



**Emerging Investigator
Heterotrimetallic Sandwich Complexes Supported by
Sulfonamido Ligands**

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Heterotrimetallic Sandwich Complexes Supported by Sulfonamido Ligands

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Co^{II} complexes bearing sulfonamido ligands derived from tris(2-aminoethyl)amine (H₆tren) assemble into complex architectures in the presence of Group II ions through interactions between the Group II ion and the sulfonyl oxygens. Novel ligands where the sulfonyl groups bear *tert*-butyl substituents afford well-defined isostructural heterotrimetallic sandwich complexes where two anionic [LCo^{II}]⁻ fragments are bridged by a Group II metal ion (Mg²⁺, Ca²⁺, Sr²⁺, or Ba²⁺). Solution studies on these novel sandwich complexes by cyclic voltammetry and electronic absorption spectroscopy indicate that these structures are not dramatically altered in solution, opening the door to the exploration of reactivity at Co^{II} that is modified by Group II ions.

Introduction

The properties and reactivity of transition metals can be dramatically modified by the presence of second-sphere redox-inactive metals. This is most notably seen in the oxygen-evolving complex (OEC) of photosystem II,¹ where second-sphere calcium or strontium² is required for the formation of O₂ from water at the manganese cluster. Synthetic models of the OEC³ have corroborated the importance of the redox-inert ion by demonstrating a dependence of the redox potentials⁴ and reactivity⁵ of manganese clusters on the identity of the redox-inert ion. The effects of second-sphere redox-inert metals have been demonstrated in other systems as well, for example by affecting the properties and reactivity of metal-oxo^{6,7} and metal-peroxo⁸ species, by altering the rate of O₂ activation by Mn^{II} and Fe^{II},^{9,10} by controlling the accessibility and reactivity of copper-nitrene species,¹¹ by changing the reactivity of a Cu^{III}-OH species,¹² and by modulating the water-oxidation reactivity of cobalt and manganese oxides.¹³ Clearly, redox-inert metals can have a profound effect on the properties and reactivity of nearby transition metals, and new methods to access well-defined complexes with second-sphere redox-inert metals are expected to enable the discovery of altered and novel transition-metal reactivity. While heterometallic systems that involve either a 1:1 ratio of redox-active and redox-inert metal ions^{6,8,9,10,11,12} or the interaction of a redox-inert metal ion with a cluster of redox-active metals^{3,4,5,7} are common, we have been targeting systems with

a 2:1 ratio of redox-active and redox-inert metal ions that could be well suited for splitting symmetric small molecules (e.g. O₂, N₂, or RNNR). Recently, Borovik demonstrated that redox-inert ions may be brought into close proximity to transition- and main-group metals coordinated by sulfonamido ligands, which bind the redox-inert metal through the electron-rich sulfonyl oxygens.^{9,10,14-18} Accordingly, we have pursued ligands that facilitate the assembly of heterotrimetallic coordination compounds where two anionic redox-active metal moieties coordinated by sulfonamido ligands are brought together through interactions with a Group II ion (e.g. Mg²⁺, Ca²⁺, Sr²⁺, or Ba²⁺) to form sandwich compounds. In particular, we have been targeting systems where the redox-active metal ion maintains an open coordination site, as the availability of this site would form the focus of reactivity studies. In this contribution, we describe the assembly of heterotrimetallic (Co^{II}₂M) sandwich complexes (M = Mg²⁺, Ca²⁺, Sr²⁺, or Ba²⁺) supported by a new sulfonamido ligand that feature open axial coordination sites on each Co^{II} ion.

