
Solution and Solid-State Studies of Alkali Metal Aggregate Assemblies

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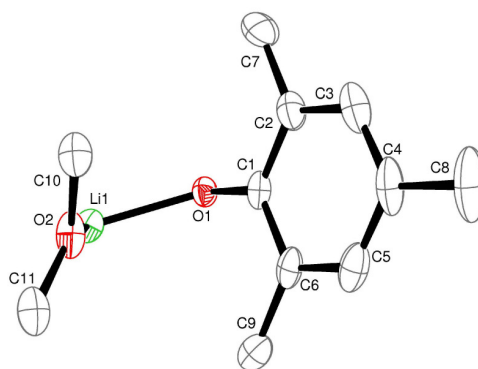
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APPENDIX

CRYSTALLOGRAPHIC INFORMATION

2.1 $\{[(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_4(\text{diox})_2] \supset 3(\text{diox})\}_\infty$

The asymmetric unit contains a lithium 2,4,6-trimethylphenoxide monomer with the lithium center solvated by a half molecule of dioxane. Symmetry expansion generates a tetrameric aggregate that is coordinated by a total of four dioxane molecules. The dioxanes bridge to

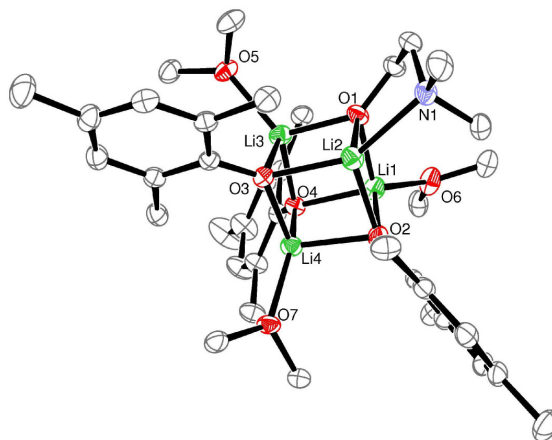


neighboring aggregates to give a three-dimensional network with **dia** topology. There are three free molecules of dioxane in the lattice. After conventional attempts to describe the disorder failed, the disorder was modeled using the SQUEEZE routine of PLATON. SQUEEZE found a total solvent accessible volume of 1956.0 \AA^3 and 623 e^- in the unit cell or 489 \AA^3 and 145.7 e^- per tetramer. Three dioxanes require approximately 144 e^- .

2.2 $\{[(\text{Me}_2\text{NC}_2\text{H}_4\text{OLi})(2,4,6\text{-Me}_3\text{-C}_6\text{H}_2\text{OLi})_3(\text{diox})_{1.5}] \supset 1/2(\text{C}_6\text{H}_{14})\}_\infty$

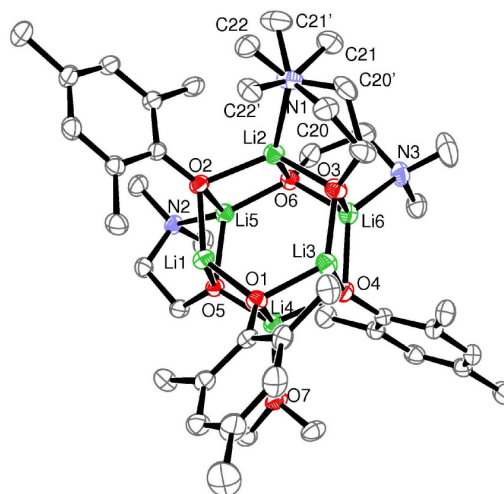
The asymmetric unit contains a mixed tetrameric lithium aggregate with three 2,4,6-trimethylphenoxide and one dimethylaminoethoxide anions. Li(1), Li(3), and Li(4) are each solvated by a half molecule of dioxane, whereas Li(2) is coordinated by the nitrogen of the dimethylaminoethoxide. Symmetry expansion generates a two-dimensional 6^3 -net

from the tetrameric aggregates. There is disordered solvent in the network lattice. After conventional attempts to describe the disorder failed, the disorder was modeled using the SQUEEZE routine of PLATON. SQUEEZE found total solvent accessible volume of 1404.4 Å³ and 289 e⁻ in the unit cell, or 175.6 Å³ and 36.13 e⁻ in the asymmetric unit. One hexane molecule, which was used in the recrystallization, contributes 50 e⁻ to the asymmetric unit.



2.3 [(Me₂NC₂H₄OLi)₃(2,4,6-Me₃-C₆H₂OLi)₃·(diox)_{0.5}](C₆H₁₄)_∞

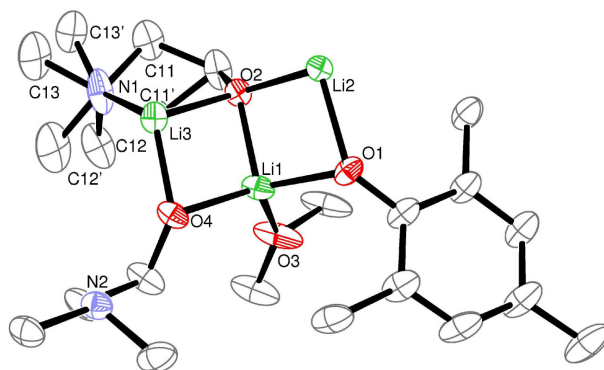
The asymmetric unit contains a mixed tetrameric lithium aggregate with three 2,4,6-trimethylphenoxide and three dimethylaminoethoxide anions. Li(2), Li(5), and Li(6) are each coordinated by the nitrogen atom of the dimethylaminoethoxide, whereas Li(4) is solvated by a half molecule of dioxane. The



carbon atoms of one of the dimethylaminoethoxide anions (C(20), C(21), C(22)) are disordered over two sites with the site occupancy of the major component freely refined to 0.512(2). Symmetry expansion generates two hexameric aggregates that are connected by one molecule of dioxane. There is one non-disordered hexane molecule per hexamer in the crystal lattice.

2.4 [(Me₂NC₂H₄OLi)₄(2,4,6-Me₃-C₆H₂OLi)₂·(diox)]_∞

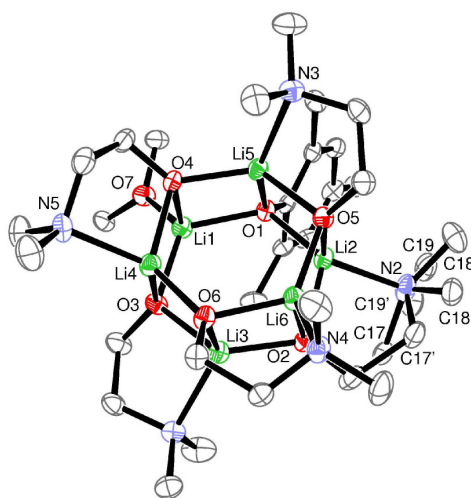
The asymmetric unit contains a mixed tetrameric lithium aggregate with one 2,4,6-trimethylphenoxide and two dimethylaminoethoxide anions. Li(1) is solvated by a half molecule of dioxane, whereas Li(3) is coordinated



by the nitrogen atom of the dimethylaminoethoxide. The carbon atoms of one of the dimethylaminoethoxide anions (C(11), C(12), C(13)) is disordered over two sites with the site occupancy of the major component freely refined to 0.755(6). Symmetry expansion generates a hexameric aggregate that is coordinated by two molecules of dioxane that bridge to other aggregates to give a one-dimensional coordination polymer.

2.5 [(Me₂NC₂H₄OLi)₅(2,4,6-Me₃-C₆H₂OLi)·(diox)_{0.5}]_∞

The asymmetric unit contains a mixed tetrameric lithium aggregate with one 2,4,6-trimethylphenoxide and five dimethylaminoethoxide anions. Li(1) is solvated by a half molecule of dioxane, whereas Li(2), Li(3), Li(4), Li(5), and Li(6) are each coordinated by the nitrogen atom of the dimethylaminoethoxide. The carbon atoms of

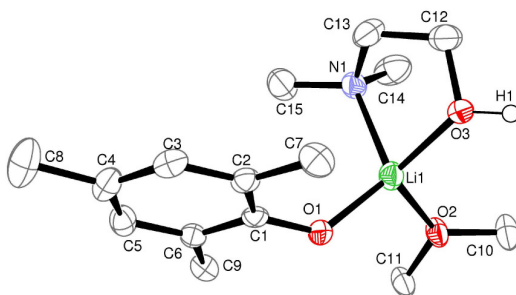


one of the dimethylaminoethoxide anions (C(17), C(18), C(19)) are disordered over two sites with the site occupancy of the major component freely refined to 0.576(3).

Symmetry expansion generates two hexameric aggregates that are connected by one molecule of dioxane.

2.6 [(2,4,6-Me₃-C₆H₂OLi)·(Me₂NC₂H₄OH)·(diox)_{0.5}]_∞

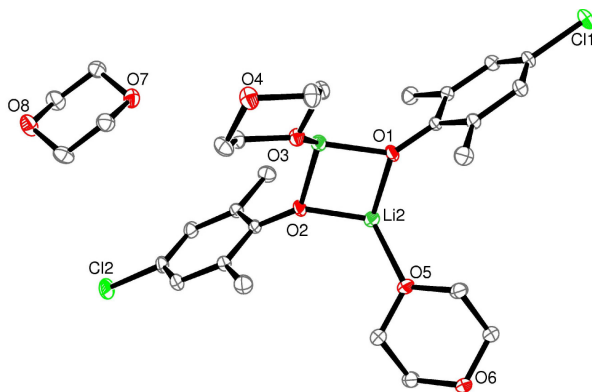
The asymmetric unit contains a lithium 2,4,6-trimethylphenoxide monomer that is chelated by one molecule of non-deprotonated dimethylethanolamine as well as one half molecule of dioxane. Symmetry expansion



generates a dimeric lithium aggregate that is coordinated through a bridging dioxane molecule. The dimers are then connected through hydrogen bonds to give a two-dimensional network.

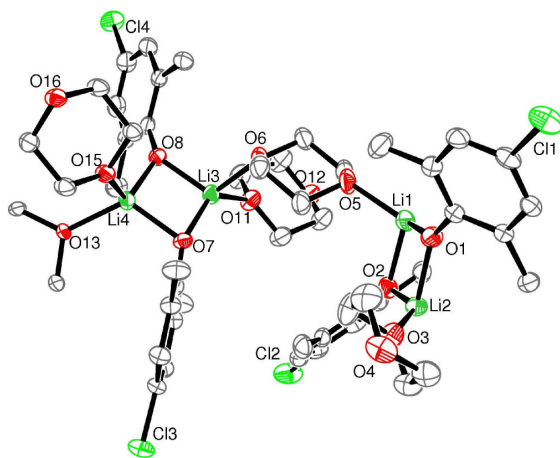
3.1 [(4-Cl-2,6-Me₂-C₆H₂OLi)₂·(dioxane)₂]_∞

The asymmetric unit contains a lithium 4-Cl-2,6-dimethylphenoxide dimer. Both lithium centers coordinate to two μ₂-aryloxy anions and are solvated by a full dioxane molecule. Additionally, there is a free molecule of dioxane in the



lattice. Symmetry expansion generates tetrasolvated dimers that are bridged to other dimers to give a two-dimensional 4⁴-network. The absolute structure was determined from anomalous dispersion effects. The system is a racemic twin with a twin ratio of 0.28(2).

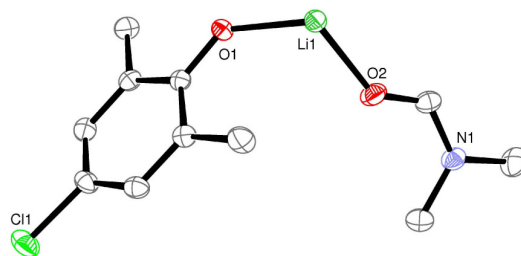
3.2 [(4-Cl-2,6-Me₂-C₆H₂OLi)₂·(dioxane)_{2.5}]_∞



The asymmetric unit contains two lithium 4-Cl-2,6-dimethylphenoxide dimers. All four lithium centers coordinate to two μ_2 -aryloxy anions. There is a total of 5 dioxane molecules between the two dimers. Li(1) and Li(3) are solvated by the dioxane that bridges between the aggregates. In addition, Li(3) is solvated by another full molecule of dioxane. Li(2) is solvated by a full molecule of dioxane, whereas Li(4) is solvated by a full and half molecule of dioxane. Symmetry expansion results in both of the dimers becoming tetrasolvated. Three of the dioxanes on each of the dimers bridge to other aggregates to give a two-dimensional network with 6³-net topology.

