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Structural-chemical aspects of complexation in metal halide – macrocyclic polyether systems

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Abstract. The review surveys data on over 200 crystal and molecular structures of metal halide complexes with oxygen-containing crown ethers. The major types of the complexes are distinguished. The characteristic features of formation of these complexes and their coordination fragments are discussed. The bibliography includes 143 references.

I. Introduction

Structural aspects of the chemistry of macrocyclic polyether complexes with metal salts have been discussed in several reviews and monographs (see, for example, Refs 1 – 3). These data were most completely surveyed in the monograph[2] containing a bibliography up to 1989. In succeeding years, a large number of publications have been devoted to structural studies of crown compounds with metal halides prepared from organic media, including those devoid of water molecules, along with studies of salts of alkali and alkaline-earth metals (which comprise the major body of structural data throughout the period of studies of these compounds). The results obtained confirmed on the whole the existence of several structural types of crown complexes, which were suggested for the first time by Dalley[4] and more recently by Poonia.[5] The first group comprises complexes in which all the oxygen atoms of the crown ether (CE) molecule are coordinated to the metal atom, which is located within or outside the CE cavity (type A). The second group includes complexes in which only some of the oxygen atoms are involved in the coordination sphere of the metal atom (type B). The third group contains complexes in which the metal atom is located outside the cavity of the crown ether and is not directly bound to the oxygen atoms of the CE molecule (type C). Finally, complexes of the 'half-sandwich' type in which the metal atom deviates substantially from the mean plane through the oxygen atoms of the CE molecule (type D) are documented.

The structural classification of crown compounds has been based on CE as such.[2,3] At that time, this was quite reasonable because the data on structurally characterised crown ethers were scarce in the literature. Presently, it seems difficult to use this classification. In the present review, we consider structural features and compositions of crown compounds with metals in the order of increasing atomic numbers. We deliberately exclude CE complexes with sodium halides and with halides of the heaviest alkali metals from consideration since their structures are rather trivial and have been reported many times.

II. Systems with halides of the first-row elements

1. Lithium halides

The reaction of anhydrous lithium chloride with 12-crown-4 (12C4) afforded a molecular complex with composition $[(LiCl)\cdot(12C4)]$ (**1**).[6] The lithium atom is coordinated by the chlorine atom (Li – Cl = 2.290 Å) and four oxygen atoms (Li – O = 2.128 Å) and deviates from the mean plane through the oxygen atoms by 0.929 Å (Fig. 1).

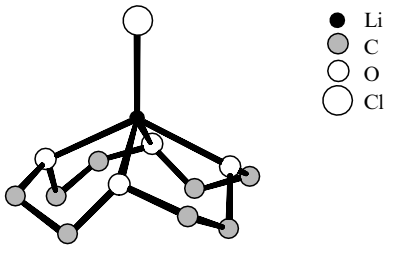


Figure 1. Structure of the complex **1**.

The reaction of lithium chloride dihydrate with 18-crown-6 (18C6) in dry diethyl ether gave a molecular binuclear complex with composition $[(H_2O)_2\cdot(LiCl)_2\cdot(18C6)]$ (**2**).[7] Therefore, the CE molecule with a large inner cavity serves as a 'host' simultaneously for two lithium atoms. The coordination environment about each lithium atom is a strongly distorted tetrahedron formed by two oxygen atoms of the polyether, one oxygen atom of the water molecule and one chlorine atom. This coordination

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results in small five-membered rings with the following distances: $Li-O_{cr}$ = 1.980 and 2.065 Å, $Li-O_w$ = 1.865 Å and Li–Cl = 2.277 Å (Fig. 2). The five-membered metallocycles in complex **2** adopt an envelope conformation.

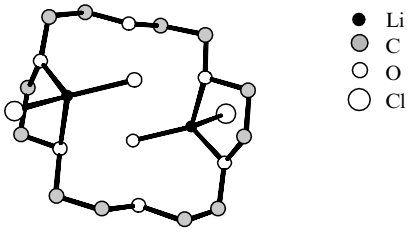


Figure 2. Structure of the complex **2**.

By contrast, this reaction in a typical solvent, which have not been dehydrated,[8] gave structurally different ionic complexes with compositions $\{[(Li)_2\cdot(H_2O)_4\cdot(18C6)]^{2+} + 2X^-\}$, where X = Cl (**3**) or Br (**4**), with a unique structure. In these compounds, two lithium atoms are also 'guests' but they are arranged nonsymmetrically with respect to the centre of the CE molecule. Both cations have a trigonal-bipyramidal environment (Fig. 3), one of them being coordinated by three oxygen atoms of the ether molecule and two oxygen atoms of water molecules, while the second cation, on the contrary, being coordinated by two oxygen atoms of the ether molecule and three oxygen atoms of water molecules. The bipyramids are linked to each other through a shared vertex formed by the bridging oxygen atoms. The $Li-O_{cr}$ bond lengths vary from 1.88 to 2.12 Å and the $Li-O_w$ bond lengths are in the range 1.90 to 2.00 Å. In the crystal structure, an extensive three-dimensional network of OH···O and OH···X intermolecular hydrogen bonds exists.

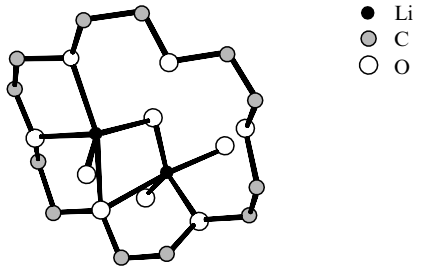


Figure 3. Structure of the cation in the complex **3**.

2. Beryllium chloride

Only one complex of $BeCl_2$ with crown ethers, *viz*., $[(BeCl_2)\cdot(15C5)]$ (**5**), which was prepared by the reaction of anhydrous beryllium chloride with the polyether in anhydrous diethyl ether, was structurally characterised.[9] In this complex, the beryllium atom retains the typical tetrahedral coordination formed by two oxygen atoms of the crown ether molecule ($Be-O_{cr}$ = 1.64 and 1.73 Å) and two chlorine atoms (Be–Cl = 1.88 and 2.0 Å) (Fig. 4). Therefore, complex **5** is a typical representative of type B compounds. The bond angles in the O_2BeCl_2 tetrahedron vary from 90 to 118 °, which is associated with steric hindrances due to coordination of two closely arranged oxygen atoms of the polyether.

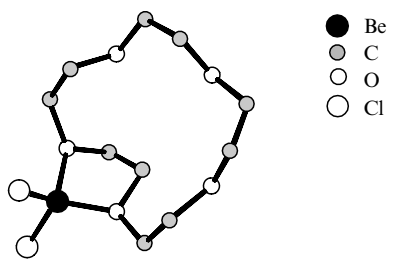


Figure 4. Structure of the complex **5**.

3. Boron trifluoride

Presently, two complexes of BF_3 with 18C6, which have been prepared by the reaction of boron trifluoride etherate with the polyether, are known, *viz*., the complex with composition $\{[(BF_3)\cdot(OH_2)] + (18C6)\}$ (**6**) solvated with toluene[10] and the complex $\{2[(BF_3)\cdot(H_2O)] + (18C6) + (H_2O)_2\}$ (**7**) obtained when BF_3 and CE were taken in a 2 : 1 ratio.[11] Both compounds belong to type C complexes because the tetrahedral boron-containing fragments interact with the CE molecule through hydrogen bonds between the coordinated water molecules and the oxygen atoms of the crown ether molecule. In structure **6**, only two oxygen atoms of the ether molecule are involved in 'guest – host' interactions, while in structure **7** all six oxygen atoms of the ether molecule participate in these interactions.

The reaction of the complex $BF_3\cdot Et_2O$ with dicyclohexyl-18-crown-6 (DCHex18C6) in the presence of atmospheric moisture[11] afforded a product with composition $\{[(BF_3)\cdot(H_2O)_2] + (DCHex18C6)\}$ with intramolecular H-bonds analogous to those observed in structure **7**.

III. Systems with halides of the second-row elements

1. Magnesium chlorides

In the compound $\{[(Mg)\cdot(H_2O)_6]^{2+} + (12C4) + 2Cl^-\}$ (**8**) (Fig. 5), which was prepared by the reaction of $MgCl_2\cdot 6H_2O$ with 12C4, the metal atom is not involved in direct bonding with the oxygen atoms of the CE molecule.[12] Hence, this complex should be assigned to type C. In the crystal structure of **8**, the $[(Mg)\cdot(H_2O)_6]$ octahedra, the CE molecules and the chloride ions are linked to each other through a complex system of OH···O and OH···Cl hydrogen bonds. The $Mg-O_w$ distances in the cation vary from 2.052 to 2.082 Å.

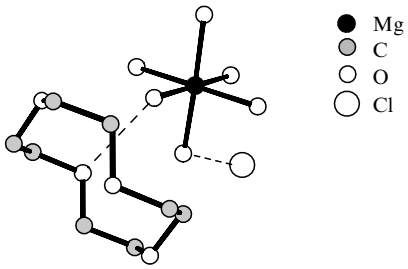


Figure 5. Structure of the complex **8**.

The reactions of slightly hydrated magnesium chloride with 15C5 in acetonitrile or chloroform gave related compounds with compositions $\{[(H_2O)\cdot(MgCl)\cdot(15C5)]^+ + Cl^-\}\cdot(L)$, where L = CH_3CN (**9**) or $CHCl_3$ (**10**), respectively. The magnesium atom is located in the cavity of the CE molecule (type A complex) and has a pentagonal-bipyramidal coordination.[13] Five oxygen atoms of the crown ether molecule occupy the equatorial plane of the polyhedron ($Mg-O_{cr}$ = 2.11 – 2.23 Å). The water molecules ($Mg-O_w$ = 2.05 and 2.06 Å) and the chlorine atoms (Mg–Cl = 2.42 and 2.44 Å) are located in the apical positions (Fig. 6). The coordinated water molecule forms intermolecular hydrogen bonds with the chloride ions ($OH\cdots Cl^-$ = 3.10 – 3.11 Å).

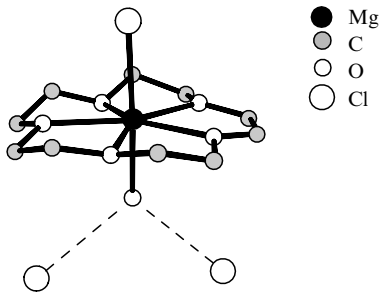


Figure 6. Structure of the complex **9**.

In the case of complete hydration of the above-described complexes, which is achieved by keeping these complexes in an atmosphere with 100% humidity,[14] the apical chlorine atom is replaced by the second water molecule and the composition of the complex corresponds to the formula $\{[(Mg)\cdot(H_2O)_2\cdot(15C5)]^{2+} + 2Cl^- + (H_2O)\}$ (**11**). The $Mg-O_{cr}$ distances vary from 2.086 to 2.225 Å and $Mg-O_w$ = 2.045 Å. In this crystal, the system of $O_wH\cdots O_w$ and $OH\cdots Cl$ hydrogen bonds is more complex than those observed in crystals of **9** and **10**.

The reaction of anhydrous magnesium chloride with 18C6 in anhydrous tetrahydrofuran[15] afforded a molecular complex $[(MgCl_2)\cdot(18C6)]$ (**12**) (Fig. 7). The coordination polyhedron

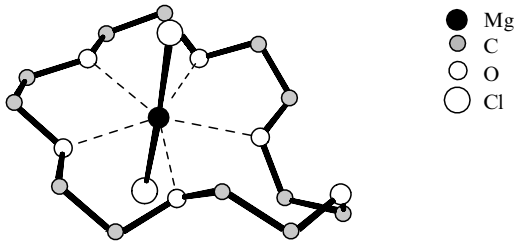


Figure 7. Structure of the complex **12**.

about the magnesium atom is a pentagonal pyramid. The coordination number of the Mg atom is 7, which is very untypical of this metal. The Mg–O distances in complex **12** vary from 2.220 to 2.331 Å. The CE molecule also adopts an unusual conformation due to coordination of the metal atom by only five out of the six oxygen atoms. The magnesium atom has analogous coordination in the complex $\{[(MgCl_2)\cdot(18C6)]\cdot(HCl)_2\}$ (**13**) (Fig. 8),[16] which was prepared by the reaction of $MgCl_2$ with the clathrate of composition $\{[(H_3O)\cdot(18C6)]^+ + [HCl_2]^-\}$. This complex is considered[16] as a purely ionic compound with composition $\{[(Mg)\cdot(18C6)]^{2+} + 2[HCl_2]^-\}$. However, the Mg–Cl distances in **13** (2.428 and 2.454 Å) and in **12** (2.429 Å) are close to the sum of the covalent radii of both elements and, in our opinion, it is more reasonable to describe both compounds as molecular complexes.

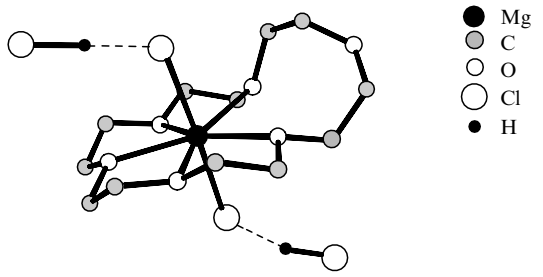


Figure 8. Structure of the complex **13**.

