

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 Mg^{2+} ($[\text{Mg}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_2]\text{Cl}\cdot\text{I}$) (1), Ca^{2+} ($[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)\cdot 3\text{H}_2\text{O}]\text{Cl}_2$) (2), $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_2]\text{I}_2$ (3),

$[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_3]\text{I}_2\cdot\text{H}_2\text{O}$ (4), $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{I}$ (5), Sr^{2+} ($[\text{Sr}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_4]\text{Cl}_2$) (6), $[\text{Sr}(\text{C}_8\text{H}_{18}\text{O}_5)_2]\text{I}_2\cdot\text{CHCl}_3$ (7) and Ba^{2+} ($[\text{Ba}(\text{C}_8\text{H}_{18}\text{O}_5)_2]\text{I}_2$) (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 ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$) and YBCO ($\text{YBa}_2\text{Cu}_3\text{O}_7$).^[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 exam-

ples for polyethylene glycol complexes, which are used in CVD-processes as precursors:

–For example, procedures for the synthesis of YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$), 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 HTC superconductors.^[15,16]

–In works of *McAlleese* et al., tetraethylene glycol dimethyl (tetraglyme) is used for growing a thin film of gadolinia (Gd_2O_3) 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.^[18–21] 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

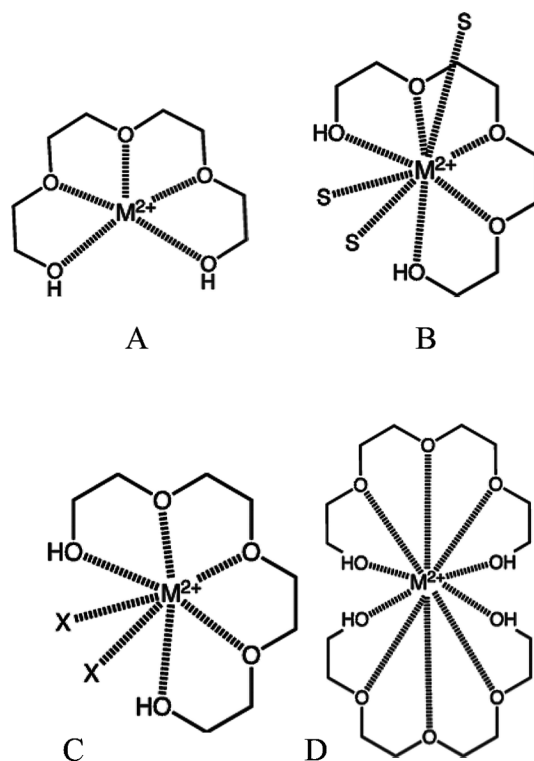
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two ligands for larger cations (Sr^{2+} , Ba^{2+}) are shown in Scheme 1. In this Scheme all complexes are protonated.



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

When MgI_2 reacts with tetraethylene glycol in chloroform, yellow crystals of compound $[\text{Mg}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_2]\text{Cl}\cdot\text{I}$ (**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 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.

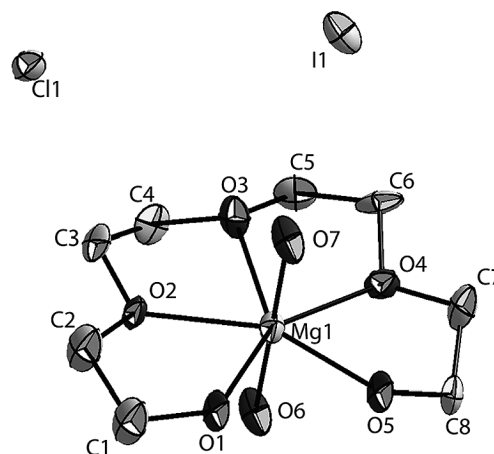


Figure 1. Representation of complex **1**, the hydrogen atoms are omitted for clarity, 60% probability.

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] $\text{Mg}-\text{O}$ 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 glycol 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.