3.3 [(4-Cl-2,6-Me₂-C₆H₂OLi)₄·(dmf)₄]

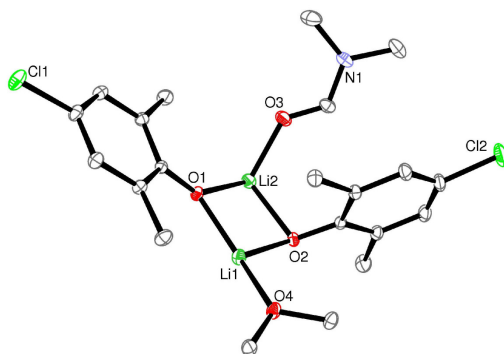
The asymmetric unit contains a lithium 4-Cl-2,6-dimethylphenoxide monomer. The lithium is solvated by one molecule of DMF. Symmetry expansion results in a



molecular tetrameric cubane aggregate where each of the lithium centers is monosolvated. The system is a racemic twin with a twin ratio of 0.25(4).

3.4 [(4-Cl-2,6-Me₂-C₆H₂OLi)₄·(dioxane)·(dmf)₂]_∞

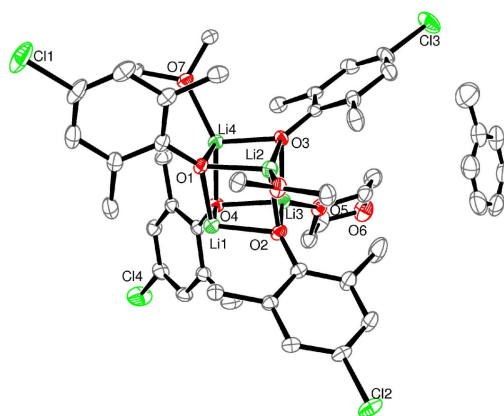
The asymmetric unit contains a lithium 4-Cl-2,6-dimethylphenoxide dimer. Both lithium centers coordinate to two μ_2 -aryloxy anions. Li(1) is solvated by a half molecule of dioxane, whereas Li(2) is solvated by a molecule of DMF. Symmetry



expansion results in a tetrameric aggregate where two of the lithium centers are solvated by dioxane and two of the lithium centers are solvated by DMF. The two dioxanes bridge to other aggregates to give a one-dimensional coordination polymer.

3.5 [(4-Cl-2,6-Me₂-C₆H₂OLi)₄·(dioxane)₂]_∞

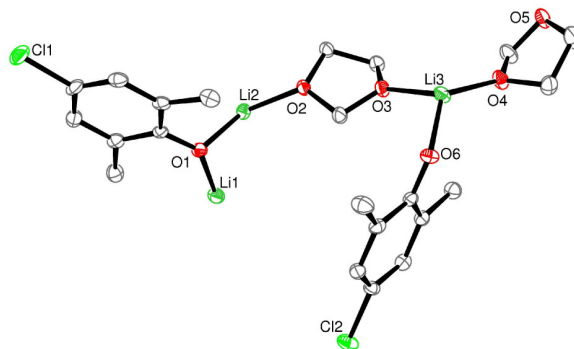
The asymmetric unit contains a lithium 4-Cl-2,6-dimethylphenoxide tetramer. Each of the lithium centers coordinate to three μ_3 -aryloxy anions. Li(3) is solvated by a terminal molecule of dioxane, whereas Li(2) and Li(4) are solvated by a half



molecule of dioxane. Li(1) is unsolvated. In addition, there is one free molecule of toluene per asymmetric unit in the network lattice. Symmetry expansion results in the tetrameric aggregate bridging to other aggregates through two dioxanes to give a one-dimensional coordination polymer.

3.6 [(4-Cl-2,6-Me₂-C₆H₂OLi)₂·(dioxolane)₂]_∞

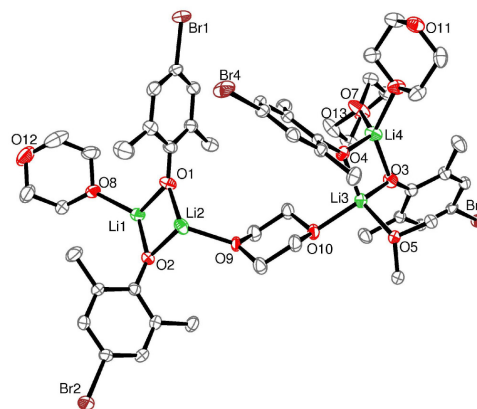
The asymmetric unit contains a lithium dimer with only one 4-Cl-2,6-dimethylphenoxide ligand as well as a lithium 4-Cl-2,6-dimethylphenoxide monomer. One dioxolane molecule bridges between Li(2) of the dimer and



Li(3) of the monomer. In addition, Li(3) is solvated by a second molecule of dioxolane. Symmetry expansion results in two separate dimeric aggregates that are tetrasolvated by dioxolane to give an extended 3D network with diamondoid topology.

3.7 [{(4-Br-2,6-Me-C₆H₂OLi)₂·(dioxane)₂} {(4-Br-2,6-Me-C₆H₂OLi)₂·(dioxane)_{2.5}}]_∞

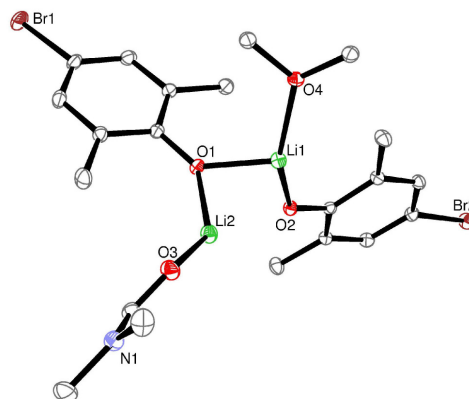
The asymmetric unit contains two lithium 4-Br-2,6-dimethylphenoxide dimers. Both of the lithium centers in each dimer coordinate to two μ_2 -aryloxide anions. Li(1) is solvated by a full molecule of dioxane. Li(2) is solvated by the dioxane molecule that bridges to Li(3) in



the second dimer. Li(3) is additionally solvated by a half molecule of dioxane. Li(4) is solvated by two full molecules of dioxane. Symmetry expansion results in the formation of a bilayer structure. One of the dimeric aggregates acts as a tetrahedral node and the second dimeric aggregates acts a trigonal node.

3.8 [(4-Br-2,6-Me₂-C₆H₂OLi)₄·(dioxane)₁·(dmf)₂]_∞

The asymmetric unit contains a lithium 4-Br-2,6-dimethylphenoxide dimer. Li(1) is solvated by a half molecule of dioxane, whereas Li(2) is solvated by a molecule of DMF. Symmetry expansion results in a tetrameric aggregate that is solvated by two molecules of dioxane and two molecules of DMF. The two dioxanes bridge to

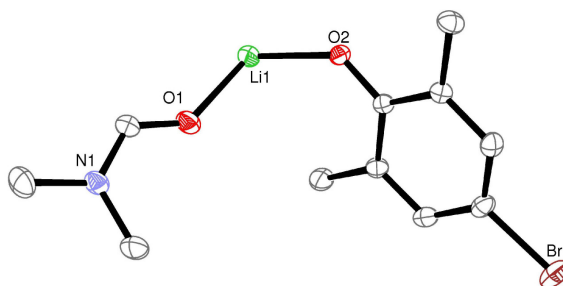


other tetrameric aggregates to give a one-dimensional coordination polymer.

3.9 [(4-Br-2,6-Me₂-C₆H₂OLi)₄·(dmf)₄]

The asymmetric unit contains a lithium 4-Br-2,6-dimethylphenoxide monomer.

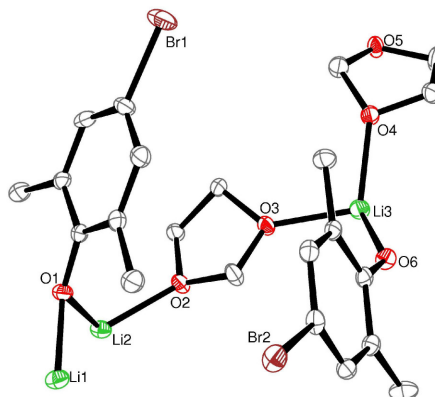
Li(1) is solvated by one molecule of DMF. Symmetry expansion results in a molecular tetrameric cubane aggregate



that is tetrasolvated by DMF. The system is a racemic twin with a twin ratio of 0.138(4).

3.10 [(4-Br-2,6-Me₂-C₆H₂OLi)₂·(dioxolane)₂]_∞

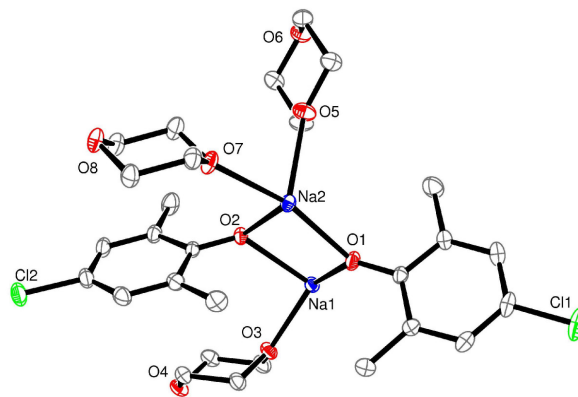
The asymmetric unit contains a lithium dimer with only one 4-Br-2,6-dimethylphenoxide ligand as well as a lithium 4-Br-2,6-dimethylphenoxide monomer. One dioxolane molecule bridges between Li(2) of the dimer and Li(3) of the monomer. In addition, Li(3) is



solvated by a second molecule of dioxolane. Symmetry expansion results in two separate dimeric aggregates that are tetrasolvated by dioxolane to give an extended 3D network with diamondoid topology.

4.1 [(4-Cl-2,6-Me₂-C₆H₂ONa)₂·(dioxane)₃]_∞

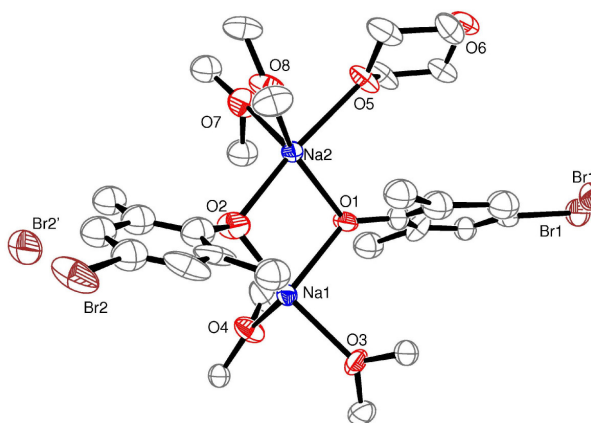
The asymmetric unit contains a sodium 4-Cl-2,6-dimethylphenoxide dimer where each sodium center is coordinated to two μ_2 -aryloxide anions. Na(1) is solvated by one full dioxane molecule and Na(2) is solvated by two full dioxane molecules.



Symmetry expansion gives a dimeric aggregate that is coordinated by six bridging dioxane molecules. The extended structure is considered a 5-connected net because of a dioxane double bridge.

4.2 [(4-Br-2,6-Me₂-C₆H₂ONa)₂·(dioxane)₃]_∞

The asymmetric unit contains a sodium 4-Br-2,6-dimethylphenoxide dimer where each sodium center is coordinated to two μ_2 -aryloxide anions. Na(1) is solvated by two dioxane molecules and Na(2) is solvated by three dioxane molecules.

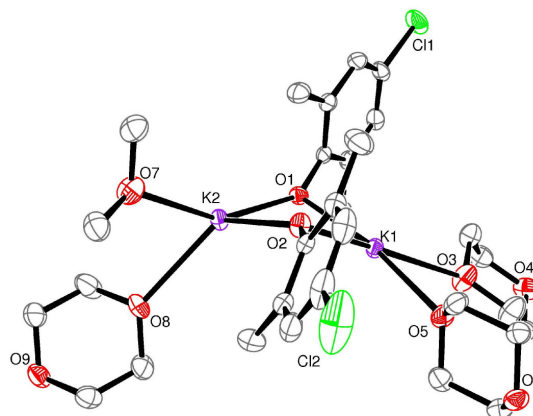


Symmetry expansion gives a dimeric aggregate that is coordinated by six bridging dioxane molecules. The extended structure is only a 5-connected net because of a dioxane

double bridge. Br(1) and Br(2) are disordered over two sites with a site occupancy of 0.503(5) and 0.521(5), respectively for the major component.

4.3 [(4-Cl-2,6-Me₂-C₆H₂OK)₂·(dioxane)_{3.5}]_∞

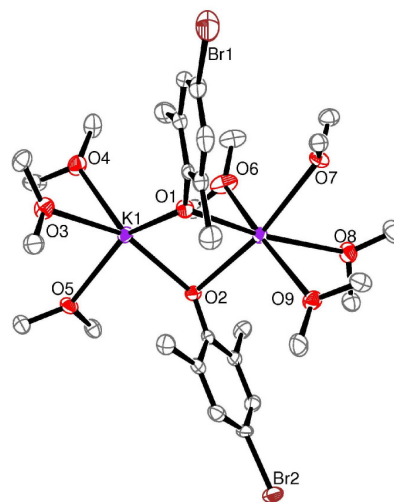
The asymmetric unit contains a potassium 4-Cl-2,6-dimethylphenoxide dimer where each potassium center is coordinated to two μ_2 -aryloxy anions. K(1) is also solvated by two full dioxane molecules and K(2) is solvated by one full and one half dioxane molecules. Symmetry



expansion gives a dimeric aggregate that is coordinated by seven bridging dioxane molecules. The extended structure forms a 7-connected network.