2. Aluminium chloride

A complex with composition $\{[(AlCl_2)\cdot(15C5)]^+ + [AlCl_4]^-\}$ (**14**) was produced by the reaction of anhydrous $AlCl_3$ with 15C5 in anhydrous ether.[17] The coordination number of the aluminium atom in the cation is 7. The coordination polyhedron about the metal atom is a pentagonal bipyramid with the oxygen atoms of the crown ether molecule in the equatorial plane and the chlorine atoms in the axial positions. This type of the polyhedron and the coordination number are untypical of aluminium compounds. The Al–O distances vary from 2.081 to 2.142 Å and the Al–Cl distances are 2.188 and 2.210 Å. The statistically disordered crown ether molecule in **14** is located on the mirror plane (Fig. 9). The complex of $AlEtCl_2$ with benzo-15-crown-5 (**15**) has an analogous structure.[18]

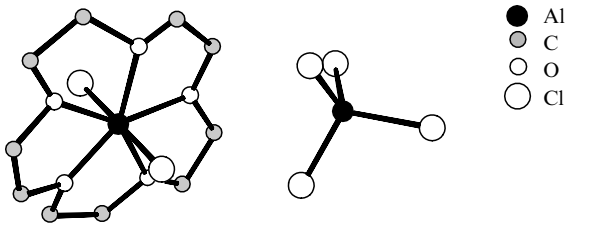


Figure 9. Structure of the complex **14**.

Complete hydration of complex **14** gave a compound with composition $\{[(Al)\cdot(H_2O)_6]^{3+} + (15C5) + 3Cl^- + (H_2O)_4\}$ (**16**)[7] in which the metal atom is not coordinated by the oxygen atoms of the crown ether molecule and the individual structural units are linked to each other through a complex network of $OH\cdots O$ and $OH\cdots Cl$ hydrogen bonds.

3. Silicon tetrafluoride

The only silicon-containing complex with CE known to date was prepared by the reaction of SiF_4 with 18C6.[19] The compound has the composition $\{[(SiF_4)\cdot(H_2O)_2] + (18C6) + (H_2O)_2\}$ (**17**) and belongs to type C complexes. The silicon atom is in an octahedral environment. The isolated structural fragments are linked to each other through intermolecular $OH\cdots O$ hydrogen bonds with the participation of water and CE molecules.

IV. Systems with halides of the third-row elements

1. Calcium chloride

The reaction of crown ether 12C4 with an aqueous solution of calcium chloride afforded a compound with composition $\{[(Ca)\cdot(12C4)\cdot(H_2O)_4]^{2+} + 2Cl^- + (H_2O)_2\}$ (**18**).[20] The calcium atom is located above the mean plane of the macrocycle and is coordinated by all the four oxygen atoms of CE and the four water molecules (Fig. 10). The Ca–O distances vary from 2.380 to

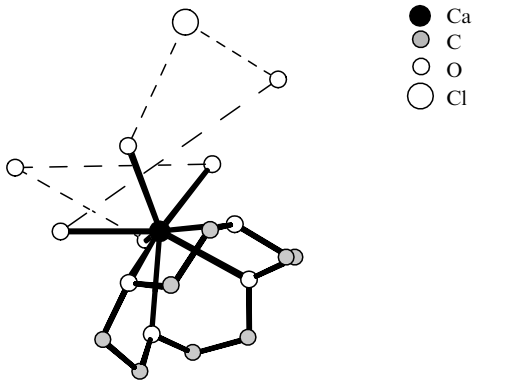


Figure 10. Structure of the complex **18**.

2.540 Å. In the crystal structure of **18**, a complex network of OH···O and OH···Cl intermolecular hydrogen bonds with the participation of all water molecules is realised.

The reaction of molten $CaCl_2$ with 18C6 in acetone yielded [7] a complex with composition $\{[(Ca)\cdot(18C6)\cdot(H_2O)_2]^{2+} + 2Cl^- + (H_2O)_2\}$ (**19**), which is a typical representative of type A crown compounds. The calcium atom is located exactly in the centre of the cavity of the CE molecule ($Ca-O_{cr} = 2.555-2.604$ Å) and is additionally coordinated by two water molecules ($Ca-O_w = 2.29$ Å) which are located above and below the mean plane of the macrocycle.

2. Scandium chloride

Data on homometallic complexes of scandium halides with CE molecules are unavailable in the literature. The structures of heterometallic halides have been studied.[21–23] These complexes were prepared by the following reactions:

$$2ScCl_3 + CuCl_2 + 2\,15C5 \longrightarrow \{2[(ScCl_2)\cdot(15C5)]^+ + [CuCl_4]^{2-}\}, \quad \mathbf{20}$$

$$ScCl_3 + SbCl_5 + 18C6 \longrightarrow \{[(ScCl_2)\cdot(18C6)]^+ + [SbCl_6]^-\}, \quad \mathbf{21}$$

$$ScCl_3 + SbCl_5 + DB24C8 \longrightarrow \{[(ScCl_2)\cdot(DB24C8)]^+ + [SbCl_6]^-\}, \quad \mathbf{22}$$

$$ScCl_3 + SbCl_5 + DB30C10 \longrightarrow \{[(ScCl_2)\cdot(DB30C10)]^+ + [SbCl_6]^-\}. \quad \mathbf{23}$$

In compounds **20**–**23**, the scandium atom is located in the centre of the cavity of the CE molecule and has a bipyramidal coordination. The Sc–O distances vary from 2.09 to 2.30 Å.

3. Titanium chlorides

The compositions and structures of complexes of $TiCl_4$ with various CE reflect the general tendency of interactions between metal halides in the highest oxidation states and polyethers, which is associated with destruction of the latter and the formation of various reactive oxygen-containing fragments.

Only one complex of $TiCl_4$ with 12C4, which was prepared by the reaction of a mixture of $TiCl_4$ and $SbCl_5$ in acetonitrile, was reported in the literature.[24] This reaction yielded a complex with composition $\{[(TiCl_3)\cdot(CH_3CN)_3]^+ + [SbCl_6]^-\}$ as an intermediate. Treatment of the latter with 12C4 in dichloromethane afforded a compound with composition $\{[(TiCl)_2(\mu_2\text{-}O)\cdot(12C4)]_2^{+} + [SbCl_6]^- + (CH_2Cl_2)\}$ (**24**). The bridging oxygen atoms in this structure occur apparently due to destruction of a portion of CE molecules. The structure of the Ti-containing fragment is shown in Fig. 11. The $Ti-O_\mu$ distances (1.81 and 1.82 Å) are intermediate between the length of the double bond in titanyl chloride and the coordination bond. The $Ti-O_{cr}$ distances vary from 2.12 to 2.38 Å, *i.e.*, these bonds are nonequivalent. The coordination number of the Ti atom is 7. The coordination polyhedron about the metal atom is a distorted pentagonal bipyramid with the oxygen and chlorine atoms in the apical positions.

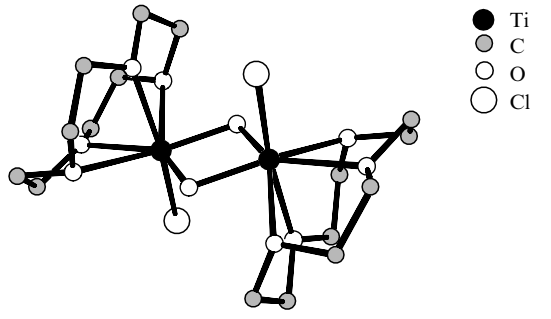


Figure 11. Structure of the $[(TiCl)(\mu_2\text{-}O)\cdot(12C4)]_2^+$ fragment in the complex **24**.

Apparently, analogous destruction of CE to form titanyl chloride as an intermediate occurs in the reaction of $TiCl_4$ with 15C5 in acetonitrile.[25] The resulting complex has the composition $[(TiCl)\cdot(15C5)\cdot(\mu_2\text{-}O)(TiCl_5)]$ (**25**) (Fig. 12). Unlike the above-described compound, the Ti–O distances in **25** are essentially nonequivalent (1.691 and 2.014 Å), which is indicative of the predominant formation of the Ti(1)–O double bond and the Ti(2)–O coordination interaction due to the lone electron pair of the bridging oxygen atom. The $Ti-O_{cr}$ distances vary from 2.073 to 2.140 Å. The coordination polyhedra about the Ti(1) and Ti(2) atoms are a pentagonal bipyramid and a typical octahedron, respectively.

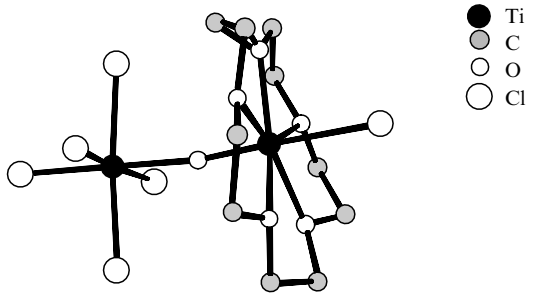


Figure 12. Structure of the complex **25**.

It was demonstrated [25] that destruction of CE is suppressed upon introduction of metal halides with readily ionisable M–X bonds which are not prone to autocomplexation. Thus the reaction of $TiCl_4$ with 15C5 in the presence of $MgCl_2$ in acetonitrile afforded the complex $\{[(Mg)\cdot(CH_3CN)_2\cdot(15C5)]^{2+} + [TiCl_6]^{2-}\}$ (**26**) in virtually quantitative yield. As in the compounds **9**–**11**, the magnesium atom in the complex **26** has a pentagonal-bipyramidal environment. The anion has a usual octahedral structure with the Ti–Cl distances varying from 2.324 to 2.354 Å. The reaction of $TiCl_3$ and $AlCl_3$ with 15C5 in tetrahydrofuran [25] gave a complex with composition $\{[(TiCl_2)\cdot(15C5)]^+ + [AlCl_4]^-\}$ (**27**). In **27**, the titanium atom is located in the centre of the cavity of the CE molecule. The Ti–O distances vary from 2.12 to 2.20 Å and Ti–Cl = 2.38 Å. The structure of the anion is analogous to that of the anion in the complex **14**.

According to the published data, the reaction of $TiCl_4$ with 18C6 did not lead to destruction of the CE molecule. Thus a distinct type B complex with composition $[(TiCl_4)\cdot(18C6)]$ (**28**) was prepared.[26] The coordination polyhedron about the titanium atom in this compound is an octahedron formed by four chlorine atoms and two oxygen atoms of the CE molecule (Ti–O = 2.125 and 2.145 Å). The CE molecule is strongly distorted (Fig. 13). The reaction of $TiCl_4$ with 18C6 in ethanol [27] afforded a type C

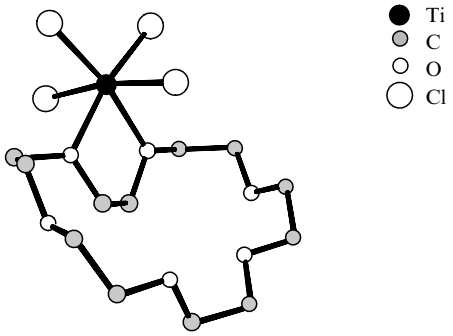


Figure 13. Structure of the complex **28**.

complex with composition $[(TiCl_3)\cdot(OC_2H_5)\cdot(C_2H_5OH)_2\cdot(18C6)_2]$ (**29**). The environment about the titanium atom is an octahedron (Fig. 14) formed by three chlorine atoms (Ti – Cl = 2.337 – 2.387 Å), the oxygen atom of the ethoxy group (Ti – O = 1.726 Å) and two coordinated ethanol molecules (Ti – O = 2.030 and 2.033 Å). The coordinated ethanol molecules interact with the macrocycle molecules through OH···O hydrogen bonds (2.63 and 2.64 Å).

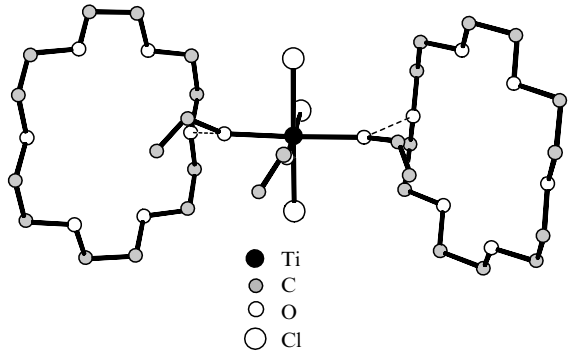


Figure 14. Structure of the complex **29**.

4. Vanadium chlorides

The reaction of VCl_4 with 15C5 in acetonitrile in the presence of water was accompanied by disproportionation of the halide to form a complex with composition $\{[(V^{III}Cl_2)\cdot(15C5)]^+ + [V^{V}OCl_4]^-\}$ (**30**).[28] The coordination polyhedron about the vanadium atom in the cation is a pentagonal bipyramid formed by the five oxygen atoms of the macrocycle (V – O = 2.08 – 2.11 Å) and the two apical chlorine atoms (V – Cl = 2.34 and 2.35 Å). The coordination environment about the vanadium atom in the anion is a tetragonal pyramid formed by four chlorine atoms (V – Cl = 2.23 – 2.26 Å) and one oxygen atom (V – O = 1.548 Å).

The structure of the complex prepared by the reaction of $VOCl_2$ with 18C6 in aqueous ethanol was reported [29, 30] to belong to type C and it is described by the formula $\{[(VOCl_2)\cdot(H_2O)_2] + [(18C6)\cdot(H_2O)]\}$ (**31**). The coordination polyhedron about the vanadium atom is a slightly distorted tetragonal pyramid (V – O = 1.573 Å, V – O_w = 1.964 and 2.024 Å and V – Cl = 2.215 and 2.362 Å). Both fragments of the structure are linked to each other through OH···O intermolecular hydrogen bonds with the participation of water and CE molecules.