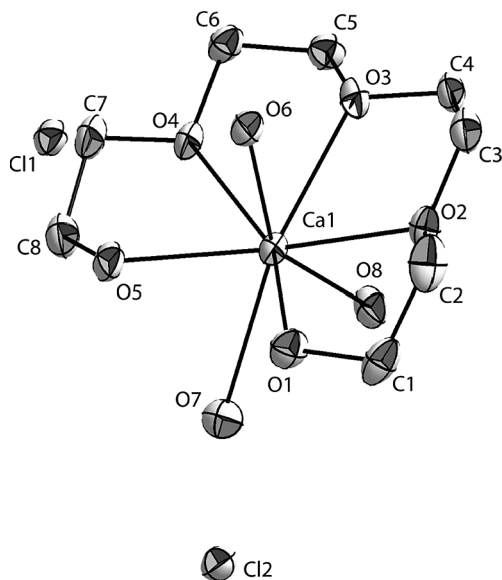
Compound $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)\cdot 3\text{H}_2\text{O}]\text{Cl}_2$ (**2**)

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 $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)\cdot 3\text{H}_2\text{O}]\text{Cl}_2$ (**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.

	<i>M</i> –OH	<i>M</i> –O	<i>M</i> –OH ₂	BVS	CooN
	(terminal) /Å	(ether) /Å	/Å		
1	2.150(1)	2.236(7)	2.032(1)	2.07	7
2	2.450(3)	2.477(3)	2.440(9)	2.17	8
3	2.362(2)	2.411(9)	2.348(7)	2.30	7
4	2.409(6)	2.489(1)	2.454(4)	2.21	8
5	2.406(4)	2.499(1)	2.418(2)	2.21	8
6	2.704	2.616	2.6916	2.06	9
				2.04	
7	2.718(8)	2.690(4)	–	2.08	10
8	2.739(5)	2.922(7)	–	2.24	10

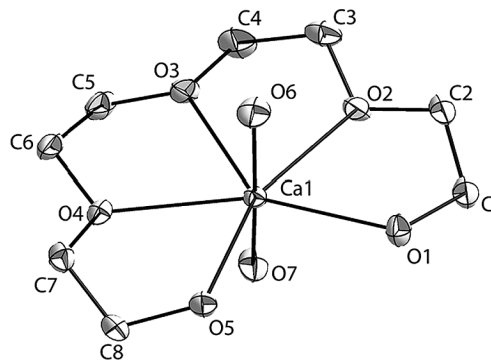
ing a distorted monocapped pentagonal bipyramidal coordination. A structure representation is shown in Figure 2.

**Figure 2.** Representation of complex **2**, the hydrogen atoms are omitted for clarity, 50% probability.

The calcium ion forms coordination bonds of average distance of 2.457(5) Å to the five oxygen atoms of the glycol 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 $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_2]\text{I}_2$ (**3**)

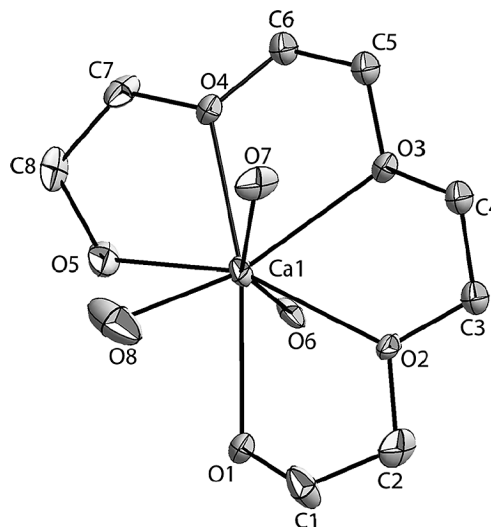
When CaI_2 reacts with tetraethylene glycol in THF, a yellow solution is obtained. After crystallization of the mother liquor by slow evaporation, yellow crystals of $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_2]\text{I}_2$ (**3**) are obtained. Compound **3** crystallizes in the centrosymmetric, monoclinic space group $P2_1/c$. 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**.

