the weaker donor  $\text{CH}_3\text{CN}$  ( $DN = 14.0$ ;  $\epsilon = 38.0$  [7]) but, nevertheless, expels water from the coordination sphere of the Zn atom only when it reacts with  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$  in ether ( $DN = 19.2$ ;  $\epsilon = 4.3$  [7]) or acetone ( $DN = 17.0$ ;  $\epsilon = 20.7$  [7]) to form the complex  $2\text{ZnCl}_2 \cdot 18\text{-crown-6}$ , the attempts to explain the experimental findings, in terms of differ-

ences in the basicity and dielectric constants of the solvent and 18-crown-6 of metal ions, appear to be obviously superficial.

The data available in the literature on the complexation of the Lewis acids with macrocyclic polyethers in aprotic organic solvents give good evidence of the conclusion that the intracavity complexes form only the anhydrous or partially hydrated salts that are able to ionize and autocomplex in the chosen solvent (eqns. (2)–(4)). Unfortunately, at present limited quantitative data on the ionization of various salts in these solvents do not provide unambiguous support for this assumption and substantiating the rules for selecting ‘solvent–crown’ pairs suitable for direct synthesis of the intracavity complexes. Nevertheless, it can be seen that with 18-crown-6, the sufficiently ionic complex  $\text{CoCl}_2$  ( $r(\text{Co}^{2+}) = 0.74$  Å) even in acetonitrile gives an intracavity complex (eqn. (4)) ( $r_{\text{cav.}} = 1.74$  Å) [22] with the following composition  $[\text{Co} \cdot 18\text{-crown-6} \cdot \text{CH}_3\text{CN}]^{2+}[\text{CoCl}_4]^{2-}$  [16].



etc.



Although the complexes of  $\text{MgCl}_2$  ( $r(\text{Mg}^{2+}) = 0.65$  Å) [3] and  $\text{HgI}_2$  ( $r(\text{Hg}^{2+}) = 1.10$  Å) [4] with 18-crown-6 crystallize from solutions as molecular compounds, there is no doubt, however, that their formation also occurs via ionization of the M–X bond (eqn. (2)). In fact, all non-dissociative mechanisms (incorporation of the linear chain  $^{-\delta}\text{X}-\text{M}-\text{X}^{+\delta}$  into the negatively charged cavity by the thread-needle principle or cleavage of the ring at the C–O bond, capture of the  $\text{MX}_2$  molecules and reclosure of the ring) seem to be fabulous and artificially devised. In contrast, the step of the M–X bond ionization looks very natural and enables the reasons for forming all the intracavity complexes of crown-ethers (the ‘head ( $\text{X}^-$ ) to tail ( $\text{MX}^+$ )’ mechanism) to be explained.

Zinc chloride ( $r(\text{Zn}^{2+}) = 0.74$  Å) in the series of these compounds is most covalent and, in terms of compound compositions isolated from THF and  $\text{CH}_3\text{CN}$ , exists chiefly as molecular complexes (eqn. (1)) of  $\text{ZnCl}_2 \cdot 2\text{L}$  in organic solvents. Putting a more basic ligand than L, for example, 15-crown-5, into the system  $\text{ZnCl}_2-\text{L}$  shifts the equilibria 2–4 to the right and gives rise to ionic intracavity complexes. Less basic 18-crown-6 does not increase the ionization of the salt and is not reactive towards  $\text{ZnCl}_2$  under homogenous conditions ( $\text{CH}_3\text{CN}$ ; THF). Similar considerations but with some allowance may be used for explaining the absence of interactions in the systems  $\text{BeCl}_2-\text{THF}-15\text{-crown-5}$  (18-crown-6) [1],  $\text{AlCl}_3-\text{THF}-18\text{-crown-6}$  [14], etc.

Virtually all the metal halides soluble in diethyl ether, including  $\text{ZnCl}_2$ , react with 18-crown-6. This, however, seems to be accounted for by highly low solubility of the products that instantly crystallize as microcrystalline powders when the first portions of crown-ether solution are added. The structure of these products has not been established, but their negligible solubility in  $\text{Et}_2\text{O}$  suggests that they might be of ionic or polymeric nature.

It is evident that if the basic properties of macrocyclic unsubstituted polyethers decrease with a greater number of oxygen atoms, the reactions with anhydrous metal halides in aprotic solvating solvents to yield intracavity complexes (via the ionic mechanism) either will not take place in general or will occur only when there are sufficiently greater numbers of units ( $-\text{OCCO}-$ ) that will cause substantial conformational changes in the molecule of the macrocycle (e.g. through coordination of the metal atom with five oxygen atoms in the macrocycle) without great expenditure of energy.

The structure and composition of the reaction products of CE and fully hydrated molecular complexes of metal halides  $\text{MX}_n \cdot k\text{H}_2\text{O}$  that are soluble in protic organic solvents seem to be rather clear. The data available in the literature indicate that the molecular compounds, whose macrocycle molecule

is in the second coordination sphere and the linkage between the metal atom and ligand is accomplished via the hydrogen bridges  $\text{O}_w-\text{H}\cdots\text{O}(\text{CE})$ , are predominantly formed ( $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} \cdot 15\text{-crown-5}$  [8],  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O} \cdot 15\text{-crown-5}$  [23],  $\text{SnMe}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O} \cdot 18\text{-crown-6}$  [24]). A similar bonding is likely to be common for all compounds of CE and metal salts solvated with proton-containing ligands such as  $\text{TiCl}_3\text{OEt} \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot (18\text{-crown-6})_2$  [25]. It is very difficult to say what structure and composition the products of CE and fully or partially hydrated metal salts will have when involved in aprotic organic solvents. Here, both molecular and ionic complexes may be expected to be formed depending on the nature of metal halides, basicity of crown-ether and the nature of the solvent.

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