5. Chromium trichloride

Presently, only one structure of the chromium-containing complex with composition $[(CrCl_3)\cdot(H_2O)\cdot(15C5)]$ (**32**) (Fig. 15) is known.[31] This complex was prepared by the reaction of $CrCl_3$ with 15C5 in aqueous acetonitrile. In the monomolecular complex of type B, the coordination environment about the chromium atom is an octahedron formed by three chlorine atoms, one oxygen atom of the water molecule and two (of five) oxygen atoms of the CE molecule (Cr – O_{cr} = 2.05 – 2.10 Å).

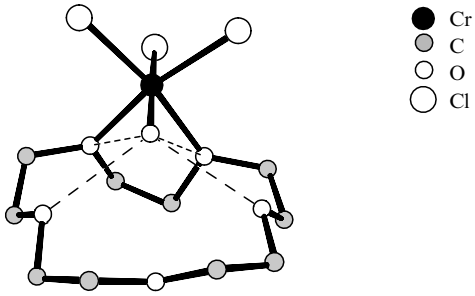


Figure 15. Structure of the complex **32**.

6. Manganese halides

The reaction of manganese bis(tribromide) with 12C4 gave the sandwich complex $\{[(Mn)\cdot(12C4)_2]^{2+} + 2[Br_3]^-\}$ (**33**) (Fig. 16).[32] The Mn – O distances vary from 2.241 to 2.369 Å.

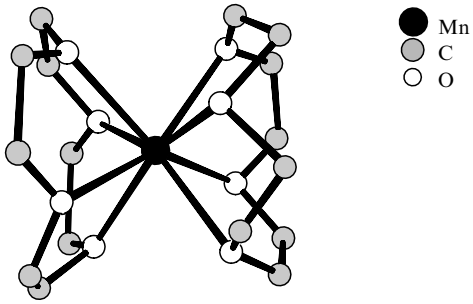


Figure 16. Structure of the $[(Mn)\cdot(12C4)_2]^{2+}$ cation in the complex **33**.

One product of the reaction of $MnCl_2$ with 18C6 in tetrahydrofuran is a compound with composition $\{2[(H_3O)\cdot(18C6)]^+ + [MnCl_4]^{2-}\}$ (**34**). Its formation can only be attributed to partial hydrolysis in the solution or to the use of the reagents containing water.[33] The oxonium ion in **34** is located in the centre of the cavity of the CE molecule. In the nearly regular tetrahedral anion, the Mn – Cl distances vary from 2.35 to 2.37 Å. Interestingly, hydrolysis products were not detected in the analogous reaction performed in the presence of an excess of water. In this case, the salt underwent complete ionisation and the cation was hydrated.[34, 35] The structure of the Mn-containing fragment is more complex and the CE molecule is located in the second coordination sphere.

$$2MnCl_2 + 18C6 + 8H_2O =$$
$$= \{[(H_2O)_4\cdot Mn(\mu\text{-}Cl_2)Mn\cdot(H_2O)_4]^{2+} + 2Cl^- + (18C6)\}.$$
35

Individual fragments of the structure **35** (Fig. 17) are linked to each other through a complex system of OH···O and OH···Cl hydrogen bonds.

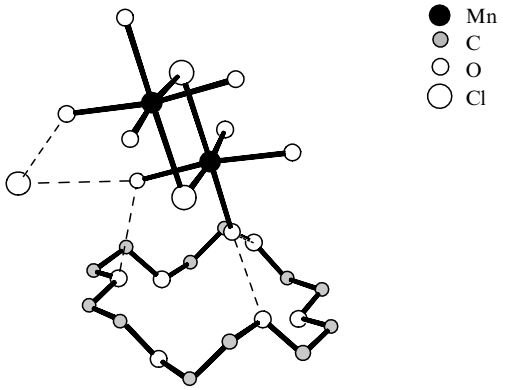


Figure 17. Structure of the $[(H_2O)_4\cdot Mn(\mu\text{-}Cl_2)Mn\cdot(H_2O)_4]^{2+}$ cation in the complex **35**.

7. Iron halides

The reaction of $FeBr_2$ with 15C5 in dry dichloromethane afforded a complex of type A with composition $\{[(FeBr_2)\cdot(15C5)] + (CH_2Cl_2)]$ (**36**) with the iron atom in the pentagonal-bipyramidal

environment. The Fe–O distances in the equatorial plane vary from 2.18 to 2.26 Å and the Fe–Br distances (the Br atoms are located in the apical positions) are in the range of 2.623–2.628 Å.[36]

The reaction of $FeCl_3$ with 15C5 in dry tetrahydrofuran proceeded analogously to the reaction of aluminium chloride with this CE (see the preparation of **14**). The process yielded an ionic complex with composition $\{[(FeCl_2)\cdot(15C5)]^+ + [FeCl_4]^-\}$ (**37**) as the final product.[37] The $Fe-O_{cr}$ distances in the cation vary from 2.112 to 2.192 Å.

The reaction of $FeCl_3$ or $FeBr_3$ with 18C6 in ordinary terahydrofuran containing water resembles the above-considered reaction of $MnCl_2$ with 18C6, *i.e.*, this reaction proceeded as hydrolysis to form type C complexes with composition $\{[FeX_4]^- + [(H_3O)\cdot(18C6)]^+\}$ [X = Cl (**38**) or Br (**39**)]. In the resulting complexes, the oxonium ion is a 'guest.' The cations have a flattened tetrahedral structure.[38,39] An analogous reaction performed in a mixture of dry tetrahydrofuran and diethyl ether afforded an unusual sandwich complex of type B with composition $\{[(FeCl)\cdot(18C6)_2]^{2+} + 2[FeCl_4]^-\}$ (**40**) (Fig. 18).[40] Crystals of this complex contain the dications $[(FeCl)\cdot(18C6)_2]^{2+}$ in which the five-coordinate iron atom exists in two equally probable orientations. The coordination environment about the iron atom in the cation is a distorted octahedron formed by two chlorine atoms [statistically disordered positions (50%)] and four of the six oxygen atoms of the CE molecule (the $Fe-O_{cr}$ distances vary from 2.156 to 2.209 Å). The anion has a flattened tetrahedral structure.

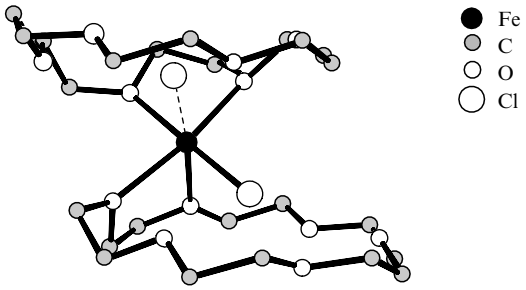


Figure 18. Structure of the $[(FeCl)\cdot(18C6)_2]^{2+}$ cation in the complex **40**.

The reaction of an equimolar mixture of $FeCl_2$ and $FeCl_3$ with 18C6 in tetrahydrofuran gave a product with an interesting structure.[41] In the complex of type B, the Fe^{II} atoms form complex cations $\{2[(Fe)\cdot(H_2O)\cdot(C_4H_8O)\cdot(18C6)](\mu_2\text{-}Cl_2)\}^{2+}$ (**41**) (Fig. 19). The coordination polyhedron about the metal atom is an octahedron. The equatorial plane is formed by two chlorine atoms (Fe–Cl = 2.43–2.47 Å) and two oxygen atoms of the CE molecule ($Fe-O_{cr}$ = 2.14–2.18 Å). The apical positions are occupied by the oxygen atom of the water molecule (2.06 Å) and the oxygen atom of the tetrahydrofuran molecule (2.13 Å). The Fe^{III} atoms form tetrahedral anions $[FeCl_4]^-$.

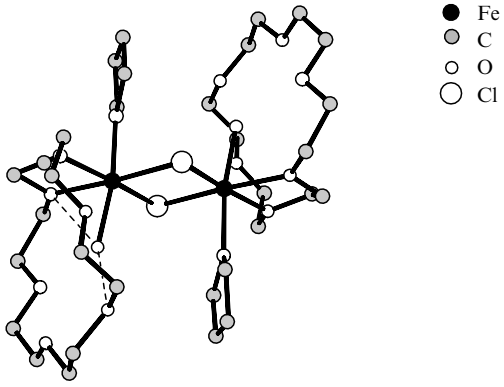


Figure 19. Structure of the cation $\{2[(FeCl)\cdot(H_2O)\cdot(C_4H_8O)\cdot(18C6)(\mu\text{-}Cl_2)]\}^{2+}$ in the complex **41**.

8. Cobalt chlorides

The reactions of $CoCl_2$ with 15C5 were studied in a series of works.[42–47] This reaction in acetonitrile always afforded the inner-cavity cation $[(Co)\cdot(CH_3CN)_2\cdot(15C5)]^{2+}$ but the composition of the anion in the complex varied from $[(CoCl_3)\cdot(CH_3CN)]^-$ (**42**) and $[CoCl_4]^{2-}$ (**43**) (mononuclear tetrahedral) to $[Co_2Cl_6]^{2-}$ (**44**) (binuclear bridging) depending on the concentration of $CoCl_2$. The presence of water in organic solvents resulted only in hydration of the complex rather than in hydrolysis of the salt. In this case, the acetonitrile molecules located in the apical positions of the pentagonal bipyramid (the coordination polyhedron about the cobalt atom) were replaced by water molecules with retention of the structural type of the cation $[(Co)\cdot(H_2O)_2\cdot(15C5)]^{2+}$ (see Ref. 44). Only free Cl^- ions (**45**) or tetrahedral anions $[CoCl_4]^{2-}$ (**46**) act as anions. In all the structures under consideration, the coordination polyhedron about the cobalt atom is a pentagonal bipyramid. The $Co-O_{cr}$ distances vary from 2.07 to 2.40 Å.

The reaction of anhydrous $CoCl_2$ with 15C5 in ethanol yielded a complex of type A with composition $\{[(Co)\cdot(EtOH)_2\cdot\cdot(15C5)]^{2+} + [CoCl_4]^{2-}\}$ (**47**).[45] The $Co-O_{Et}$ distances vary from 2.11 to 2.13 Å.

The reaction of $CoCl_2$ with 15C5 in the presence of an equimolar amount of $MgCl_2$ in acetonitrile afforded an inner-cavity magnesium complex with CE with composition $\{[(Mg)\cdot(CH_3CN)_2\cdot(15C5)]^{2+} + [CoCl_4]^{2-} + (CH_3CN)\}$ (**48**).[42] One product of hydration of this compound is a homometallic complex with composition $\{[(Co)\cdot(H_2O)_2\cdot(15C5)]^{2+} + 2Cl^- + (H_2O)_{2.5}\}$ (**49**). The cobalt atom is in the typical pentagonal-bipyramidal coordination. The structural fragments are linked to each other through a system of $OH\cdots O$ and $OH\cdots Cl$ intermolecular hydrogen bonds.[42]

The reaction of a mixture of cobalt chloride and copper chloride with 15C5 in acetonitrile gave a complex with composition $\{[(Co)\cdot(CH_3CN)_2\cdot(15C5)]^{2+} + [Cu_2Cl_6]^{2-}\}$ (**50**). The $Co-O_{cr}$ distances in this compound vary from 2.103 to 2.269 Å, Co–N = 2.097 Å. Complete hydration of this complex led to changes in the composition of the cation and in the structure of the anion. The resulting compound has the composition $\{[(Co)\cdot(H_2O)_2\cdot(15C5)]^{2+} + [CuCl_4]^{2-}\}$ (**51**).

The reaction of anhydrous $CoCl_2$ with 18C6 in acetonitrile yielded a compound with composition $\{[(Co)\cdot(CH_3CN)\cdot\cdot(18C6)]^{2+} + [CoCl_4]^{2-}\}$ (**52**). In this complex, the cobalt atom has a rather untypical hexagonal-pyramidal coordination (the coordination number is 7). The metal atom is coordinated to all the six oxygen atoms of the CE molecule ($Co-O_{cr}$ = 2.26 Å) and to the nitrogen atom (Co–N = 1.83 Å) and deviates from the mean plane through the oxygen atoms by 0.5 Å. The values of the torsion angles indicate that the CE molecule is highly strained.[45]

The reaction of $CoCl_2\cdot 6H_2O$ with 18C6 in acetone afforded a complex with composition $\{[(Co)\cdot(H_2O)_6]^{2+} + [CoCl_4]^{2-} + (18C6) + [(CH_3)_2CO]\}$ (**53**). All structural units of this complex are linked to each other through a branched system of $OH\cdots O$ and $OH\cdots Cl$ hydrogen bonds.[48]

The reaction of a mixture of $CoCl_2$ and $BaCl_2$ with 18C6 gave a compound $\{[(Ba)\cdot(H_2O)_2\cdot(18C6)]^{2+} + [CoCl_4]^{2-}\}$ (**54**).[49]

9. Nickel chloride

The reaction of anhydrous $NiCl_2$ and NaCl with 15C5 gave a complex with composition $\{2[(Na)\cdot(15C5)]^+ + [NiCl_4]^{2-}\}$ (**55**) in which the tetrahedral anion and the complex cation are linked through an $Na\cdots Cl$ interaction (2.65 Å).[50]

The reaction of nickel chloride dihydrate with 18C6 in methanol afforded a compound $\{[(H_2O)_4\cdot Ni(\mu\text{-}Cl_2)Ni\cdot(H_2O)_4]^{2+} + (18C6) + 2Cl^-\}$ (**56**) the structure and composition of which are analogous to those of the manganese complex **35**.[51]

10. Copper halides

The products of reactions of a mixture of monovalent copper iodide and KI with various CE in acetone were studied by Rath and Holt.[52] Complexes containing potassium cations, CE molecules (dibenzo-24-crown-8, DB24C8, or dibenzo-18-crown-6, DB18C6) and $[Cu_xI_y]^{n-}$ anions of different compositions were prepared according to the following reactions:

$$12CuI + 7KI + 6\,12C4 \longrightarrow \longrightarrow [Cu_4I_6]^{2-} + [Cu_8I_{13}]^{5-} + 7K^+ + 6\,12C4\,, \quad \mathbf{57}$$

$$4CuI + 2KI + 2\,15C5 \longrightarrow [Cu_4I_6]^{2-} + 2K^+ + 2\,15C5\,, \quad \mathbf{58}$$

$$3CuI + KI + DB24C8 \longrightarrow [Cu_3I_4]^- + K^+ + DB24C8\,. \quad \mathbf{59}$$

The reaction of CuI with DB18C6 in acetonitrile gave a molecular complex of composition $\{[(Cu_4I_4)\cdot(CH_3CN)_4] + (DB18C6)\}$ (**60**) with fragments that are not linked to each other.[53]

Only one structure of a monomolecular complex of $CuCl_2$ with 12C4 (**61**) (Fig. 20) has been reported.[54] In this complex, the copper atom has an octahedral coordination formed by four oxygen atoms of the CE molecule and two chlorine atoms ($Cu-O_{cr} = 2.113-2.403$ Å and $Cu-Cl = 2.214-2.228$ Å).