**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 and^[15]).

Compound $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_3]\text{I}_2 \cdot \text{H}_2\text{O}$ (**4**)

Among the crystals of **3**, it was possible to find a different kind of crystals, namely $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_3]\text{I}_2 \cdot \text{H}_2\text{O}$ (**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 $P2_1/c$. The unit cell consists of four molecules. Due to the additional coordinated water molecule, the packing is different compared to **3** and **2**.

**Figure 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).

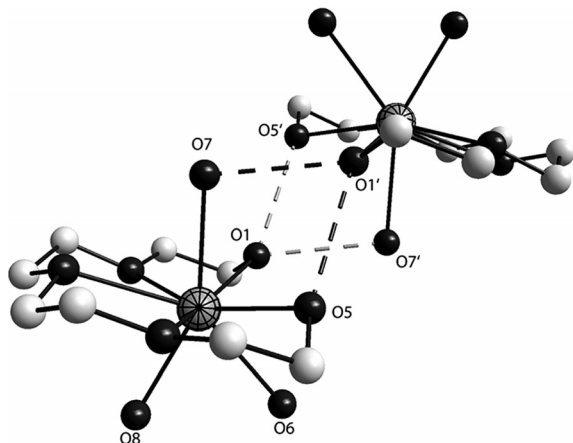


Figure 5. Dimer formation of **4**.

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 $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{I}$ (**5**)

The reaction of CaI_2 with tetraethylene glycol in chloroform affords not only **3** and **4**, but, upon long crystallization times also $[\text{Ca}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{I}$ (**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, CaI_2 , CaCl_2 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 $P2_1/n$ (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

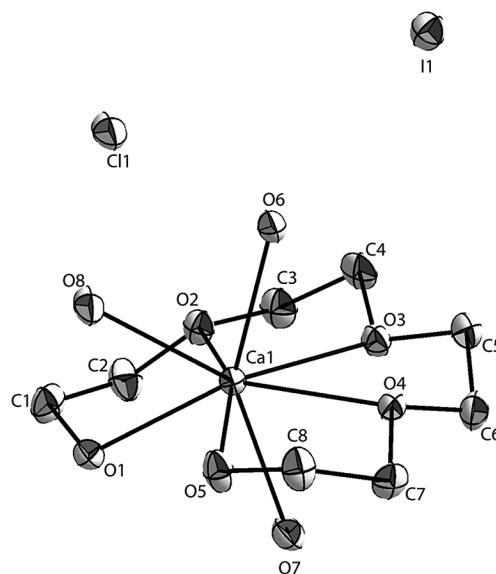


Figure 6. Representation of complex **5**, the hydrogen atoms are omitted for clarity, 50 % probability.

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 $[\text{Sr}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_4]\text{Cl}_2$ (**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 SrI_2 . Only once it was possible to measure quite bad crystals of this complex $[\text{Sr}(\text{C}_8\text{H}_{18}\text{O}_5)(\text{H}_2\text{O})_4]\text{Cl}_2$ (**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 $C22_1$ 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.

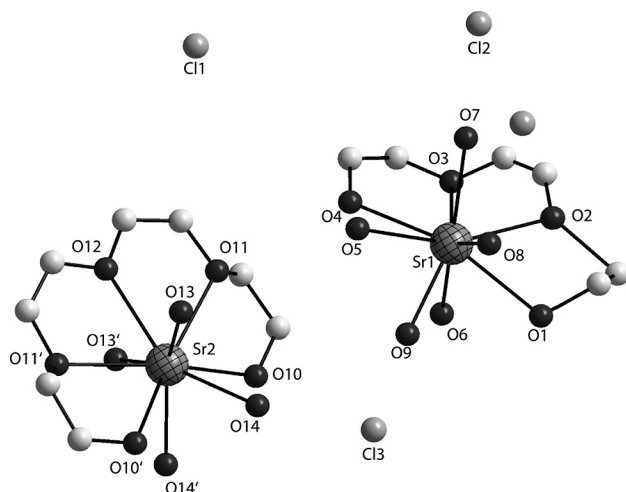


Figure 7. Representation of the unambiguous part of the asymmetric unit of **6**, the hydrogen atoms and Cl4 are omitted for clarity, 50% probability.