4.4 [(4-Br-2,6-Me₂-C₆H₂OK)₂·(dioxane)_{3.5}]_∞

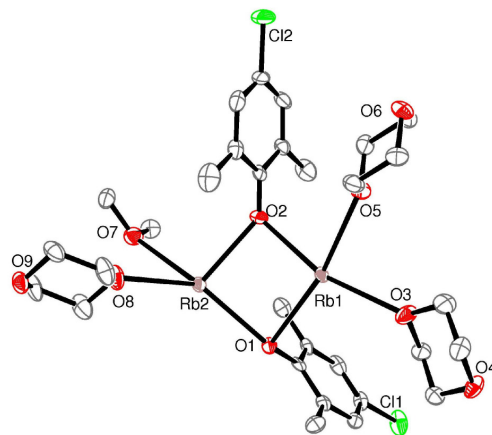
The asymmetric unit contains a potassium 4-Br-2,6-dimethylphenoxide dimer where each potassium center is coordinated to two μ_2 -aryloxy anions. K(1) is also solvated by three half dioxane molecules and K(2) is solvated by four half dioxane molecules. Symmetry expansion gives a dimeric aggregate that is coordinated by a total of seven



bridging dioxane molecules. The extended structure forms a 7-connected network.

4.5 [(4-Cl-2,6-Me₂-C₆H₂ORb)₂·(dioxane)_{3.5}]_∞

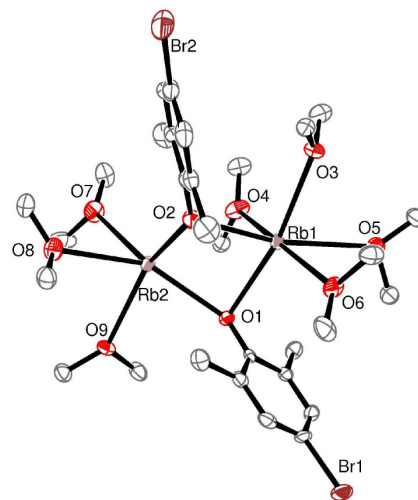
The asymmetric unit contains a rubidium 4-Cl-2,6-dimethylphenoxide dimer where each rubidium center is coordinated to two μ_2 -aryloxide anions. Rb(1) is also solvated by two full dioxane molecules and Rb(2) is solvated by one full and one half dioxane molecules. Symmetry expansion gives a dimeric aggregate



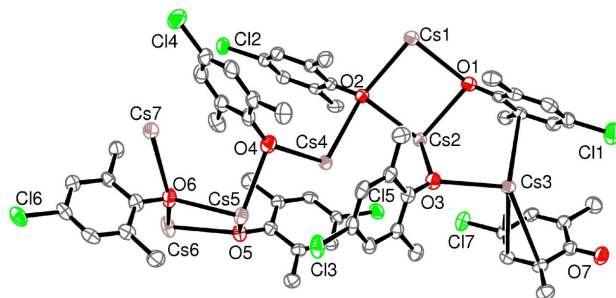
that is coordinated by seven bridging dioxane molecules. The extended structure forms a 7-connected network.

4.6 [(4-Br-2,6-Me₂-C₆H₂ORb)₂·(dioxane)_{3.5}]_∞

The asymmetric unit contains a rubidium 4-Br-2,6-dimethylphenoxide dimer where each rubidium center is coordinated to two μ_2 -aryloxide anions. Rb(1) is also solvated by four half dioxane molecules and Rb(2) is solvated by three half dioxane molecules. Symmetry expansion gives a dimeric aggregate that is coordinated by seven bridging dioxane molecules. The extended structure forms a 7-connected network.



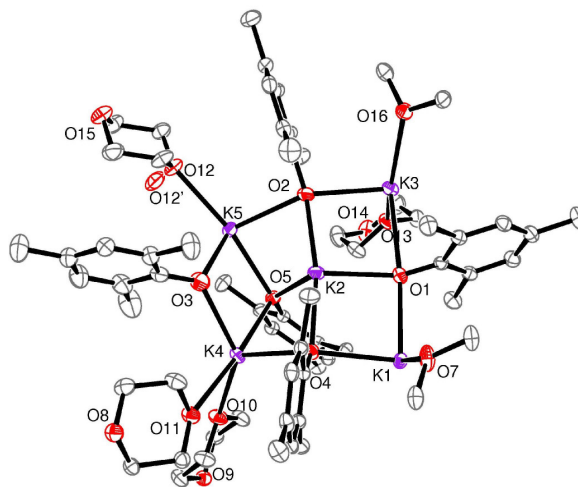
4.7 [(4-Cl-2,6-Me₂-C₆H₂OCs)₇·(dioxane)₁]_∞



The asymmetric unit contains seven cesium 4-Cl-2,6-dimethylphenoxides and no coordinated dioxane. There are three different cesium bonding environments in the structure. The first group (Cs(1), Cs(2), Cs(5)) each coordinate to two μ_3 -aryloxide anions and one μ_2 -aryloxide anion. The second group (Cs(3), Cs(4), Cs(7)) each coordinate to one μ_3 -aryloxide anion and one μ_2 -aryloxide anion. This group also coordinates to three different aryloxide rings through Cs-C_{Ar} cation- π interactions. The final cesium, Cs(6), coordinates to two μ_3 -aryloxide anions as well as three different aryloxide rings through Cs-C_{Ar} cation- π interactions. There is one molecule of free dioxane in the lattice per asymmetric unit that was removed using the SQUEEZE program in PLATON because the disorder could not be modeled. SQUEEZE found a total solvent accessible volume of 2312.7 Å³ and 867 e⁻ in the unit cell or 128.5 Å³ and 48.12 e⁻ per asymmetric unit. One dioxane molecule requires approximately 48 e⁻. Symmetry expansion of the asymmetric unit gives a tubular structure made from Cs-O_{Ar} interactions.

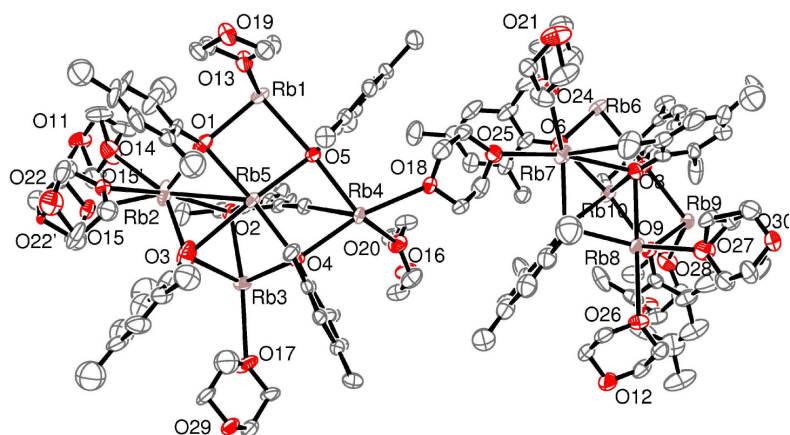
4.8 [(2,4,6-Me₃-C₆H₂OK)₅·(dioxane)₅]_∞

The asymmetric unit contains a pentameric potassium 2,4,6-trimethylphenoxide pentamer where each of the potassium centers and aryloxide anions are in different bonding environments. K(1) coordinates to two μ_3 -aryloxide anions and is solvated by one half dioxane



molecule, which bridges to another aggregate. K(2) coordinates to four μ_3 -aryloxide anions and is not solvated by dioxane. K(3) coordinates to two μ_3 -aryloxide anions and is solvated by one half and one full dioxane, all of which bridge to other aggregates. K(4) coordinates to two μ_3 -aryloxide anions, and one μ_2 -aryloxide anion. It is also solvated by two full dioxane molecules, both which bridge to other aggregates. K(5) coordinates to two μ_3 -aryloxide anions, and one μ_2 -aryloxide anion. It is also solvated by one full dioxane, which is terminal. O(12) is disordered over two sites with a site occupancy of 0.804(3) for the major component. Symmetry expansion gives the pentameric aggregate that is coordinated by seven bridging dioxane molecules. The extended structure forms a 7-connected network.

4.9 [(2,4,6-Me₃-C₆H₂ORb)₅·(dioxane)₅]_∞

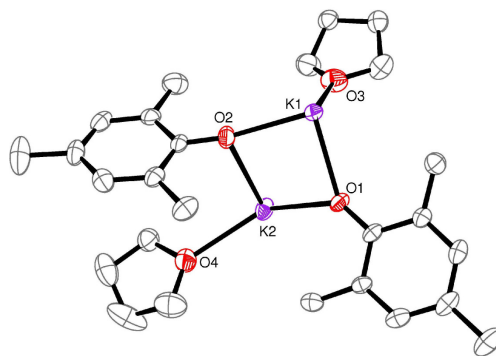


The asymmetric unit contains two different pentameric rubidium 2,4,6-trimethylphenoxide aggregates that are structurally similar. In the first pentameric aggregate Rb(1) coordinates to two μ_3 -aryloxy anions and solvated by one full dioxane molecule. Rb(2) coordinates to three μ_3 -aryloxy anions and is solvated by two full dioxane molecules. Both of these dioxanes are either fully or partially disorder over two sites. One of the dioxanes (O(15), C(97), C(98), C(115), C(116), O(22)) has a site occupancy of 0.770(8) for the major component. The carbon atoms of the second dioxane (C(92), C(100)) have a site occupancy of 0.565(15) for the major component. Rb(3) coordinates to three μ_3 -aryloxy anions and solvated by one full dioxane. Rb(4) coordinates to two μ_3 -aryloxy anions and solvated by one full and one half dioxane. Rb(5) coordinates to five μ_3 -aryloxy anions. In the second pentameric aggregate Rb(6) coordinates to two μ_3 -aryloxy anions. Rb(7) coordinates to three μ_3 -aryloxy anions and solvated by one full and one half dioxane molecule. Rb(8) coordinates to three μ_3 -aryloxy anions and solvated by two full dioxane. The carbon atoms of the dioxane (C(122) and C(123)) are disordered over two sites with a site occupancy of 0.709(12) for the

major component. Rb(9) coordinates to two μ_3 -aryloxide anions and is solvated by one full dioxane molecule. Rb(1) coordinates to five μ_3 -aryloxide anions. Symmetry expansion gives the two pentameric aggregates that are each deca-coordinated by dioxane. The extended structure is an eight-connected network with **bcu** topology. The structure, initially thought to have a c-centered orthorhombic setting, is pseudomerohedrally twinned with a BASF of 0.4553(6) and a twin law of 0 0 1 0 -1 0 1 0 0.

4.10 [(2,4,6-Me₃-C₆H₂OK)₄·(thf)₄]_∞

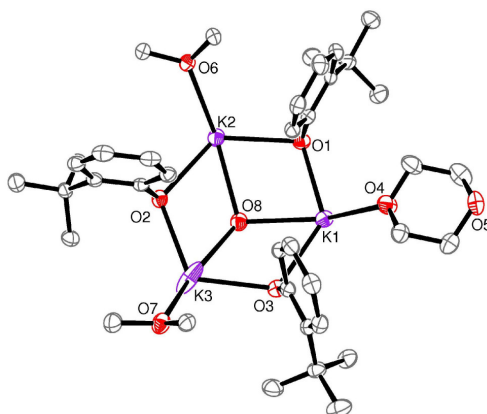
The asymmetric unit contains a potassium 2,4,6-trimethylphenoxide dimer where each potassium center is coordinated to two μ_2 -aryloxide anions. Additionally, both potassium centers are solvated by a THF molecule. Symmetry expansion gives a



tetrameric ladder aggregate. K(2) and K(2)' are η^6 -coordinated to the aryloxide ring of a neighboring aggregate through a cation- π interaction. This gives a one-dimensional chain polymer built up through this interaction.

5.1 [{(2-*t*Bu-C₆H₄OK)₆⊃(H₂O)}·(dioxane)₄]_∞

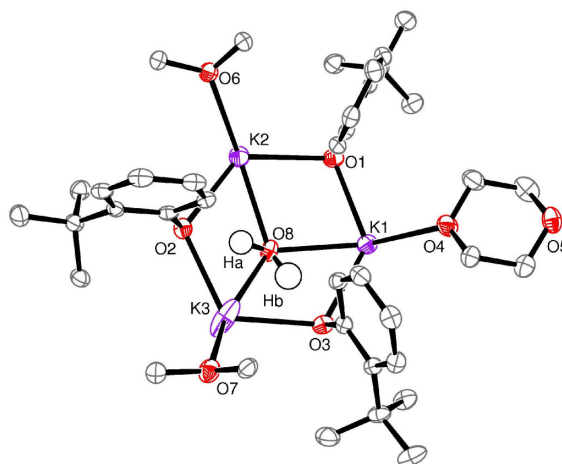
The asymmetric unit contains a potassium 2-*t*-butylphenoxide trimer where each potassium center is coordinated to two μ_2 -aryloxide anions. K(1) is solvated by a full molecule of dioxane, whereas K(2) and K(3) are solvated by a half molecule of dioxane.



