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Synthesis of Novel Alkaline Earth Tosylate Complexes through Donor Studies

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and Renée Crown University Honors

May 2012

Honors Capstone Project in Chemistry

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Date: April 25, 2012

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Abstract

Salt metathesis has become a critical reaction pathway in organometallic chemistry; however, for alkaline earth metals this process is hindered by the need of highly pure and expensive metal iodides as starting materials. This contribution highlights recent attempts to identify inexpensive reagents for salt metathesis. Alkaline earth-tosylates can be prepared cost effectively using p-toluenesulfonic acid in one-pot reactions in water. The coordinated water molecules can be removed by gentle heating under vacuum. The anhydrous tosylates, however, have major solubility limitations as the result of extensive aggregation networks. The goal of this study was to increase the solubility of the tosylates by the addition of electron donating crown ethers, which may reduce aggregations. Crown ethers are known for their ability to coordinate metal ions in the cavity of the macrocycles and form sandwich or club sandwich complexes.

Four new complexes were synthesized and characterized using X-ray crystallography, $\{[\text{Ca}(\text{OH}_2)_2(18\text{-crown-6})]_3[\text{OTs}]_3 \cdot 2\text{H}_2\text{O}\}_\infty$, $\{[\text{Ca}(\text{OH}_2)_2(18\text{-crown-6})]_2[\text{OTs}]_4\}_\infty$, $[\text{Sr}(\text{OTs})_2(18\text{-crown-6})(\text{OH}_2)]_\infty$, and $[\text{Ba}(\text{OTs})_2(18\text{-crown-6})(\text{OH}_2)_2]_\infty$. The two calcium complexes exhibit unique metal center environments while the strontium and barium complexes show distinct coordination numbers and arrangements of coordinating ligands. The arrangement of tosylate anions in the structures is determined by the coordination atmosphere of water molecules to the metal centers. All four characterized compounds were found to be soluble in pyridine, which improves upon previous studies that only show tosylate complexes soluble in water.

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Abbreviations:

12-crown-4, 12-c-4: 1,4,7,10- Tetraoxacyclodecane

15-crown-5, 15-c-5: 1,4,7,10,13- Pentaoxacyclopentadecane

18-crown-6, 18-c-6: 1,4,7,10,13,16- Hexaoxacyclooctadecane

A: Alkali

Ae: Alkaline-Earth

Bp: Boiling Point

CVD: Chemical vapor deposition

diglyme: Diethylene glycol dimethyl ether

FT-IR: Fourier Transform Infrared Spectroscopy

HMDS: Hexamethyldisilazane

Ln: Lanthanide

Mp: Melting Point

MOCVD: Metal organic chemical vapor deposition

NMR: Nuclear magnetic resonance spectroscopy

OTs: *p*-toluenesulfonic acid

PMDTA: N,N,N',N',N''- pentamethyldiethylenetriamine

Pyr: Pyridine

RT: Room temperature

TGA: Thermogravimetric Analysis

THF: Tetrahydrofuran

TMEDA: N,N,N',N' - Tetramethylethylenediamine

Acknowledgements:

I am happy to thank Dr. Karin Ruhlandt-Senge for allowing me to become and continue to be a part of the Ruhlandt-Senge research group from 2008 to 2012. I would also like to thank Dr. Ruhlandt-Senge for the chance to participate in the Research Experience for Undergraduates (REU) program at Syracuse University in 2011. My undergraduate research experience would not have been complete without the help of William Buchanan and Peter Rosado, who taught me the essentials of inorganic chemistry during my four years of college. I would like to thank the rest of the Ruhlandt-Senge laboratory for their support and assistance during my academic career. Professor Mathew Maye has been a great professor and reviewer of this work and deserves thanks for his help.

Besides all of the assistance from Dr. Ruhlandt-Senge and her laboratory, I would like to thank my parents for making it possible for me to attend Syracuse University. Without their help, I would not have been nearly as successful in my collegiate career.

I would last like to thank Syracuse University for hosting the Research Experience for Undergraduates (REU) program, the Syracuse Chemistry Department faculty for all of their help and advice, the National Science Foundation, and the Renee Crown University Honors Program.

1. Introduction

1.1 Alkaline Earth Metal Chemistry

The alkaline earth metals are well known for their use in organometallic chemistry. The group 2 metals are found in the earth's crust and critical for various biological processes, but they are highly oxophilic and hydrophilic in their pure metal form. As a result, strict synthetic considerations such as the use of inert gas conditions are needed.^[1] With the emergence of "Grignard" reagents based on magnesium metal, organo magnesium complexes can be successfully and efficiently synthesized if oxygen is avoided.^[2] "Grignard" reagents, as well as their heavier metal counterparts, have been explored as polymerization initiators,^[1] precursors for perovskite metal oxides in metal organic chemical vapor deposition (MOCVD)^[3], and target metals for lightweight metal-organic frameworks for gas storage and release.^[4]

Trends among the s-block metals can be useful into determining the properties and reactivity of group 2 metal compounds. Ion-association in solution and solid states can determine the coordination of alkaline earth metals to ligands based on the strength of the metal-ligand bond and capability of the anion to distribute negative charge. Contact molecules have direct bonds between the metal and organic ligands while dissociated ion pairs are observed when the cation is sufficiently saturated by a coordinated, stabilizing ligand.

The ionic radius trend for the group 2 metals can determine the coordination atmosphere. As the ionic radii increases upon descending the group, the electronegativity decreases. As a result, metal-carbon bonds increase in polar bond character. The decreasing charge to size ratio for the heavier metals limits

the polarization of ligand, and thus covalency of the resulting bond. Alkaline earth metals are able to form a wide variety of compounds, preferentially with small, highly electronegative ligands. The smaller metals, including beryllium and magnesium, support polar covalent bonds, while the larger metals, such as strontium and barium, display compounds with predominant ionic bonds. Due to the large size of the heavier metals, strategies to prevent aggregation need to be developed. The use of bulky ligands has proven successful in preventing aggregation and supporting monomeric species.

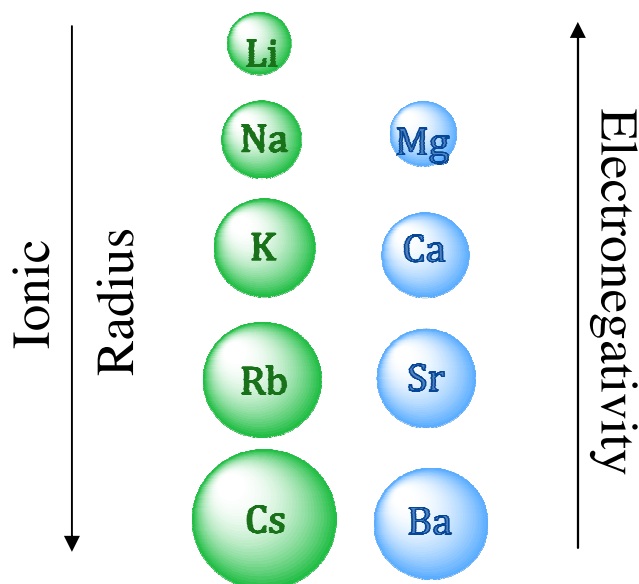


Figure 1.1. Periodic trends for group 1 and 2 metals

The alkaline earth metal compounds exhibit a wide range of coordination numbers depending on the nature of the ligands. As the diameters of the alkaline earth metals increase significantly descending the group, high coordination numbers and poor compound solubility are common. Calcium may exhibit coordination numbers ranging from three to eleven, with the most common being

six, seven, and eight.^[5] The larger size of strontium and barium results in higher coordination numbers, with typical numbers of six to twelve.^[5] To saturate these metal spheres, the use of sterically impeding or neutral co-ligands is needed.

The larger size of the alkaline earth metal centers make π interactions favorable. These interactions may be quite extensive, especially for the heaviest metals, and may be favored over metal-donor interactions. One reason for this would be if the π interactions can exist involving the entire π system of a phenyl ring.

1.2 Alkaline Earth Amides

Alkaline earth amides are amongst the best known molecular species, with multiple species focusing on the $[\text{N}(\text{SiMe}_3)_2]^-$ amide system. Isostructural dimers of the form $\{\text{Ae}[\text{N}(\text{SiMe}_3)_2]_2\}_2$ exist for all group 2 metals except beryllium.^[6] There are several studies investigating the effect of a lewis base on the overall structures. The rationale for investigating these compounds lies in their importance as starting materials in a range of synthetic applications. The $\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{donor})_n$ are typically soluble in a wide variety of solvents facilitating their synthetic process.^[6]

Aside from their use in synthetic applications, the amides have been utilized as MOCVD as well as polymerization initiators.^[6] Despite these applications, synthetic access to the amides has been limited, with salt-metathesis being a reliable synthetic route for Ca, Sr, and Ba species. Salt metathesis reactions enforce a strict stoichiometric ratio of starting materials in order to avoid

halide containing products.^[7] While an earlier report mentions the successful treatment of BaCl_2 with $\text{LiN}(\text{SiMe}_3)_2$ to obtain the target compounds, newer methodologies rely on the treatment of soluble AeI_2 with $\text{KN}(\text{SiMe}_3)_2$.^[7] The combination of an iodide and potassium ensures the clean precipitation of potassium salts.

In a two step process potassium hydride is combined with HMDS, hexamethyldisilazane (Figure 1.2), where metallation of the amide occurs through the reaction with AeI_2 . The product is then reacted with the desired alkaline earth iodide to create the alkaline earth complex along with potassium iodide.

Precipitation of potassium iodide salts shifts the reaction equilibria towards the products. Scheme 1.1 shows the reaction sequence during this reaction.

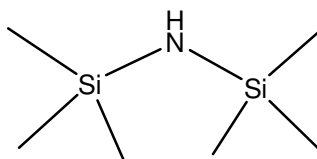
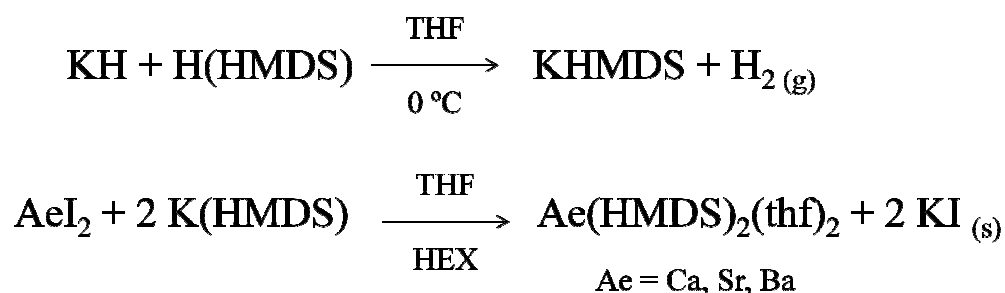


Figure 1.2. HMDS ligand



Scheme 1.1. Salt Metathesis Reaction

While salt-metathesis provides the target amides in good yields and purity, a major setback is the required high purity of the metal iodides, which are very expensive (Sigma Aldrich, 2009-2010 – BaI₂, 5g, \$113.00). Furthermore, stoichiometric control is essential, as halide containing side-products can form under the presence of excess AeI₂.^[7]

1.3 Alkaline Earth Iodide Alternatives

At least two studies have discussed the use of alternative, less expensive starting materials to replace the pricier iodides in salt metathesis regimes.

Previous studies based on trifluoromethane sulfonates (Figure 1.4) afforded the alkaline earth amides in high yields for Sr and Ba.^[8] A previous paper by Frankland and Lappert discussed arene sulfonates as potential alternative materials, but little detail is discussed in the paper on experimental synthesis.^[8]

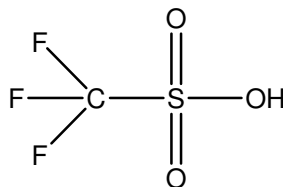


Figure 1.3. Diagram of Trifluoromethanesulfonate

The highly acidic *p*-toluenesulfonic acid (Figure 1.5) has been noted as a strong leaving group in organic chemistry, but in the inorganic sphere, it is shown to be superior to trifluoromethanesulfonate.^[8] *p*-Toluenesulfonic acid is commercially available and the corresponding alkaline earth metal species are made by simple acid base chemistry based on the alkaline earth metal carbonates, as described in Scheme 1.2.