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 $[\text{Sr}(\text{C}_8\text{H}_{18}\text{O}_5)_2]\text{I}_2 \cdot \text{CHCl}_3$ (**7**)

SrI_2 and tetraethylene glycol were reacted in chloroform to obtain yellow crystals of $[\text{Sr}(\text{C}_8\text{H}_{18}\text{O}_5)_2]\text{I}_2 \cdot \text{CHCl}_3$ (**7**). This compound crystallizes in the orthorhombic space group $P2_12_12_1$ 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 chloroform molecules are intercalated between the complex units. The chloroform molecule does not interact directly with the cationic complex, but has a short contact over C22 to I1'. A simple packing system can be observed in x -direction, where the complexes are arranged in rows (Figure S8, Supporting Information). Between each complex a chloroform molecule is lo-

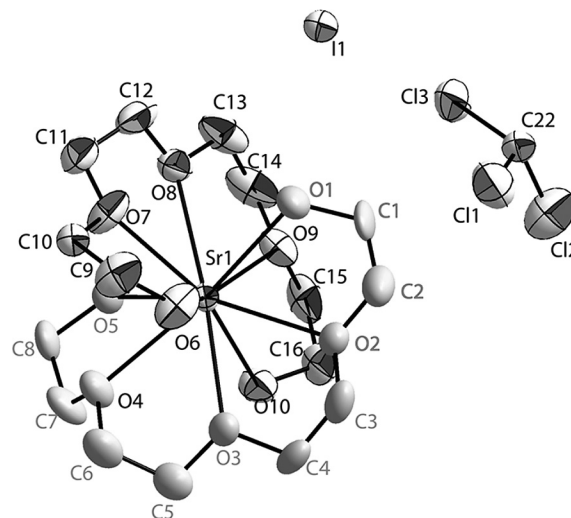


Figure 8. Representation of the complex **7**, the hydrogen atoms and I1' are omitted for clarity, 50% probability.

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.^[36,44] Strontium complexes with open glycols (or glymes) are also known, for example, in the work of Rogers et al.^[45–47] and Fromm et al.^[48–50] 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.^[51,55] 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 $[\text{Ba}(\text{C}_8\text{H}_{18}\text{O}_5)_2]\text{I}_2$ (**8**)

When BaI_2 reacts with tetraethylene glycol in dichloromethane, a light yellow solution is obtained. After overlaying the reaction solution with hexane, big light yellow crystals of $[\text{Ba}(\text{C}_8\text{H}_{18}\text{O}_5)_2]\text{I}_2$ (**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

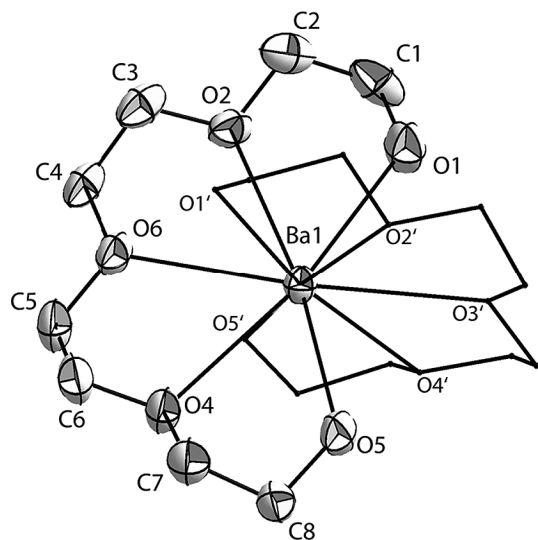


Figure 9. Representation of the cationic unit of **8**, the hydrogen atoms are omitted for clarity, 50 % probability.