Symmetry expansion gives a prismatic hexamer that is coordinated by a total of six dioxane molecules. Four of the dioxanes bridge to other aggregates to give a two-dimensional 4^4 -net. A water molecule is encapsulated inside the potassium aggregate and is disordered over two sites related by symmetry. The occupancy of the oxygen freely refined to 50% at each site, so the site occupancy was fixed at that value.

5.1_n [$\{(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})\}\cdot(\text{dioxane})_4$]_∞

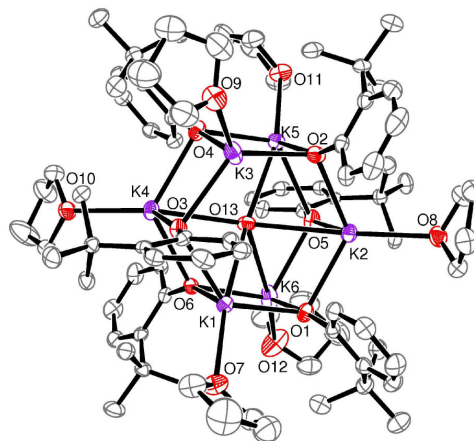
This is the same structure as **5.1**, but was solved by neutron diffraction. The asymmetric unit contains a potassium 2-*t*-butylphenoxide trimer where each potassium center is coordinated to two μ_2 -aryloxy anions. K(1) is solvated by a full molecule of dioxane, whereas K(2) and



K(3) are solvated by a half molecule of dioxane. Symmetry expansion gives a prismatic hexamer that is coordinated by a total of six dioxane molecules. Four of the dioxanes bridge to other aggregates to give a two-dimensional 4^4 -net. A water molecule is encapsulated inside the potassium aggregate and is disordered over two sites related by symmetry. The occupancy of the oxygen freely refined to 50% at each site, so the site occupancy was fixed at that value.

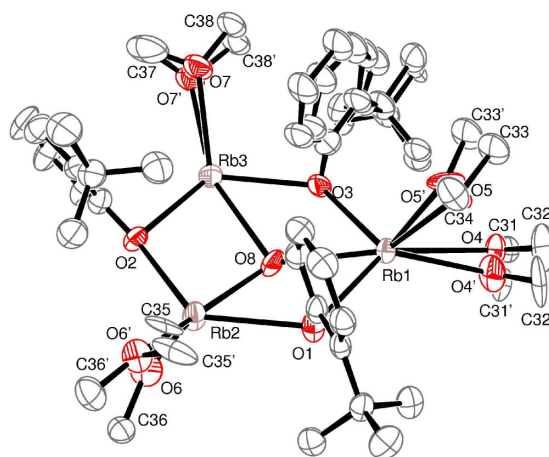
5.2 $[(2\text{-}t\text{Bu-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})]\cdot(\text{THF})_6$

The asymmetric unit contains a potassium 2-*t*-butylphenoxide hexamer where each potassium center is coordinated to three μ_3 -aryloxide anions. Additionally, each potassium is coordinated by a molecule of THF. The encapsulated water molecule (O13) is disordered over two sites with a site occupancy of 50% at each site.



5.3 $[\{(2\text{-}t\text{Bu-C}_6\text{H}_4\text{ORb})_6\supset(\text{H}_2\text{O})\}\cdot(\text{dioxane})_4]\cdot(\text{dioxane})_\infty$

The asymmetric unit contains a rubidium 2-*t*-butylphenoxide trimer where each potassium center is coordinated to two μ_2 -aryloxide anions. Rb(1) is solvated by two half molecules of dioxane, whereas Rb(2) and Rb(3) are solvated by a half molecule of dioxane. Symmetry expansion gives a

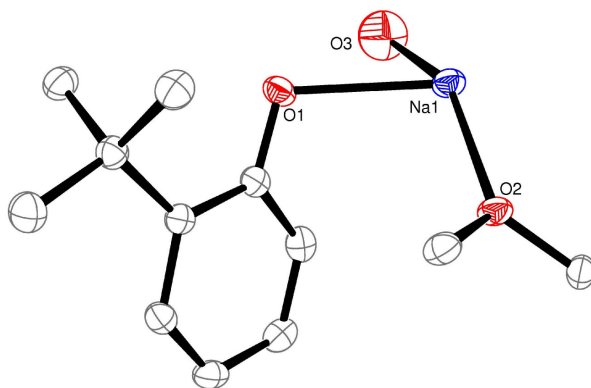


prismatic hexamer that is coordinated by a total of eight dioxane molecules. All of the dioxanes bridge to other aggregates to give 3D network with **bcu** topology. A water molecule is encapsulated inside the rubidium aggregate and is disordered over two sites related by symmetry. The site occupancy of the oxygen atom was allowed to freely refine to 0.114(9) at each site. The carbon atoms of one of the aryloxide ligands (C(22) – C(30)) were disordered over two sites with an occupancy of 0.620(7) for the major component.

In addition, four dioxane molecules were disordered over two sites. The site occupancies for the major component are: (i) O(6), C(35), C(36): 0.457(14); (ii) O(4), C(31), C(32): 0.767(20); (iii) O(7), C(38): 0.831(6); (iv) O(5), C(33): 0.638(13).

5.4 $\{[(2\text{-}i\text{Bu-C}_6\text{H}_4\text{ONa})_6\supset(\text{H}_2\text{O})]\cdot(\text{dioxane})_3\}_\infty$

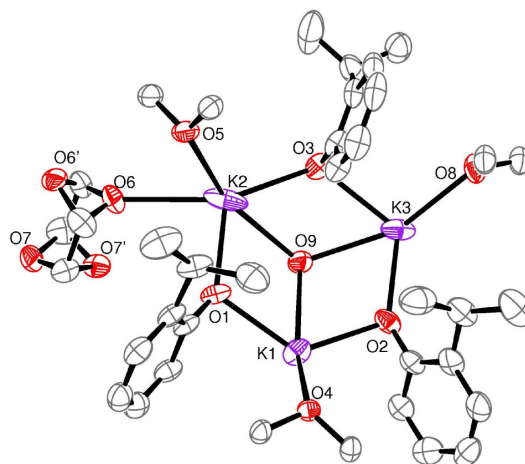
The asymmetric unit contains a sodium 2-*i*-butylphenoxide monomer with the sodium center solvated by a half molecule of dioxane and a molecule of water. Symmetry expansion gives a



a total of six dioxane molecules. All of the dioxanes bridge to other aggregates to give 3D network with **pcu** topology. The water molecule is disordered over two sites within the aggregate, with a site occupancy of 0.207(9) for the major component. The structure is pseudo-merohedrally twinned with a BASF of 0.438(1) and a twin law of 0 -1 0 -1 0 0 0 1.

5.5 $\{[(2\text{-}i\text{Pr-C}_6\text{H}_4\text{OK})_6\supset(\text{H}_2\text{O})]\cdot(\text{dioxane})_5\cdot(\text{dioxane})\}_\infty$

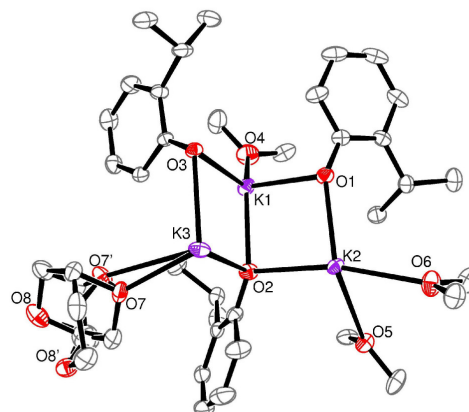
The asymmetric unit contains a potassium 2-*i*-propylphenoxide trimer where each potassium center is coordinated to two μ_2 -aryloxy anions. K(1) and K(3) are solvated by a half molecule of dioxane, whereas K(2) is solvated by a full and half molecule of dioxane. The oxygen atoms of



the full molecule of dioxane (O(6) and O(7)) are disordered over two sites, with an occupancy for the major component that freely refined to 0.643(5). Symmetry expansion generates a prismatic hexamer that is coordinated by a total of eight dioxane molecules. Six of the dioxanes bridge to other aggregates to give a 3D network with **pcu** topology. A water molecule (O(9)) is encapsulated inside the potassium aggregate and is disordered over two sites related by symmetry. The occupancy of the oxygen initially freely refined to 50% at each site so the site occupancy was fixed at that value.

5.6 [(2-*i*Pr-C₆H₄OK)₆·(dioxane)₅]_∞

The asymmetric unit contains a potassium 2-*i*-propylphenoxide trimer where each potassium center is coordinated to two μ_2 -aryloxide and one μ_3 -aryloxide. K(1) is solvated by a half molecule of dioxane, K(2) is solvated by two half molecules of dioxane, and K(3) is solvated



by one full molecule of dioxane. The full molecule of dioxane (O(7), O(8), C(34), C(35), C(36), C(37)) is disordered over two sites, with an occupancy for the major component that freely refined to 0.717(3). Symmetry expansion gives a triple-stack of dimers that is coordinated by a total of eight dioxane molecules. Six of the dioxanes bridge to other aggregates to give a 3D network with **pcu** topology.

5.7 $[(2\text{-}^i\text{Pr-C}_6\text{H}_4\text{OK})_6\cdot(\text{H}_2\text{O})_2]\cdot(\text{dioxane})_{5.5}]_\infty$

The asymmetric unit contains a potassium

2-*i*-propylphenoxide hexamer. K(1)

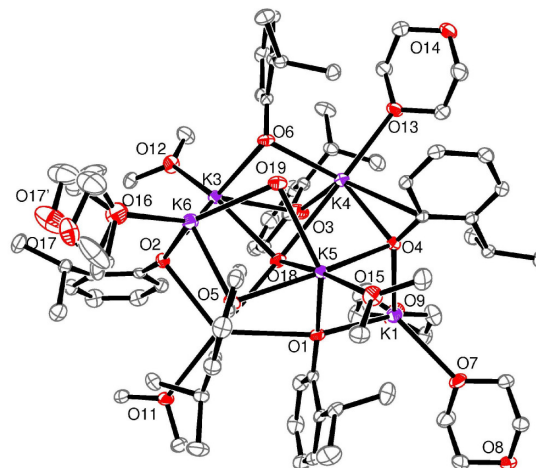
coordinates to two μ_3 -aryloxy anions and

is solvated by two full molecules of

dioxane. K(2) coordinates to three μ_3 -

aryloxy anions and is solvated by one

half molecule of dioxane and one water.



K(3) coordinates to one μ_3 -aryloxy and two μ_2 -aryloxy anions, and is solvated by one

half molecule of dioxane and one water. K(4) coordinates to one μ_3 -aryloxy and two

μ_2 -aryloxy anions, and is solvated by one full molecule of dioxane and one water. K(5)

coordinates to three μ_3 -aryloxy anions and is solvated by one half molecule of dioxane

and two waters. K(6) coordinates to two μ_3 -aryloxy anions and is solvated by one full

molecule of dioxane and one water. The molecule of dioxane (O(16), O(17), C(73),

C(74), C(75), C(76)) is disordered over two sites, with an occupancy for the major

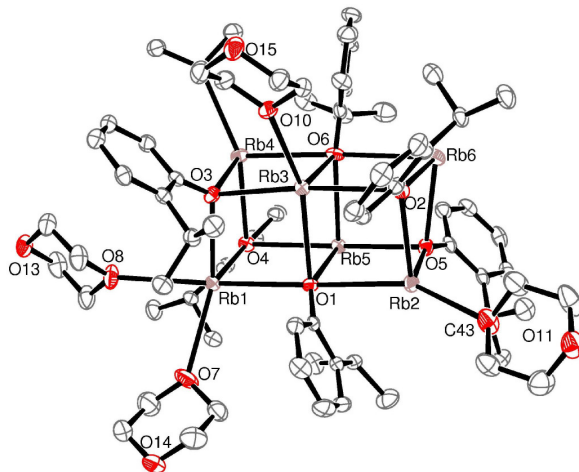
component that freely refined to 0.505(8). Symmetry expansion generates a hexameric

aggregate with eight coordinated dioxane. Five of the dioxanes bridge to other aggregates

to give a bilayer structure.