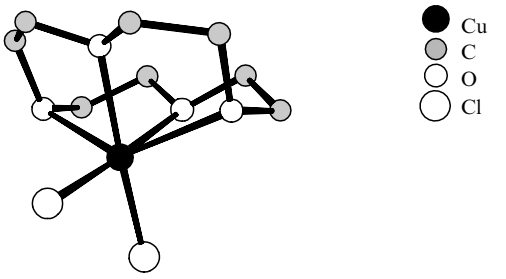


Figure 20. Structure of the complex **61**.

The reaction of $CuCl_2$ with 15C5 in acetonitrile was studied in several works.[55–57] Ionic complexes of the type $\{[(Cu)\cdot\cdot(CH_3CN)_{2-x}\cdot Cl_x\cdot(15C5)] + A\}$, where $x = 0$ or 1 and A is an anion in which the coordination environment about the copper atom is a pentagonal bipyramid, were synthesised. The following complexes were obtained depending on the halide : CE : solvent ratio:

$$4CuCl_2 + 2\,15C5 + 2CH_3CN \longrightarrow \longrightarrow \{2[(CuCl)\cdot(CH_3CN)\cdot(15C5)]^+ + [Cu_2Cl_6]^{2-}\}\,, \quad \mathbf{62}$$

$$4CuCl_2 + 15C5 + 2CH_3CN \longrightarrow \longrightarrow \{[(Cu)\cdot(CH_3CN)_2\cdot(15C5)]^{2+} + [Cu_3Cl_8]^{2-}\}\,. \quad \mathbf{63}$$

The Cu – O distances in these compounds vary from 2.16 to 2.34 Å and the Cu – N distances are in the range of 1.95 – 1.99 Å. In the complex **63**, the anion exists as an infinite chain of alternating tetragonal-bipyramidal and tetragonal-pyramidal fragments linked through bridging chlorine atoms (Fig. 21). The Cu – Cl distances are in the range of 2.255 – 2.787 Å. Hydration of compounds **62** and **63** with water vapour resulted in the removal of the CE molecules from the coordination sphere of the metal atom and in the change in the type of the complex from A to C.[57] In this case, compounds with compositions $\{[(Cu)\cdot(H_2O)_4]^{2+} + [(Cu_3Cl_8)\cdot(H_2O)_2]^{2-} + (15C5)_2\}$ (**64**) and $\{2[(CuCl_2)\cdot(H_2O)_2] + (15C5)\}$ (**65**) were formed along with $CuCl_2\cdot 2H_2O$. Separate fragments in **64** and **65** are linked to each other through $OH_w\cdots O_{cr}$ hydrogen bonds (Figs 22 and 23, respectively).

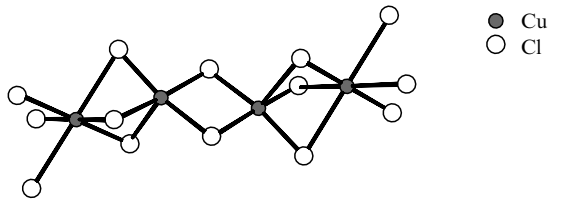


Figure 21. Structure of the $[Cu_3Cl_8]^{2-}$ anion in the complex **63**.

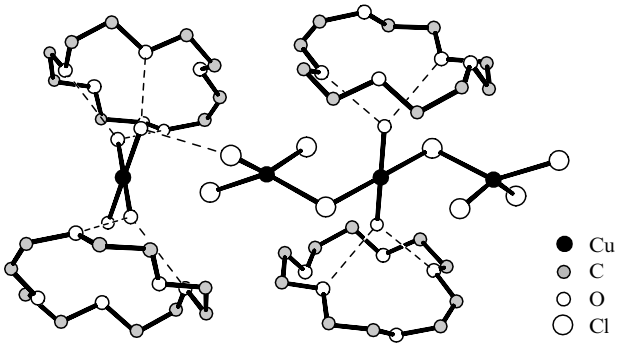


Figure 22. Structure of the complex **64**.

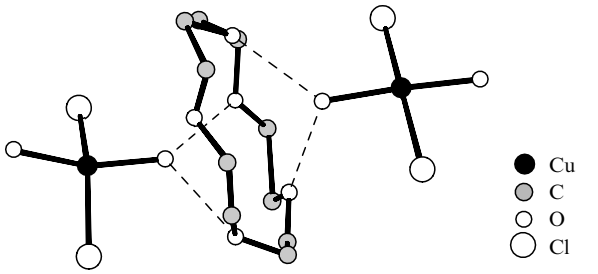


Figure 23. Structure of the complex **65**.

The reaction of anhydrous $CuCl_2$ with 15C5 in aqueous methanol gave a complex of type C with composition $\{[(CuCl_2)\cdot(H_2O)_2\cdot(CH_3OH)] + (15C5)\}$ (**66**).[58] The coordination environment about the copper atom is a square pyramid. In the crystal structure of the complex, OH···O intermolecular hydrogen bonds with the participation of water, methanol and CE molecules are realised. The reaction of $CuBr_2$ with 15C5 yielded a complex with composition $\{[(H_2O)_2\cdot(CuBr_2)] + (15C5)\}$ (**67**). The coordination polyhedron about the copper atom is a strongly flattened tetrahedron.[59]

The structures of a number of products which were formed in the reactions of a mixture of $CuCl_2$ and $MgCl_2$ with 15C5 in acetonitrile where the reagents were taken in different ratios and at various concentrations were reported.[60]

$$CuCl_2 + MgCl_2 + 15C5 + CH_3CN \longrightarrow \longrightarrow \{[(CH_3CN)\cdot(Mg)\cdot(15C5)\cdot(\mu_2\text{-}Cl)\cdot(CuCl_3)]\}\,, \quad \mathbf{68}$$

$$2CuCl_2 + MgCl_2 + 15C5 + 2CH_3CN \longrightarrow \longrightarrow \{[(CH_3CN)_2\cdot(Mg)\cdot(15C5)]^{2+} + [Cu_2Cl_6]^{2-}\}\,, \quad \mathbf{69}$$

$$3CuCl_2 + MgCl_2 + 15C5 + 2CH_3CN \longrightarrow \longrightarrow \{[(CH_3CN)_2\cdot(Mg)\cdot(15C5)]^{2+} + [Cu_3Cl_8]^{2-}\}\,. \quad \mathbf{70}$$

The structure **68** consists of monomolecular fragments (Fig. 24), while structures **69** and **70** are ionic. In all the three compounds, the magnesium atom is located in the centre of the cavity of the CE molecule and has a pentagonal-bipyramidal

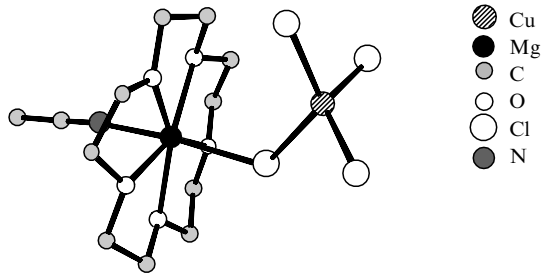


Figure 24. Structure of the complex **68**.

coordination. In compound **70**, the chain anion is analogous to that observed in the structure **63**. Hydration of compounds **68**–**70** with water vapour gave complexes with compositions $\{[(H_2O)_2\cdot(Mg)\cdot(15C5)]^{2+} + [CuCl_4]^{2-}\}$ (**71**) and $\{[(Cu_3Cl_8)\cdot\cdot(H_2O)_2]^{2-} + [(Mg)\cdot(H_2O)_6]^{2+} + (15C5)_2\}$ (**72**). The structure of the cation in **71** is analogous to that in **11**. The metal atom in the cation of **72** has an octahedral coordination. The central copper atom in the anion has an octahedral coordination formed by two oxygen atoms of the water molecules and four chlorine atoms. The terminal copper atoms have a tetrahedral environment. The fragments are linked to each other through $OH_w\cdots O_{cr}$ and $OH_w\cdots Cl$ hydrogen bonds.

The reactions of copper chloride with 18C6 in the presence of halides of alkali or alkaline-earth metals gave complexes in which the metal atoms are coordinated by CE molecules and the copper atoms form the $[Cu_2Cl_6]^{2-}$ anions.[61]

$$2CuCl_2 + 2RbCl + 2\,18C6 \longrightarrow 2[(Rb)\cdot(18C6)]^+ + [Cu_2Cl_6]^{2-}, \quad \mathbf{73}$$

$$2CuCl_2 + BaCl_2 + 18C6 \longrightarrow [(Ba)\cdot(18C6)]^{2+} + [Cu_2Cl_6]^{2-}. \quad \mathbf{74}$$

The product of the reaction of $CuCl_2$ with benzo-15-crown-5 (B15C5) in chloroform was also structurally characterised.[62] The product has the composition $\{[(CuCl_2)\cdot(B15C5)] + (CHCl_3)\}$ (**75**). The copper atom is located in the centre of the cavity of the CE molecule and has a pentagonal-bipyramidal coordination. This reaction in acetonitrile in the presence of NaCl gave a complex $\{2[(Na)\cdot(B15C5)]^+ + [Cu_2Cl_6]^{2-}\}$ (**76**).[63] An analogous product with composition $\{2[(Na)\cdot(DB18C6)]^+ + [Cu_2Cl_6]^{2-}\}$ (**77**) was formed when DB18C6 was used as a polyether.[63] The reaction with KCl and naphtho-15-crown-5 (N15C5) yielded a compound with a similar composition, $\{2[(K)\cdot(N15C5)]^+ + [Cu_2Cl_6]^{2-} + (H_2O)\}$ (**78**), containing a water molecule of crystallisation.[64]

11. Zinc halides

The reactions of anhydrous $ZnCl_2$ with 15C5 in different solvents gave complexes of type A of the general formula $\{[(Zn)\cdot(L_1)\cdot(L_2)\cdot(15C5)]^{2+} + [Zn_2Cl_6]^{2-}\}$, where L_1 = Cl and $L_2 = (CH_3)_2CO$ (**79**), L_1 = Cl and $L_2 = H_2O$ (**80**) (both prepared in acetone), $L_1 = L_2 = C_4H_8O$ (**81**) (in tetrahydrofuran) and $L_1 = L_2 = CH_3CN$ (**82**) (in acetonitrile).[65,66] In all the structures under consideration, the zinc atom is located in the cavity of the CE molecule and has a pentagonal-bipyramidal coordination. The $Zn-O_{cr}$ distances vary from 2.13 to 2.27 Å.

The reaction of zinc chloride dihydrate with 15C5 in methanol yielded a typical complex of type C with composition $\{[(H_2O)_2\cdot(ZnCl_2)] + (15C5)\}$ (**83**).[67] In this complex, the zinc atom has a tetrahedral coordination. The structural fragments are linked to each other through $OH\cdots O$ hydrogen bonds.

In going from 15C5 to 18C6, the compositions and structures of zinc chloride complexes become more diversified. Thus the reaction in tetrahydrofuran[66,68] gave a complex of type B with composition $[(H_2O)\cdot(ZnCl_2)\cdot(18C6)]$ (**84**). The coordination polyhedron about the zinc atom is a tetrahedron formed by two chlorine atoms (Zn–Cl = 2.20 and 2.23 Å), one water molecule ($Zn-O_w$ = 1.97 Å) and one oxygen atom of the CE molecule ($Zn-O_{cr}$ = 2.08 Å). The water molecule, in turn, forms an intramolecular hydrogen bond with another O_{cr} atom (2.77 Å) resulting in strong distortion of the macrocycle (Fig. 25).

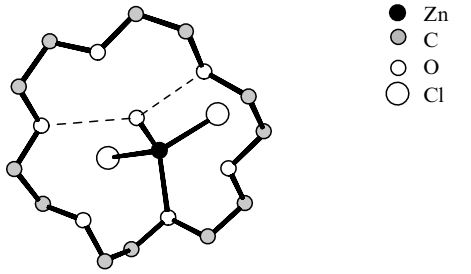


Figure 25. Structure of the complex **84**.