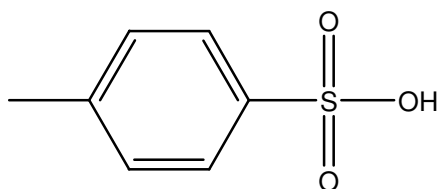
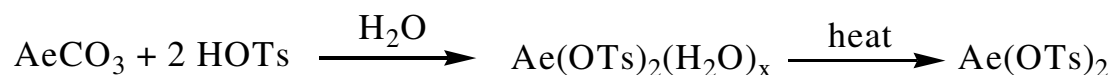


Figure 1.4. *p*-Toluenesulfonic acid

The conversion from *p*-toluenesulfonic acid monohydrate to its dehydrated form is easily achieved, requiring the heating of acid under dynamic vacuum at mild temperatures (Scheme 1.2).



Scheme 1.2. Synthesis of alkaline earth metal tosylates.

Ae = Sr, Ba

X = Mg= 6; Ca= 4; Sr, Ba=1

Literature evidence exists for the use of anhydrous Sr and Ba tosylates in salt metathesis chemistry towards the respective HMDS amides. However, the anhydrous materials aggregate under dramatic reduction of solubility, rendering heterogeneous reaction conditions associated with extended reaction times and low product yields.

Consequently the solubility of the tosylates is a key synthetic challenge to overcome the tosylates in salt metathesis chemistry. Studies formed on improving the solubility of alkaline-earth tosylates by introduction of lewis bases are not available.^[7]

1.4 Aggregations

A major obstacle in utilizing alkaline earth *p*-toluene sulfonates as starting materials for salt metathesis reactions is their low solubility in the anhydrous state. In their water coordinated state, the structure is propagated by an extensive hydrogen bonded network. Upon dehydration, removal of the hydrogen bonded

networks results in aggregations. Figure 1.5 provides a schematic representation of the deaggregation process upon addition of donors.

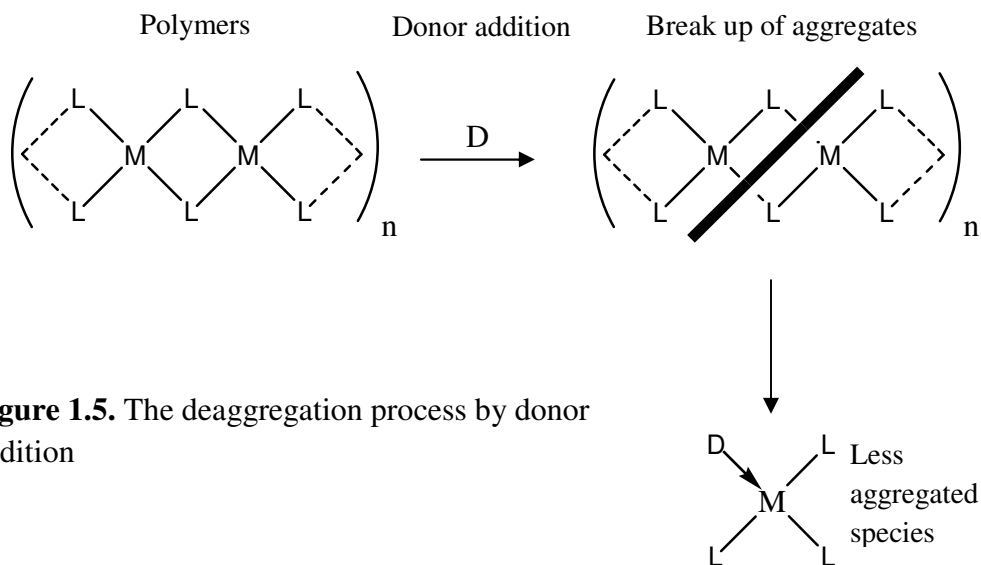


Figure 1.5. The deaggregation process by donor addition

For a donor to function as an agent to break up a polymer, the energetics of a potential M-donor bond need to outweigh that of the M-L aggregate. As an example, in AeI_2 , the iodide aggregation is relatively weak and THF as a donor can easily compete under formations of the THF adducts, hence why AeI_2 shows good solubility in THF. In contrast, AeCl_2 forms stronger aggregate bonds and a potential Ae-thf interaction cannot compete, hence, the chlorides are insoluble in THF. As an example, $[\text{BaI}_2(\mu_2\text{-H}_2\text{O})_2]_{3/\infty}$ has recently been characterized with water acting as the chemical competitor for BaI_2 .^[9] Another factor into the structural integrity of compounds after the competition of bonds depends on the sterics of more demanding donor ligands. Such is evidenced when THF is used with BaI_2 : $\text{BaI}_2(\text{thf})_5$, a seven coordinate monomer, is obtained.^[10] An identical

species exists for $\text{SrI}_2(\text{thf})_5$, whereas the calcium species $\text{CaI}_2(\text{thf})_4$ is six coordinate.^[10]

1.5 Goals

The goal of this project is to find cost effective precursors for salt metathesis using *p*-toluenesulfonic acid. The alkaline earth iodides are very expensive so the goal is that the alkaline earth tosylates will provide efficient, alternative synthetic routes in salt metathesis. While solubility of the tosylates has proved challenging in previous studies, our objective is to create more soluble complexes with the addition of donor molecules. Donor molecules can act as competitors with the already present water molecules and alter the properties of resulting complexes with increased solubility. Thus, it is desired that the synthesis and characterization of novel alkaline earth tosylate complexes be completed through this study.

2. Donor Studies

As discussed above, neutral co-ligands, often called donors, have been effective in breaking up insoluble aggregates. Donors containing multiple attachment sites, often called multidentate, have been especially effective in this process.

Among those multidentate ligands, macrocycles are especially effective and offer great accessibility to organometallics.^[11] The macrocycles exhibit hydrophilic cavities with electronegative or electropositive binding atoms and flexible hydrophobic exteriors.^[11] The use of these macrocycles with alkali and alkaline earth metals serve as viable options, as the macrocycles exhibit a strong

affinity and selective cation binding properties.^[12] One such a macrocycle are crown ethers, whose role in metal binding sites has been widely studied. In crown ether chemistry, metal complexes are formed, with the metal ions located in the cavity of the ether ring while anions are provided from various substrates.^[13] A 1:1 polyether-metal complex formed allows for a metal ion to be bound in the center of the cavity of the polyether ring.^[11] However, the metal ion is not necessarily bound in the center of the cavity as the ion may be too large or small to fit exactly in the hole.^[11] “Sandwich” and “Club Sandwich” complexes have been observed based on infrared, magnetic, and crystallographic data.^[11] Structural evidence indicates that the sizes of the polyether cavity and the metal’s ionic radius correlate to the stoichiometry of the resulting complex.^[11] A barium difluorenyl and cyclic dimethyldibenzo-18-crown-6 complex was found to be in a 1:1 ratio with the barium ion sitting in the cavity of the ring sandwiched between two fluorenyl moieties.^[11] The formation of a 3:2 potassium benzo-15-crown-5 complex was postulated to be a club sandwich complex, with three polyether molecules arranged in three tiers, each separated from the next by a metal ion.^[11] Table 2.1 shows the ionic and cavity diameters of various alkali, alkaline earth and polyethers.

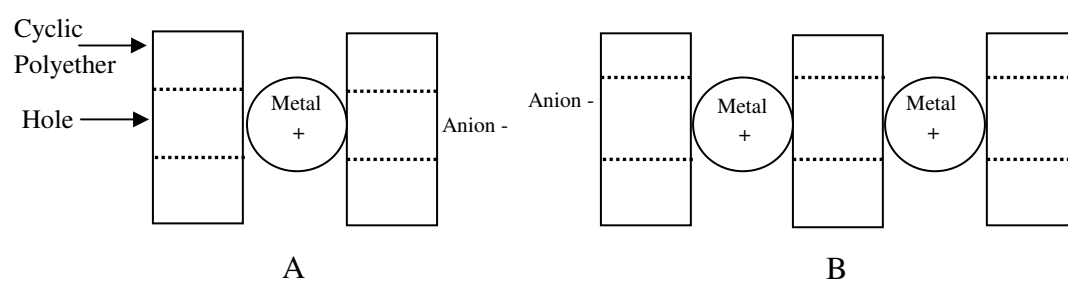
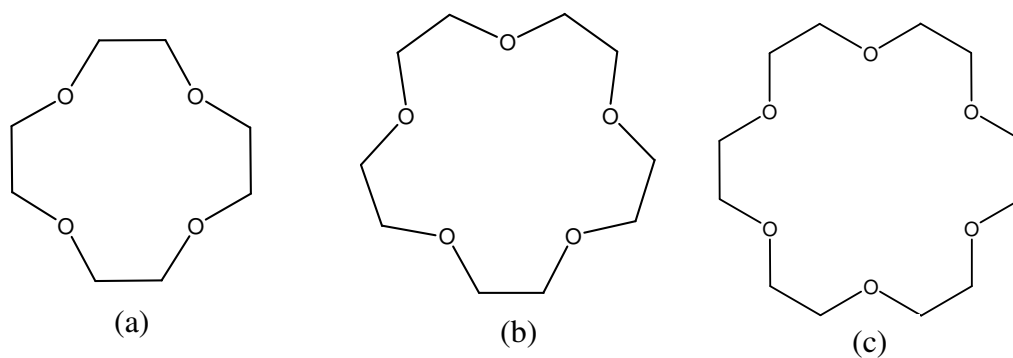


Figure 2.1. Sandwich (A) and Club Sandwich Orientations (B)

Table 2.1. Ionic and Cavity Diameters of A, Ae, and Crown Ethers.¹¹

Cation	Ionic Radius (Å)	Polyether	Diameter of Cavity (Å)
Lithium	0.90	12-crown-4	1.2-1.4
Sodium	1.16	15-crown-5	1.7-2.2
Potassium	1.52	18-crown-6	2.6-3.2
Magnesium	0.86	15-crown-5	1.7-2.2
Calcium	1.14	18-crown-6	2.6-3.2
Strontium	1.32	18-crown-6	2.6-3.2
Barium	1.49	18-crown-6	2.6-3.2

**Figure 2.2.** Example of crown ethers: (a) 12-crown-4, (b) 15-crown-5, (c) 18-crown-6

Water plays a factor with crown ether complexes as hydrogen bonding has been shown to play a significant role in propagating extended networks.^[6] Recent studies have found that hydrated metal salts form hydrogen-bonded networks or oligomeric/polymeric arrays with crown ethers acting as spacer units via the H-

bond accepting heteroatoms in the macrocycle.^[12] Fewings et.al. reported on three 15-crown-5 tosylate complexes incorporating Mn, Co, and Zn. The compounds display pentagonal bipyramidal metal centers with the metal located in the center of the crown ether, bound to five oxygen atoms. The axial water molecules form hydrogen bonded networks to oxygen atoms of the sulfonate ions that bridge successive $[M(H_2O)_2 15\text{-crown-5}]^{2+}$ units forming a one-dimensional polymeric strand.^[12]

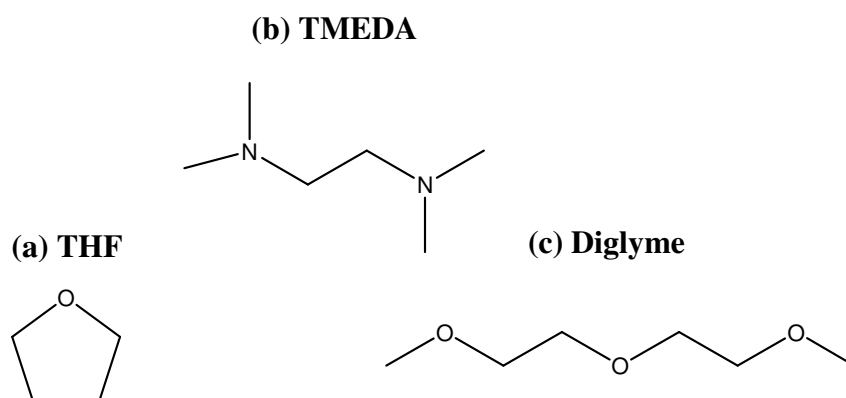
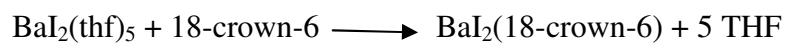


Figure 2.3. Various donors explored. (a): Tetrahydrofuran (THF) ; (b): Tetramethylethylenediamine (TMEDA) ; (c): bis(2-methoxyethyl) ether (Diglyme);

The exploration of donors besides crown ethers has been studied. Figure 2.1 shows three donors with oxygen or nitrogen donating groups. These donors allow the successive introduction of oxygen or nitrogen atoms, as options exist to introduce one (THF), two (dimethoxyethane, DME), three (diglyme shown above), or more donor atoms. The success of introducing multidentate donors is based on

the chelate effect, where chelate coordination is entropically favored. Scheme 2.1 shows the increased disorder of a reaction based on the chelate effect.



Scheme 2.1. Chelate Effect

The chelate effect for TMEDA and digylme promote them as good donors for the alkaline earth metals. THF's polarity allows for it to be used as a solvent as well as a coordinating ligand.