5.8 [2-ⁱPr-C₆H₄ORb)₆·(dioxane)_{4.5}]_∞

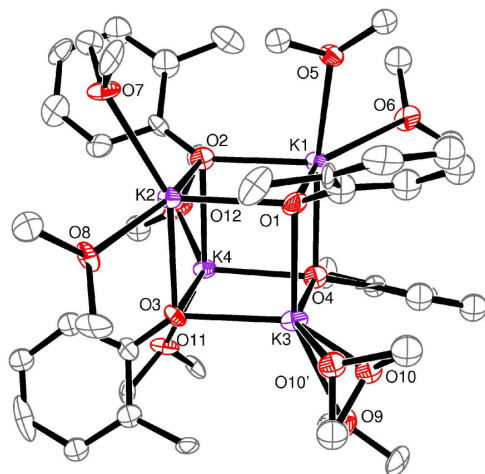
The asymmetric unit contains a rubidium 2-*i*-propylphenoxide triple-stack of dimers aggregate. Rb(1) coordinates to three μ₃-aryloxy anions and is solvated by two full molecules of dioxane. Rb(2) coordinates to three μ₃-aryloxy anions and is solvated by one full molecule of



dioxane. Rb(3) coordinates to four μ₃-aryloxy anions and is solvated by one full molecule of dioxane. Rb(4) coordinates to three μ₃-aryloxy anions and is solvated by one half molecule of dioxane. Rb(5) coordinates to four μ₃-aryloxy anions and Rb(6) coordinates to three μ₃-aryloxy anions. Symmetry expansion generates the hexameric aggregate with nine coordinated dioxane. All of the dioxanes bridge to other aggregates to give a nine-connected network with **ncd** topology.

5.10 [(2-Me-C₆H₄OK)₄·(dioxane)₄]_∞

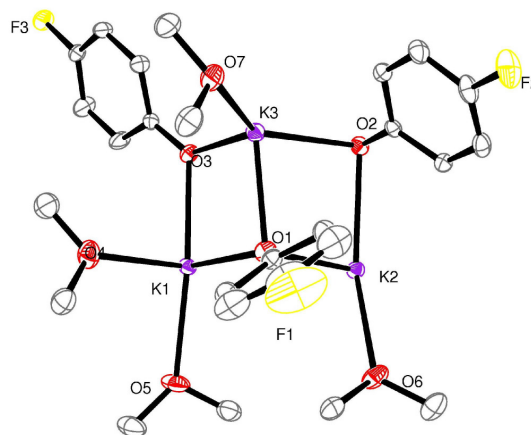
The asymmetric unit contains a tetrameric potassium 2-methylphenoxide aggregate. The four potassium centers coordinate to three μ₃-aryloxy anions and are solvated by two half molecules of dioxane. The oxygen of one of the dioxane molecules is disordered over two sites with an occupancy for the major component that freely refined to 0.562(12). Symmetry expansion generates the tetrameric aggregate



coordinated by eight dioxane molecules. The dioxanes bridge to six different aggregates to give a 3D network with **sxc** topology. The structure is pseudo-merohedrally twinned with a BASF of 0.468(2) and a twin law of 0 1 0 1 0 0 0 -1.

6.1 [(4-F-C₆H₄OK)₆·(dioxane)₄]_∞

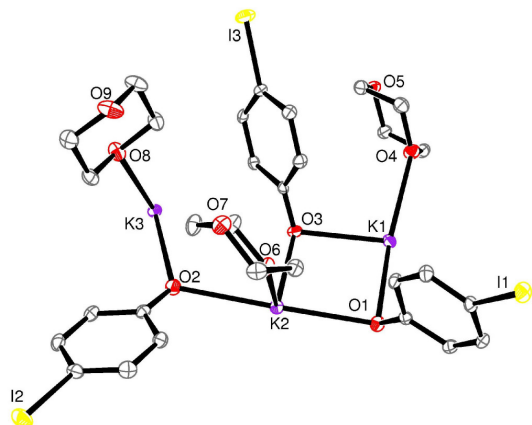
The asymmetric unit contains a potassium 4-F-phenoxide trimer. K(1) and K(2) coordinate to one μ_2 -aryloxide anion and one μ_3 -aryloxide anion, whereas K(3) coordinates to two μ_2 -aryloxide anions and one μ_3 -aryloxide anion. K(1) is solvated by two half molecules of dioxane. K(2) and



K(3) are solvated by one half molecule of dioxane each. Symmetry expansion generates a hexameric aggregate coordinated by a total of eight dioxane molecules. In addition to the dioxane bridges, there are transannular K-F_{Ar} interactions. With all eight dioxanes bridging to other aggregates, plus the K-F_{Ar} interactions, the hexameric aggregate has sixteen connections to other aggregates. The aggregate is only considered an 8-connected node because each of the connections is a double bridge. The resulting 3D network has **bcu** topology.

6.2 [(4-I-C₆H₄OK)₆·(dioxane)₆]_∞

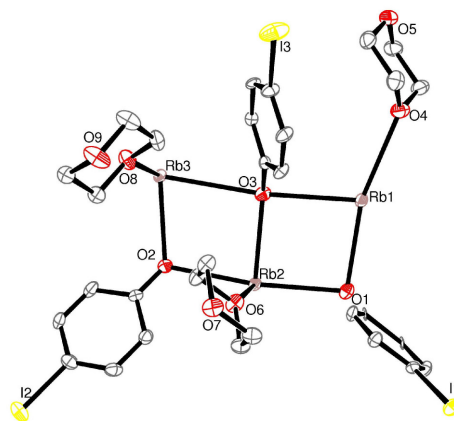
The asymmetric unit contains a potassium 4-I-phenoxide trimer. K(1) coordinates to two μ_2 -aryloxide anions, K(2) coordinates to three μ_2 -aryloxide anions, and K(3) coordinates to one μ_2 -aryloxide anion. Each of the potassium centers is solvated by a full molecule of dioxane. Symmetry expansion



gives a hexameric aggregate that is coordinated a total of twelve dioxane molecules. However, the aggregate is only linked to six neighboring aggregates because each link is formed through a dioxane double bridge. The 6-connected extended structure forms an extended structure with **pcu** topology.

6.3 [(4-I-C₆H₄ORb)₆·(dioxane)₆]_∞

The asymmetric unit contains a rubidium 4-I-phenoxide trimer. Rb(1) and Rb(2) coordinate to one μ_2 -aryloxide anion and one μ_3 -aryloxide anion. Rb(3) coordinates to two μ_2 -aryloxide anions and one μ_3 -aryloxide anion. Each of the rubidium centers are coordinated by a full

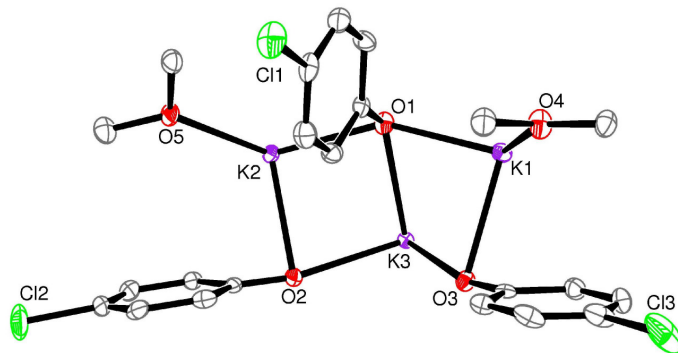


molecule of dioxane. Symmetry expansion gives a hexameric aggregate that is coordinated a total of twelve dioxane molecules. However, the aggregate is only linked to six neighboring aggregates because each link is formed through a dioxane double bridge.

The 6-connected extended structure forms an extended structure with primitive cubic topology.

6.4 [(4-Cl-C₆H₄OK)₃·(dioxane)]_∞

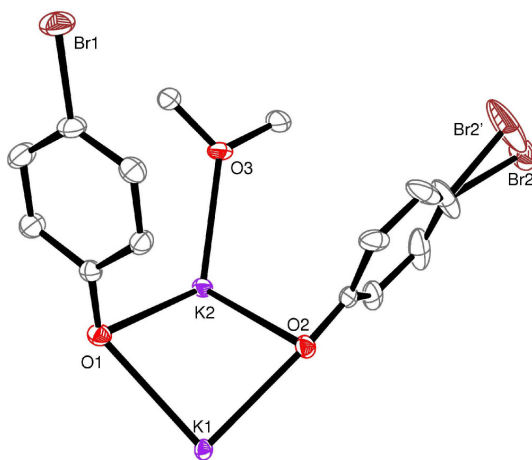
The asymmetric unit contains a potassium 4-Cl-phenoxide trimer. There are two different bonding environments for the potassiums. Both K(1) and K(2) coordinate to one μ_2 -aryloxide



anion and one μ_3 -aryloxide anion as well as being solvated by one half molecule of dioxane. K(3) coordinates to two μ_2 -aryloxide anions and one μ_3 -aryloxide anion. Symmetry expansion generates an inorganic rod built from K-O_{Ar} interactions. Each inorganic rod is linked to four other rods through a dioxane bridge to give an extended hybrid inorganic/organic network.

6.5 [(4-Br-C₆H₄OK)₂·(dioxane)_{0.5}]_∞

The asymmetric unit contains a potassium 4-Br-phenoxide dimer. Both potassium centers coordinate to two μ_2 -aryloxide anions. In addition, K(2) is solvated by a half molecule of dioxane. Symmetry expansion results in an inorganic rod built from K-O_{Ar}

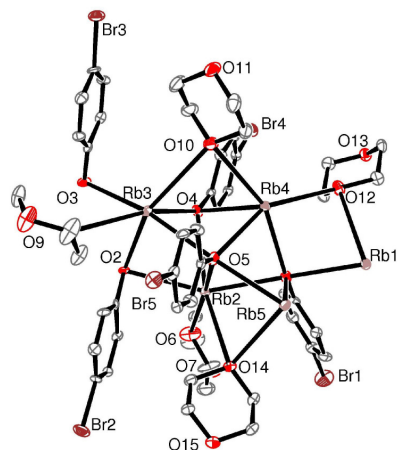


four other rods through a dioxane bridge to give an extended hybrid inorganic/organic

network. Br(2) is disordered over two sites with a site occupancy of 0.529(7) for the major component.

6.6 [(4-Br-C₆H₄ORb)₅·(dioxane)₅]_∞

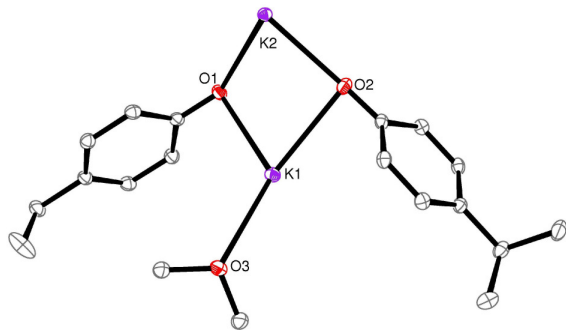
The asymmetric unit contains a rubidium 4-Br-phenoxide pentamer with each metal is coordinated by a full dioxane molecule. All of the rubidium centers are coordinated to four μ_4 -aryloxide anions. There are three different dioxane bonding environments for the five rubidium centers. Rb(1) and Rb(5) are coordinated by one μ_2 -dioxane, while Rb(2) and Rb(3) are coordinated



by one μ_1 -dioxane and one μ_2 -dioxane, and Rb(4) is coordinated by two μ_2 -dioxane molecules. Symmetry expansion results in an inorganic rod built from Rb-O_{Ar} interactions.

6.7 [(4-ⁱPr-C₆H₄OK)₂·(dioxane)_{0.5}]_∞

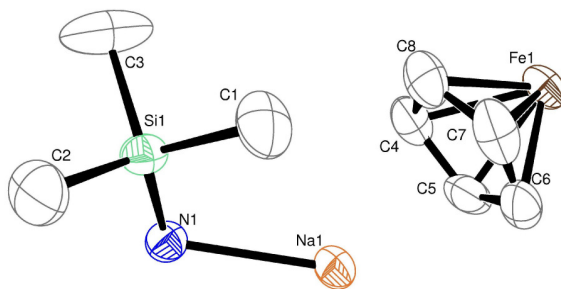
The asymmetric unit contains a potassium 4-ⁱPr-phenoxide dimer. Both of the potassium centers coordinate to μ_2 -aryloxide anions. In addition, K(1) is solvated by a half molecule of dioxane.



Symmetry expansion results in an inorganic rod built from K-O_{Ar} interactions. Each inorganic rod is linked to four other rods through a dioxane bridge to give an extended hybrid inorganic/organic network.

7.1 $[(\text{Me}_3\text{Si})_2\text{NNa}]_2 \cdot (\text{Cp}_2\text{Fe})_\infty$

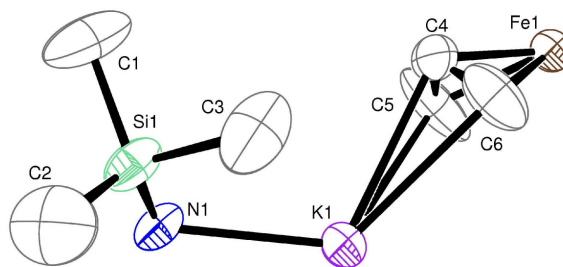
The asymmetric unit contains a Na(HMDS) monomer that is η^5 -coordinated by half a molecule of ferrocene. Symmetry expansion



generates a one-dimensional polymeric chain of Na_2N_2 ring dimers connected through doubly η^5 -coordinated ferrocene molecules. The five atoms of the Cp ring were fixed as a five-membered ring with one-half site occupancy. Symmetry expansion of the molecule gives the second orientation of the ring.