–3.258 Å).^[29,40] In this structure, the H-bonding system is quite simple due to the high symmetry of the complex and the fact that only OH groups O1 and O5 can form H-bonds. Layer over layer, **8** forms channels in both directions *x* and *y* and the iodide fills the free space between the complexes. (Figure S9 and S10, Supporting Information).

In conclusion, the series with the homotopic tetraethylene glycol gave a good understanding of the behavior of alkaline earth metals with polyethylene glycols. In the next paragraph their potential towards halide exchange, followed by their potential towards evaporation and thermal decomposition, will be described.

Halogen Exchange

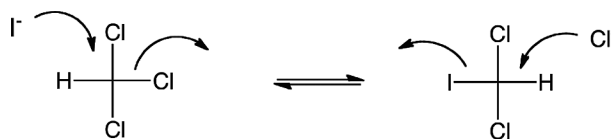
In the complexation of MgI_2 with tetraethylene glycol described above, an iodide atom has been substituted by one chloride atom from the solvent. This substitution has been observed in several complexation reactions investigated during this research, which were performed in dichloromethane and chloroform. 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.^[52] This type of reaction is known in organic chemistry as Finkelstein reaction,^[53,54] where the treatment of a primary alkyl halide or a pseudohalide with an alkali metal halide (for example, KI or KF) leads to a replacement of the halogen atom via an $\text{S}_{\text{N}}2$ -reaction.^[55] Normally this type of reaction takes place with an excess of metal halides. The equilibrium of this substitution reaction depends also on the solubility of the used metal salt in the solvent. Furthermore, the equilibrium position of these substitution reactions depend i) on the nucleophilicity of the anion, ii) the quality of the leaving group iii) the stabilization of the anion in the given solvent. A new type of Finkelstein reaction using ionic liquids

as solvent and catalyst has been studied by Chi et al.^[53] using nucleophilic fluorination of *tert*-alcohol as model reaction. Halogen exchange reactions are also widely used in different anion exchange membranes, for instance for electrodialysis,^[56] and many standard commercials offer also anion exchange resins.^[57,58]

Generally iodide is quite a good leaving group followed by chloride and bromide.



This classical theory is the contrary to the observed experiences. Due to equilibrium reactions, the unfavored reaction of chloride being substituted via $\text{S}_{\text{N}}2$ -mechanism by iodide is probable (Scheme 2).



Scheme 2. Proposed iodide substitution via $\text{S}_{\text{N}}2$ -reaction mechanism.

In a small test series we investigated how fast the exchange I^- to Cl^- happens. In a simple qualitative test AgNO_3 was added to chloroform. No precipitated formation of AgCl was observed, but upon addition of a MI_2 , 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.^[59] 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.^[60]

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/BaCO_3 . 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 BaCO_3 (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^{-5} mmbar. The best growth rate is at 120 °C with $0.5 \text{ Å} \cdot \text{s}^{-1}$. Passing 150°, the powder melts and then decomposes to a black solid. This remaining powder was analyzed by PXRD, and one phase could be identified as $\text{Ba}_4\text{C}_{4.02}\text{O}_{12.5}$, a phase similar to BaCO_3 . 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 CO_3^{2-} .^[62] A weak band at 2956 cm^{-1} shows that there are still C–C bonds. This could be remaining organic decomposition products. A silicone 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.

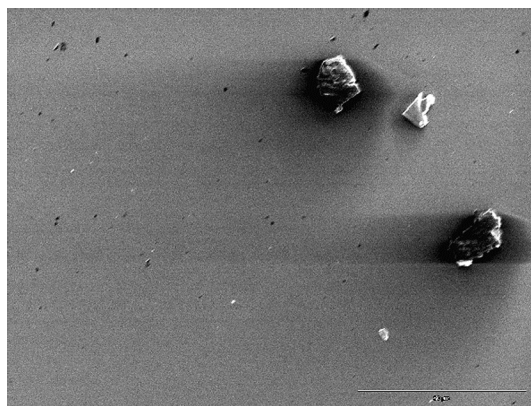


Figure 10. SEM pictures of the deposition of compound **8**, grown on a silicon substrate.

