Tetraethylene Glycol Adducts of Alkaline Earth Halides

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In Memory of Professor Kurt Dehnicke

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Abstract. Reaction of commercially available tetraethylene glycol with different alkaline earth metal halides affords tetraethylene glycol complexes with different coordination numbers at the metal ion and structural features; depending on the ionic radius of the metal ion, one or two ligand molecules will be coordinated to the metal ion. In this article we will first present complexes with Mg2+ ([Mg(C8H18O5)(H2O)2]Cl) (1), Ca2+ ([Ca(C8H18O5)(H2O)3]Cl2) (2), [Ca(C8H18O5)(H2O)2]I2 (3), [Ca(C6H5O2)(H2O)2]I (4), ([Ca(C6H5O2)(H2O)3]Cl) (5), Sr2+ ([Sr(C6H5O2)(H2O)3]Cl2) (6), [Sr(C6H5O2)2]Cl2·CHCl3 (7) and Ba2+ ([Ba(C6H5O2)2]I2) (8). Secondly we will show preliminary tests for the combustion of some selected compounds and their thermal decomposition behavior. Furthermore, selected compounds were evaporated by MOCVD (metal organic chemical vapor deposition) to evaluate their capacity as future single source precursors for oxide materials.

Introduction

The design and synthesis of volatile compounds of group 2 metal ions have generated considerable attraction because of the need for these compounds as (MO)CVD precursors for the preparation of oxide thin films.[1,2] Metal ion containing thin films are of particular interest as active components in functional materials. Metal complexes with group 2 metals have a wide range of well-defined coordination arrangements and diverse properties that are relevant to electronic, optical, magnetic, and catalytic applications. Precursors with alkaline earth metal ions are very attracting for high-temperature superconductors like BSCCO (Bi2Sr2CaCu2O8) and YBCO (YBa2Cu3O7).[3–8] Enhanced volatility and suitable thermal stability, accomplished by the formation of saturated metal ion environments, are two of the most essential requirements for the good performance of these CVD precursors. The addition of ligands with sufficient oxygen or nitrogen donor atoms to a formally unsaturated metal complex is a method to achieve coordinative saturation. For example, crown ether, glyme and polyamine based chelate molecules or polyethylene glycols have been successfully employed in improving the volatility of the group 2 metal complexes.[9–13] There exist a few examples for polyethylene glycol complexes, which are used in CVD-processes as precursors:

–For example, procedures for the synthesis of YAG (Y3Al5O12), where yttrium oxide and ammonium cerium nitrate are complexed with ethylene glycol.[14]

–Previous research in the Fromm group shows the potential of ethylene glycol and glymes and their complexes of alkaline earth ions as precursors for HTS superconductors.[15,16]

–In works of McAlleese et al., tetraethylene glycol dimethyl (tetruglyme) is used for growing a thin film of gadolinia (Gd2O3) via MOCVD.[17]

The use of polyethylene glycol for the sol-gel and colloid synthesis of metal complexes, which are used as precursors in MOCVD techniques or spray pyrolysis has been described.[18–20] For these reasons we decided to investigate alkaline earth metal halide adducts of polyethylene glycols. These monotopic ligands are expected to give good precursors for testing i) the complexation and ii) the synthesis of oxidic materials. We chose the commercial monotopic ligand tetraethylene glycol for several reasons: i) Only few complexes have been studied so far with it,[22–26] ii) the four ethylene oxide moieties can take up larger alkaline earth ions and iii) the free OH groups provide a possibility for H-bonding and therefore self-assembly systems or supramolecular architectures in contrary to methylated glycols like DME or glymes. Furthermore almost all our future multitopic target ligands have a polyethylene chain as building unit.[27] For this reason it was obvious to synthesize complexes with tetraethylene glycol as ligand in order to study its complexation behavior towards different metal ions. Different proposed coordination modes for tetraethylene glycol, A) simple coordination only with one ligand, B) coordination with solvent shell, C) coordination with halide (for reaction under inert conditions) or D) coordination with
two ligands for larger cations (Sr$^{2+}$, Ba$^{2+}$) are shown in Scheme 1. In this Scheme all complexes are protonated.