7.2 $[(\text{Me}_3\text{Si})_2\text{NK}]_2 \cdot (\text{Cp}_2\text{Fe})_\infty$

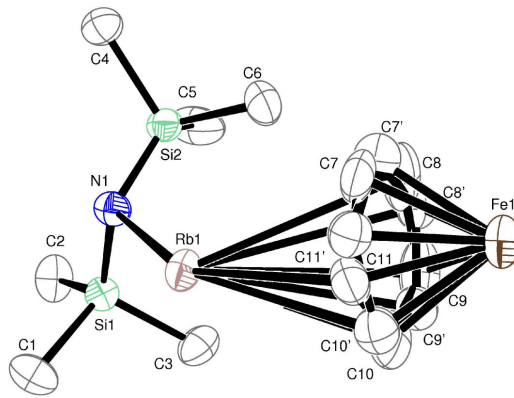
The asymmetric unit contains a K(HMDS) monomer that is η^3 -coordinated by a partial molecule of ferrocene. Symmetry expansion generates a one-dimensional polymeric



chain of K_2N_2 ring dimers connected through doubly η^5 -coordinated ferrocene molecules.

7.3 $[(\text{Me}_3\text{Si})_2\text{NRb}]_2 \cdot (\text{Cp}_2\text{Fe})_\infty$

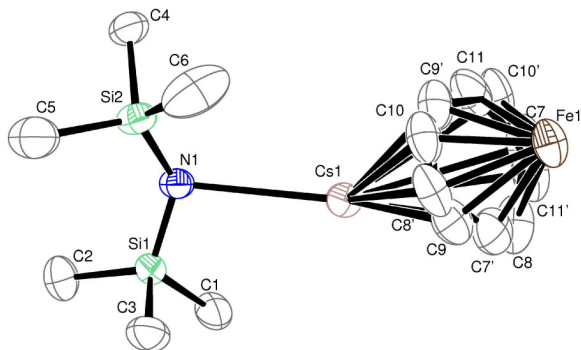
The asymmetric unit contains a Rb(HMDS) monomer that is η^5 -coordinated by half a molecule of ferrocene. Symmetry expansion generates a one-dimensional polymeric chain of Rb_2N_2 ring dimers connected through



doubly η^5 -coordinated ferrocene molecules. The carbon atoms of the ferrocene ring (C(7), C(8), C(9), C(10), C(11)) are disordered over two sites with the site occupancy of the major component freely refined to 0.652(11). The ISOR command (0.002) was used on all of the atoms of the minor component of the disordered Cp ring.

7.4 $[(\text{Me}_3\text{Si})_2\text{NCs}]_2 \cdot (\text{Cp}_2\text{Fe})_\infty$

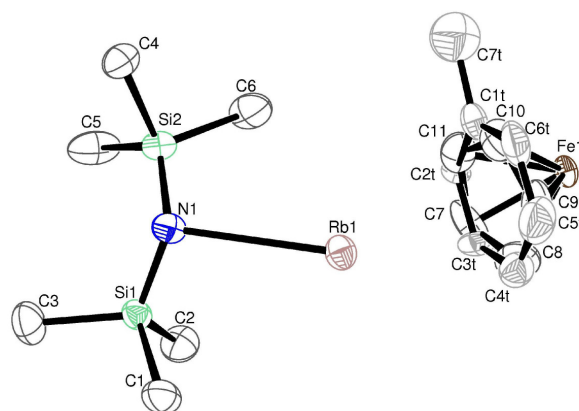
The asymmetric unit contains a Cs(HMDS) monomer that is η^5 -coordinated by half a molecule of ferrocene. Symmetry expansion generates a one-dimensional polymeric



chain of Cs_2N_2 ring dimers connected through doubly η^5 -coordinated ferrocene molecules. The carbon atoms of the ferrocene (C(7), C(8), C(9), C(10), C(11)) are disordered over two sites with the site occupancy of the major component freely refined to 0.550(22).

7.5 $[(\text{Me}_3\text{Si})_2\text{NRb}]_2 \cdot (\text{Cp}_2\text{Fe})_{0.6} \cdot (\text{C}_7\text{H}_8)_{0.8} \cdot \infty$

The asymmetric unit contains a Rb(HMDS) monomer that is η^5 -coordinated by half a molecule of ferrocene and η^6 -coordinated by one molecule of toluene. Since the toluene and Cp ring occupy nearly the same site,

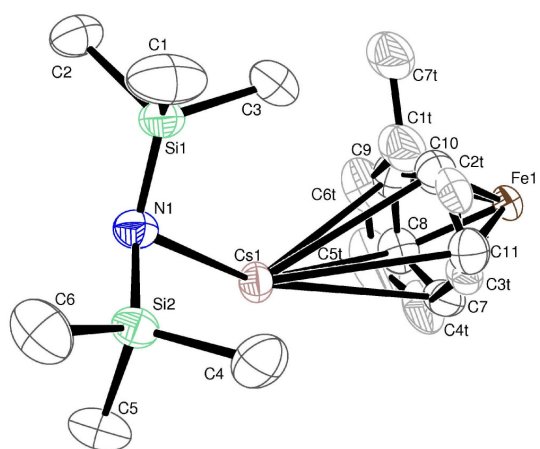


the two were modeled as disordered. The Cp ring is the major component with a site occupancy of 0.595(6). The site occupancy of the Fe atom was changed to match the site

occupancy of the Cp ring, since the Fe can only be present in the structure when the Cp ring is present. The carbon atoms of the Cp ring were fixed as a five-membered ring and the anisotropic thermal parameters were modeled using the ISOR command. Likewise, the six ring carbons of the toluene molecule were fixed as a six-membered ring. Symmetry expansion generates a one-dimensional polymeric chain of Rb_2N_2 ring dimers connected through doubly η^5 -coordinated ferrocene molecules.

7.6 $\{[(\text{Me}_3\text{Si})_2\text{NCs}]_2 \cdot (\text{Cp}_2\text{Fe})_{0.5} \cdot (\text{C}_7\text{H}_8)\}_\infty$

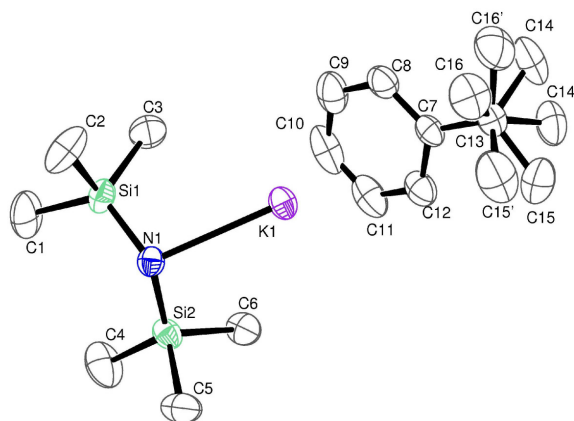
The asymmetric unit contains a $\text{Cs}(\text{HMDS})$ monomer that is η^5 -coordinated by half a molecule of ferrocene and η^6 -coordinated by one molecule of toluene. Since the toluene and Cp ring occupy nearly the same site, the two were modeled as disordered. The Cp ring is the minor component with a site



occupancy of 0.495(6). The site occupancy of the Fe atom was changed to match the site occupancy of the Cp ring, since the Fe can only be present in the structure when the Cp ring is present. The carbon atoms of the Cp ring were fixed as a five-membered ring and the anisotropic thermal parameters were modeled using the ISOR command. Likewise, the six ring carbons of the toluene molecule were fixed as a six-membered ring. The EADP command was used for C(7T) and C(1T). Symmetry expansion generates a one-dimensional polymeric chain of Cs_2N_2 ring dimers connected through doubly η^5 -coordinated ferrocene molecules.

7.14 $[\{\text{Me}_3\text{Si}\}_2\text{NK}\}\cdot(\text{}^t\text{Bu-C}_6\text{H}_5)]_2$

The asymmetric unit contains a K(HMDS) monomer that is η^6 -coordinated by one molecule of *tert*-butylbenzene. Symmetry expansion generates a K_2N_2 ring dimer that is doubly solvated by *tert*-butylbenzene. The *t*-butyl group is disordered over two sites with the site occupancy of the major component freely refined to 0.660(3).



7.15 $[\{\text{Me}_3\text{Si}\}_2\text{NK}\}\cdot(\text{Me}_3\text{-C}_6\text{H}_3)]_2$

The asymmetric unit contains a K(HMDS) monomer that is η^6 -coordinated by one molecule of mesitylene. Symmetry expansion generates a K_2N_2 ring dimer that is doubly solvated by mesitylene.

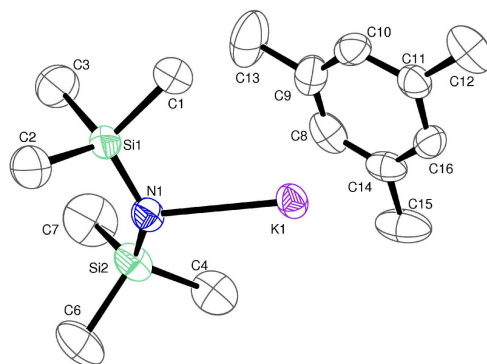


Table A.1
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **2.1-2.5**

	2.1	2.2	2.3	2.4	2.5
Formula	C ₅₆ H ₈₄ Li ₄ O ₁₄	C ₃₇ H ₅₅ Li ₄ N ₁ O ₇	C ₉₄ H ₁₆₂ Li ₁₂ N ₆ O ₁₄	C ₁₉ H ₃₅ Li ₃ N ₂ O ₄	C ₆₂ H ₁₃₀ Li ₁₂ N ₁₀ O ₁₄
Formula Wt.	1008.99	653.58	1683.58	376.31	1323.04
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 4 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a (Å)	15.260(1)	30.862(7)	11.0932(3)	10.6238(6)	11.3217(5)
b (Å)	15.260(1)	15.082(3)	13.5887(4)	11.3639(6)	11.3930(5)
c (Å)	24.138(4)	21.712(5)	18.7141(5)	11.4918(7)	17.6387(7)
α (deg)	90	90	98.329(1)	65.516(3)	84.165(2)
β (deg)	90	123.1(1)	97.972(2)	88.273(4)	84.919(2)
γ (deg)	90	90	109.910(1)	62.920(3)	63.925(2)
Volume (Å ³)	5629.9(1)	8472.5(3)	2570.25(12)	1102.48(10)	2030.57(15)
Z	4	8	1	2	1
Density (Mg/m ³)	1.192	1.235	1.088	1.134	1.082
μ (λ) (mm ⁻¹)	0.083	1.025	0.069	0.076	0.073
Crystal size (mm ⁻¹)	0.20x0.20x0.20	0.25x0.22x0.21	0.35x0.32x0.25	0.35x0.35x0.28	0.25x0.25x0.20
θ range (deg)	2.53 – 30.37	2.40 – 27.00	2.38 – 30.44	2.20 – 24.75	2.28 – 27.50
T _{max} / T _{min}	0.98 / 0.98	0.97 / 0.99	0.98 / 0.99	0.97 / 0.98	0.98 / 0.99
Refln. Collected	34,879	53,338	52,006	15,828	40,041
Ind. Refln.	7,132	9,500	10,338	3,773	9,075
Obs. Refln. [I > 2σ(I)]	5,472	6,872	8,944	2,922	6,574
GOF on F ²	1.105	1.078	1.035	1.086	1.080
R1,wR2 [I > 2 σ (I)]	0.0522, 0.1482	0.0558, 0.1420	0.0401, 0.1085	0.0588, 0.1482	0.0414, 0.1011
R1, wR2 (all data)	0.0662, 0.1543	0.0791, 0.1541	0.0471, 0.1153	0.0788, 0.1651	0.0699, 0.1244
Largest peak/hole (e·Å ⁻³)	0.252 / -0.213	0.350 / -0.378	0.371 / -0.328	0.442 / -0.357	0.399 / -0.328

Table A.2
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **2.6**, **3.1-3.4**