The reaction of $ZnCl_2$ with 18C6 in diethyl ether afforded a complex of type B with composition $\{2(H_2O)_2\cdot(ZnCl)\cdot\cdot(18C6)]^+ + [Zn_2Cl_6]^{2-}\}$ (**85**).[69] The zinc atom is coordinated by one chlorine atom, one oxygen atom of the water molecule and three (of six) oxygen atoms of the CE molecule. Recrystallisation of this compound from a mixture of acetone and CCl_4 gave a complex of type C with composition $\{[(Zn)\cdot(H_2O)_6]^{2+} + 2[(ZnCl_3)\cdot(H_2O)]^- + (18C6) + [(CH_3)_2CO]\}$ (**86**). In the crystal structure of this complex, an extensive system of intermolecular hydrogen bonds exists. The reaction of $ZnCl_2$ with 18C6 in terahydrofuran yielded a product with composition $\{[ZnCl_4]^{2-} + 2[(H_3O)\cdot(18C6)]^-\}$ (**87**) with the oxonium ion occupying the centre of the cavity of the CE molecule.[32] Under analogous conditions, the reaction of ZnI_2 with 18C6 afforded the compound $\{[(H_2O)_2\cdot(ZnI_2)] + (18C6)_2 + (H_2O)\}$ (**88**) in which the tetrahedral zinc-containing fragments are located between two CE molecules and are bound to the CE molecules through $OH\cdots O$ hydrogen bonds (Fig. 26).

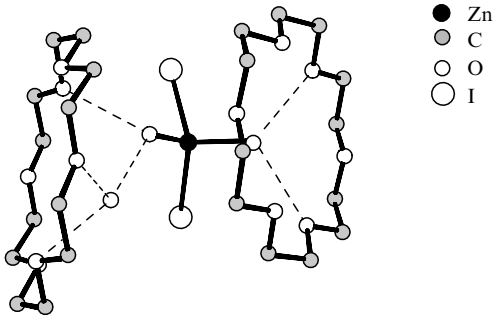


Figure 26. Structure of the complex **88**.

12. Gallium halides

It was shown[70] that the complexes prepared by reactions of gallium halides with 15C5 have the composition $\{[(GaX_2)\cdot(15C5)]^+ + [GaX_4]^-\}$, where X = Cl (**89**) or Br (**90**). These complexes are isostructural to the aluminium complex **14**.

The reaction of $GaCl_3$ with 18C6 in acetonitrile afforded the compounds $\{[GaCl_4]^- + [(H_3O)\cdot(18C6)]^+\}$ (**91**) with the oxonium ion occupying the centre of the CE molecule. The structure of this complex is analogous to that of the above-described manganese complex **34**.

13. Arsenic halides

The structures of the molecular complexes $[(AsCl_3)\cdot(12C4)]$ (**92**) (Fig. 27) and $[(AsCl_3)\cdot(15C5)]$ (**93**) were reported.[71] The $As-O_{cr}$ distances in these compounds vary from 2.776 to 2.915 Å and from 2.944 to 3.156 Å, respectively, which are only slightly smaller than the sum of the van der Waals radii. In general, a complex of arsenic bromide with 15C5 has an analogous structure.[72] However, the As···O bonds in the latter complex are nonequivalent: four bonds vary from 3.12 to 3.29 Å and the fifth bond is substantially longer (3.85 Å).

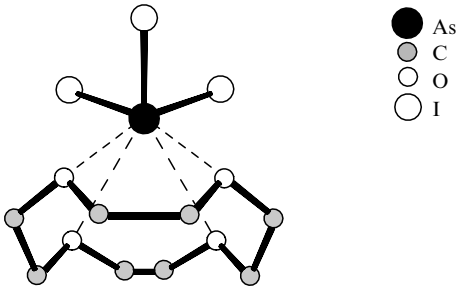


Figure 27. Structure of the complex **92**.

V. Systems with halides of the fourth-row elements

1. Zirconium tetrachloride

The reactions of metal halides in the highest oxidation states with CE were accompanied by destruction of the latter. The reaction of $ZrCl_4$ with 18C6 in tetrahydrofuran is a typical example.[73] The resulting product (Fig. 28) has the composition $\{[(ZrCl_5)\cdot\cdot(C_4H_8O)]^- + [(ZrCl_2)\cdot(O_5C_8H_{16}(CH_2)_2O(CH_2)_2Cl)]^+\}$ (**94**). The Zr – O distances (1.93 and 2.24 – 2.33 Å) in the cation indicate that both covalent and coordination interactions exist between the zirconium and oxygen atoms.

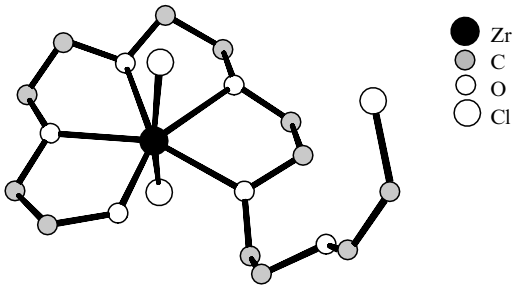


Figure 28. Structure of $[(ZrCl_2)\cdot(O_4C_8H_{16}(CH_2)_2O(CH_2)_2Cl)]^+$ cation in the complex **94**.

2. Molybdenum halides

The reaction of $MoCl_5$ with 15C5 in 1,2-dimethoxyethane (L) in the presence of sodium silicide was accompanied by reduction of Mo^V to Mo^{IV} (see Ref. 74). The resulting complex of type C has the composition $\{[(MoCl_4)\cdot(L)] + (15C5)\}$ (**95**). The coordination polyhedron about the molybdenum atom is a distorted octahedron. The $Mo-O_{cr}$ distances vary from 2.14 to 2.18 Å.

The reaction of $MoCl_5$ with 15C5 in acetonitrile in the presence of $AlCl_3$ gave the compound $\{[(MoOCl_4)\cdot(CH_3CN)]^- + [(AlCl_2)\cdot(15C5)]^+ + (CH_3CN)\}$ (**96**). It was assumed[75] that the oxychloride was formed as a result of decomposition of the CE molecule under the action of the strong Lewis acid, *viz*., $MoCl_5$. The coordination polyhedron about the molybdenum atom in the anion of **96** is an octahedron. The structure of the cation of **96** is analogous to that of the complex **14**.

The reactions of molybdenum oxychloride Mo^VOCl_3 with 12C4 or 18C6 yielded complexes containing the octahedral cations $[(MoOCl_4)\cdot(H_2O)]^-$ and the oxonium-containing cations of the type $[(H_3O)\cdot(CE)]^+$, *viz*., $\{[(MoOCl_4)\cdot(H_2O)]^- + [(H_3O)\cdot\cdot(12C4)]^+\}$ (**97**) and $\{[(MoOCl_4)\cdot(H_2O)]^- + [(H_3O)\cdot(18C6)]^+\}$ (**98**), respectively.[76, 77] The Mo – O and Mo – O_w distances in these complexes are 1.641 (1.654) and 2.285 (2.355) Å, respectively. Separate structural fragments are linked to each other through a system of OH···O and OH···Cl hydrogen bonds. The reaction with $MoOBr_3$ gave a complex with an analogous structure $\{[(MoOBr_3)\cdot(H_2O)]^- + [(H_3O)\cdot(18C6)]^+\}$ (**99**).[78]

3. Palladium chloride

The reaction of $PdCl_2$ with 18C6 in a tetrahydrofuran solution of hydrochloric acid afforded a binuclear complex $\{[Pd_2Cl_6]^{2-} + 2[(H_3O)\cdot(18C6)]^+\}$ (**100**) of type C.[38] The palladium atoms in the planar anion have a square coordination. The Pd – Cl distances are 2.326 Å (for the terminal bond) and 2.668 Å (for the bridging bond).

4. Silver halides

The reactions of silver halides with DB18C6 in dimethylformamide in the presence of alkali metal halides were studied by Helgesson and Jagner.[79]

$$AgCl + 3KCl + 3\,DB18C6 \longrightarrow \longrightarrow \{3[(K)\cdot(DB18C6)]^+ + [AgCl_3]^{2-} + Cl^-\},$$
101

$$AgCl + 3RbCl + 3\,DB18C6 \longrightarrow \longrightarrow \{3[(Rb)\cdot(DB18C6)]^+ + [AgCl_3]^{2-} + Cl^-\},$$
102

$$AgBr + 3KBr + 3\,DB18C6 \longrightarrow \longrightarrow \{3[(K)\cdot(DB18C6)]^+ + [AgBr_3]^{2-} + Br^-\},$$
103

$$AgBr + 3RbBr + 3\,DB18C6 \longrightarrow \longrightarrow \{3[(Rb)\cdot(DB18C6)]^+ + [AgBr_3]^{2-} + Br^-\}.$$
104

In all cases, complexes containing planar anions of silver halides were detected (Fig. 29).

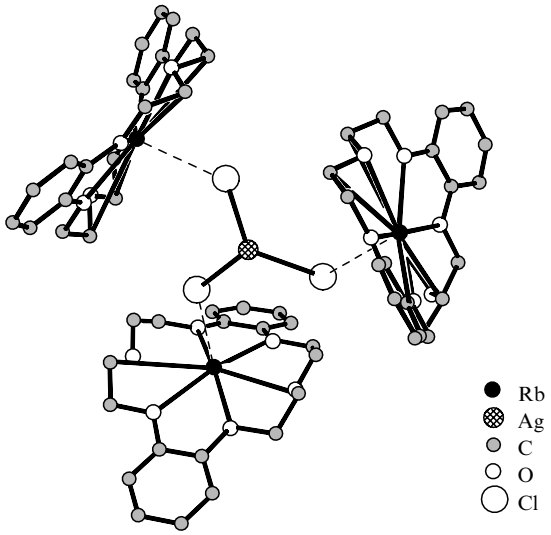


Figure 29. Structure of the complex **102**.

5. Cadmium halides

The reactions of cadmium halides with 18C6 gave typical complexes of type A with composition $[(CdCl_2)\cdot(18C6)]$ (**105**), $[(CdBr_2)\cdot(18C6)]$ (**106**) and $[(CdI_2)\cdot(18C6)]$ (**107**) in which the cadmium atom is located in the centre of the cavity of the CE molecule and has a hexagonal-bipyramidal coordination.[80,81] The $Cd-O_{cr}$ distances in the complexes vary from 2.36 to 2.75 Å.

6. Indium halides

The reactions of indium(III) halide hydrates with 15C5 or 18C6 always yielded complexes of type C in which direct $In-O_{cr}$ contacts were absent. Thus the reaction of $InCl_3\cdot 4H_2O$ with 15C5 gave the complex $\{[(InCl_3)\cdot(H_2O)_2] + (15C5)\}$ (**108**).[82] The coordination environment about the indium atom in this complex is a slightly distorted trigonal bipyramid. The $In-O_w$ distances are in the range of 2.201–2.218 Å. The fragments are linked to each other through $O_wH\cdots O_{cr}$ hydrogen bonds. An analogous reaction with 18C6 afforded the complex $\{[(InCl_3)\cdot(H_2O)_3] + (18C6)\}$ (**109**). In this compound, the indium atom has an octahedral environment. The $In-O_w$ distances vary from 2.23 to 2.25 Å.

The reaction of $InCl_3$ with 18C6 in tetrahydrofuran afforded the compound $\{[InCl_4]^- + [(H_3O)\cdot(18C6)]^+\}$ (**110**) isostructural to the complex **38**.[38] The formation of the tetrahedral anions of the same type was also observed in the reactions of indium mixed halides with alkali metal halides and alkyl derivatives.[83–85]

$$InCl_3 + CH_3Li + 15C5 \longrightarrow \{[(Li)\cdot(15C5)]^+ + [(InCl_3)\cdot(CH_3)]^-\}, \quad \textbf{111}$$

$$InClI_2 + KI + 18C6 \longrightarrow \{[(K)\cdot(18C6)]^+ + [InClI_3]^-\}, \quad \textbf{112}$$

$$InClPr^i_2 + KCl + 15C5 \longrightarrow \{[(K)\cdot(15C5)]^+ + [InCl_2Pr^i_2]^-\}. \quad \textbf{113}$$

7. Tin chlorides

Only one example of complexation of $SnCl_2$ with CE (18C6) in methanol saturated with hydrogen chloride is documented.[86] This reaction gave the complex $\{[(SnCl)\cdot(18C6)]^+ + [SnCl_3]^-\}$ (**114**) with a very unusual structure (Fig. 30). The tin atom in the cation has a nontypical hexagonal-pyramidal coordination with the Sn–O distances varying from 2.59 to 2.88 Å. The tin atom in the anion has a pyramidal coordination and is located in the mean plane of the base of the pyramid. Oxidation of $SnCl_2$ in aqueous methanol containing 15C5 with atmospheric oxygen at 120 K yielded the complex of type C with composition $\{[(Sn^{IV}Cl_4)\cdot(H_2O)_2] + [15C5]\}$ (**115**).[86] The coordination polyhedron about the tin atom is an octahedron. The $Sn-O_w$ distances vary from 2.107 to 2.125 Å. The fragments in this compound are linked to each other through $O_wH\cdots O_{cr}$ hydrogen bonds.

The reaction of $SnCl_4$ with 15C5 in acetonitrile resulted in decomposition of the CE molecule.[88] In this case, two C–O bonds were cleaved, one $-CH_2-CH_2-$ unit was eliminated in the form of dichloroethane and two tin atoms were μ_2-coordinated by two terminal oxygen atoms (Fig. 31). The resulting complex has the composition $\{[(SnCl_4)\cdot(O_5C_8H_{16}SnCl_2)] + (CH_3CN)\}$ (**116**). The coordination environment about the Sn(1) atom is a pentagonal bipyramid. The $Sn(1)-O_{cr}$ coordination bonds are in the range of 2.237–2.239 Å. The $Sn(1)-O_\mu$ covalent bond is 2.074 Å. The Sn(2) atom has an octahedral coordination with the $Sn(2)-O_\mu$ distances of 2.149 Å.