![Scheme 1](image1)

**Scheme 1.** Different coordination modes of tetraethylene glycol: A coordination of the ligand alone, B coordination with supplemental solvent molecules (S), C coordination of the counterions (X), D coordination of two ligand molecules.

Results and Discussion

In the first part of the results section, we will present eight new tetraethylene glycol compounds; one magnesium, three calcium, and two strontium complexes, as well as one barium complex, with coordination numbers ranging from seven to ten. Each compound is presented with a short description and also in comparison to the other structures.

**Compound [Mg(C$_8$H$_{18}$O$_5$)(H$_2$O)$_2$]Cl·I (1)**

When MgI$_2$ reacts with tetraethylene glycol in chloroform, yellow crystals of compound [Mg(C$_8$H$_{18}$O$_5$)(H$_2$O)$_2$]Cl·I (1) can be obtained. The compound crystallizes in the monoclinic space group $P2_1/n$ with four asymmetric units in a unit cell. The asymmetric unit of 1 is shown in Figure 1 with a representation of the structure with the numbering of the cationic unit. The asymmetric unit consists of one magnesium tetraethylene glycol complex with two water molecules coordinating at the magnesium central ion; there are two counterions, one chloride and one iodide ion. The tetraethylene glycol molecule adopts a half circle shape around the magnesium central ion, at which two supplementary water molecules O6 and O7 are coordinated in axial positions of a pentagonal bipyramid.

![Figure 1](image2)

Figure 1. Representation of complex 1, the hydrogen atoms are omitted for clarity, 60% probability.

In total, there are four positions where hydrogen bonds can exist: both hydroxyl groups and both water molecules. This hydrogen bonding system is presented in Figure S1 (Supporting Information). Looking along $x$-direction, 1 arranges in rows with chloride and iodide ions between adjacent rows. The halogen exchange from MgI$_2$ is explained in the section “halogen exchange”.

Magnesium complexes are widely used in research, especially in medicine or for biotechnological research (enzymes, antibody, ATP, …), but also for catalysis or other applications as for example reagents in organic synthesis (for example Grignard reagents). The magnesium complex reported in this paper, has the less frequent seven coordination. Indeed in the Cambridge Database$^{[28]}$ there exist around 600 magnesium complexes with oxygen coordination and only 12 of them have a coordination number of seven. These seven-coordinate magnesium compounds are often found in crown ether chemistry.$^{[29–31]}$ Mg–O distances for the literature compounds of seven-coordinate magnesium complexes can be found between 1.982 Å–2.557 Å. The value of 1 (2.236(7) Å) lies perfectly in this range. The BVS. (bond valence sum$^{[32–34]}$) of the magnesium tetraethylene complex is close to 2, which shows that the ratio of charge of the magnesium ion to the distance of the ligand is optimal. A selection of metric data can be found in Table 1.

**Compound [Ca(C$_8$H$_{18}$O$_5$)·3H$_2$O]Cl$_2$ (2)**

After the successful reaction of magnesium iodide with tetraethylene glycol, the next step is to use calcium salts, for example CaCl$_2$ and CaI$_2$. The reaction of CaCl$_2$ with tetraethylene glycol in methanol occurs fast to form a colorless precipitate of [Ca(C$_8$H$_{18}$O$_5$)·3H$_2$O]Cl$_2$ (2) in high yield. Independent of the stoichiometry no other compound could be observed, which was confirmed by further test reactions. X-ray diffraction reveals a very similar structure to 1, but with three coordinated water molecules instead of two. The calcium ion is surrounded by one tetraethylene glycol unit and three water molecules adopting a coordination number of eight and form-
Table 1. M–O distances, bond valence sum and the coordination number (CooN) of the synthesized tetraethylene glycol complexes.