	2.6	3.1	3.2	3.3	3.4
Formula	C ₃₀ H ₅₂ Li ₂ N ₂ O ₆	C ₂₈ H ₄₀ Cl ₂ Li ₂ O ₈	C ₅₂ H ₇₀ Cl ₄ Li ₄ O ₁₄	C ₄₄ H ₆₀ Cl ₄ Li ₄ N ₄ O ₈	C ₂₁ H ₂₇ Cl ₂ Li ₂ NO ₄
Formula Wt.	550.62	589.38	1081.28	942.52	442.22
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Tetragonal	Monoclinic
Space group	<i>P2₁/n</i>	<i>Pna2₁</i>	<i>P2₁/c</i>	<i>I-4</i>	<i>C2/c</i>
a (Å)	12.809(5)	22.2796(3)	10.700(2)	15.5400(5)	22.200(4)
b (Å)	9.254(3)	15.8706(2)	44.305(1)	15.5400(5)	10.830(2)
c (Å)	14.881(5)	8.5835(1)	12.727(3)	10.5170(10)	18.690(4)
α (deg)	90	90	90	90	90
β (deg)	111.88(2)	90	109.02(2)	90	100.04(3)
γ (deg)	90	90	90	90	90
Volume (Å ³)	1636.83(10)	3035.05(7)	5704.01(13)	2539.8(3)	4424.7(15)
Z	2	4	4	2	8
Density (Mg/m ³)	1.117	1.290	1.259	1.232	1.328
μ (λ)(mm ⁻¹)	1.105	0.259	0.265	0.284	0.320
Crystal size (mm ⁻¹)	0.25x0.30x0.0.3	0.36x0.58x0.63	0.30x0.35x0.36	0.23x0.27x0.36	0.17x0.35x0.38
Radiation	X-ray	X-ray	X-ray	X-ray	X-ray
T _{min} / T _{max}	0.70 / 0.80	0.85 / 0.91	0.91 / 0.93	0.90 / 0.94	0.88 / 0.95
Refln. Collected	9,158	59,780	83,221	11,920	43,160
Ind. Refln.	2,442	14,159	18,858	2,601	8,427
Obs. Refln. [I > 2σ(I)]	1,932	12,961	11,654	2,472	7,497
GOF on F ²	1.041	1.045	1.046	1.061	1.028
R1,wR2 [I > 2 σ (I)]	0.0587, 0.1425	0.0317, 0.0809	0.0692, 0.1904	0.0249, 0.0606	0.0308, 0.0838
R1, wR2 (all data)	0.0758, 0.1539	0.0362, 0.0832	0.1165, 0.2136	0.0276, 0.0621	0.0348, 0.0870
Largest peak/hole	0.338 / -0.200	0.627 / -0.206	0.959 / -0.369	0.171 / -0.118	0.587 / -0.179

Table A.3
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **3.5-3.9**

	3.5	3.6	3.7	3.8	3.9
Formula	C ₄₇ H ₅₆ Cl ₄ Li ₄ O ₈	C ₂₂ H ₂₈ Cl ₂ Li ₂ O ₆	C ₅₀ H ₆₈ Br ₄ Li ₄ O ₁₃	C ₂₁ H ₂₇ Br ₂ Li ₂ NO ₄	C ₄₄ H ₆₀ Br ₄ Li ₄ N ₄ O ₈
Formula Wt.	918.48	473.22	1223.44	531.14	1120.36
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Tetragonal	Triclinic	Monoclinic	Tetragonal
Space group	<i>P</i> -1	<i>I</i> -42 <i>d</i>	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>I</i> -4
a (Å)	13.792(3)	18.3300(3)	10.7494(2)	22.3470(8)	15.6067(2)
b (Å)	14.024(3)	18.3300(3)	12.7727(3)	10.9388(4)	15.6067(2)
c (Å)	14.085(3)	28.3790(7)	22.2935(5)	18.9663(7)	10.5227(2)
α (deg)	74.51(3)	90	95.936(1)	90	90
β (deg)	82.82(3)	90	97.949(1)	100.090(2)	90
γ (deg)	79.54(3)	90	111.018(1)	90	90
Volume (Å ³)	2573.3(9)	9535.0(3)	2790.74(10)	4565.6(3)	2563.00(7)
Z	2	16	2	8	2
Density (Mg/m ³)	1.185	1.319	1.457	1.546	1.452
μ (λ)(mm ⁻¹)	0.276	0.306	2.942	3.578	3.191
Crystal size (mm ⁻¹)	0.14x0.20x0.38	0.21x0.27x0.33	0.27x0.44x0.50	0.35x0.42x0.45	0.37x0.39x0.44
Radiation	X-ray	X-ray	X-ray	X-ray	X-ray
T _{min} / T _{max}	0.90 / 0.96	0.91 / 0.94	0.46 / 0.25	0.36 / 0.20	0.38 / 0.25
Refln. Collected	37,232	20,341	54,858	41,166	19,989
Ind. Refln.	10,499	4,225	12,758	8,708	4,841
Obs. Refln. [I > 2σ(I)]	8,504	3,917	10,879	7,316	4,474
GOF on F ²	1.061	1.037	1.036	1.048	1.006
R1,wR2 [I > 2 σ (I)]	0.0431, 0.1105	0.0260, 0.0594	0.0267, 0.0657	0.0255, 0.0617	0.0203, 0.0474
R1, wR2 (all data)	0.0545, 0.1153	0.0303, 0.0615	0.0343, 0.0686	0.0354, 0.0645	0.0243, 0.484
Largest peak/hole (e·Å ⁻³)	0.880 / -0.050	0.203 / -0.149	0.672 / -0.537	0.645 / -0.602	0.345 / -0.290

Table A.4
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **3.10**, **4.1-4.4**

	3.10	4.1	4.2	4.3	4.4
Formula	C ₂₂ H ₂₈ Br ₂ Li ₂ O ₆	C ₂₈ H ₄₀ Cl ₂ Na ₂ O ₈	C ₂₈ H ₄₀ Br ₂ Na ₂ O ₈	C ₃₀ H ₄₄ Cl ₂ K ₂ O ₉	C ₃₀ H ₄₄ Br ₂ K ₂ O ₉
Formula Wt.	562.14	621.48	710.40	697.75	786.67
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Tetragonal	Tetragonal	Tetragonal	Orthorhombic	Orthorhombic
Space group	<i>I</i> -42 <i>d</i>	<i>I</i> 4 ₁ <i>cd</i>	<i>I</i> 4 ₁ <i>cd</i>	<i>Pbca</i>	<i>Pbca</i>
a (Å)	18.4920(5)	24.136(3)	24.2812(2)	10.9385(3)	11.020(2)
b (Å)	18.4920(5)	24.136(3)	24.2812(2)	19.5849(5)	19.780(4)
c (Å)	28.562(1)	21.614(4)	21.8474(5)	32.2466(8)	32.080(6)
α (deg)	90	90	90	90	90
β (deg)	90	90	90	90	90
γ (deg)	90	90	90	90	90
Volume (Å ³)	9766.9(5)	12591(4)	12880.7(3)	6908.2(3)	6993(2)
Z	16	16	16	8	8
Density (Mg/m ³)	1.529	1.311	1.465	1.342	1.494
μ (λ) (mm ⁻¹)	3.353	0.279	2.589	0.477	2.604
Crystal size (mm ⁻¹)	0.13x0.25x0.30	0.47x0.47x0.54	0.20x0.45x0.45	0.25x0.3x0.35	0.20x0.37x0.44
Radiation	X-ray	X-ray	X-ray	X-ray	X-ray
T _{max} / T _{min}	0.65 / 0.38	0.84 / 0.82	0.65 / 0.35	0.89 / 0.84	0.65 / 0.40
Refln. Collected	58,978	70,482	53,246	56,225	84,050
Ind. Refln.	6,036	11,374	5,392	8,172	6,891
Obs. Refln. [I > 2σ(I)]	5,308	10,418	4,117	7,233	5,626
GOF on F ²	0.986	1.049	1.054	1.151	1.022
R1,wR2 [I > 2 σ (I)]	0.0239, 0.0456	0.0409, 0.1125	0.0715, 0.1541	0.0479, 0.1086	0.0370, 0.0714
R1, wR2 (all data)	0.0322, 0.0472	0.0463, 0.1181	0.1041, 0.1822	0.0555, 0.1123	0.0527, 0.779
Largest peak/hole (e·Å ⁻³)	0.346 / -0.238	0.599 / -0.403	1.403 / -0.766	0.914 / -0.336	0.855 / -1.469

Table A.5
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **4.5-4.9**

	4.5	4.6	4.7	4.8	4.9
Formula	C ₃₀ H ₄₄ Cl ₂ O ₉ Rb ₂	C ₃₀ H ₄₄ Br ₂ O ₉ Rb ₂	C ₅₆ H ₅₆ C ₁₇ Cs ₇ O ₇	C ₆₅ H ₉₅ K ₅ O ₁₅	C ₂₆ H ₃₈ K ₂ O ₄
Formula Wt.	790.49	879.41	2019.53	1311.91	492.76
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic	Rhombohedral	Monoclinic	Triclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>R</i> -3	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
a (Å)	11.324(2)	11.2931(7)	41.8031(7)	18.380(4)	9.2965(6)
b (Å)	19.659(4)	19.7565(13)	41.8031(7)	21.550(4)	11.8019(7)
c (Å)	32.308(7)	32.173(2)	20.8283(9)	17.740(4)	12.7143(8)
α (deg)	90	90	90	90	90.663(3)
β (deg)	90	90	90	91.30(3)	101.569(3)
γ (deg)	90	90	120	90	98.122(3)
Volume (Å ³)	7192(2)	7178.3(8)	31521(2)	7025(3)	1351.77(15)
Z	8	8	18	4	2
Density (Mg/m ³)	1.460	1.627	1.915	1.240	1.211
μ (λ) (mm ⁻¹)	2.917	5.000	3.912	0.373	0.378
Crystal size (mm ⁻¹)	0.15x0.37x0.44	0.19x0.35x0.37	0.22x0.22x0.36	0.29x0.40x0.44	0.28x0.30x0.38
Radiation	X-ray	X-ray	X-ray	X-ray	X-ray
T _{max} / T _{min}	0.65 / 0.30	0.45 / 0.20	0.48 / 0.34	0.90 / 0.84	0.92 / 0.88
Refln. Collected	36,628	167,398	109,342	105,361	31,134
Ind. Refln.	6,412	7,067	17,391	20,144	4,580
Obs. Refln. [I > 2σ(I)]	5,011	5,784	13,340	17,304	2,946
GOF on F ²	1.129	1.015	1.059	1.069	1.021
R1,wR2 [I > 2 σ (I)]	0.0561, 0.1269	0.0284, 0.0538	0.0315, 0.0736	0.0438, 0.1011	0.0443, 0.0861
R1, wR2 (all data)	0.0765, 0.1356	0.0434, 0.0589	0.0456, 0.0794	0.0531, 0.1076	0.0885, 0.0998
Largest peak/hole (e·Å ⁻³)	1.433 / -1.054	1.495 / -2.031	0.992 / -1.092	0.829 / -0.34	0.362 / -0.212

Table A.6 CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **4.10**, **5.1-5.3**

	4.10	5.1	5.1_n	5.2	5.3
Formula	C ₁₃₀ H ₁₉₀ O ₃₀ Rb ₁₀	C ₇₆ H ₁₁₀ K ₆ O ₁₅	C ₇₆ H ₁₁₂ K ₆ O ₁₅	C ₈₄ H ₁₂₅ K ₆ O _{12.5}	C ₃₈ H _{53.93} O _{7.11} Rb ₃
Formula Wt.	3087.52	1498.24	1500.29	1569.44	880.99
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Tetragonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>I</i> 4 ₁ / <i>acd</i>
a (Å)	27.8767(9)	26.3510(7)	26.418(6)	16.3888(5)	30.4836(3)
b (Å)	18.6139(6)	16.1465(5)	16.043(4)	22.4490(7)	30.4836(3)
c (Å)	27.8767(9)	19.9042(5)	19.841(5)	24.0814(7)	35.6583(8)
α (deg)	90	90	90	90	90
β (deg)	101.33	106.209(1)	106.34(2)	90	90
γ (deg)	90	90	90	90	90
Volume (Å ³)	14183.0(8)	8132.1(4)	8069.44(5)	8859.8(5)	33135.5(9)
Z	4	4	4	4	32
Density (Mg/m ³)	1.446	1.224	1.235	1.177	1.413
μ (λ) (mm ⁻¹)	3.486	0.380	1.373 + 1.893 λ	0.350	3.573
Crystal size (mm ⁻¹)	0.26x0.36x0.42	0.35x0.22x0.15	2x2x1	0.28x0.24x0.22	0.42x0.35x0.20
Radiation	X-ray	X-ray	Neutron and X-ray	X-ray	X-ray
T _{max} / T _{min}	0.40 / 0.25	0.947 / 0.915	0.7604 / 0.2689	0.94 / 0.91	0.55 / 0.31
Refln. Collected	183,154	37,481	7651	180,195	95,974
Ind. Refln.	25,192	7,951	---	15,445	7,325
Obs. Refln. [I > 2σ(I)] ^a	21,641	5,632	3448 ^b	13,100	6,039
GOF on F ²	1.053	1.048	0.896	1.068	1.066
R1,wR2 [I > 2 σ (I)] ^a	0.0455, 0.1012	0.0544, 0.1123	0.045, 0.075, ^c	0.0413, 0.0889	0.0405, 0.0904
R1, wR2 (all data)	0.0595, 0.1085	0.0882, 0.1300	0.065, 0.089 ^{d,e}	0.0570, 0.0984	0.0579, 0.0953
Largest peak/hole (e·Å ⁻³)	1.469 / -1.063	1.256 / -1.667	0.711 / -0.672 ^f	0.628 / -0.398	0.588 / -0.487