Results and Discussion

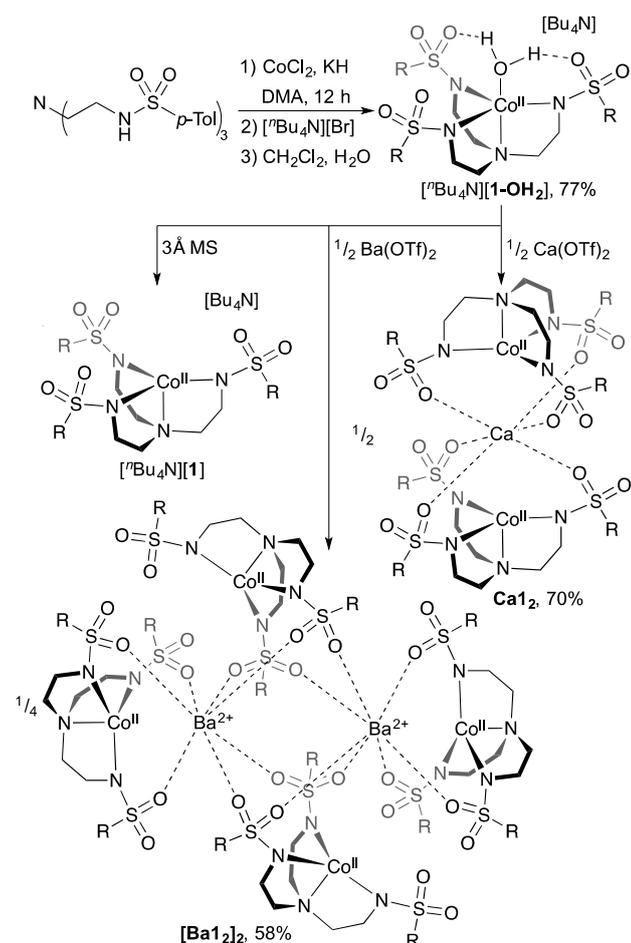
We reasoned that heterotrimetallic sandwich compounds would be accessible from ligands of the type [(RSO₂NCH₂CH₂)₃N]³⁻ ([[(RSO₂)₃tren]³⁻), which have been demonstrated by Borovik to furnish heterobimetallic complexes where the sulfonyl oxygens of [((RSO₂)₃tren)M^{II}]⁻ coordinate redox-active¹⁶ or redox-inert^{9,10,14,17} metal ions in the second sphere of M^{II}.¹⁸ Our first efforts employed Ts₃H₃tren (R = *p*-tolyl), a readily accessible ligand that has been used in the synthesis of heterobimetallic species.¹⁰ [Ts₃tren]³⁻ is smaller than the R = mesityl derivative employed in the

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synthesis of heterobimetallic cobalt complexes,¹⁴ and we reasoned that this diminished size might be important for assembly of heterotrimetallic systems.

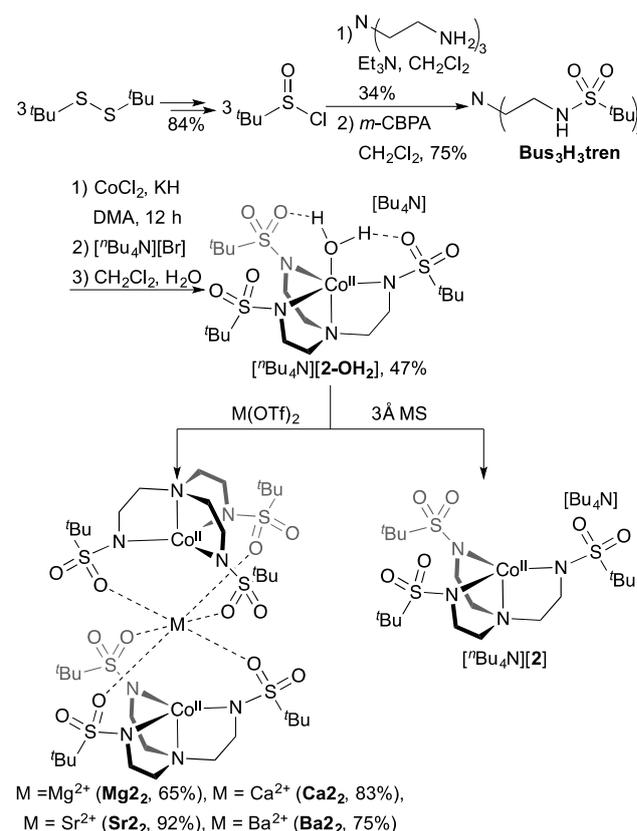
Combining Ts₃H₃tren with Co^{II}Cl₂ and NaH in DMF, followed by addition of [ⁿBu₄N][Br] and aqueous workup provided [ⁿBu₄N][(Ts₃tren)Co^{II}(OH₂)] ([ⁿBu₄N][1-OH₂]) in 77% crystalline yield (Scheme 1). Combining [ⁿBu₄N][1-OH₂] with 3 Å molecular sieves generated the four-coordinate species [ⁿBu₄N][1], which formed crystals of X-ray quality from CH₂Cl₂/Et₂O (Figure 1).[‡] Heating Ca(OTf)₂ and [ⁿBu₄N][1] in methanol/glyme to 85 °C provided a novel sandwich compound that crystallized upon cooling (Figure 1), wherein two [1]⁻ units are bonded to Ca²⁺ through one sulfonyl oxygen of each ligand arm to afford the sandwich compound **Ca1₂**, a species that is octahedral at Ca²⁺ and trigonal monopyramidal at the two Co^{II} ions. Attempts to prepare structurally related species using Mg(OTf)₂ were unsuccessful. A related procedure employing Ba(OTf)₂ in place of Ca(OTf)₂ afforded crystalline [**Ba1₂**]₂ (Figure 1), which features two seven-coordinate Ba²⁺ ions bridging four [1]⁻ units. We were also unsuccessful in accessing **Sr1₂**, but we were able to crystallize a partially hydrated form of this species (see Supplementary Information).