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 Mg^{2+} , four complexes with Ca^{2+} , two complexes with Sr^{2+} and one complex with Ba^{2+} . We could show the coordination of one ligand to the metal salt for Mg^{2+} and Ca^{2+} 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 tetraethylene 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]

Experimental Section

The commercially available ligand tetraethylene glycol, metal salts and solvents were used without further purification.

[Mg(C₈H₁₈O₅)(H₂O)₂]Cl·H (1): MgI_2 (0.277 g, 1 mmol) was dissolved in dichloromethane (15 mL) and tetraethylene glycol (0.197 g, 1 mmol) was added to the solution. The reaction was stirred for 4 hours at room temperature. Finally, the yellow solution was filtered. Yellow single crystals of **1** could be grown at low temperature (−4 °C). Yield 30%. FT-IR: 3225 (O–H), 2989 and 2931 (C–C), 1645 (O–H deformation), 1091 (C–O) cm^{-1} . ¹H NMR (360 MHz, CDCl_3 , 300 K, TMS, values given in ppm): δ = 4.23 (broad, 2 H, OH), 3.62 (s, 4 H, H1, H8), 3.57 (s, 8 H, H2, H3, H6, H7), 3.51 (s, 4 H, H4, H5). ¹³C NMR (90 MHz, CDCl_3 , 300 K, TMS, values given in ppm): δ = 72.1 (C2, C7), 69.9 and 69.4 (C3, C4, C5, C6), 60.9 (C1, C8). BVS: 2.078. TGA: decomposition at around 450 °C to MgCO_3 . MOCVD: 120 °C at 10^{-5} mbar.

[Ca(C₈H₁₈O₅)(H₂O)₃]Cl₂ (2): CaCl_2 (0.109 g, 1 mmol) was dissolved in methanol (15 mL) and tetraethylene glycol (0.197 g, 1 mmol) was added to the solution. The reaction was stirred for 4 hours at room temperature. Finally the yellow solution was filtered. Yellow single crystals of **2** could be grown by overlaying the mother liquor with ethyl ether and let it diffuse over 4 days at room temperature. Yield 72%. FT-IR: 3288 (OH), 2988 and 2871 (C–C), 1658 (O–H deformation), 1398 (C–H), 1017 (C–O) cm^{-1} . Elemental analysis ($\text{C}_8\text{H}_{24}\text{CaCl}_2\text{O}_8$) Calcd. C 26.75, H 6.73; found C 26.81, H 6.45. BVS: 2.17. TGA: decomposition at around 450 °C to CaCO_3 . MOCVD: 110 °C–150 °C at 10^{-5} mbar

[Ca(C₈H₁₈O₅)(H₂O)₂]₂ (3) and [Ca(C₈H₁₈O₅)(H₂O)₃]₂ (4): CaI_2 (0.293 g, 1 mmol) was dissolved in dichloromethane (15 mL) and tetraethylene glycol (0.197 g, 1 mmol) was added to the solution. The reaction was stirred for 5 hours at room temperature. Finally, the yellow solution was filtered. Yellow single crystals of **3** could be grown by overlaying the mother liquor with hexane and let it diffuse over 1 week at room temperature while crystals of **4** were grown at low temperature (−24 °C). Yield 72%. Analyses in solution are drawn together: ¹H NMR (360 MHz, CDCl_3 , 300 K, TMS, values given in ppm): δ = 4.62 (broad, 2 H, OH), 3.80 (d, 4 H, H1, H8, J = 5.2 Hz), 3.75 (m, 8 H, H2, H3, H6, H7), 3.71 (d, 4 H, H4, H5, J = 3.6 Hz). ¹³C NMR (90 MHz, CDCl_3 , 300K, TMS, values given in ppm): δ = 72.3 (C2, C7), 70.1 and 69.6 (C3, C4, C5, C6), 60.9 (C1, C8) (**3**) BVS: 2.30. (**4**) FT-IR: 3288 (OH), 2988 and 2871 (C–C), 1658 (O–H deformation), 1398 (C–H), 1017 (C–O) cm^{-1} . Elemental analysis for **4** ($\text{C}_8\text{H}_{24}\text{Ca}_2\text{O}_8$) Calcd. C 17.72, H 4.46; found C 17.89, H 4.31. BVS: 2.21. Combustion: around 450 °C, CaCO_3 .