3. Experimental

3.1 General Experimental

While many of the alkaline earth metals are air and moisture sensitive, the use of an inert atmosphere was not needed as the alkaline earth tosylates formed in Scheme 1.2 were hydrated. All reactions were carried out on the bench top and the resulting products were placed in vials for further characterization. THF solvent was collected from a Vacuum Atmospheres solvent system. All alkaline earth metal carbonates were purchased from commercial suppliers in +99.9% purity.

Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 series instrument (TA Instruments-Waters LLC) under an N₂ balance/sample purge flow of 40 mL/min and 60 mL/min, respectively. The sample was loaded onto a platinum pan and heated using a ramp method from room temperature to 750 °C.

All crystal data was collected using a Bruker SMART system with a 3-circle goniometer and an APEX-CCD detector. Data were collected using MoK α radiation and a low temperature device built by H. Hope (UC Davis). The crystals were submerged in highly viscous hydrocarbon oil (Infineum), mounted on a glass fiber and placed in the low temperature stream on the diffractometer, as described in detail previously.^[14] Data collection parameters and refinement details have been described in detail (Table 4.1).^[14] The crystal structures were solved using Direct Methods and subsequent refinement by full-matrix least-squares method on F^2 .^[15] All non-hydrogen atoms were refined anisotropically.

Hydrogen atoms, except those of water molecules, were calculated to fixed positions using restraints. Water hydrogens were located directly in the difference map. An absorption correction was performed using the SADABS program.^[16]

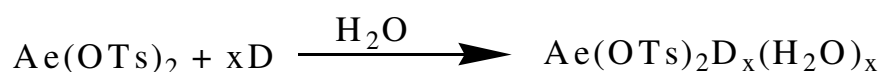
IR spectra (4000-400 cm^{-1}) were obtained on a Nicolet IR200 FTIR spectrometer for mineral oil mulls prepared between KBr plates. Melting point determinations (uncalibrated) were made using capillary tubes in a Mel-Temp II melting point apparatus.

3.2 Synthetic Routes

Two synthetic methodologies were explored for synthesis of the target compounds, donor addition reactions and direct metallation reactions.

3.2.1 Donor Addition

As this work focuses on evaluating the role of donors in the structural chemistry of heavy alkaline earth tosylates, reactions explored preformed alkaline earth tosylates dissolved in water with the various donors employed. Scheme 3.1 shows the donor addition reactions.



Scheme 3.1. Donor addition reactions

Ae- Ca, Sr, Ba

D = THF, TMEDA, Diglyme, 15-crown-5, 18-crown-6

3.2.2 Direct Metallation

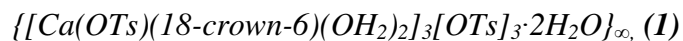
Donors may also be introduced during the preparation of the complexes, as investigated in direct metallation reactions. In these reactions, metal filings were combined with *p*-toluenesulfonic acid, donors, and solvents. Water was not used as a solvent or donor in the hopes of creating anhydrous complexes.

3.3 Alkaline Earth Crown Tosylates

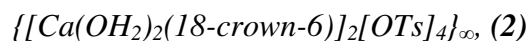
Synthetic Route A

A 1:1 or 1:2mmol ratio of Ae(tosylate)(H₂O):crown ether was added to a 25mL beaker. Slowly, a small amount of distilled H₂O (3-10mL) was added to the beaker until both compounds dissolved. On a few occasions, 2-3mL of THF was added to the solution. The beaker was placed on a stir plate and left to stir for fifteen minutes. The solution was then filtered into small vials and left to slowly evaporate.

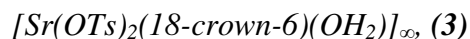
3.3.1 Specific Syntheses



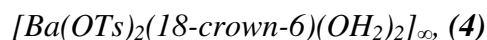
In a 25mL beaker, 0.38g (1mmol) Ca(OTs)₂(H₂O)_n was added with 0.26g (1mmol) 18-crown-6. 5mL of distilled H₂O was added to the beaker until the solids dissolved followed by stirring for fifteen minutes. The resulting colorless solution was filtered into a vial. The solution was left to evaporate for fourteen days, when crystal formation occurred. The product was soluble in pyridine and water, but no other solvents. Mp: Brown at 260°C, dark brown at 290°C, black at 305°C. Yield % (non-optimized): 94%. IR (cm⁻¹): 3448 (br, w); 2926 (s); 1250 (m); 1195 (m); 1011 (w); 824 (m); 684 (s); 568 (s).



In a 25mL beaker, 0.38g (1mmol) $Ca(OTs)_2(H_2O)_n$ was added with 0.53g (2mmol) 18-crown-6. 5mL of distilled H_2O was added to the beaker until the solids dissolved. The beaker was placed on a stir plate for fifteen minutes, and then filtered into a vial. The solution was left to evaporate for fifteen days, when crystal formation occurred. The product was soluble in pyridine and water, but no other solvents. Mp: Brown at 255°C, dark brown at 290°C, and black at 305°C. Yield % (non-optimized): 59%. IR (cm^{-1}): 3460 (br, s); 2890 (s); 1637 (m); 1475 (m); 1203 (m); 1107 (m); 1011 (w).



In a 25 mL beaker, 0.430g (1mmol) $Sr(OTs)_2(H_2O)_n$ was added with 0.26g (1mmol) 18-crown-6. 5mL of distilled H_2O was added to the beaker until the solids dissolved, when 3mL of THF was added. The beaker was placed on a stir plate for fifteen minutes, and then filtered into a vial. The solution was left to evaporate for five days, when crystal formation occurred. The product was soluble in pyridine and water, but no other solvents. Mp: Brown at 255°C, dark brown at 310°C, and black at 350°C. Yield % (non-optimized): 87%. IR (cm^{-1}): 3473 (br, s); 2920 (s); 1475 (s); 1016 (s); 684 (s); 565 (s).



In a 25mL beaker, 0.480g (1mmol) $Ba(OTs)_2(H_2O)_n$ was added with 0.26g (1mmol) 18-crown-6. 5mL of distilled H_2O was added to the beaker until the solids dissolved. The beaker was placed on a stir plate for fifteen minutes, and

then filtered into a vial. The solution was left to evaporate for eight days, when crystal formation occurred. The product was soluble in pyridine and water, but not in other solvents. Mp: Brown at 250°C, dark brown at 280°C, and black at 295°C. Yield % (non-optimized): 86%. IR (cm^{-1}): 3423 (br, s); 2920 (m); 1467 (m); 1011 (s); 813 (w); 566 (s).

4.0 Results and Discussion:

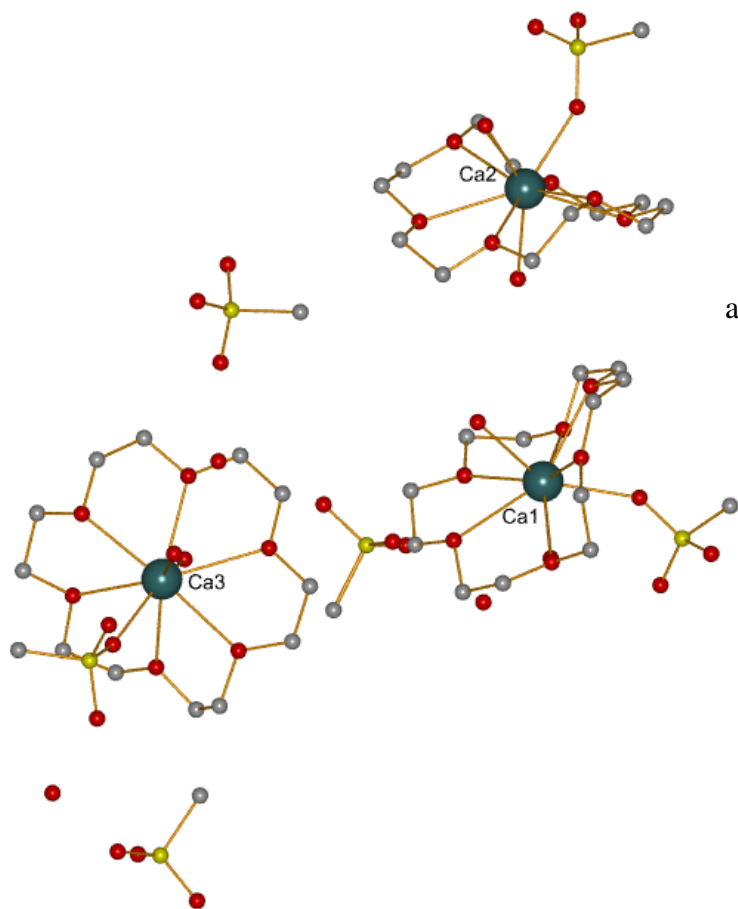
4.1 Structural characterization for Compounds 1-4

Table 4.1. Crystallographic data and structural refinement for compounds **1-4**.

Compound	1	2	3	4
Empirical formula	C ₇₈ H ₁₃₂ Ca ₃ S ₆ O	C ₂₆ H ₄₂ CaS ₂ O ₁	C ₂₆ H ₄₀ SrS ₂ O ₁	C ₂₆ H ₄₂ BaS ₂ O ₁
Formula weight	⁴⁵ 2102.50	⁴ 688.80	³ 712.34	⁴ 780.07
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	Pc	P2 ₁ 2 ₁ 2 ₁	P-1	P2 ₁ /c
T (K)	86(1)	86(2)	86(1)	83(2)
Unit cell dimensions (Å, °)				
a	8.3932(9)	13.1482(8)	9.0390(18)	13.801(2)
b	44.372(4)	19.4443(13)	11.397(2)	15.090(2)
c	14.6394(13)	24.4742(17)	15.142(3)	14.965(2)
α, γ	90	90	93.02(3); 92/49(3)	90
β	118.199(5)		91.87(3)	91.959(2)
Volume (Å ³), Z	4805.0(8), 2	6257.0(7), 8	1555.3(5), 2	3114.8(7), 4
Calculated density (Mg/m ⁻³)	1.451	1.462	1.453	1.663
Absorption coefficient (mm ⁻¹)	0.396	0.401	1.862	1.476
2θ range	3.59 to 25.68°	1.66 to 30.37°	1.35 to 28.24°	0.92 to 28.33°
Unique reflections	15251	18717	6899	7033
Total reflections	29092	55690	13755	26867
Goodness-of-fit on F ²	1.008	0.929	1.035	0.975
R ₁ , wR ₂ (all data)	R ₁ = 0.1007, wR ₂ = 0.1116	R ₁ = 0.0644, wR ₂ = 0.0906	R ₁ = 0.0327, wR ₂ = 0.0709	R ₁ = 0.0392, wR ₂ = 0.0730
R ₁ , wR ₂ (Final)	R ₁ = 0.0606, wR ₂ = 0.0988	R ₁ = 0.0399, wR ₂ = 0.0802	R ₁ = 0.0274, wR ₂ = 0.084	R ₁ = 0.0316, wR ₂ = 0.0708
F(0 0 0)	2226	2920	708	1592

4.1.1 Structural characterization of $\{[Ca(OTs)(18\text{-crown-6})(OH_2)_2]_3 [OTs]_3 \cdot 2H_2O\}_\infty$ (**1**)

Compound **1** crystallizes in the monoclinic spacegroup Pc. The complex demonstrates three nine-coordinate crystallographically independent calcium centers. Each calcium center achieves coordination through six oxygen atoms coming from the 18-crown-6 donor molecule, two axial water co-ligands and metal bound sulfonate oxygens (Figure 4.1). Distances and angles for Ca-O and O-Ca-O bonds lie within reported values and are summarized in Table 2, with shorter distances and larger angles possibly due to the twisting of the crown molecule.^[17]



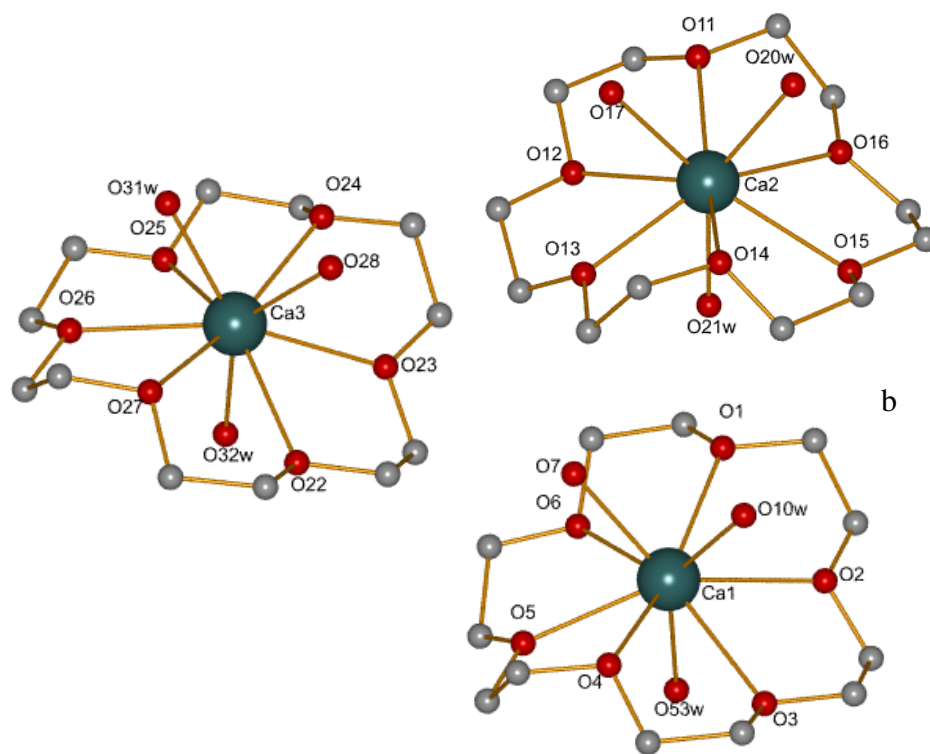


Figure 4.1. (a) Nine coordinate calcium centers. (b) Individual calcium centers with labels. Phenyl groups and hydrogens removed for clarity.