Scheme 1. Synthesis of [ⁿBu₄N][1-OH₂], [ⁿBu₄N][1], **Ca1₂**, and [**Ba1₂**]₂. Yields are of crystalline product. R = *p*-tolyl.

In order to facilitate a direct comparison between sandwich complexes with different Group II ions, we reasoned that a

ligand with more electron-rich sulfonyl oxygens would be beneficial for accessing compounds where the Group II metals all feature the same coordination number. This led us to explore alkylsulfonyl groups that would provide more electron-rich oxygen donors than the arylsulfonyl ligands in **Ca1₂**. This reasoning is supported by the higher acidity of PhSO₂NH₂ than CH₃SO₂NH₂ (*p*K_a = 16.1 vs. 17.5, respectively).¹⁹ Ms₃H₃tren²⁰ was not targeted owing to its water solubility; instead, we targeted (^tBuSO₂NHCH₂CH₂)₃N (Bus₃H₃tren, Bus = busyl). Bus₃H₃tren had not been reported, and accessing this ligand in an analogous manner to Ts₃H₃tren is not feasible because ^tBuSO₂Cl is not an effective sulfonyl transfer agent (^tBuSO₂Cl decomposes into isobutylene, SO₂, and HCl on addition to amines).²¹ However, busyl amides are accessible from amine sulfonylation with ^tBuSOCl²² followed by oxygen-atom transfer to sulphur with *m*-CPBA.²³ We accessed Bus₃H₃tren from commercially available ^tBuSS^tBu over four steps in 21% overall yield (Scheme 2). This ligand was metallated analogously to Ts₃H₃tren, providing crystalline [ⁿBu₄N][(Bus₃tren)Co^{II}(OH₂)] ([ⁿBu₄N][2-OH₂]) in 47% yield (Scheme 2, Figure 2). As with [ⁿBu₄N][1-OH₂], [ⁿBu₄N][2-OH₂] could be readily dehydrated with 3 Å molecular sieves to afford the crystalline four-coordinate complex [ⁿBu₄N][2] (Figure 2).



Scheme 2. Synthesis of [ⁿBu₄N][2-OH₂], [ⁿBu₄N][2], **Mg₂**, **Ca₂**, **Sr₂**, and **Ba₂**. Yields are of crystalline products.