[Ca(C₈H₁₈O₅)(H₂O)₃]Cl·H (5): CaI_2 (0.293 g, 0.5 mmol) and CaCl_2 (0.054 g, 0.5 mmol) were dissolved in a mixture of dichloromethane and methanol (10 mL/10 mL). Afterwards, tetraethylene glycol (0.197 g, 1 mmol) was added to the solution. The reaction was stirred for 4 hours at room temperature. Finally, the yellow solution was filtered. Yellow single crystals of **5** could be grown by slow evaporation of the mother liquor overnight at room temperature. Yield: 33%. FT-IR: 3340 (OH), 2956 and 2819 (C–C), 1645 (O–H deformation), 1352 (C–H vibrations), 1095 (C–O) cm^{-1} . Elemental analysis

(C₈H₂₄CaClO₈) Calcd. C 21.32, H 5.37; found C 20.99, H 5.47. BVS: 2.21. Combustion: around 450 °C, CaCO₃.

[Sr(C₈H₁₈O₅)(H₂O)₄]Cl₂ (**6**): SrCl₂ (0.157 g, 1 mmol) was dissolved in technical dichloromethane (15 mL) and tetraethylene glycol (0.197 g, 1 mmol) was added to the solution. The reaction was stirred for 1 day 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.

[Sr(C₈H₁₈O₅)₂]₂·CHCl₃ (**7**): SrI₂ (0.341 g, 1 mmol) was dissolved in chloroform or in dichloromethane (15 mL) and tetraethylene 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. Yellow single crystals of **7** were obtained by overlaying the solution with heptane. Yield 55%. FT-IR: 3386 (OH), 2941 and 2887 (C–C), 1678 (O–H deformation), 1475 (C–H vibrations), 1352 (C–H), 1098 (C–O) cm^{−1}. ¹H NMR (360 MHz, CDCl₃, TMS, values given in ppm): δ = 4.06 (broad, 4 H, OH), 3.66 (d, 8 H, H1, H8, *J* = 4.1 Hz) 3.64 (s, 16 H, H2, H3, H6, H7), 3.56 (d, 8 H, H4, H5, *J* = 4.3 Hz). ¹³C 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): (SrI₂C₁₈O₁₀H₃₆·0.85CH₂Cl₂) Calcd. C 27.25, H 5.18; found C 27.24, H 5.21. BVS: 2.08

[Ba(C₈H₁₈O₅)₂]I₂ (**8**): BaI₂ (0.391 g, 1 mmol) was dissolved in chloroform (15 mL) and tetraethylene glycol (0.197 g, 1 mmol) was added to the solution. The reaction was stirred for 12 hours at room temperature. Finally, the yellow solution was filtered. Yellow single crystals of **7** were obtained by overlaying the solution with ethyl ether or by slow evaporation. Yield 75%. FT-IR: 3383 (OH), 2950 and 2885 (C–C), 1670 (O–H deformation), 1359 (C–H vibrations), 1074 (C–O) cm^{−1}. ¹H NMR (360 MHz, CDCl₃, 300 K, TMS, values given in ppm): δ = 4.09 (s, 4 H, OH), 3.68 (d, 8 H, H1, H8, *J* = 3.2 Hz) 3.61 (s, 16 H, H2, H3, H6, H7), 3.56 (d, 8 H, H4, H5, *J* = 3.4 Hz). ¹³C NMR (90 MHz, CDCl₃, 300 K, 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 with one supplemental crystallized chloroform molecule per complete unit): BaI₂C₁₈O₁₀H₃₆·CHCl₃, calcd. C 24.74, H 4.04; found C 24.36 H 4.60. BVS: 2.244. TGA: (N₂) one decomposition

step at 305 °C to BaCO₃ and a second step at 809 °C with a conversion to BaO. MOCVD: 85 °C at 10^{−5} mbar.