Unassociated tosylate ligands serve as counter ions and provide the anchor points for the hydrogen bonded network in the 3D structure (Table 4.3). The uncoordinated lattice water also participates in hydrogen bonding, extending the network further (Figure 4.2).

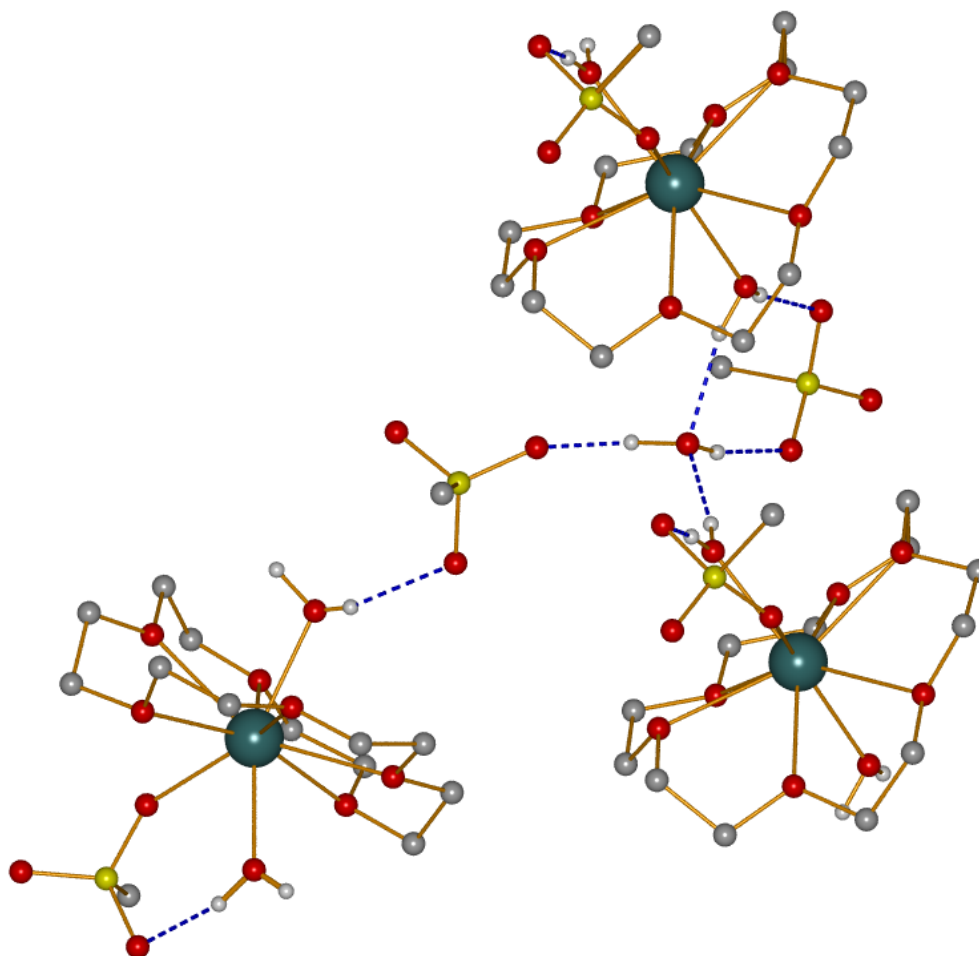


Figure 4.2. Example of the hydrogen bonded network between calcium centers, phenyl rings on the tosylate ligands and all non-water bound hydrogens removed for clarity. Complete hydrogen bonded network not shown due to the very dense nature of the structure.

Table 4.2 Selected bond lengths (Å) and angles (°) for **1**

Ca(1)-O(10)w	2.370(5)	O(10)-Ca(1)-O(7)	75.05(18)
Ca(1)-O(7)w	2.393(4)	O(10)-Ca(1)-O(53)	143.7(10)
Ca(1)-O(53)	2.425(5)	O(7)-Ca(1)-O(53)	141.3(17)

Ca(1)-O(5)	2.510(4)	O(20)w-Ca(2)-	74.97(17)
Ca(2)-O(20)w	2.370(5)	O(17)	144.9(2)
Ca(2)-O(17)	2.371(4)	O(20)w-Ca(2)-	133.0(17)
Ca(2)-O(21)w	2.398(6)	O(21)w	139.9(17)
Ca(2)-O(13)	2.542(4)	O(20)w-Ca(2)-	145.9(17)
		O(13)	
		O(17)-Ca(2)-	
		O(21)w	
		O(31)w-Ca(3)-	
		O(32)w	
Ca(3)-O(31)w	2.351(5)	O(31)w-Ca(3)-	141.7(16)
		O(28)w	
Ca(3)-O(32)	2.388(4)	O(32)w-Ca(3)-	72.21(15)
		O(23)	
Ca(3)-O(28)w	2.404(4)	O(28)-Ca(3)-O(23)	72.52(13)
Ca(3)-O(23)	2.523(6)	O(31)-Ca(3)-O(27)	78.16(14)

Table 4.3 Selected hydrogen bonding distances (Å) and angles (°) for **1**

D-H...A	<DHA	d(D...A)
O(31)-H(88)...O(29)	162.86	2.775
O(31)-H(88)...S(6)	131.00	3.338
O(50)-H(96)...O(30)	163.93	2.785
O(52)-H(84)...O(33)	170.13	2.761
O(50)-H(95)...O(37)	148.31	2.753
O(52)-H(85)...O(40)	171.78	2.758
O(10)-H(80)...O(52)	167.29	2.791
O(10)-H(79)...O(9)	163.97	2.765
O(10)-H(79)...S(4)	133.77	3.394
O(21)-H(90)...O(36)	165.96	2.760
O(21)-H(90)...S(3)	142.61	3.691
O(53)-H(81)...O(52)	165.95	2.836
O(31)-H(89)...O(51)	169.67	2.766
O(20)-H(92)...O(50)	153.80	2.829

4.1.2 Structural characterization of $\{[Ca(OH_2)_2(18\text{-crown-}6)_2]_2[OTs]_4\}_{\infty}$ (**2**)

Compound **2** crystallizes in the orthorhombic spacegroup $P2_12_12_1$. The complex demonstrates two eight coordinate calcium centers with six oxygens coming from the crown macrocycle and two water molecules at the axial positions (Table 4.4). Table 5 shows selected bond lengths and angles for the complex.

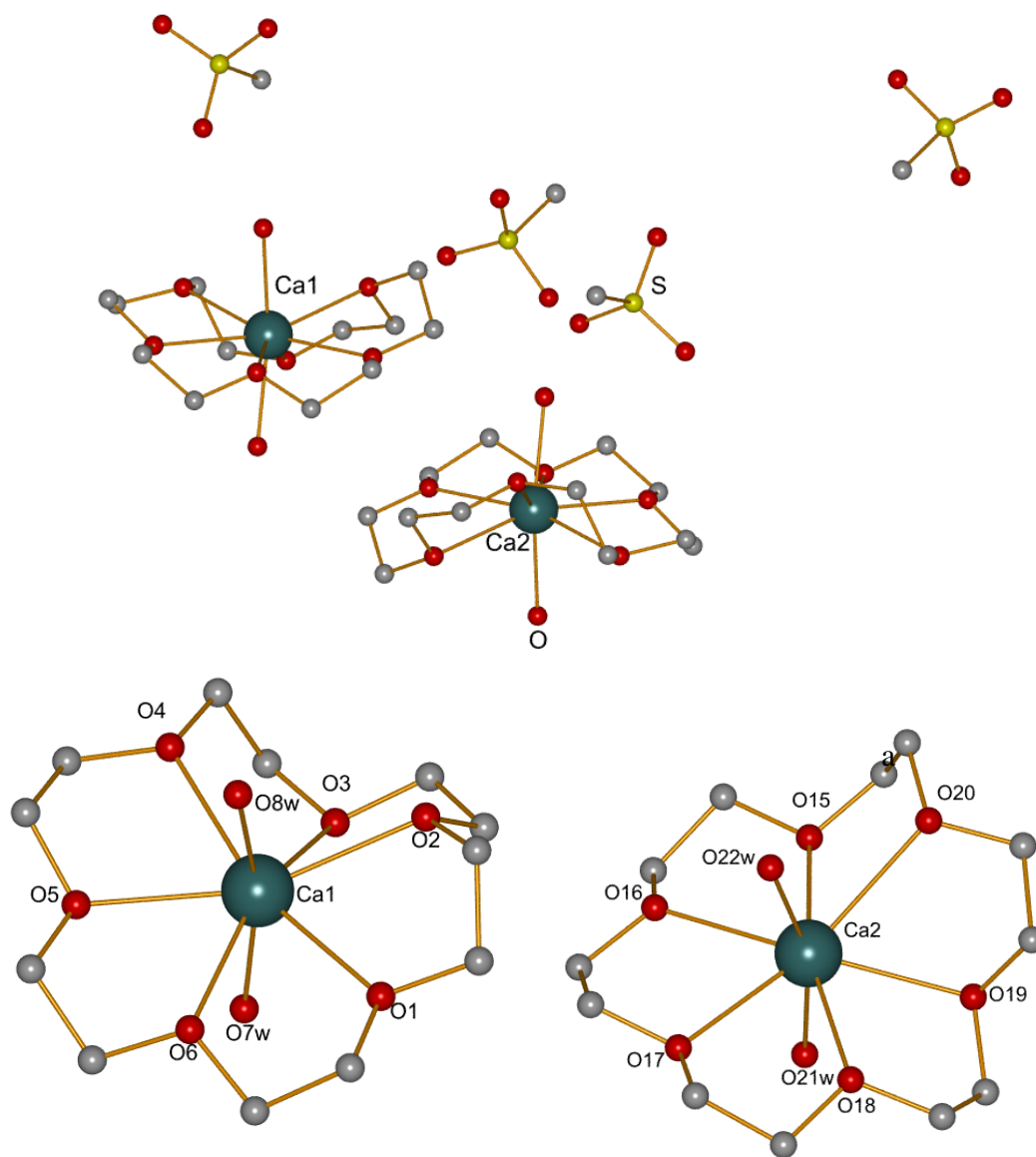


Figure 4.3. (a) Eight coordinate calcium centers with fully separated tosylate ligands. Hydrogens removed for clarity. (b) Labeled calcium environments. All hydrogen atoms and phenyl groups removed for clarity.

The extended structure shows propagation into 1D chains *via* a complex hydrogen bonded network (Table 4.5) between the unassociated [OTs]⁻ ligands and the coordinated waters (Figure 4.4).