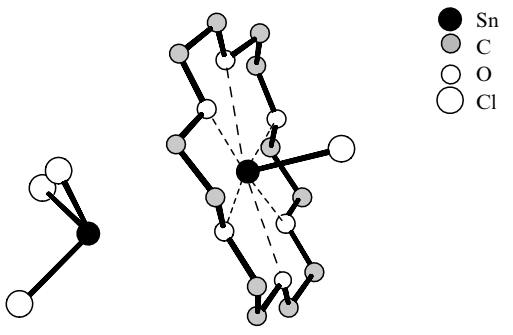


Figure 30. Structure of the complex **114**.

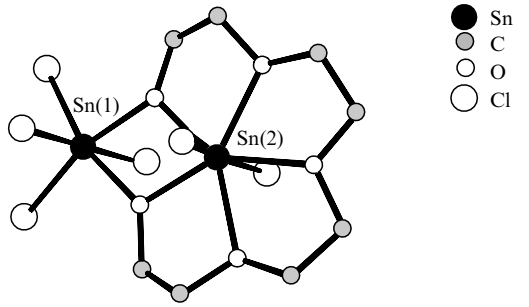


Figure 31. Structure of the complex **116**.

The reaction of $SnCl_4$ with 18C6 in chloroform gave a complex of type C with composition $\{[(SnCl_4)\cdot(H_2O)_2] + (18C6) + (CHCl_3) + (H_2O)\}$ (**117**).[89,90] The octahedral tin-containing fragment is linked to the CE molecule through $O_wH\cdots O_{cr}$ hydrogen bonds. In addition, there are H-bonds between the coordinated water molecules and the water molecules of crystallisation.

8. Antimony halides

The complex $[(SbCl_3)\cdot(12C4)]$ (**118**)[71,91] has a structure analogous to that of the complex **92**. The reaction of a mixture of $SbCl_3$ and $SbCl_5$ with 12C4 in acetonitrile gave a compound with composition $\{[(Sb^{III})\cdot(12C4)_2]^{3+} + 3[Sb^VCl_6]^- + (CH_3CN)\}$ (**119**).[92] The $Sb-O_{cr}$ distances in the sandwich cation vary from 2.325 to 2.530 Å.

The reaction of $SbCl_3$ with 15C5 afforded the monomolecular complex $[(SbCl_3)\cdot(15C5)]$ (**120**).[93] The pyramidal $SbCl_3$ molecule is hanging over the mean plane of the CE molecule and the lone electron pair of the antimony atom is directed toward the polyether molecule. The $Sb-O_{cr}$ distances vary from 2.787 to 2.997 Å. The reaction of $SbBr_3$ with 15C5 and the reaction of $SbCl_3$ with DB18C6 in chloroform afforded analogous structures [**121**[94] and **122** (Fig. 32), respectively].†

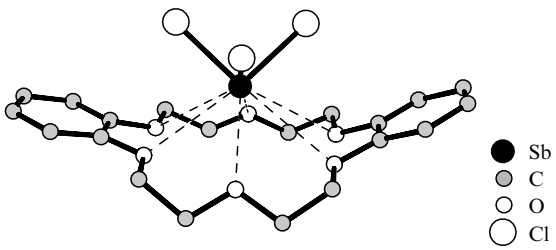


Figure 32. Structure of the complex **122**.

The reaction of a mixture of tri- and pentavalent antimony chlorides with 18C6 in acetonitrile afforded a compound with composition $\{[(Sb^{III}Cl_2)\cdot(18C6)]^+ + [SbCl_6]^-\}$ (**123**)[95] in which the antimony(III) atom is coordinated by two chlorine atoms and only two oxygen atoms of the CE molecule. The coordination polyhedron about this atom (taking into account the lone electron pair) is a trigonal bipyramid. The anion in the complex **123** has the typical octahedral structure.

† V K Belsky. Unpublished data.

9. Tellurium tetrachloride

The reaction of $TeCl_4$ with a mixture of $SbCl_5$ and 15C5 gave a bimetallic ionic complex with composition $\{[(TeCl_3)\cdot(15C5)]^+ + [SbCl_6]^-\}$ (**124**). The Te – O_{cr} distances vary from 2.66 to 2.79 Å.[96]

VI. Systems with halides of the fifth-row elements

1. Barium bromide

Only one structure of the complex formed by the reaction of barium bromide hydrate with 15C5 was reported in the literature.[97] The resulting compound has the composition $\{[(Ba)\cdot(15C5)_2]^{2+} + 2Br^- + (H_2O)_2\}$ (**125**). The barium ion is located in the centre of the sandwich formed by CE molecules. The Ba···O distances are in the range of 2.749 – 2.880 Å. In the crystal, the Br^- anions and the water molecules are involved in the formation of a network of OH···Br intermolecular hydrogen bonds (3.326 – 3.493 Å).

2. Lanthanide and yttrium halides

The structures of complexes of lanthanide halide hydrates with 12C4, which were crystallised from a mixture of methanol with acetonitrile, are known.[98,99] Compounds of three different structural types were obtained depending on the nature of the metal atom and the reaction temperature. In the case of lanthanide and yttrium chlorides, the compositions and structures of the resulting complexes are similar, *viz*., $\{[(Ln)\cdot(H_2O)_5\cdot(12C4)]^{3+} + 3Cl^- + (H_2O)_2\}$, where Ln = Ce (**126**) (Fig. 33), Nd (**127**), Sm (**128**), Eu (**129**), Gd (**130**), Dy (**131**), Y (**132**), Ho (**133**), Er (**134**) or Yb (**135**). In these complexes, the coordination environment about the metal atom is a monocapped tetragonal antiprism formed by four oxygen atoms of the CE molecule and five oxygen atoms of the water molecules ($Ln-O_{cr}$ = 2.42 – 2.63 Å and $Ln-O_w$ = 2.23 – 2.51 Å). All water molecules (both coordinated and of crystallisation) and chloride ions are involved in the formation of a complex system of OH···Cl intermolecular hydrogen bonds.

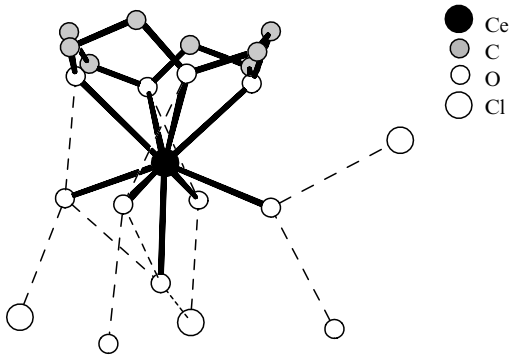


Figure 33. Structure of the complex **126**.

In complexes with composition $\{[(H_2O)_2\cdot(LnCl_2)\cdot(12C4)]^+ + Cl^-\}$, where Ln = Ho (**136**), Er (**137**), Tm (**138**), Yb (**139**) or Lu (**140**) (Fig. 34), the coordination environment about the metal atom is a bicapped trigonal prism formed by four oxygen atoms of the CE molecule, two oxygen atoms of the water molecules and two chlorine atoms. The structural fragments are linked to each other through a system of OH···Cl hydrogen bonds.

The reaction of yttrium chloride with 12C4 afforded a complex with composition $\{[(H_2O)\cdot(YCl_2)\cdot(CH_3OH)\cdot(12C4)]^+ + Cl^-\}$ (**141**) in which one water molecule is replaced by the methanol molecule. Though the yttrium atom retains the coordination number of 8, it has a different coordination environment (a square antiprism, Fig. 35).

The praseodymium complexes with compositions $\{[(H_2O)\cdot(PrCl_3)\cdot(12C4)] + (12C4) + (CH_3OH)\}$ (**142**) and $[(CH_3OH)\cdot(PrCl_3)\cdot(12C4)]$ (**143**) were also described in the literature.[100] In both structures, the coordination environment

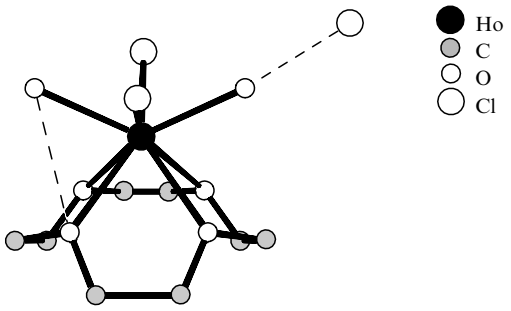


Figure 34. Structure of the complex **136**.

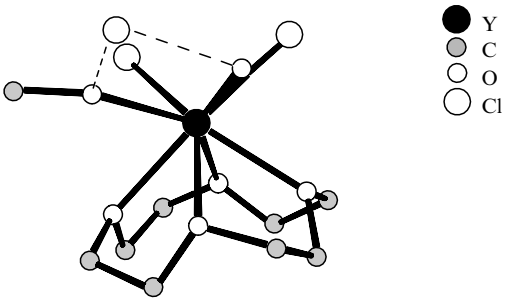


Figure 35. Structure of the complex **141**.

about the metal atom is a tetragonal antiprism with Pr – O_{cr} = 2.56 – 2.63 Å, $Pr-OCH_3OH$ = 2.51 Å and Pr – O_w = 2.48 Å. In the complex **142**, the structural fragments are linked to each other through $O_wH\cdots O_{cr}$ hydrogen bonds (Fig. 36).

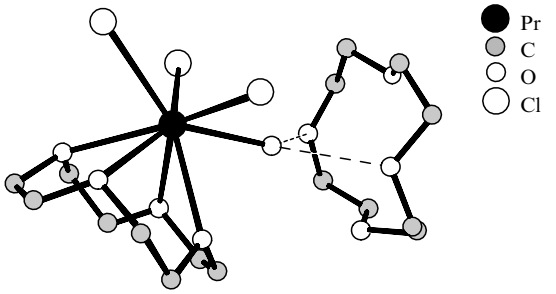


Figure 36. Structure of the complex **142**.

Complete hydration of complexes of lutetium chloride with 12C4 gave eight-coordinate (square antiprism) octaaqualutetium ions.[101,102]

$$LuCl_3 + 12C4 + 9H_2O \longrightarrow \{[(Lu)\cdot(H_2O)_8]^{3+} + 3Cl^- + (12C4) + (H_2O)\}\ (\text{at } -150\ ^\circ C)\,,$$

144

$$LuCl_3 + NaCl + 2\,12C4 + 9H_2O \longrightarrow \{[(Lu)\cdot(H_2O)_8]^{3+} + [(Na)\cdot(12C4)_2]^+ + 4Cl^- + (H_2O)\}\,.$$

145

The reactions of $LnCl_3$ with 15C5 generally gave complexes of two types. The complexes of the first type, *viz*., $[(LnCl_3)\cdot(15C5)]$, were formed when anhydrous chlorides of praseodymium (**146**), neodymium (**147**) or samarium (**148**) were used.[103,104] The structures of these complexes are analogous to those of trihalides of Group V elements (see, for example, structure **93**). The pyramidal $LnCl_3$ molecule is located above the mean plane of the CE molecule. The $Ln-O_{cr}$ distances vary from 2.50 to 2.75 Å. The stabilities of these complexes were calculated by the INDO method.[105]

Complexes of the second type have the composition $\{[(Ln)\cdot(H_2O)_8]^{3+} + (15C5) + 3Cl^- + (H_2O)_n\}$. These compounds were obtained by the reactions with metal chloride hydrates in aqueous solvents or by hydration of lanthanide salts with water vapour. The complexes with Ln = Y (**149**), Gd (**150**) and Lu (**151**) were prepared.[106–109] In all cases, the coordination polyhedron about the metal atom is a distorted dodecahedron. Complex systems of OH···O and OH···Cl hydrogen bonds are observed in all the structures under consideration.

Products of complexation of chlorides of rare-earth elements with 18C6 are characterised by different types of crystal structures.[110,111] The reactions performed in a 1 : 3 mixture of methanol and acetonitrile afforded complexes with compositions $\{[(H_2O)_2\cdot(LnCl)\cdot(18C6)]^{2+} + 2Cl^- + (H_2O)_2\}$, where Ln = Nd (**152**), Sm (**153**), Gd (**154**), Tb (**155**), Pr (**156**) or Eu (**157**). The metal atom is coordinated by six oxygen atoms of the CE molecule, one chlorine atom (located 'above' the mean plane of CE) and two water molecules (located 'below' the mean plane of CE) (Fig. 37).

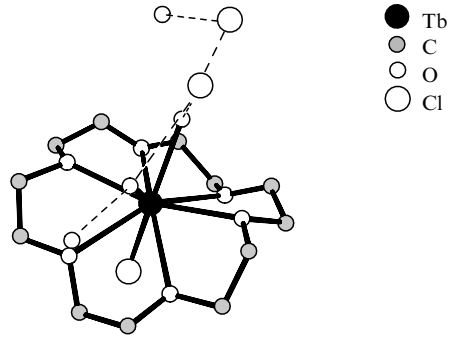


Figure 37. Structure of the complex **155**.