<table>
<thead>
<tr>
<th></th>
<th>M–OH (terminal) /Å</th>
<th>M–O (ether) /Å</th>
<th>M–OH₂ BVS</th>
<th>CooN</th>
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<td>2.690(4)</td>
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<td>2.08 10</td>
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<td>8</td>
<td>2.739(5)</td>
<td>2.922(7)</td>
<td>–</td>
<td>2.24 10</td>
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</table>

The calcium ion forms coordination bonds of average distance of 2.457(5) Å to the five oxygen atoms of the polyether and distances of 2.399(3) Å, 2.530(3) Å and 2.393(3) Å to the water molecules O6, O7 and O8 respectively. O6, O7 and O8 connect via H-bridges with Cl1 and Cl2. A coordination schematic similar to a pentagram can be seen in Figure S2 (Supporting Information). A 3D structure with a chain motive ordered in ABAB-system (row of complexes and a row of chlorides) is formed (Figure S3, Supporting Information).

Compound [Ca(C₆H₁₂O₅)(H₂O)₂]I₂ (3)

When CaI₂ reacts with tetraethylene glycol in THF, a yellow solution is obtained. After crystallization of the mother liquor by slow evaporation, yellow crystals of [Ca(C₆H₁₂O₅)(H₂O)₂]I₂ (3) are obtained. Compound 3 crystallizes in the monoclinic space group P2₁/c. The unit cell consists of four complete cationic molecules of 3 and eight iodides, two for each complex (Figure 3). In total this compound is almost identical to compound 1.

Compound [Ca(C₆H₁₂O₅)(H₂O)₃]I₂·H₂O (4)

Among the crystals of 3, it was possible to find a different kind of crystals, namely [Ca(C₆H₁₂O₅)(H₂O)₃]I₂·H₂O (4). This one is almost identical to 3 with the difference that three water molecules (O6, O7, O8) are coordinating to the calcium ion and affording in this way an eight coordination of calcium in 4. This leads to a monocapped pentagonal bipyramid almost identical to 2. Furthermore, there are also two iodides and one free water molecule per unit (Figure 4). Compound 4 crystallizes in the monoclinic space group P2₁/c. The unit cell consists of four molecules. Due to the additional coordinated water molecule, the packing is different compared to 3 and 2.

Figure 3. Ortep plot of the cationic complex of 3, the hydrogen atoms are omitted for clarity, 50% probability.

The Ca–O distances are on average 2.391(7) Å for the five oxygen atoms of the polyether and 2.334(1) Å and 2.363(6) Å for the water molecules O6 and O7 (Table 1). In x-, y-, and z-direction the regular arrangement of the iodide and complexes is clearly visible, especially in y-direction with a characteristic “zigzag” formation (Figure S4 and S5, Supporting Information).

Figure 4. Cationic unit of complex 4, the hydrogen atoms are omitted for clarity, 50% probability.

The Ca–O bonds are 2.457(3) Å on average for the five oxygen atoms of the polyether and 2.553(1) Å, 2.498(1) Å and...
2.312(1) Å for the water molecules O6, O7 and O8. The hydroxyl-group oxygen atom O1 connects to oxygen atom O5’ of the neighboring molecule to form a dimer; this has not been observed for other tetraethylene glycol complexes (Figure 5).

There are also hydrogen bonds between the hydroxyl group O5 and the water molecule O6 to iodide I1, which is connected to water molecule O7’ of the neighboring molecule. Furthermore, O1 has also a connection to I1, which continues to C8 of the neighboring molecule. Water molecule O8 connects to I2 and its symmetry equivalent I2’ and O6 connects to the free water molecule O9. This one forms also a hydrogen bond to I2. The chains are ordered in an ABAB-Scheme in which the neighboring molecules point into opposite directions (Figure S6 Supporting Information).

**Compound [Ca(C₈H₁₈O₅)(H₂O)₃]Cl·I (5)**

The reaction of CaI₂ with tetraethylene glycol in chloroform affords not only 3 and 4, but, upon long crystallization times also [Ca(C₈H₁₈O₅)(H₂O)₃]Cl·I (5). The crystal structure shows that one iodide atom was substituted by one chloride atom. Repeating this reaction led always to 3 or 4. In a last attempt, Ca₂, CaCl₂ and tetraethylene glycol were mixed in ethanol in a ratio 1:1:2. After only one night at 4 °C, the desired compound 5 could be confirmed by X-ray measurement. Compound 5 crystallizes in the monoclinic space group P2₁/n (Figure 6).