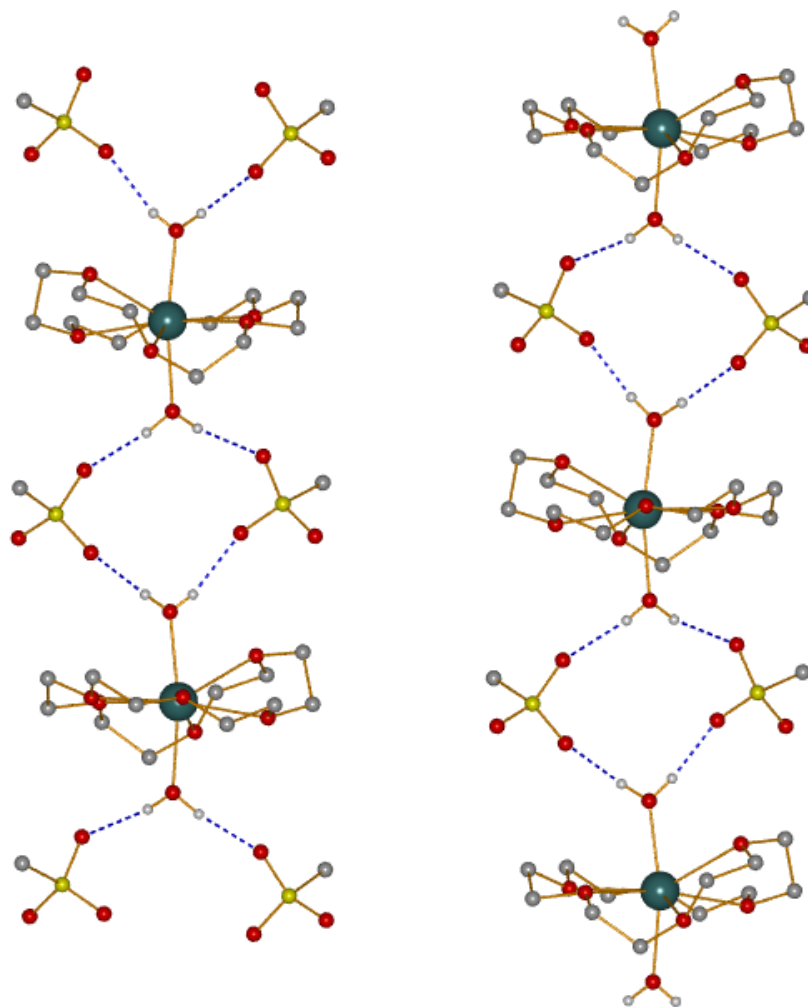


Figure 4.4. Extended hydrogen bonded network of **2**. All non-water bound hydrogens removed for clarity.

Table 4.4. Selected bond lengths (Å) for **2**

Ca(1)-O(4)	2.504(18)
Ca(1)-O(6)	2.526(18)
Ca(1)-O(5)	2.489(19)
Ca(1)-O(1)	2.491(18)
Ca(1)-O(2)	2.511(19)
Ca(2)-O(20)	2.650(19)
Ca(2)-O(16)	2.483(17)
Ca(2)-O(19)	2.508(20)

Table 4.5. Selected hydrogen bonding distances (Å) and angles (°) for **2**

D-H...A	<DHA	d(D...A)
O(7)-H(60)...O(9)	167.67	2.698
O(7)-H(59)...O(14)	177.23	2.690
O(8)-H(57)...O(10)	165.64	2.793
O(8)-H(57)...S(1)	162.56	3.697
O(8)-H(58)...O(12)	167.87	2.750
O(21)-H(56)...O(23)	163.20	2.793
O(21)-H(56)...S(3)	167.58	3.681
O(21)-H(55)...O(28)	169.67	2.744
O(22)-H(53)...O(25)	168.30	2.695
O(22)-H(54)...O(26)	174.53	2.697

Contrary to compound **1**, compound **2** was prepared utilizing 2 equivalents of 18-crown-6 in an effort to obtain a sandwich complex. In compound **1**, three calcium centers, two of which portray similar environments, are observed that coordinate 18-crown-6 ligand, tosylate anions, and two or three water molecules. Whilst in compound **2** only two crystallographically independent calcium centers are observed. Compound **1** exhibits partial separation of the tosylate ligands

where one tosylate is bound and the other is unassociated but plays an important role in hydrogen bonding. In compound **2**, the tosylate ligands do not coordinate to the metal, but act as anchor points for the bonding interactions, further propagating the chain structure.

4.1.3 Structural characterization of $[\text{Sr}(\text{OTs})_2(18\text{-crown-6})(\text{OH}_2)]_\infty$, (3)

Compound **3** crystallizes in the triclinic spacegroup P-1. The complex consists of a nine coordinate strontium center (Figure 11), with six oxygens coming from the crown macrocycle, two ligands and one water. Sr-O distances and angles between the metal center and the 18-crown-6, tosylate, and water molecules lay within reported values.^[18] Table 4.8 summarizes selected bond lengths and angles for the title compound. The extended structure consists of 1D chains that propagate *via* hydrogen bonds (Table 4.9) between the metal bound water molecule to the *trans* positioned tosylate ligands (Figure 4.6).

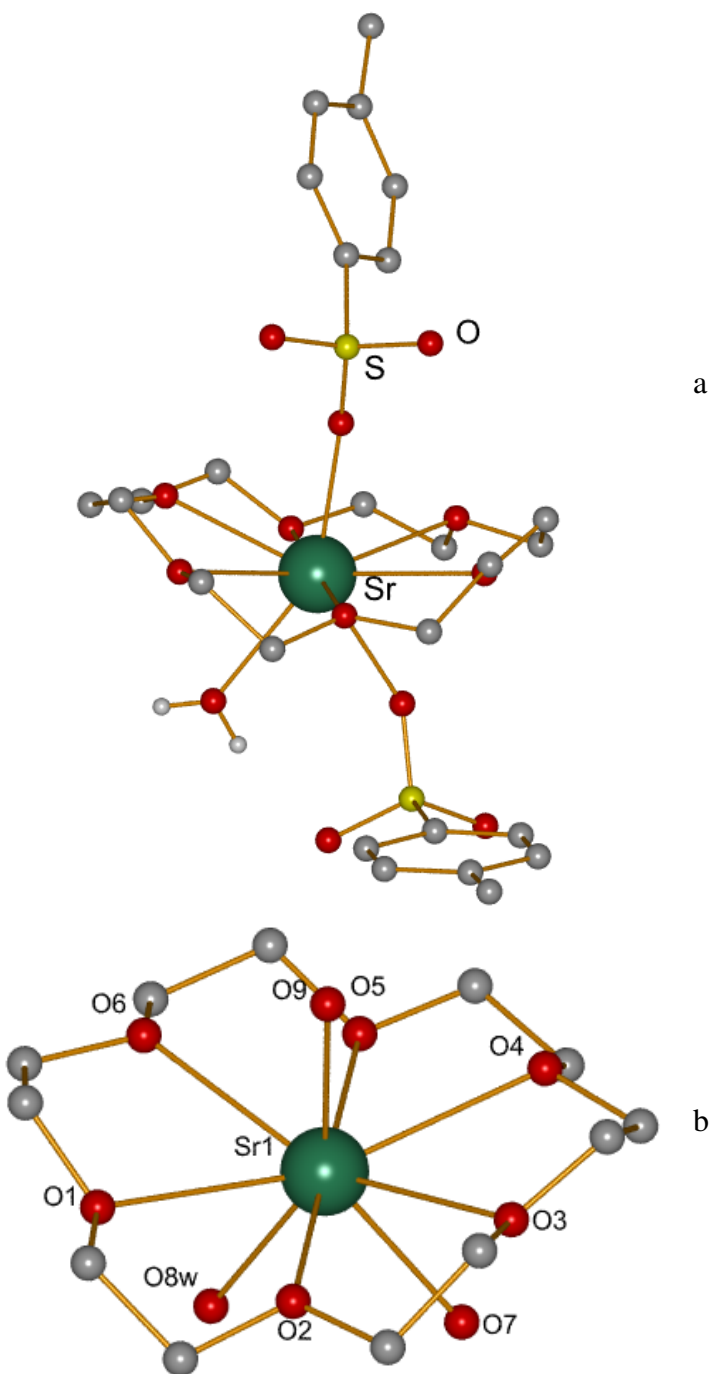
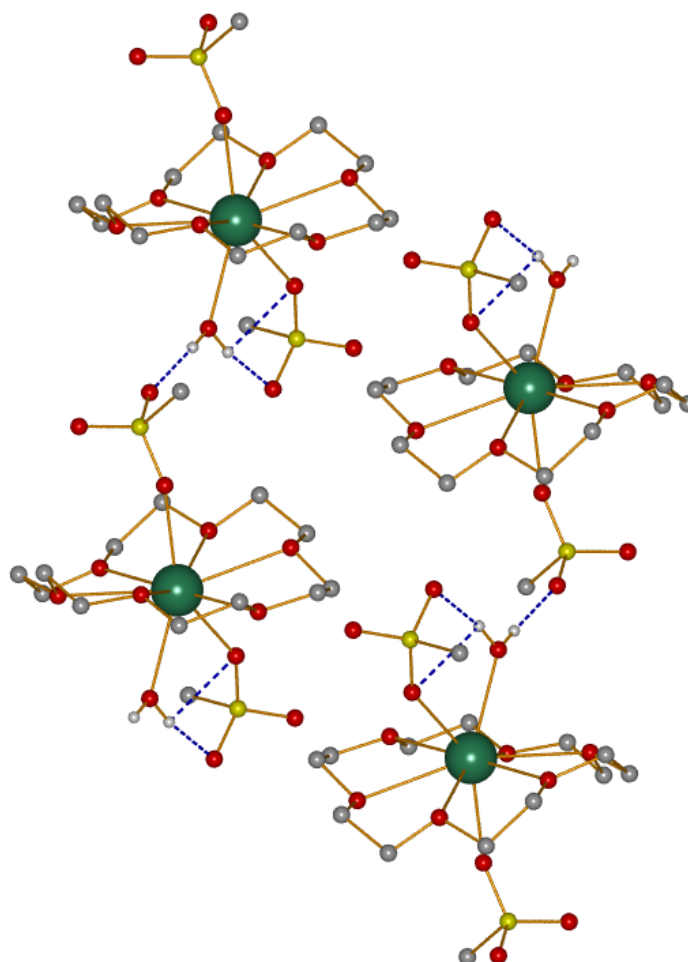


Figure 4.5. (a) Nine coordinate strontium center. Hydrogen atoms on crown ether and tosylate ligands removed for clarity. (b) Labeled metal environment core, tosylate ligands on O7 and O9 removed for clarity.

Table 4.6. Selected bond lengths (Å) for **3**

Sr(1)-O(1)	2.779(14)
Sr(1)-O(2)	2.624(15)
Sr(1)-O(3)	2.766(15)
Sr(1)-O(4)	2.782(14)
Sr(1)-O(5)	2.732(15)
Sr(1)-O(6)	2.695(15)
Sr(1)-O(7)	2.513(14)
Sr(1)-O(8)w	2.577(15)
Sr(1)-O(9)	2.470(14)

**Figure 4.6.** Hydrogen bonded network in 3D. Phenyl groups on the tosylate ligands and all non-water bound hydrogens removed for clarity. Shown are two strands.

The tosylate ligands themselves are in *trans* positions (to each other, do not participate in π --- π stacking interactions as is typical for aromatic ligand systems.

Table 4.7. Selected hydrogen bonding distances (Å) and angles (°) for **3**

D-H...A	<DHA	d(D...A)
O(8)-H(45)...O(12)	177.07	2.805
O(8)-H(46)...O(10)	161.62	2.836
O(8)-H(46)...S(3)	132.33	3.391

4.1.4 Structural characterization of $[Ba(OTs)_2(18\text{-crown-6})(OH_2)_2]_\infty$ (**4**)

Compound **4** crystallizes in the monoclinic spacegroup $P2_1/c$. The complex consists of a ten coordinate barium centers, with oxygens originating from the crown macrocycle, two ligands in *cis* positions and two *trans* waters (Figure 4.7). Further, the Ba-O distances and angles lying within reported values for previously reported complexes.^[17,19] Table 4.8 shows selected bond lengths and angles for the title compound. The wider angles and longer distances in **4** as compared to **3**, are associated with the difference in ionic radii of barium as opposed to strontium (0.16Å).^[20]