The Ln–O_{cr} and Ln–O_w distances are in the ranges of 2.53–2.55 and 2.36–2.45 Å, respectively. In all cases, the coordination polyhedron about the lanthanide atom is a tricapped trigonal prism. The lanthanide atoms have the same coordination in another type of complexes in which one coordinated water molecule is replaced by the chlorine atom or the methanol molecule:[111] $\{[(CH_3OH)\cdot(LaCl_2)\cdot(18C6)]^+ + Cl^- + (H_2O)_{1.5}\}$ (**158**), $\{[(H_2O)\cdot(LaCl_2)\cdot(18C6)]^+ + Cl^-\}$ (**159**) and $\{[(H_2O)\cdot(CeCl_2)\cdot(18C6)]^+ + Cl^- + (H_2O)_2\}$ (**160**).

An anhydrous lanthanum complex $[(LaCl_3)\cdot(18C6)]$ (**161**) was prepared by crystallisation at 70 °C.[111] The coordination polyhedron in the complex **161** is also similar to a tricapped trigonal prism (formed by six oxygen atoms of the CE molecule and three chlorine atoms).

The addition of the salting-out reagent, LiCl, to a solution of $[(GdCl_3)\cdot(H_2O)_6 + (18C6)]$ in methanol afforded a compound with a more complex composition, $\{[GdCl_6]^{3-} + 3[(H_2O)\cdot(GdCl_2)\cdot(18C6)]^+ + 2[CH_3OH]\}$ (**162**).[111] The chlorine atoms and water molecules in the cation are statistically disordered. The structure of the complex **162** is analogous to those of compounds **159** and **160**.

The reactions of lanthanide chloride hexahydrates $LnCl_3\cdot 6H_2O$ with 18C6 in a methanol : acetonitrile mixture under argon[112] gave complexes with composition $\{[(H_2O)_7\cdot(Ln)\cdot(CH_3OH)]^{3+} + 2[(H_2O)_2\cdot(LnCl)\cdot(18C6)]^{2+} + 7Cl^- + (H_2O)_2\}$, where Ln = Y (**163**) or Dy (**164**) (X-ray data were collected at −150 °C). The structures of the double-charged cations are analogous to those observed in the complexes **152**–**157**. The trivalent cation has an octahedral environment. All the water and methanol molecules and noncoordinated chloride ions are involved in intermolecular hydrogen bonding.

In addition, two more types of complexes of $DyCl_3$ with 18C6 were reported. One of them was formed in acetonitrile and has the composition $\{[(Dy)\cdot(H_2O)_8]^{3+} + (18C6) + 3Cl^-\}$ (**165**).[113] The coordination polyhedron about the dysprosium atom is a bicapped trigonal prism. In a complex with triethylene glycol (L) with composition $\{[(DyCl_3)\cdot(L)] + (18C6)\}$ (**166**), the dysprosium atom has a pentagonal-bipyramidal environment.[114]

3. Tantalum chlorides

As mentioned above, the reaction of CE with strong Lewis acids (halides of metals in the highest oxidation states) are often accompanied by opening and decomposition of the macrocycle to produce large amounts of water, hydrogen chloride (due to hydrolysis), $-O-CH_2-CH_2-O-$ fragments and products of their interactions. The products of the reaction of anhydrous $TaCl_5$ with 15C5 have been studied most thoroughly.[115] The reaction in dry acetonitrile afforded a mixture of several compounds. Thus crystals of an ionic complex with composition $\{[(TaCl_2)\cdot(C_8H_{16}O_5)]^+ + [TaCl_6]^-\}$ (**167**) were isolated at room temperature. The structure of the cation of this compound (Fig. 38) is analogous to that of the complex **116**. The Ta(1) is located in the centre of the mean plane formed by five oxygen atoms of the CE molecule. However, as in the case of the complex **116**, the metal atom is bound to three oxygen atoms [O(1), O(4) and O(4a)] through donor-acceptor bonds (Ta–O = 2.24–2.27 Å) and to two oxygen atoms [O(7) and O(7a)] through covalent bonds (Ta–O = 1.89 Å).

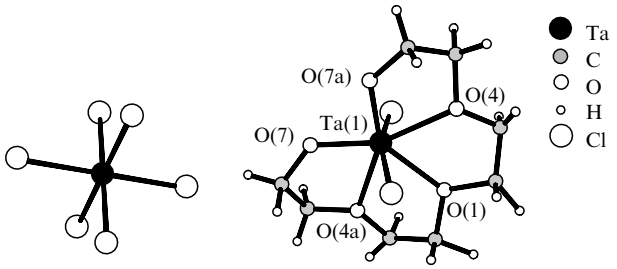


Figure 38. Structure of the complex **167**.

The coordination polyhedron about the tantalum atom is a slightly distorted pentagonal bipyramid. The Cl–Ta–Cl angle is 162°.

Heating of the reaction mixture to 35–40 °C afforded a complex with composition $\{[TaCl_6]^- + [(H_3O)\cdot(18C6)]^+\}$ (**168**).[115] The structure of the cation in this compound is analogous to those, for example, of the complexes **34**, **87** and **91**. The appearance of a new CE (18C6) in the $TaCl_5$–15C5–CH_3CN system was attributed to processes of profound destruction of 15C5, chain extension of the open-chain polyether and closure of the latter. Apparently, these processes are accompanied by the formation of water molecules and hydrolysis of $TaCl_5$ as follows from the presence of the oxonium ion in the complex **168** and the concurrent formation of complexes with compositions $\{[(H_2Cl)\cdot(15C5)_2]^+ + [TaCl_6]^-\}$ (**169**) and $\{[(15C5)\cdot(CH_3C(Cl)=NH_2)]^+ + [TaCl_6]^-\}$ (**170**). The fragments in the cation of the last-mentioned compound are linked to each other through NH···O hydrogen bonds (Fig. 39).

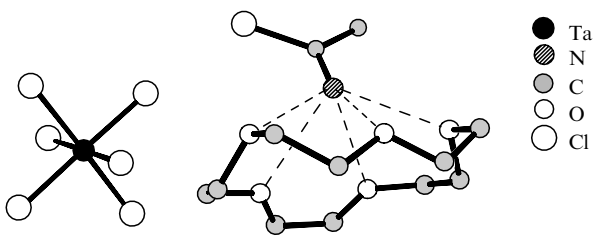


Figure 39. Structure of the complex **170**.

Introduction of an additional component, namely, a tertiary amine or a quaternary ammonium salt, into the $TaCl_5$ – 15C5 – acetonitrile system afforded the complex $\{[((C_2H_5)_3NH)\cdot(15C5)]^+ + [TaCl_6]^-\}$ (**171**) in which the fragments of the cation interact through NH···O hydrogen bonds and a complex tantalum oxychloride with composition $\{[Ta_3O_3Cl_{12}]^{3-} + 3[N(CH_3)_4]^+ + (CH_3CN)\}$ (**172**), which contains no CE molecules. The structure of the cation in the complex **172** is shown in Fig. 40.

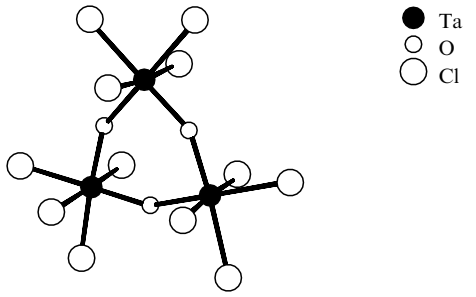


Figure 40. Structure of the $Ta_3O_3Cl_{12}$ fragment in the complex **172**.

The reaction of $TaCl_5$ with 15C5 in acetonitrile in the presence of LiCl gave complexes in which the lithium atom is a 'guest' for the CE molecule and the tantalum atom forms anions of different compositions depending on the ratio of halide molecules.[116] Two products with compositions $\{[(TaCl_5)_2O]^{2-} + 2[(Li)\cdot(CH_3CN)\cdot\cdot(15C5)]^+\}$ (**173**) (Fig. 41) and $\{[TaCl_6]^- + [(Li)\cdot(CH_3CN)\cdot\cdot(15C5)]^+\}$ (**174**) were identified. The structures of the cations in both compounds are identical. The lithium atom has a pentagonal-pyramidal coordination and deviates from the mean plane through the oxygen atoms of the CE molecule by 0.45 Å. The Li – O_{cr} distances vary from 2.08 to 2.39 Å. The Li – N distance is 2.11 Å.

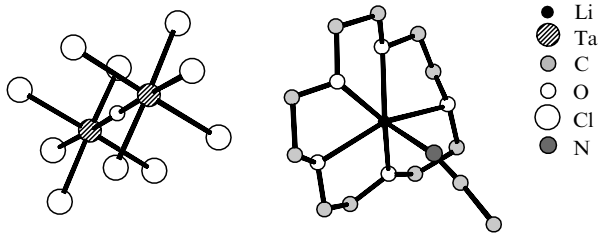


Figure 41. Structure of the complex **173**.

4. Rhenium halides

The reactions of $ReOCl_3$ and $ReOBr_3$ with 12C4 and 18C6 in the presence of water gave complexes with compositions $\{[(ReOX_4)\cdot(H_2O)]^- + [(H_3O)\cdot(12C4)]^+\}$, where X = Cl (**175**) and Br (**176**), respectively. The reaction of $ReOCl_2$ with 18C6 yielded the complex $\{[(ReOCl_4)\cdot(H_2O)]^- + [(H_3O)\cdot(18C6)]^+\}$ (**177**).[76, 117] The structures of the anions in the compounds **175** – **177** are analogous to that in the complex **98**.

The reaction of a mixture of $ReCl_4$ and LiCl with 12C4 in acetonitrile afforded a product with composition $\{(ReCl_5)\cdot\cdot(CH_3CN)]^- + [(Li)\cdot(12C4)_2]^+ + [(CH_3CN)]$ (**178**) containing the octahedral anion.[117]

5. Gold trichloride

The reaction of a mixture of gold trichloride and potassium chloride with 15C5 yielded a compound with composition $\{[(K)\cdot(15C5)_2]^+ + [AuCl_4]^-\}$ (**178**) containing the tetrahedral anion $[AuCl_4]^-$.

6. Mercury halides

The reactions of $HgCl_2$ and $HgBr_2$ with 18C6 gave typical complexes of type A with composition $[(HgX_2)\cdot(18C6)]$, where X = Cl (**180**) and Br (**181**), respectively. The mercury atom is located in the cavity of the CE molecule and has a hexagonal-bipyramidal coordination. The Hg – O_{cr} distances vary from 2.31 to 2.86 Å.[81, 118]

7. Thallium halides

The reaction of a mixture of TlCl and $SbCl_5$ with 12C4 afforded a bimolecular complex with composition $\{[SbCl_6]^- + [(Tl)\cdot(12C4)_2]^+\}$ (**182**).[119] The thallium atom in the sandwich cation is located between two CE molecules. The Tl – O_{cr} distances vary from 2.865 to 2.904 Å. The reaction of an equimolar mixture of $TlBr_3$ and RbBr with 15C5 yielded a complex with composition $\{[TlBr_4]^- + [(Rb)\cdot(15C5)_2]^+\}$ (**183**) with the thallium atom in the tetrahedral anion and the rubidium atom in the sandwich cation.[49]

The reactions of mixtures of TlX and TlX_3 with 18C6 in the presence of copper or manganese dihalides gave complexes with the analogous composition $\{4[(Tl^I)\cdot(18C6)]^+ + 2[Tl^{III}X_4]^- + [MX_4]^{2-}\}$, where M = Cu and X = Cl (**184**) or Br (**185**); or M = Mn, X = Cl (**186**).[49, 61, 120] In all the structures, the thallium(I) atom deviates from the mean plane through the oxygen atoms of the CE molecule by ~0.9 Å. The Tl – O_{cr} distances vary from 2.93 to 3.01 Å.

8. Lead halides

The reaction of lead dibromide with 18C6 in a hot aqueous solution gave a complex of type A with composition $\{[(PbBr_2)\cdot(18C6)] + (H_2O)\}$ (**187**). The coordination number of the lead atom is 8 (the Pb – O_{cr} distances with the six oxygen atoms of the CE molecule vary from 2.77 to 2.80 Å; Pb – Br = 2.924 and 2.927 Å).[121] In the crystal, the complex molecules are linked to each other through OH···Br intermolecular hydrogen bonds (3.37 Å) with the participation of water molecules. The complexes $[(PbI_2)\cdot(18C6)]$ (**188**)[122] and $[(PbCl_2)\cdot(DCHex18C6)]$, where DCHex18C6 is dicyclohexyl-18-crown-6, (**189**) [123] have analogous structures. The reaction of a 1 : 2 mixture of $PbCl_2$ and $SbCl_5$ with 18C6 in acetonitrile afforded a compound with composition $\{[(CH_3CN)_3\cdot(Pb)\cdot(18C6)]^{2+} + 2[SbCl_6]^-\}$ (**190**) in which the lead atom is also located in the centre of the CE cavity and is additionally coordinated by three acetonitrile molecules (one molecule is located 'above' the mean plane of the macrocycle and two molecules are located 'below' this plane).[124]

9. Bismuth halides

Complexes of $BiCl_3$ with 12C4 (**191**) and of $BiBr_3$ with 12C4 (**192**) are structurally similar to the corresponding arsenic complex (**92**).[125, 126] A 1 : 1 mixture of $BiCl_3$ and $SbCl_3$ reacted with 12C4 in acetonitrile to yield a product with composition $\{[(Bi)\cdot(12C4)_2]^{3+} + 3[SbCl_6]^- + [CH_3CN]\}$ (**193**),[92] which is isostructural to the antimony complex **119**.