Single-Crystal X-ray Structures: All crystals were mounted on loops and all geometric and intensity data were taken from one single crystal. Data collection using Mo-*K*_α radiation (λ = 0.71073 Å) was performed at 150 K with a STOE IPDS-II diffractometer equipped with an Oxford Cryosystem open flow cryostat.^[64] Absorption correction was partially integrated in the data reduction procedure. The structure was solved by Direct Methods and refined using full-matrix least-squares on *F*² with the SHELX-97 package.^[64–65] All heavy atoms could be refined anisotropically. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions. Table 2 contains the crystallographic data and details of the structure analyses. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depositary numbers CCDC-814643, -814644, -814645, -814646, -814647, -814648, -814649 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Additional pictures and analyses are available as Supporting Information.

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Table 2. Crystal structure data for **1–8**.

	1	2	3	4	5	6	7	8
Formula sum	C ₈ H ₂₂ ClIMgO ₇	C ₈ H ₂₄ CaCl ₂ O ₈	C ₈ H ₂₂ CaI ₂ O ₇	C ₈ H ₂₆ CaI ₂ O ₉	C ₈ H ₂₄ CaClO ₈	C ₁₆ H ₄₄ Sr ₂ Cl ₄ O ₁₄	C ₁₇ H ₃₇ SrCl ₃ I ₂ O ₁₀	C ₁₆ H ₃₆ BaI ₂ O ₁₀
Formula weight	416.92	359.25	524.14	560.17	450.70	757.56	847.22	779.59
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 222 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> ccn
<i>T</i> / °C	202	202	202	202	202	202	202	202.00
<i>a</i> / Å	7.050(1)	7.483(2)	9.692(8)	13.689(9)	8.701(1)	8.573(2)	8.283(6)	10.556(2)
<i>b</i> / Å	12.770(3)	14.385(3)	14.141(3)	10.392(8)	14.841(9)	14.88(3)	12.736(3)	15.625(3)
<i>c</i> / Å	18.151(4)	15.227(3)	13.363(3)	14.430(5)	13.647(6)	41.258(8)	29.942(6)	16.004(3)
<i>α</i> / deg	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
<i>β</i> / deg	91.41(3)	90.00	105.93(3)	109.11	99.94(0)	90.00	90.00	90.00
<i>γ</i> / deg	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
<i>V</i> / Å ³	1634.8(6)	1639.0(6)	1761.2(6)	1940.0(2)	1735.9(9)	5265.6(2)	3159.0(1)	2639.8(9)
<i>r</i> _{calc} / g·cm ^{−3}	1.69	1.46	1.98	1.918	1.72	0.95	1.78	1.96
<i>μ</i> / cm ^{−1}	2.18	0.74	3.88	3.536	2.32	2.25	3.96	3.89
<i>Z</i>	4	4	4	4	4	4	4	4
<i>R</i>	0.08	0.05	0.02	0.08	0.06	0.16	0.06	0.04
<i>wR2</i>	0.10	0.10	0.05	0.0902	0.11	0.19	0.12	0.07
Completeness <i>θ</i>	0.94	0.99	1.00	1.00	1.00	0.9	0.99	1.00
Goodness-of-Fit <i>F</i> ²	1.00	1.08	1.07	0.944	1.05	1.12	1.05	1.14
Reflections collected/unique	7032/2015	17925/2965	15015/4216	10420/2895	14817/4145	15799/5369	17132/4737	27063/2631
<i>F</i> (000)	832.00	760.00	1008	1088	904	1536	1648	1496

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