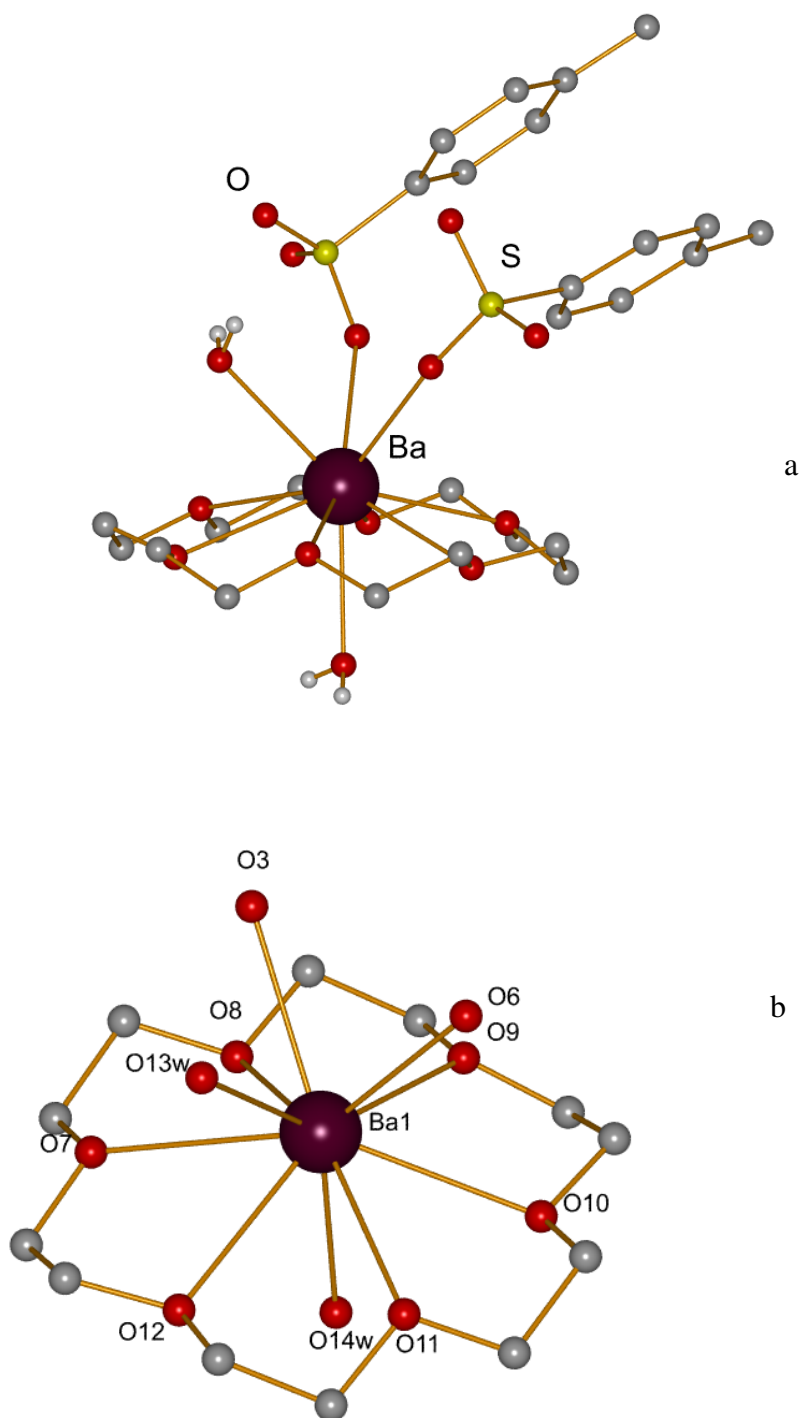


Figure 4.7. (a) Ten coordinate barium center. Hydrogens on crown ether and ligands removed for clarity. (b) Labeled metal environment core, tosylate ligands on O3 and O6 removed for clarity.

Table 4.8. Selected bond lengths (Å) for **4**

Ba(1)-O(6)	2.750(3)
Ba(1)-O(201)w	2.787(4)
Ba(1)-O(200)w	2.819(3)
Ba(1)-O(3)	2.851(3)
Ba(1)-O(19)	2.854(20)
Ba(1)-O(24)	2.866(3)
Ba(1)-O(21)	2.888(3)
Ba(1)-O(22)	2.912(3)

The extended structure of **4** consists in 1D chains that propagate *via* hydrogen bonds between water coordinated molecules to the *cis* tosylate ligands (Table 4.9, Figure 4.8). As possible due to the *cis* ligand arrangement, the ligands are involved in π --- π interactions (centroid-centroid distance: 3.66 Å), the value being in agreement with literature.^[21]

Table 4.9. Selected hydrogen bonding distances (Å) and angles (°) for **4**

D-H...A	<DHA	d(D...A)
O(13)-H(53)...O(14)	153.81	2.849
O(14)-H(55)...O(2)	161.34	2.804
O(14)-H(56)...O(4)	175.96	2.800
O(13)-H(54)...O(2)	152.43	3.007

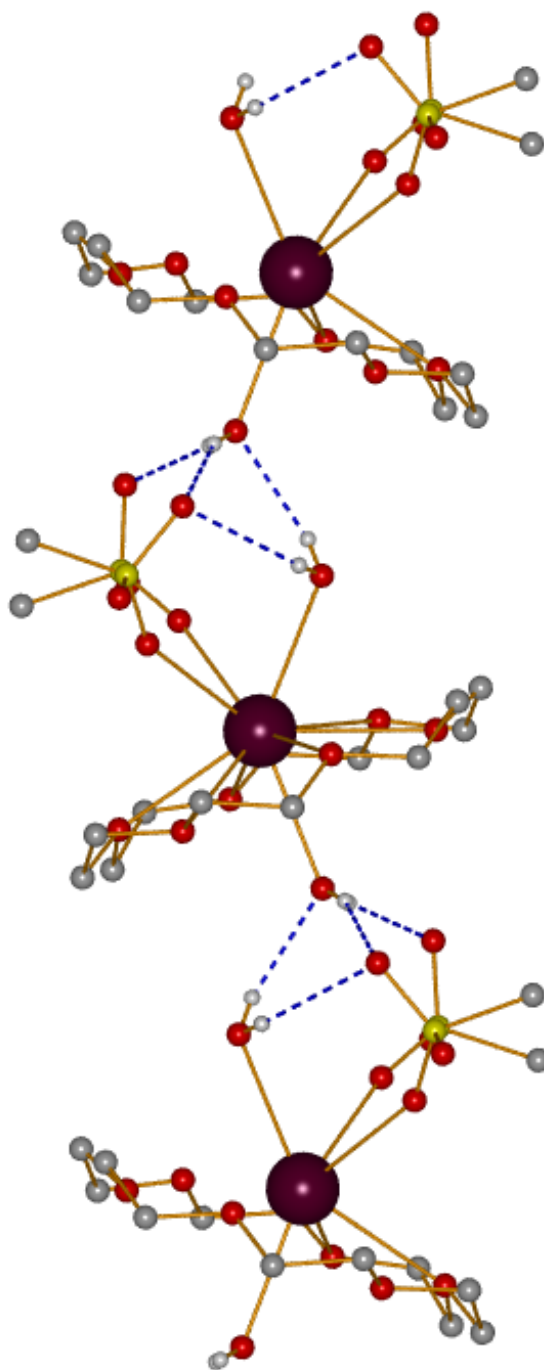


Figure 4.8. Hydrogen bonded network in **4**. Phenyl groups on tosylate ligands and some hydrogens removed for clarity

4.2 Thermogravimetric Analysis

As compounds **1-4** all contain water, either metal bound or as water of crystallization, thermogravimetric analysis was performed to investigate at which temperatures the water will be lost.

4.2.1 TGA of $\{[Ca_3(OTs)_3(18\text{-crown-}6)_3(OH_2)_6][OTs]_3 \cdot 2H_2O\}_\infty$ (**1**)

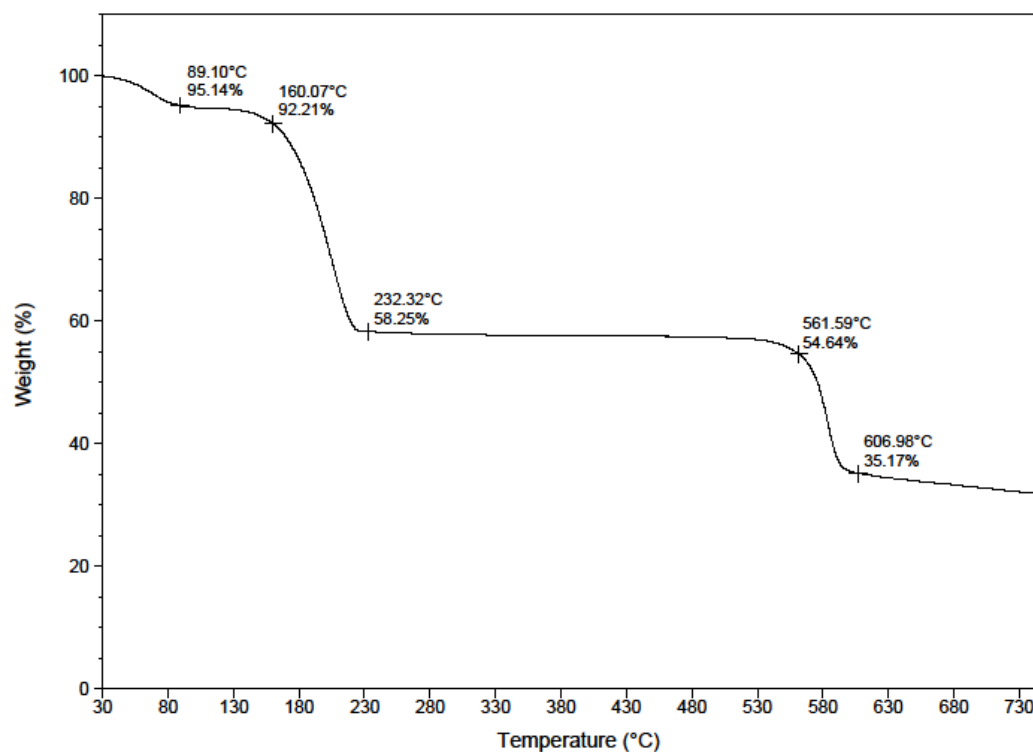


Figure 4.9. TGA of **1** showing the loss of water molecules, crown molecules and thermal decomposition.

A TGA study was performed on **1**, to observe its thermal properties. The TGA plot shows loss of six water molecules at 89°C (exp. 4.86%, calc. 5.13%). Further, the weight loss between 160-232°C indicates the loss of 18-crown-6 molecules (exp. 33.96%, calc. 37.71%). No further weight loss is observed

between 232-561 °C, although further weight loss beyond this temperature might indicate decomposition.

4.2.2 TGA of $\{[Ca_2(OH)_2(18\text{-crown-}6)_2][OTs]_4\}_n$ (**2**)

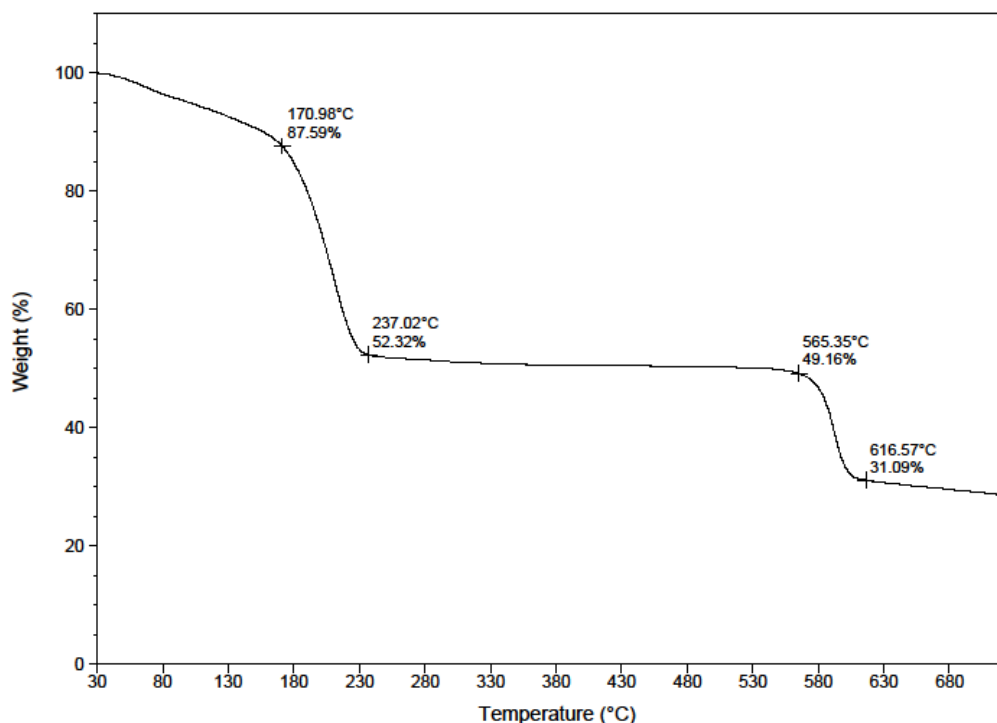


Figure 4.10. TGA of **2** showing the loss of water molecules, crown molecules and consequent decomposition above 565 °C.

A TGA study was performed on **2**, to observe its thermal properties. The TGA plot shows initial loss of water molecules (exp. 12.41%, calc. 10.54%) to 170 °C. Above 170 °C, loss of 1 crown molecule occurs until 237 °C (exp. 35.27%, calc. 38.71%). No further weight loss is observed between 237-565 °C, although further weight loss beyond this temperature might indicate decomposition.