Addition of M(OTf)₂ to [ⁿBu₄N][2] with heat provided crystalline samples of **M2₂**, where M = Mg, Ca, Sr, and Ba (Scheme 2, Figure 3). In contrast to compounds containing [1]⁻, the Group II ion in each of these species is octahedral, and

each member of the series is isostructural: the redox-inert metal ion is bound symmetrically by one sulfonyl oxygen of each busyl group. The ability to access this isostructural series that was inaccessible with $[1]^-$ may at least partially result from the increased electron density of the sulfonyl oxygens of busyl vs. tosyl groups. Table 1 highlights relevant crystallographic distances. The Co–N_{ax} distance is sensitive to the coordination number at cobalt, where this bond in species

containing $[2]^-$ elongates by ~ 0.1 Å upon coordination of H₂O. Differences between the Co–N_{ax} distances for all four-coordinate species containing $[2]^-$ are within 3σ . The Co–N_{eq} bond lengths are sensitive to the coordination number of cobalt, but to a lesser extent than the Co–N_{ax} distance. No clear trends in Co–N bond lengths are observed for the $M2_2$ series; however, the Co–M distance increases monotonically with increasing size of the Group II ion.

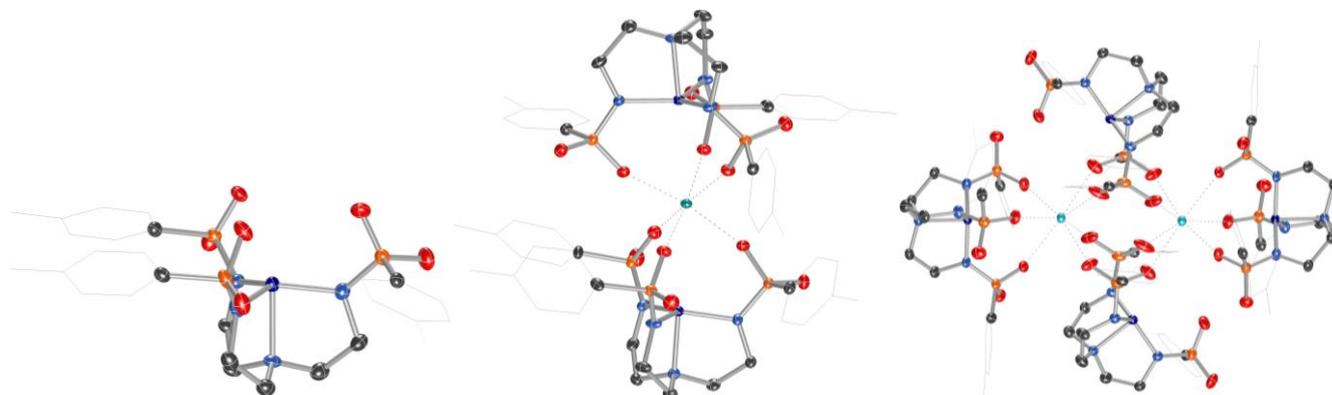


Figure 1. Solid-state molecular structures of the anion in $[n\text{Bu}_4\text{N}][1]$ (left), $\text{Ca}1_2$ (middle), and $[\text{Ba}1_2]_2$ (right).

We next explored the Co^{II}/Co^{III} redox couple of $[n\text{Bu}_4\text{N}][1\text{-OH}_2]$, $[n\text{Bu}_4\text{N}][2\text{-OH}_2]$, $[n\text{Bu}_4\text{N}][1]$, and $[n\text{Bu}_4\text{N}][2]$ in CH_2Cl_2 using cyclic voltammetry to probe the effect of coordination number and ligand identity on redox potential as a benchmark for probing the members of the $M2_2$ series. Borovik recently demonstrated that the Fe^{II}/Fe^{III} redox couple in $[\text{Me}_4\text{N}][(\text{ArSO}_2)_3\text{trenFe}^{\text{II}}(\text{OH}_2)]$ is sensitive to the electronic properties of the aryl group,¹⁵ so we wanted to probe the extent to which the Co^{II}/Co^{III} couple is sensitive to the nature of the sulfonyl substituent (*p*-tolyl vs. *tert*-butyl). The electrochemical data are summarized in Table 2. Both species containing $[2]^-$ are more easily oxidized than the corresponding $[1]^-$ species, where the onset of oxidation was shifted by -30 and -60 mV for the respective hydrated and anhydrous $[2]^-$ species compared to the $[1]^-$ species in CH_2Cl_2 , consistent with busyl amides being more electron rich than tosyl amides. Furthermore, the onset of oxidation for the four-coordinate species $[n\text{Bu}_4\text{N}][1]$ and $[n\text{Bu}_4\text{N}][2]$ were shifted by $+270$ and $+240$ mV from the corresponding hydrated species, revealing a strong dependence of the Co^{II}/Co^{III} couple on coordination number.⁵ These data clearly demonstrate the stronger donor strength of $[\text{Bus}_3\text{tren}]^{3-}$ compared to $[\text{Ts}_3\text{tren}]^{3-}$, and also provide a benchmark for electrochemical studies of the members of the $M2_2$ series.