The structure of 5 is almost identical to the one of 2. The calcium ion has an average coordination distance of 2.462(3) Å to the five oxygen atoms O1–O5 and a distance of 2.405(5), 2.428(5), and 2.420(5) Å to the water molecules O6, O7, and O8. The only difference to the other calcium tetraethylene glycol complexes is that all three water molecules (O6, O7, O8) coordinate to two counterions, and also both hydroxyl groups (O1, O5) form H-bridges to the chloride ion or the iodide ion leading to a highly organized 3D packing.

**Comparison of Calcium Compounds**

A wide range of open polyethylene glycol or crown ether derivatives of calcium exist in literature[16,35–41] Comparing our new calcium adducts reveals no surprising structural differences. Only one of the four complexes shows a seven coordination of the cation. The general Ca–O distances for seven coordinated calcium compounds are between 2.37 Å and 2.82 Å.[28,42,43] Compound 3 has a mean Ca–O distance (average of all Ca–O bonds) of 2.374 Å. This is due to the stronger electron attraction of the calcium ion and a tight bonding of the ligand. The BVS. of 3 with 2.305 is also quite high and shows a more than sufficient coordination environment of the calcium ion.

**Compound [Sr(C₈H₁₈O₅)(H₂O)₄]Cl₂ (6)**

After the successful coordination of calcium, we started to investigate complexation with strontium ions. First crystalline structures always showed that two ligands wrap around one strontium ion. Even so, theoretically speaking it should be possible to obtain a strontium complex with one ligand and additional solvent molecules. This structure would be the perfect link between calcium tetraethylene complexes with one ligand and the strontium complexes with two ligands. The reaction was performed in technical solvent with a 1:1 ratio of ligand and SrI₂. Only once it was possible to measure quite bad crystals of this complex [Sr(C₈H₁₈O₅)(H₂O)₄]Cl₂ (6). The yellow crystals melt easily at room temperature when they are taken out of their mother liquor. In spite of the unsatisfactory crystal quality, the structure could be solved to see the main part unambiguously. It will be presented herein since it shows a very interesting feature: Normally a strontium ion takes up two ligands of tetraethylene glycol to fill its preferred 10-coordination. But in this case only one ligand coordinates to strontium whereas four supplementary water molecules complete the coordination sphere of the cation. Two chloride ions are balancing the charge. The strontium atom has now a nine-coordination and adopts a pentagonal double-capped bipyramidal con-
formation. The bad crystals and their short lifetime show that this complex is not very stable and decomposes spontaneously to form the two-ligand variation or, even more probable, to form strontium-hexaaqua or other aqua- or hydrate complexes. This latter species will only form when the solvent contains water. Compound 6 crystallizes in the orthorhombic space group C2221 with two complexes and four chloride ions in the asymmetric unit. Most of the carbon atoms are disordered. A representation of the compound is given in Figure 7.

**Figure 7.** Representation of the unambiguous part of the asymmetric unit of 6, the hydrogen atoms and Cl4 are omitted for clarity, 50 % probability.

Since all hydroxyl groups and all water molecules form H-bonds to chlorides, an overall 3D H-bonding system is created. The packing of the structures is very regular, and the row-like arrangement of the chlorides with the complexes is clearly visible. In x-direction an ABC-A’B’C’ arrangement can be observed (see Figure S7, Supporting Information).

**Compound [Sr(C8H18O5)2]I2·CHCl3 (7)**

SrI2 and tetraethylene glycol were reacted in chloroform to obtain yellow crystals of [Sr(C8H18O5)2]I2·CHCl3 (7). This compound crystallizes in the orthorhombic space group P212121 as a monomer with two tetraethylene glycol molecules wrapping perpendicularly around the strontium ion. Two iodides and one chloroform molecule complete the asymmetric unit. A representation of 7 is given in Figure 8.