4.2.3 TGA of $[Sr(OTs)_2(18\text{-crown-6})(OH_2)]_{\infty}$ (**3**)

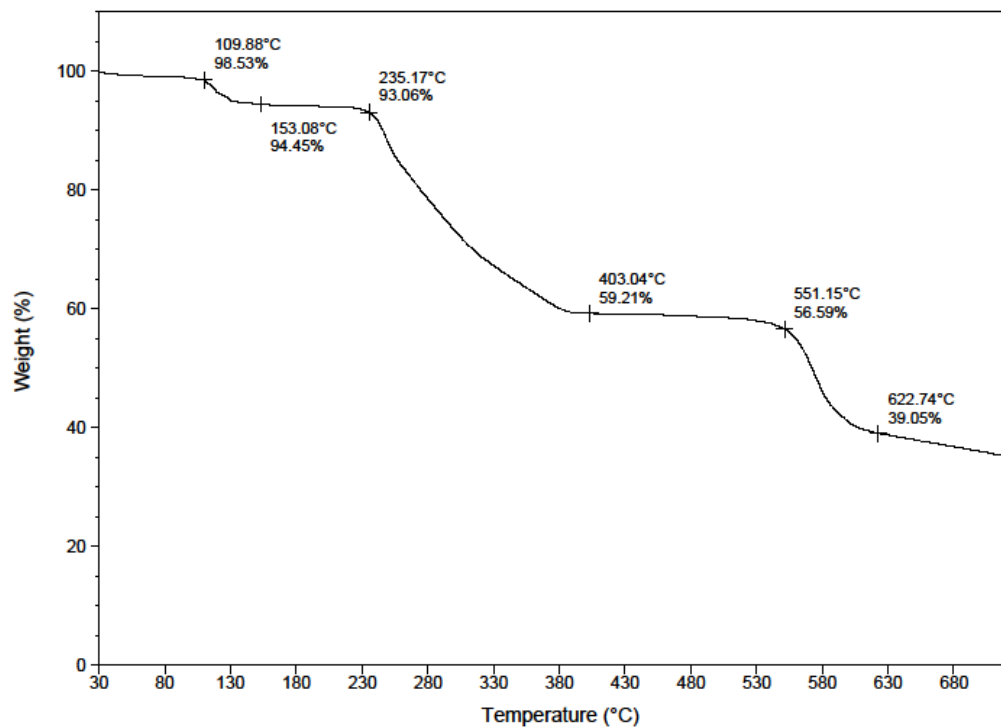


Figure 4.11. TGA of **3** showing loss of water molecule, crown molecule and consequent decomposition above 551°C.

A TGA study was performed on **3**, to observe its thermal properties. The TGA plot shows initial loss of ~1 water molecule (exp. 1.47%, calc. 2.52%) to 109°C. Further, loss of 1 crown molecule occurs from 235-403°C (exp. 33.85%, calc. 37.10%). No further weight loss is observed between 403-551°C, where the start of decomposition processes are believed to occur.

4.2.4 TGA of $[Ba(OTs)_2(18\text{-crown-6})(OH_2)_2]_{\infty}$ (**4**)

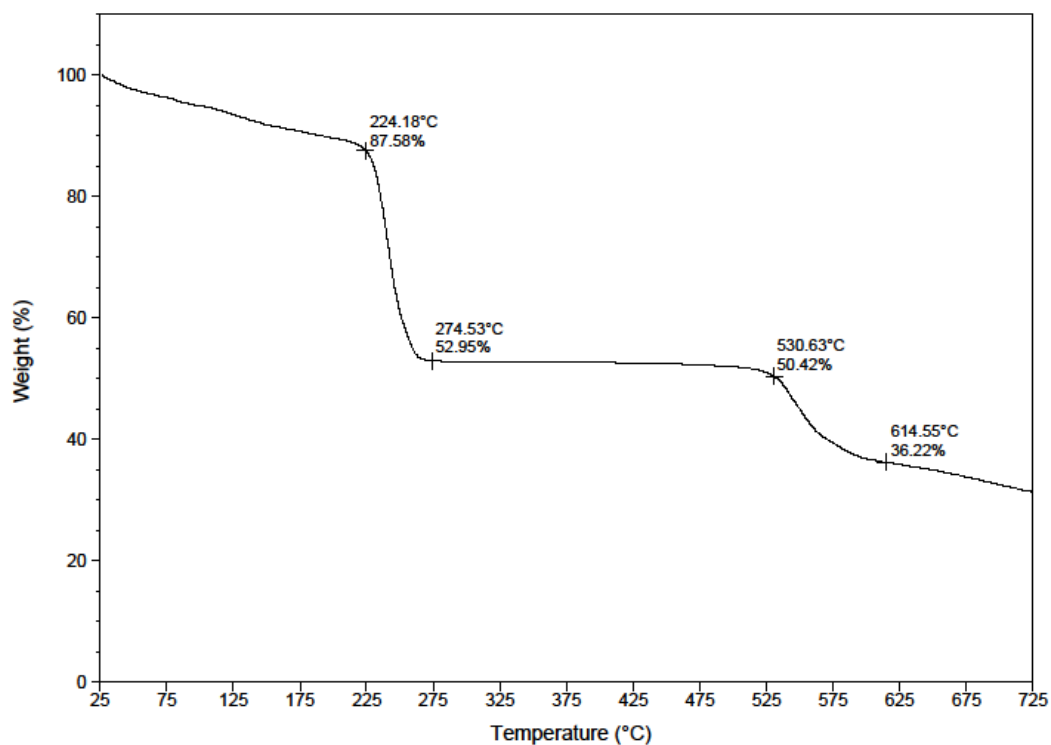


Figure 4.12. TGA of **4** showing loss of water molecules, crown molecule and consequent decomposition

A TGA study was performed on **4**, to observe its thermal properties. The TGA plot shows initial loss of ~2 water molecules (with a possibility of lattice solvents) (exp. 12.42%, calc. 4.61%) from the total weight from room temperature to 224°C. Further, loss of 1 crown molecule occurs from 224-274°C (exp. 34.63%, calc. 33.88%). No further weight loss is observed until 530°C, where the start of decomposition processes is believed to occur.

By comparing all four compounds, several trends can be observed. The bond lengths between the metal centers and the oxygen atoms of 18-crown-6, tosylate ligands, and water molecules corresponds to the increasing atomic radii of the metals. Compound **1** shows Ca-O bond lengths between 2.370 and 2.542 Å

while compound **2** exhibits Ca-O bond lengths between 2.483 and 2.650 Å. Compound **3** has Sr-O bonds ranging from 2.471 to 2.782 Å while compound **4** incorporates Ba-O bonds ranging from 2.750 to 2.912 Å. The calcium complexes exhibit different bond ranges, possibly due to twisting of the crown ligands affecting the placement of the metal center. Compound **3** has the largest range of Sr-O bond lengths and with a 140.38° angle between the two tosylate ligands in *trans* position, the presence of the one water molecule may explain how twisting of the crown molecule occurs to create space for both tosylate ligands and the water.

4.3 Infrared Spectroscopy

4.3.1 IR of $\{[Ca_3(OTs)_3(18\text{-crown-6})_3(OH_2)_6][OTs]_3 \cdot 2H_2O\}_\infty$ (**1**)

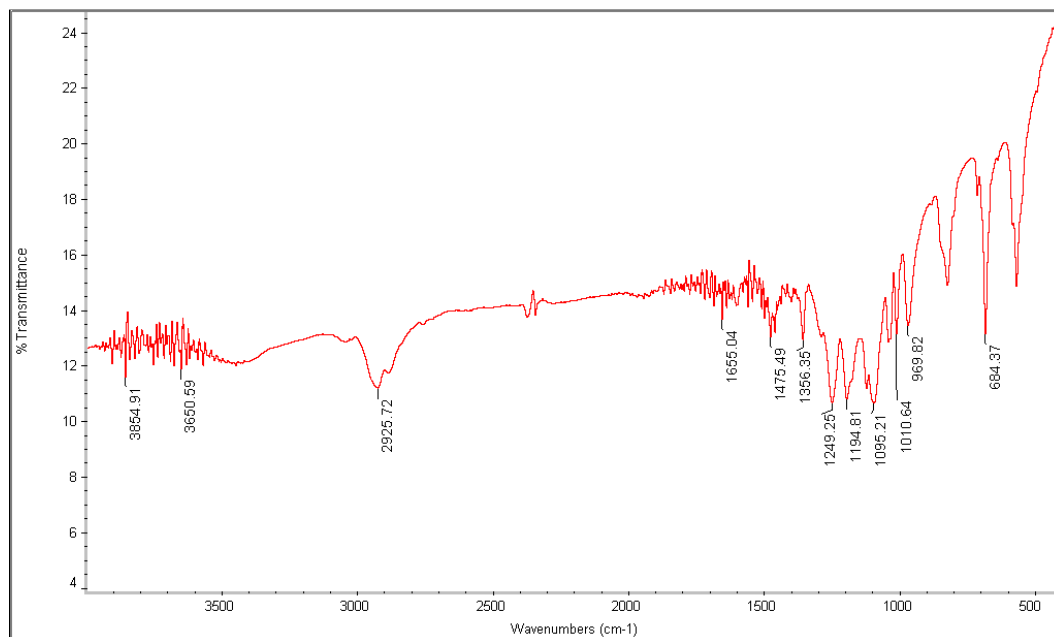


Figure 4.13. IR of **1** showing a H₂O peak from 3300-3600cm⁻¹, indicating hydrogen bonding.

4.3.2 IR of $\{[Ca_2(OH_2)_4(18\text{-crown-6})_2][OTs]_4\}_\infty$ (2)

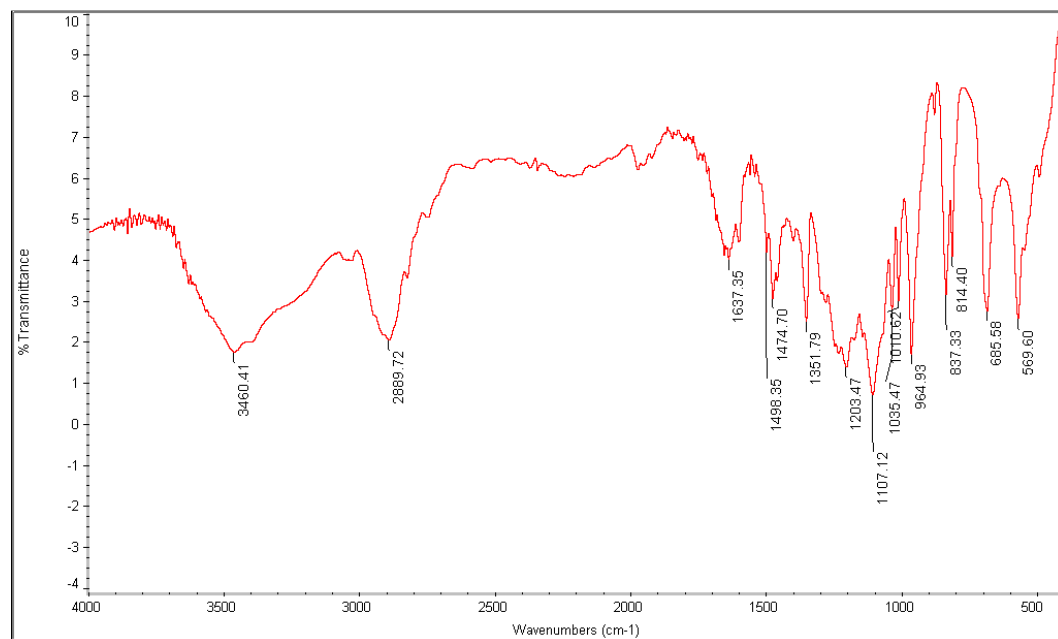


Figure 4.14. IR of **2** showing a broad H₂O peak from 3050-3700cm⁻¹, indicating hydrogen bonding.