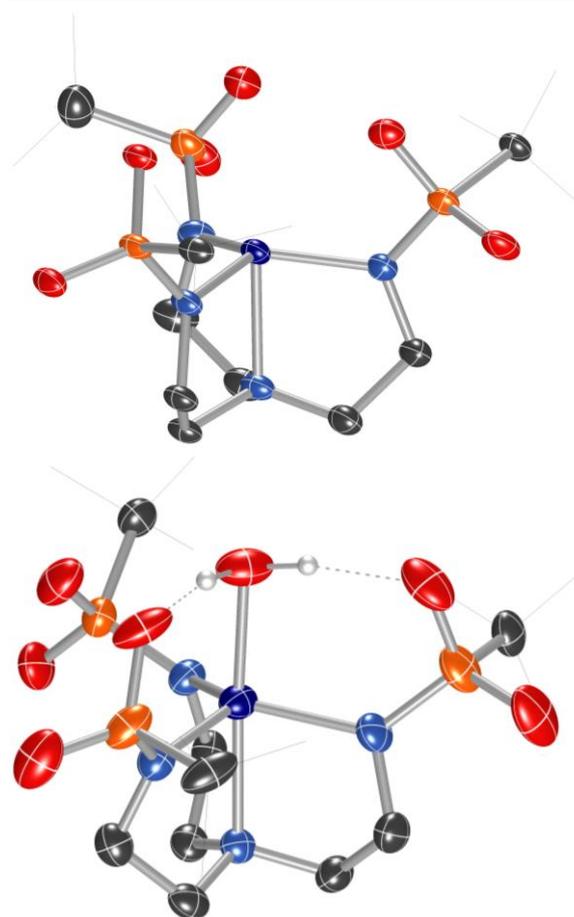


Figure 2. Solid-state molecular structures of the anions in $[n\text{Bu}_4\text{N}][2]$ (top) and $[n\text{Bu}_4\text{N}][2\text{-OH}_2]$ (bottom).

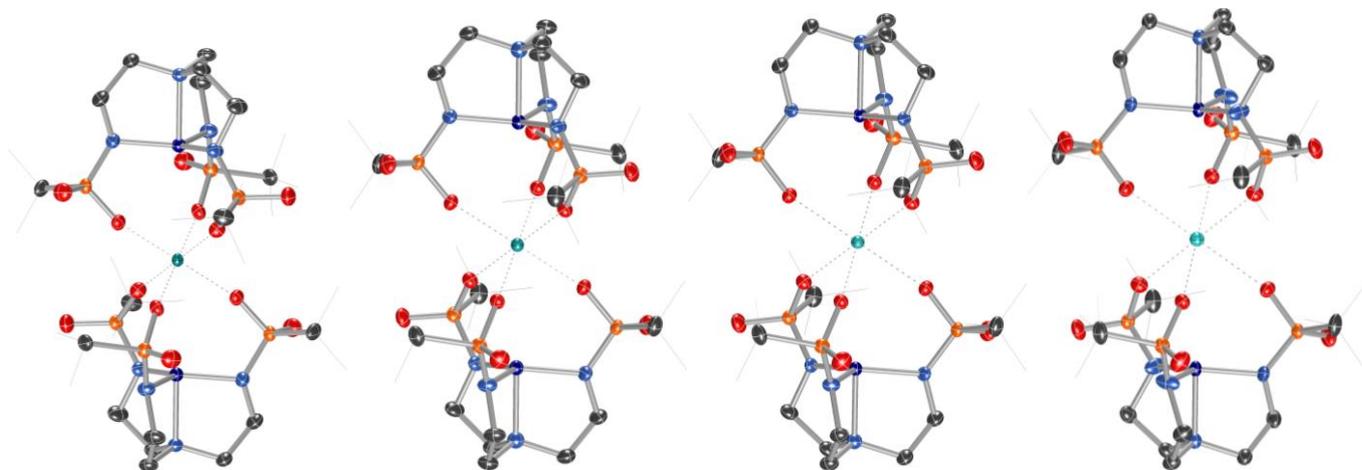
Table 1. Crystallographic distances for compounds containing [2]⁻.