The reaction of a 1 : 1 mixture of $BiCl_3$ and $SbCl_5$ with 15C5 in acetonitrile afforded the complex $\{[(CH_3CN)\cdot(BiCl_2)\cdot(15C5)]^+ + [SbCl_6]^-\}$ (**194**) in which the $[(BiCl_2)\cdot(CH_3CN)]$ fragment is located above the mean plane through the oxygen atoms of the CE molecule.[127] The analogous reaction of a 1 : 2 mixture of tri- and pentachlorides of bismuth and antimony with 18C6 gave a product with composition $\{[(CH_3CN)_2\cdot(BiCl)\cdot(18C6)]^{2+} + 2[SbCl_6]^-\}$ (**195**) in which the bismuth atom is coordinated by one chlorine atom, two nitrogen atoms and four (of six) oxygen atoms of the CE molecule.[127]

VII. Systems with actinide halides

The reaction of uranium(VI) oxychloride with 12C4 in tetrahydrofuran containing water yielded a compound with composition $\{[(H_2O)_2\cdot(UO_2Cl_2)\cdot(12C4)] + [12C4]\}$ (**196**).[128, 129] The coordination environment about the uranium atom is a pentagonal bipyramid formed by two oxygen atoms of the water molecules

($U-O_w$ = 2.41 Å), two chlorine atoms (U – Cl = 2.68 – 2.71 Å), two oxygen atoms of the uranyl fragment (U – O = 1.76 Å) and one oxygen atom of the CE molecule ($U-O_{cr}$ = 2.55 Å) (Fig. 42).

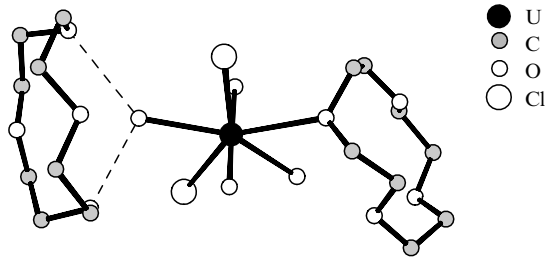


Figure 42. Structure of the complex **196**.

The reaction of uranyl chloride with 12C4 in the presence of NaCl afforded the complex $\{[UO_2Cl_4]^{2-} + 2[(Na)\cdot(12C4)]^+\}$ (**197**) containing the octahedral anion.[130,131] The reaction of uranyl chloride with benzo-15-crown-5 (B15C5) proceeded analogously to form a complex with composition $\{[UO_2Cl_4]^{2-} + 2[(Na)\cdot(B15C5)]^+\}$ (**198**).[132]

Thorium tetrachlorides reacted with various CE in solvents containing water to produce complexes of type C in which the thorium atom is not directly bound to oxygen atoms of the CE molecules.[133–135]

$$ThCl_4 + 18C6 + 9H_2O \longrightarrow \longrightarrow \{[(ThCl_2)\cdot(H_2O)_7]^{2+} + 2Cl^- + (18C6) + (H_2O)_2\}, \quad \mathbf{199}$$

$$ThCl_4 + 18C6 + 3CH_3OH + 2H_2O \longrightarrow \longrightarrow \{[(ThCl_4)\cdot(CH_3OH)_3\cdot(H_2O)] + (18C6) + (H_2O)\}, \quad \mathbf{200}$$

$$ThCl_4 + 15C5 + 2CH_3OH + CH_3CN + 2H_2O \longrightarrow \longrightarrow \{[(ThCl_4)\cdot(CH_3OH)_2\cdot(H_2O)_2] + (15C5) + (CH_3CN)\}. \quad \mathbf{201}$$

The coordination polyhedron about the thorium atom in the complexes **199**, **200** and **201** is a tricapped trigonal prism, a square antiprism and a distorted dodecahedron, respectively.

The reactions of UCl_4 with crown ethers 15C5, DB18C6 and DCHex18C6 in air proceeded with oxidation of U^{4+} to U^{6+} (see Refs 131 and 136–138).

$$UCl_4 + CaCl_2 + 15C5 + H_2O \longrightarrow \longrightarrow \{[(H_2O)_3\cdot(Ca)\cdot(15C5)]^{2+} + [UO_2Cl_4]^{2-}\}, \quad \mathbf{202}$$

$$UCl_4 + 2NH_4Cl + 4DB18C6 + CH_3CN \longrightarrow \longrightarrow \{[UO_2Cl_4]^{2-} + 2[(NH_4)\cdot(DB18C6)_2]^+ + (CH_3CN)\}, \quad \mathbf{203}$$

$$UCl_4 + CH_3OH + 2DB18C6 + H_2O \longrightarrow \longrightarrow \{[UO_2Cl_4]^{2-} + 2[(H_3O)\cdot(DB18C6)]^+ + (CH_3OH)\}, \quad \mathbf{204}$$

$$UCl_4 + 2NH_4Cl + 15C5 + CH_3CN \longrightarrow \longrightarrow \{[UO_2Cl_4]^{2-} + 2[(NH_4)\cdot(15C5)_2]^+ + 2(CH_3CN)\}. \quad \mathbf{205}$$

In the absence of air, the reaction of UCl_4 with B15C5 in the presence of NH_4Cl afforded the octahedral anion $[UCl_6]^{2-}$ and the cation $[(NH_4)\cdot(B15C5)]^+$ (**206**).[131] The reaction of uranium tetrachloride with DCHex18C6 gave compounds with compositions $\{[UCl_6]^{2-} + 2[(H_3O)\cdot(DCHex18C6)]^+\}$ (**207**)[137] and $\{[UCl_6]^{2-} + 2[(UCl_3)\cdot(DCHex18C6)]^+\}$ (**208**)[139] depending on the reaction conditions. The coordination number of the uranium atom in the cation of **208** is equal to 9. The metal atom is coordinated by three chlorine atoms and all the six oxygen atoms of the CE molecule.

The reaction of a 1 : 1 mixture of UCl_4 and NH_4Cl with 18C6 in acetonitrile yielded a compound with composition $\{[UCl_6]^{2-} + 2[(NH_4)\cdot(18C6)]^+ + (CH_3CN)_2\}$ (**209**).[140]

An interesting example of a redox process that occurred in the reaction of UCl_4 with 18C6 in tetrahydrofuran was reported.[141] The reaction product contained the uranium(IV) and uranium(VI) atoms.

$$3UCl_4 + 18C6 \xrightarrow{H_2O} \longrightarrow \{2[(U^{IV}Cl_3)\cdot(18C6)]^+ + [(U^{VI}O_2Cl_3)\cdot(OH)\cdot(H_2O)]^{2-}\}. \quad \mathbf{210}$$

The uranium(VI) atom in the anion has a pentagonal-bipyramidal environment and the uranium(IV) atom in the cation is coordinated by all the six oxygen atoms of the CE molecule ($U-O_{cr}$ = 2.48 – 2.61 Å) and three chlorine atoms.

VIII. Conclusions

To date, crown compounds of the majority of metal and semimetal halides in the highest oxidation states have been prepared and structurally characterised. However, data on the structures of this class of compounds with metal halides in the lowest oxidation states are virtually unavailable. As has been mentioned in the Introduction, the structures of the great majority of crown compounds can be actually classed into three major types, *viz*., A, B and C, and their variations. Homonuclear molecular complexes of crown ethers with halides of semimetals, such as As, Sb and Bi, as well as complexes, the nature of bonding in which is still not clearly understood, should be assigned to exceptions or to the individual type D.

The geometrical correspondence between the dimension of the metal atom (d_m) and the dimension of the cavity (d_c) of the crown ether molecule is a necessary but not nearly sufficient condition for the formation of inner-cavity crown compounds. The principle of this correspondence virtually forbids the synthesis of these compounds only if $d_m > d_c$. Moderate-sized metal atoms in the cavity are displaced toward two or three oxygen atoms or find alternative possibilities for the formation of complexes (see, for example, complexation of halides of lithium, beryllium, metals of the arsenic subgroup and lanthanides).[142,143] In these cases, the metal atoms are generally located outside the cavity of the CE molecule. It should be noted that unusual and nontypical coordination numbers of metal atoms located in the cavity of the CE molecule (for example, of the aluminium atom in the complex with the crown ether 15C5) should not be regarded as a violation of the well-known structural principles because the above-mentioned deviations of the metal atoms are induced by the macrocyclic nature of the polyethers.

Apparently, the possibility of ionisation and/or autocomplexation of a salt in a solution should be regarded as a prerequisite for the preparation of crown-ether compounds containing the metal atom in the cavity. All the above-considered inner-cavity crown compounds were prepared in solvents of the donor type. Since the processes of ionisation and autocomplexation in these solvents occur with difficulty, complexes with metal halides in the lowest oxidation states are very poorly studied. It should be noted that these metals generally form rather stable polymeric structures.

Acceptors of halide ions are introduced into salt solutions in order to direct the reactions toward inner-cavity complexes. However, in these cases the reactions always afford hetero- or homonuclear different-valence ionic complexes in which the inner-cavity cation is formed by the metal ion with the lower affinity for the halogen atom (a weaker Lewis acid). In this respect, the conversion of the complexes based on SbX_3 from type D to type A in the presence of SbX_5 is a prominent example.

The introduction of a versatile solvent, *viz*., water, into the reaction system prevents, as a rule, the formation of inner-cavity

crown compounds or causes their destruction, *i.e.*, leads to the passage from type A to type B or C in which the fragments are linked to each other through a system of hydrogen bonds. We are aware of only three examples where the metal atoms remain in the cavity of the macrocycle in the presence of water, *viz.*, the complexes prepared by the reactions of 15C5 with $CoCl_2$ (see Ref. 42) and with $MgCl_2$ (See Ref. 14) and by the reaction of $CaCl_2$ with 18C6.[7]

The presence of water in a salt – CE – organic solvent system sharply changes the character of interactions between the components. In this case, the process involves either hydration of the cation accompanied by displacement of molecules of the organic solvent from the coordination sphere of this cation or hydrolysis accompanied by the appearance of hydrogen halide, oxonium ions, oxides, hydroxides and a number of other products in the solution. However, the reasons for the appearance of water in the reaction zone have not been a matter of discussion in the majority of works. Undoubtedly, the experiments performed with the use of crystal hydrates or ordinary (not dehydrated) solvents are quite understandable the more so that hydrated compounds are formed under these conditions in rather high yields.

The instances where the reactions which were carried out with the use of anhydrous solvents and thoroughly dehydrated salts afforded single crystals of hydrated complexes are not so unambiguous. Since the yields of these salts were no more than 5% – 8% (see, for example, Refs 7, 14 and 41), hydration of salts may be attributed to residual traces of moisture in the initial compounds and in solvents as well as to the anomalous hydrophilicity of salts of some divalent metals.

Finally, the appearance of water in reactions of crown ethers with some anhydrous metal halides in the highest oxidation states, for example, with $MoCl_5$ [75] and $TaCl_5$,[115, 116] is still unclear. The complexes prepared by these reactions never have and apparently cannot have the structures of classical intra-cavity crown compounds because these structures can be formed only if the charge of the cation is no less than 3+, which is observed in none of the above-described structures. However, these reactions always afforded a wide range of various compounds, including hydrolysis products in yields of up to 20% – 30%. These yields are substantially larger than those calculated taking into account all possible sources of residual moisture that could exist in the reaction zone. In this connection, we believe that hydrolysis can be explained only by profound decomposition of the polyether molecule accompanied by the formation of large amounts of water. In this case, residual moisture, which is introduced into the reaction zone with the initial compounds and the solvent, can act as an initiator of cleavage of the macrocycle. Taking into account the above-mentioned characteristic features of the salt behaviour, not only the results of experiments on extraction and separation of metal halides (and, apparently, compounds of other types as well) with the use of crown ethers but also the ideology of these studies are highly questionable.

Reactions of solvation and complexation are the major subject matter of coordination chemistry. However, these reactions are explicitly and implicitly involved in many processes which are far from this field of chemistry. In this respect, the chemistry of macrocyclic compounds (in particular its structural aspect) is undeniably helpful in developing general model concepts of interactions between components of complex systems which can be used in various divisions of chemistry.

For example, products of intercalation of salts of the acceptor type (generally, metal halides, Lewis acids) into the interlayer space of graphite (the so-called intercalation graphite compounds, IGC) are known. Most of these products are compounds formed by metal halides MX_n which are intercalated into graphite only in the presence of free halogen or metal halides in the highest oxidation states M^*X_m (hetero-IGC). If the graphite network is considered as a polyligand, this behaviour of salts MX_n is readily explained from the standpoint of formation of heterocrown compounds, *i.e.*, on the assumption that ionisation, autocomplexation and, finally, intercalation of ionic salts of the type $\{[M^*X_{m-1}]^+[MX_{n+1}]^-\}$ or $\{[X^+[MX_{n+1}]^-\}$ into the interlayer space occur.

Yet another example is associated with the chemistry of Ziegler – Natta catalytic systems applied onto mineral supports whose surface layers, in principle, can be considered as polyligands. It is known that introduction of magnesium salts, for example, of $MgCl_2$, into catalysts $AlRR'R'' - TiXX'X''$, where R = Alk, R′ = H, R″ = Hal; X = Hal, X′ = Alk, X″ = C_5H_5, *etc.*, increases their activity in polymerisation of alkenes by several orders of magnitude. Aluminium and titanium salts can form both cationic and anionic components of complexes, while magnesium is involved only in cations of CE complexes. Therefore, magnesium efficiently competes with the first two metals in formation of cations thus causing them to form anions. One would expect that, like $MgCl_2$, salts of other metals which can undergo ionisation and are not prone to autocomplexation (for example, $ScCl_3$), are efficient promoters of polymerisation.

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