The average Sr–O distance to the ether oxygen atoms is 2.690(3) Å and the average distances of Sr–OH are longer with 2.718(6) Å, which indicate terminal and neutral oxygen atoms; no deprotonation occurred. Two hydroxyl groups (O1 and O10) form H-bonds to I1 and I1‘ respectively. The Ba–O distances range from 2.735(5) Å for Ba1–O5 of the hydroxyl group to 2.944(4) Å for Ba–O2. These distances are in the normal range of Ba–O bonds, which can be found in the literature (2.611 Å cated. It can be noted here that no halide exchange with chloroform occurred.

**Comparison of Strontium Compounds**

Several strontium complexes can be found in the literature with glycol or crown ethers. Junk et al. synthesized different crown ether strontium complexes and studied the chelating effect. Strontium complexes with open glycols (or glymes) are also known, for example, in the work of Rogers et al. and Fromm et al. Strontium complexes can have a coordination number between 8 and 10. In compound 6 we observe a coordination number of nine for the strontium cation, and, more importantly, a bond valence sum of 2.05 for both cations Sr1 and Sr2. Compound 7 exhibits a valence sum of 2.08. The general distance for Sr–O (for ethylene glycol oxygen) in literature is 2.552 Å–2.881 Å showing that our compounds lie perfectly in the so far observed range (Table 1).

**Compound [Ba(C8H18O5)2]I2 (8)**

When BaI2 reacts with tetraethylene glycol in dichloromethane, a light yellow solution is obtained. After overlaying the reaction solution with hexane, big light yellow crystals of [Ba(C8H18O5)2]I2 (8) could be observed. Compound 8 crystallizes in the centrosymmetric, orthorhombic space group Pccn. The unit cell consists of four molecules of 8 and their eight iodide counterions (Figure 9).

Two tetraethylene glycol molecules wrap almost perpendicularly to each other (89.86°) around one barium ion to yield a coordination number of ten of the barium cation in form of a bicapped square prism arrangement. To each hydroxyl-group an iodide ion is coordinated via H-bonding (O1–I1 3.459 Å and O5–I1 3.577 Å). The Ba–O distances range from 2.735(5) Å for Ba1–O5 of the hydroxyl group to 2.944(4) Å for Ba–O2. These distances are in the normal range of Ba–O bonds, which can be found in the literature (2.611 Å...
Halogen Exchange

In the complexation of MgI₂ with tetraethylene glycol described above, an iodide atom has been substituted by one chloride atom from the solvent. This substitution has been observed in several complexation reactions investigated during this research, which were performed in dichloromethane and chloroform. Chloride, bromide and iodide ions can be added and removed using the various addition, elimination, and substitution reactions available to (organic) chemists. Exchange of chlorides and bromides were intensively studied for the reaction of primary alcohol. This type of reaction is known in organic chemistry as Finkelstein reaction, where the treatment of primary alcohol as model reaction. Halogen exchange reactions are also widely used in different anion exchange membranes, for instance for electrodialysis, and many standard commercials offer also anion exchange resins.

Generally iodide is quite a good leaving group followed by chloride and bromide. I⁻ > Cl⁻ > Br⁻. This classical theory is the contrary to the observed experiences. Due to equilibrium reactions, the unfavored reaction of chloride being substituted via S_n2-mechanism by iodide is probable (Scheme 2).

Scheme 2. Proposed iodide substitution via S_n2-reaction mechanism.

In a small test series we investigated how fast the exchange I⁻ to Cl⁻ happens. In a simple qualitative test AgNO₃ was added to chloroform. No precipitated formation of AgCl was observed, but upon addition of a MₙI₂, almost instantaneously, a white precipitate forms showing that the iodide substitution happens almost immediately. There exist also kinetic studies of exchanges in haloforms; For example, exchange reactions in solvents like tetrachloromethane or tetrabromomethane were studied by Orvik et al. He also investigated halogen exchange between chloroform and bromoform and their kinetics, nevertheless his exchange reactions were performed in a basic media. More recent studies about halogen exchange in solvents were performed by Baughman et al.