compound	Co–N _{ax} ^a	Co–N _{eq} ^b	Co–OH ₂	Co---M
[ⁿ Bu ₄ N][2-OH ₂]	2.246(3) Å	2.038(3) Å, 2.014(3) Å, 2.030(3) Å	2.134(3) Å	---
[ⁿ Bu ₄ N][2]	2.109(6) Å	1.933(5) Å, 1.937(6) Å, 1.991(6) Å	---	---
Mg ₂	2.1069(10) Å	1.9440(7) Å	---	3.4101(9) Å
Ca ₂	2.0951(19) Å	1.9344(11) Å	---	3.5485(11) Å
Sr ₂	2.087(3) Å	1.965(6) Å	---	3.6411(10) Å
Ba ₂	2.087(5) Å	1.942(3) Å	---	3.7490(7) Å

^a N_{ax} is the central nitrogen of the H₆tren-derived ligand. ^b N_{eq} depicts the three nitrogens in the trigonal plane. The presence of one value indicates that these bonds are equivalent by symmetry. ^c Bond lengths involving different cobalt centers are separated by a semicolon.

We next interrogated how the position of the Co^{II}/Co^{III} redox couple was affected by the presence and identity of a second-sphere Group II ion by examining the electrochemical properties of the members of the **M2**₂ series (M = Ca, Sr, and Ba).⁵⁵ These species are not soluble in CH₂Cl₂, but they are soluble in 2,2,2-trifluoroethanol (TFE). We therefore examined the electrochemical behaviour of [ⁿBu₄N][1-OH₂] and [ⁿBu₄N][2-OH₂] in TFE to benchmark the **M2**₂ data. We were unable to measure the electrochemical properties of [ⁿBu₄N][1] and [ⁿBu₄N][2] in TFE because UV-vis indicated that these complexes were always 5-coordinate in TFE (see below) and electrochemical studies of these compounds in TFE provided data that matched the hydrated species, indicating either that these species bind residual water in the TFE despite distillation from MgSO₄ or that TFE occupies the fifth coordination site on Co^{II} in these compounds. Nevertheless, all **M2**₂ species explored maintained a four-coordinate geometry