^aFor **5.1_n**: (*I* > 3σ(*I*)); ^bOutliers with $|F_o^2/F_c^2| > 2$ and $|F_c^2/F_o^2| > 2$ were rejected; ^c $R(F^2) = \Sigma|F_o^2 - F_c^2| / \Sigma F_o^2$; ^dAll R values for **1n** include joint refinement of neutron and X-ray data; ^e $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; ^fLargest peak / hole: fm/Å³

Table A.7
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **5.4-5.8**

	5.4	5.5	5.6	5.7	5.8
Formula	C ₁₂ H ₁₇ NaO _{2.02}	C ₇₄ H ₁₀₆ K ₆ O ₁₇	C ₃₇ H ₅₃ K ₃ O ₈	C ₇₆ H ₁₁₄ K ₆ O ₁₉	C ₇₀ H ₁₀₂ O ₁₅ Rb ₆
Formula Wt.	216.58	1502.19	743.09	1566.27	1720.36
T (K)	100(2)	100(2)	100(2)	105(2)	100(2)
Crystal system	Rhomb	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>R</i> -3	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
a (Å)	16.3626(3)	13.8683(4)	20.4983(7)	13.0417(7)	19.0470(4)
b (Å)	16.3626(3)	16.2281(5)	19.3574(7)	13.0596(6)	20.6118(5)
c (Å)	22.8182(8)	20.4910(6)	19.0737(7)	26.6715(18)	20.0105(5)
α (deg)	90	90	90	96.112(2)	90
β (deg)	90	104.715(2)	90.844(2)	92.854(2)	91.713(1)
γ (deg)	120	90	90	114.286(2)	90
Volume (Å ³)	5290.7(2)	4460.4(2)	7567.5(5)	4095.1(4)	7852.5(3)
Z	18	2	8	2	4
Density (Mg/m ³)	1.224	1.118	1.304	1.270	1.455
μ (λ) (mm ⁻¹)	0.112	0.348	0.409	0.384	3.768
Crystal size (mm ⁻¹)	0.28x0.21x0.14	0.33x0.23x0.18	0.38x0.33x0.25	0.40x0.31x0.28	0.36x0.34x0.26
Radiation	X-ray	X-ray	X-ray	X-ray	X-ray
T _{max} / T _{min}	0.99 / 0.96	0.939 / 0.895	0.92 / 0.87	0.8984 / 0.8622	0.38 / 0.26
Refln. Collected	24,001	58,080	212,276	66,202	133,299
Ind. Refln.	2,240	6996	10,197	22,529	14,914
Obs. Refln. [I > 2σ(I)]	2,037	6086	8407	15,989	11,405
GOF on F ²	1.047	1.072	1.069	1.006	1.029
R1,wR2 [I > 2 σ (I)]	0.0297, 0.0662	0.0725, 0.1391	0.0434, 0.1090	0.037, 0.078	0.029, 0.056
R1, wR2 (all data)	0.0358, 0.0689	0.0804, 0.1428	0.0577, 0.1205	0.068, 0.091	0.051, 0.062
Largest peak/hole (e·Å ⁻³)	0.197, -0.159	0.833 / -1.281	1.060 / -0.847	0.425 / -0.284	0.823 / -0.401

Table A.8
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **5.10**, **6.1-6.4**

	5.10	6.1	6.2	6.3	6.4
Formula	C ₄₄ H ₅₆ K ₄ O ₁₂	C ₂₆ H ₂₈ F ₃ K ₃ O ₇	C ₃₀ H ₃₆ I ₃ K ₃ O ₉	C ₃₀ H ₃₆ I ₃ O ₉ Rb ₃	C ₂₂ H ₂₀ Cl ₃ K ₃ O ₅
Formula Wt.	933.29	626.78	1038.59	1177.70	588.03
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Hexagonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 6 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
a (Å)	11.5501(3)	13.1101(5)	11.2104(8)	11.6779(11)	18.0451(8)
b (Å)	11.5501(3)	19.5138(7)	15.3230(12)	15.7238(14)	21.0177(10)
c (Å)	62.233(3)	11.76.26(5)	22.0706(18)	21.4171(19)	7.0816(3)
α (deg)	90	90	90	90	90
β (deg)	90	105.4(2)	103.706(4)	103.589(5)	91.869(3)
γ (deg)	120	90	90	90	90
Volume (Å ³)	7189.0(5)	2901.2(2)	3683.3(5)	3822.5(6)	2684.4(2)
Z	6	4	4	4	4
Density (Mg/m ³)	1.293	1.435	1.873	2.046	1.455
μ (λ) (mm ⁻¹)	0.428	0.531	2.932	6.294	0.836
Crystal size (mm ⁻¹)	0.37x0.32x0.25	0.18x0.27x0.28	0.17x0.19x0.30	0.23x0.28x0.33	0.12x0.12x0.38
Radiation	X-ray	X-ray	X-ray	X-ray	X-ray
T _{max} / T _{min}	0.92 / 0.87	0.91 / 0.87	0.63 / 0.47	0.31 / 0.16	0.91 / 0.74
Refln. Collected	67,292	171,979	162, 736	52,499	36, 932
Ind. Refln.	10,132	10,110	10,342	4,942	5,088
Obs. Refln. [I > 2σ(I)]	10,036	8,418	8,741	4,057	4,390
GOF on F ²	1.164	1.017	1.040	1.079	1.183
R1,wR2 [I > 2 σ (I)]	0.0859, 0.2016	0.0292, 0.0721	0.0223, 0.0439	0.0349, 0.0815	0.0664, 0.1673
R1, wR2 (all data)	0.0865, 0.2020	0.0398, 0.0775	0.0313, 0.0463	0.0501, 0.0894	0.0754, 0.1731
Largest peak/hole (e·Å ⁻³)	0.769 / -0.840	0.500 / -0.417	0.897 / -0.851	0.981 / -0.802	1.488 / -0.527

Table A.9
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **6.5-6.7**

	6.5	6.6	6.7
Formula	C ₂₂ H ₂₀ Br ₃ K ₃ O ₅	C ₅₀ H ₅₈ Br ₅ O ₁₅ Rb ₅	C ₃₁ H ₄₁ K ₃ O ₅
fw	721.41	1725.86	610.94
T (K)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pnma</i>	<i>P2₁/c</i>	<i>Pnma</i>
a (Å)	7.1981(4)	9.1298(6)	7.4165(2)
b (Å)	17.5149(8)	30.9592(16)	19.9699(4)
c (Å)	21.2140(10)	21.3492(12)	20.8900(5)
α (deg)	90	90	90
β (deg)	90	93.446(3)	90
γ (deg)	90	90	90
Volume (Å ³)	2671.5(2)	6023.5(6)	3093.95(13)
Z	4	4	4
Density (Mg/m ³)	1.792	1.903	1.312
μ (λ) (mm ⁻¹)	5.022	7.411	0.478
Crystal size (mm ⁻¹)	0.13x0.19x0.33	0.17x0.21x0.34	0.24x0.29x0.38
Radiation	X-ray	X-ray	X-ray
T _{max} / T _{min}	0.57 / 0.29	0.35 / 0.20	0.91 / 0.87
Refln. Collected	54,582	38,586	54, 413
Ind. Refln.	3,050	10,620	3,784
Obs. Refln. [I > 2σ(I)]	2,614	7,579	3,341
GOF on F ²	1.082	1.003	1.042
R1, wR2 [I > 2 σ (I)]	0.0245, 0.0517	0.0391, 0.0666	0.0255, 0.0619
R1, wR2 (all data)	0.0347, 0.0558	0.0710, 0.0745	0.0312, 0.0653
Largest peak/hole (e·Å ⁻³)	0.695 / -0.430	0.845 / -0.616	0.389 / -0.255

Table A.10
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS 7.1-7.5

	7.1	7.2	7.3	7.4	7.5
Formula	C ₂₂ H ₄₆ FeN ₂ Na ₂ Si ₄	C ₂₂ H ₃₆ FeK ₂ N ₂ Si ₄	C ₂₂ H ₄₆ FeN ₂ Rb ₂ Si ₄	C ₂₂ H ₄₆ Cs ₂ FeN ₂ Si ₄	C _{23.62} H _{48.43} Fe _{0.6} N ₂ Rb ₂ Si ₄
Formula Wt.	552.80	574.94	677.76	772.64	677.04
T (K)	200(2)	200(2)	200(2)	200(2)	200 (2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Ccca</i>	<i>Fmmm</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
a (Å)	14.664(3)	18.1618(3)	7.8880(4)	8.0580(2)	8.030(2)
b (Å)	18.019(4)	14.7669(3)	17.7157(9)	17.6804(5)	17.960(4)
c (Å)	11.956(2)	12.8125(2)	12.1361(6)	12.4615(4)	12.450(3)
α (deg)	90	90	90	90	90
β (deg)	90	90	99.414(2)	98.986(1)	99.64(3)
γ (deg)	90	90	90	90	90
Volume (Å ³)	3159.1(11)	3436.23(10)	1673.08(15)	1753.58(9)	1770.2(6)
Z	4	4	2	2	2
Density (Mg/m ³)	1.162	1.111	1.345	1.463	1.270
μ (λ) (mm ⁻¹)	0.669	0.832	3.497	2.624	3.147
Crystal size (mm ⁻¹)	0.35x0.28x0.26	0.43x0.37x0.32	0.45x0.55x0.35	0.47x0.35x0.22	0.44x0.38x0.30
θ range (deg)	2.26 - 26.33	2.24 - 28.28	2.05 - 26.41	2.02 - 29.57	2.01 - 28.36
T _{max} / T _{min}	0.8695 / 0.8109	0.8035 / 0.7116	0.3642 / 0.1991	0.5959 / 0.3687	0.4552 / 0.2875
Refln. Collected	18188	11756	31921	96709	30211
Ind. Refln.	1612	1194	3260	4907	4330
Obs. Refln. [I > 2σ(I)]	1447	1035	2642	4351	3621
GOF on F ²	1.108	1.153	1.054	1.051	1.023
R1, wR2 [I > 2 σ (I)]	0.0267, 0.0796	0.0322, 0.1140	0.0253, 0.0532	0.0236, 0.0501	0.0268, 0.0654
R1, wR2 (all data)	0.0297, 0.0834	0.0369, 0.1205	0.0422, 0.0585	0.0293, 0.0532	0.0380, 0.0702
Largest peak/hole (e·Å ⁻³)	0.245 / -0.222	0.291 / -0.251	0.408 / -0.332	0.889 / -0.755	0.689 / -0.292

Table A.11
CRYSTALLOGRAPHIC PARAMETERS FOR COMPOUNDS **7.6**, **7.14**, **7.15**

	7.6	7.14	7.15
Formula	C _{24.02} H _{49.03} Cs ₂ Fe _{0.49} N ₂ Si ₄	C ₃₂ H ₆₄ K ₂ N ₂ Si ₄	C ₃₀ H ₆₀ K ₂ N ₂ Si ₄
Formula Wt.	771.75	667.41	639.36
T (K)	200(2)	180(2)	200(2)
Crystal system	Monoclinic	monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
a (Å)	8.1328(3)	13.9696(14)	9.3181(3)
b (Å)	17.7450(7)	9.5875(10)	10.6208(3)
c (Å)	12.5957(5)	15.8298(15)	11.3909(4)
α (deg)	90	90	109.253(2)
β (deg)	98.567(2)	99.031(5)	99.479(2)
γ (deg)	90	90	100.098(2)
Volume (Å ³)	1797.49(12)	2093.9(4)	1017.31(6)
Z	2	2	1
Density (Mg/m ³)	1.426	1.059	1.044
μ (λ) (mm ⁻¹)	2.367	0.362	0.370
Crystal size (mm ⁻¹)	0.41 x 0.22 x 0.15	0.31x0.26x0.20	0.382x0.297x0.210
T _{max} / T _{min}	0.7149 / 0.4407	1.81 / 28.39	1.95 / 31.00
Refln. Collected	41565	29810	24987
Ind. Refln.	5431	5135	6444
Obs. Refln. [I > 2σ(I)]	4845	4209	5395
GOF on F ²	1.028	1.048	1.038
R1,wR2 [I > 2 σ (I)]	0.0252, 0.0593	0.0318, 0.0818	0.0360, 0.1052
R1, wR2 (all data)	0.0293, 0.0618	0.0431, 0.0881	0.0440, 0.1130
Largest peak/hole (e·Å ⁻³)	1.195 / -0.759	0.287 / -0.328	0.360 / -0.325