Preliminary Thermal Decomposition and Evaporation Tests

Since our research is focused on single source precursors, we decided to check the thermal behavior of our tetraethylene glycol complexes. The results give us valuable references for further research. Thus, some complexes of the tetraethylene glycol series were selected and synthesized in larger quantity. They were combusted in an oven or were evaporated in high vacuum. Whereas compounds 1 and 2 showed only formation of carbonates (Figures S11 and S12, Supporting Information), compound 8 decomposes in a first test into BaO/BaCO₃. In the next paragraph we will present our preliminary results for the thermal decomposition and evaporation test.

Thermal Decomposition of Compound 8

Compound 8 can be easily produced in large quantity. It is stable and therefore a good starting product for evaporation tests. Combustion in the oven at 500 °C in air for one day affords two phases; BaO and BaCO₃ (whiterite). We decided to investigate compound 8 also by MOCVD since this small complex could be a good precursor. The powder of 8 starts to
evaporate at 85 °C in a vacuum of 3 × 10⁻² mbar. The best growth rate is at 120 °C with 0.5 Å/s⁻¹. Passing 150 °C, the powder melts and then decomposes to a black solid. This remaining powder was analyzed by PXRD, and one phase could be identified as Ba₄C₄O₁₂.₅, a phase similar to BaCO₃. This phase was, until now, only obtained by heating barium carbonate to 970 °C.[23,24,53,61] We have shown previously[27] that the precursor approach can form oxide materials at much lower temperature than the classical solid state routes. It seems that there could be BaO also in the powder, but the black material is partially amorphous and the measured pattern is quite broad. Therefore, we carried out an IR spectroscopic analysis of the black powder. The IR spectrum shows bands at 1612 cm⁻¹ and 1011 cm⁻¹, which correspond to the vibration of a characteristic band of ionic carbonate CO₃²⁻.[62] A weak band at 2956 cm⁻¹ shows that there are still C–C bonds. This could be due to organic decomposition products. A silicon substrate with the coating obtained by MOCVD was investigated by SEM and EDS. A smooth surface with some particles and debris (size: 20 μm) is visible (Figure 10). The film is also sensitive to the beam and degrades rapidly.

Figure 10. SEM pictures of the deposition of compound 8, grown on a silicon substrate.

The low evaporation temperature and the fact that barium complex 8 can be obtained easily in high quantity could make this complex a good precursor for coatings in combination with other homometallic precursors or using this compound to build larger multitopic systems.

Conclusions

We synthesized a metal complex series with tetraethylene glycol; one complex with Mg²⁺, four complexes with Ca²⁺, two complexes with Sr²⁺ and one complex with Ba²⁺. We could show the coordination of one ligand to the metal salt for Mg²⁺ and Ca²⁺ ion and the coordination of two ligands to the barium ions. Strontium ions are able to take up only one ligand while completing their coordination sphere with solvent molecules or they can take up two ligands similar to barium tetaethylene glycol complexes. First tests of thermal decomposition show that especially compound 8 could be used as oxide source for the synthesis of HTC superconductors and we could gain a set of reference data, which will be useful for the development of further multitopic ligands based on tetraethylene glycol moieties.[27]
1. 1H NMR (360 MHz, CDCl₃, 300 K, TMS, values given in ppm): Sr₂(C₈H₁₈O₅)₂·CHCl₃ (7): on the compound.

3.64 (s, 16 H, H₂, H₃, H₆, H₇), 3.56 (d, 8 H, H₄, H₅, (90 MHz, CDCl₃, 300 K, TMS, values given in ppm):

11C NMR (90 MHz, CDCl₃, TMS, values given in ppm): δ = 72.8 (C₂, C₇), 70.4 (C₃, C₄, C₅, C₆), 69.9 (C₁, C₈) Elemental analysis of the bulk material (reaction performed in dichloromethane):

[Sr(C₈H₁₈O₅)₂]₂CHCl₃ (7): Sr₁ (0.341 g, 1 mmol) was dissolved in chloroform or in dichloromethane (15 mL) and tetrabutylene glycol (0.388 g, 2 mmol) was added to the solution. The reaction was stirred for 5 hours at room temperature. Finally, the yellow solution was filtered. A few yellow, in air unstable, single crystals of 6 were obtained by slow evaporation over 3 weeks. No further analysis could be performed on the compound.

Table 2. Crystal structure data for 1–8.

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