4.3.3 IR of $[Sr(OTs)_2(18\text{-crown-6})(OH_2)]_\infty$ (3)

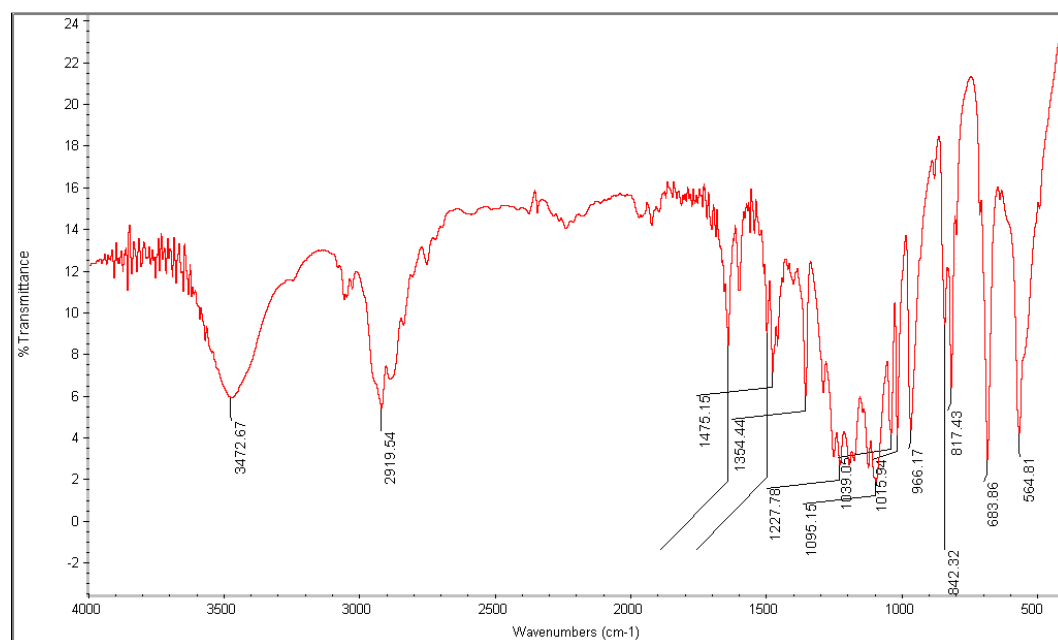


Figure 4.15. IR of **3** showing a broad H₂O peak from 3150-3650cm⁻¹, indicating hydrogen bonding.

4.3.4 IR of $[Ba(OTs)_2(18\text{-crown-6})(OH_2)_2]_{\infty}$ (**4**)

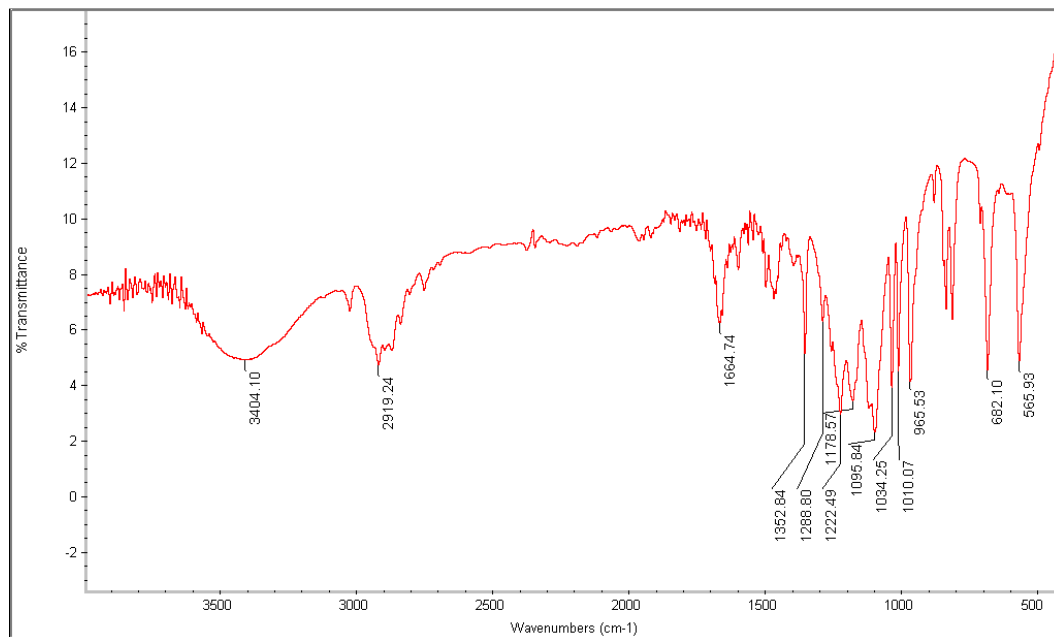


Figure 4.16. IR of **4** showing a broad H₂O peak from 3050-3650cm⁻¹, indicating hydrogen bonding

By comparing compounds **1-4**, it can be observed through the broad H₂O peaks that hydrogen bonding is occurring. As absorptions occur at various frequencies for individual molecules, the broadened peaks observed in **1-4** indicate the average of the hydrogen bonded water molecules. Compounds **2-4** observe larger ranges than **1**, possibly explaining the extent of the hydrogen bonded networks.

4.4 Solubility Studies

As the starting tosylate materials were insoluble in solvents besides water, the hope of creating more soluble tosylate complexes was proven successful. Compounds **1-4** were all soluble in pyridine and water. The importance of having complexes soluble in pyridine is the fact that pyridine is a nitrogen based donor.

As the tosylates had only been soluble in oxygen donating water previously, having complexes that are able to switch donor molecules is key. The competition between oxygen and nitrogen coordinating to the metal center can now be observed. The ligand that wins the coordination competition will have more influence on the properties of the resulting complex.

4.5 Other Reactions

All reactions using digylme, TMEDA, and PMDTA afforded the water solvated tosylates. One explanation could be how the starting tosylate complexes were not soluble in any solvent besides water. The use of water as a solvent was proposed to eliminate solubility issues; however the interactions of the water with the alkaline earth tosylates were stronger than the interactions with the donors.

^1H NMR was not used as a characterization method in this study as solubility was very limited and no information on the coordination atmosphere surrounding the metal would have been obtained.

5.0 Conclusions and Future Work

Four novel complexes were created from simple, one-pot donor addition reactions. The compounds were characterized using single crystal X-ray diffraction, thermogravimetric analysis, and infrared spectroscopy. Compounds **1** and **2**, while prepared in similar manners, exhibit unique behavior based on a change in the metal/crown stoichiometry. Compounds **3** and **4** show distinct coordination numbers and ligand positions despite using similar stoichiometry. With so many competing factors for the metal center, predicting the coordination atmosphere of novel tosylate complexes is impossible. The tosylate ligands in

compound **3** are arranged in *trans* positions while in compound **4** they are in the *cis* position and involved in a π - π stacking interaction. The coordination atmosphere of water molecules coordinated to the four compounds differs greatly. Original solubility issues with the tosylates were partially solved as all four compounds were soluble in pyridine. The alkaline earth tosylates will continue to be looked examined in conjunction with bulky donor ligands as potential methods of preventing aggregation behavior in complexes.

Future Work includes the following:

- Explore other crown ethers as potential binding ligands for alkaline earth tosylates
- Vary conditions on direct metallation reactions that promote the coordination of donors to the metal center
- Perform temperature dependent PXRD experiments on compounds **1-4** to determine structural integrity at higher temperatures and compare to the TGA plots
- Perform solubility studies on compounds **1-4** at high temperatures
- Perform salt-metathesis reactions with the characterized complexes
- Explore the use of other donors in donor addition reactions

6. References

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7. Summary

The Group 2 alkaline earth metals (magnesium, calcium, strontium, and barium) can be used in many applications including polymerization initiation, as precursors for solid state materials used as high temperature superconductors or semiconductors, as well as in organic and organometallic chemistry.

Studies utilizing Group 2 metals in organometallics have been limited until recently. Trends among the alkaline earth metals exhibit factors that have prevented further research into understanding the properties and reactivity of the metals. As the ionic radius of the metals increases down the group, a decrease in the charge (+2) to size ratio decreases the metal-ligand bond strength. The increasing electropositive character of the heavier metals increases the polarity of a metal-ligand bond.

The Group 2 metals are highly moisture and air sensitive, leading to strict synthetic considerations. The introduction of magnesium “Grignard” reagents allows for the efficient synthesis of organometallic compounds if oxygen can be avoided. With many unique traits of the alkaline earth metals, this project is aimed to prepare novel compounds that foster a clearer understanding of alkaline earth metals.

A major usage of alkaline earth compounds is for organometallic applications. Of specific interest in this work is to gain facile, inexpensive access to the amido species, as they provide convenient synthetic access to a large group of highly reactive organometallic species. Conventional synthetic access to the amides is achieved by salt metathesis based on the reaction of highly pure metal

iodides with potassium amides. The salt metathesis chemistry involves two steps: the synthesis of metal amide, and its treatment with an alkaline earth iodide to form a desired product. While the salt metathesis reactions produce products in excellent yield and purity, the starting materials are very expensive. This project aimed to find a cost-efficient alternative for alkaline earth iodides for salt metathesis reactions.

A potential alternative ligand that was examined in this work is *p*-toluenesulfonic acid. The *p*-toluenesulfonic acid ligand is an inexpensive, commercially available organic acid. The alkaline earth metal derivatives are available by the treatment of commercially available, inexpensive carbonates with the free acid. Alkaline earth tosylate complexes can be converted into their dehydrated forms by gently heating under vacuum. However, the dehydrated tosylates display highly limited solubility properties. As a result, technique to increase the solubility of the tosylates is a key challenge when exploring them for salt metathesis. One explanation for the low solubility is that upon dehydration, removal of the hydrogen bonded networks causes aggregation. In order to prevent aggregation, lewis base donors can be used as competitor ligands. After competing for the metal center, structural features of the resulting compounds are determined by the characteristics of the ligands. By using various donor ligands in this study with the alkaline earth tosylates, we hope to gain insight into factors to prevent aggregation and improve solubility.

Donor ligands provide a wide variety coordination opens for saturating metal centers. Of particular interest in this study are oxygen and nitrogen donating

ligands. Crown ethers are oxygen rich ligands that possess a series of carbon-carbon-oxygen bonds and form a ring. An example of this is 18-crown-6, where there are a total of 12 carbon atoms that are interconnected by 6 oxygen atoms. A benefit of the crown ethers is the hydrophilic center of the ring and the hydrophobic exterior of the ring. With a hydrophilic center, water molecules are able to saturate the metal center of the ring. However, with the introduction of other ligands like tosylates, the coordination number of the metal center is altered. Another factor with the crown ethers is their selective binding to metals. As the size of the crown ethers through the extension of $\text{CH}_2\text{-CH}_2\text{O}$ units to the ring varies, size of the metal can be accommodated. Only metals that are small enough to fit comfortably in the middle of the ring are coordinated to the crown ethers. For this reason, only calcium, strontium, and barium were used in this study with the 15-crown-5 and 18-crown-6 macrocycles.

The successful route employed in this study is based on the treatment of already prepared alkaline earth tosylates in combination with donors in water. This simple reaction only required the use of a beaker and stir bar to ensure the homogeneous reaction conditions. Another type of reaction, direct metallation, required metal filings to be added with *p*-toluenesulfonic acid and donor in an inert gas atmosphere. The inert gas atmosphere was provided by applying the schlenk line technique, which also prevents the incorporation of water or oxygens from the air. While both reaction types seemed feasible, only desired product was obtained from the donor addition reactions after a period of two months. As a

result, remaining efforts on producing novel complexes were focused on the donor addition reactions.

With the donor addition reactions, the stoichiometry of the reactants was altered to examine the resulting effects. Four new complexes were obtained using either a 1:1 and 1:2 metal to crown ether ratios. Calcium (**1**), strontium (**3**), and barium (**4**) tosylate complexes were obtained with 18-crown-6 using the 1:1 ratio. Another calcium complex (**2**) was able to be characterized using the 1:2 ratio. The reason for using the 1:2 ratio for calcium was to create a “sandwich” complex, where two crown ethers would create a sandwich surrounding the calcium ion. However, the reagent stoichiometry is not reflected in the final product. By grouping the two calcium complexes together, in the 1:1 calcium complex (**1**), three calcium centers are apparent, with partial tosylate ligand separation. This binding motif plays a role in hydrogen bonding between the calcium centers. The tosylate ligands in the 1:2 calcium complex (**2**) act as connectors through hydrogen bonding.

The strontium and barium complexes demonstrate the size effect of the metal centers. In the nine-coordinated strontium complex (**3**), six oxygen atoms from the crown ether, two oxygens from the tosylate ligands, and one water molecule are coordinated to the metal center. The two tosylate ligands are in the *trans* position. In the ten-coordinated barium complex (**4**), six oxygen atoms from the crown ether, two oxygens from the tosylate ligands, and two water molecules are coordinated. Besides having two waters instead of one, the barium complex displays π - π stacking geometry made possible by the *cis* positions of the ligands.

The four complexes characterized in this study exhibit unique structural features from one another. Importantly, the crown coordination resulted in improved solubility, as the complexes were found to be soluble in pyridine. This is a significant improvement over the water containing or anhydrous tosylate starting materials.