at cobalt by absorption spectroscopy (see below), suggesting that these species remain intact in solution to the extent that they prevent coordination of H₂O or TFE to the Co^{II} ions. As seen in Table 2, solvent has a strong effect on the position of the Co^{II}/Co^{III} redox couple in [ⁿBu₄N][2-OH₂] (+28 mV in CH₂Cl₂ and +390 mV in TFE), likely reflecting hydrogen bonding between TFE and the sulfonyl oxygens that pulls electron density away from the anionic nitrogen donors. The cyclic voltammograms of the members of the **M2**₂ series are distinct from the voltammogram of [ⁿBu₄N][2-OH₂] even in the presence of a large excess of [ⁿBu₄N]⁺, suggesting that these **M2**₂ species are not ionized in TFE. The voltammograms of **M2**₂ species are complicated by the presence of multiple oxidation events, which is consistent with the **M2**₂ species remaining intact in solution. However, the final return reduction events of **Ca2**₂, **Sr2**₂, and **Ba2**₂ (Table 2) approach the position of the return reduction event of [ⁿBu₄N][2-OH₂] in TFE, where **Ba2**₂ is the closest and **Ca2**₂ is the furthest of this series. This suggests that (1) the identity of the metal ion affects the potential of the return reduction event indicating that these redox-inert metal ions remain in close contact to the [2]⁻ ions throughout the electrochemical event, and (2) electrochemical oxidation results in occupation of the fifth coordination site on the electrophilic four-coordinate Co^{III} centers either by water or TFE. Electrochemical cycling experiments indicate that the overall processes are all chemically reversible, so the complexity of the oxidation events likely reflects reversible and oxidation-state-dependent occupation of the fifth coordination site on cobalt, although mixed valency and partial disruption of M---OS interactions may also play a role. From these data, we see that the interactions between the M²⁺ ion and the [2]⁻ units are still present in solution, although it is unclear whether these interactions are the same as in the solid-state structures. We next turned to electronic absorption spectroscopy to probe the extent to which the Co^{II} ions in the **M2**₂ series remain four-coordinate in solution.

**Figure 3.** From left to right, solid-state molecular structures of **Mg2**, **Ca2**, **Sr2**, and **Ba2**.

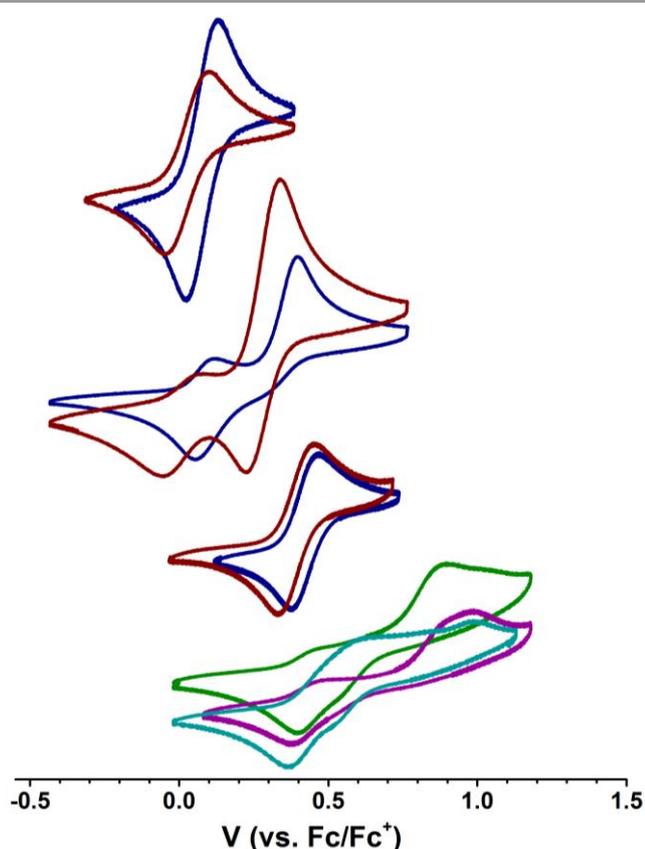


Figure 4. Cyclic voltammograms of $[\text{Bu}_4\text{N}][1\text{-OH}_2]$ (—) and $[\text{Bu}_4\text{N}][2\text{-OH}_2]$ (—) in CH_2Cl_2 (top); $[\text{Bu}_4\text{N}][1]$ (—) and $[\text{Bu}_4\text{N}][2]$ (—) in CH_2Cl_2 (second from top, smaller features are from hydrated forms derived from adventitious water in the experimental setup); $[\text{Bu}_4\text{N}][1\text{-OH}_2]$ (—) and $[\text{Bu}_4\text{N}][2\text{-OH}_2]$ (—) in TFE (second from bottom); and Ca_2_2 (—), Sr_2_2 (—), and Ba_2_2 (—) in TFE. Scan rate = 100 mV/s.

Table 2. Electrochemical data.^a

compound	solvent	E_{anodic} (mV)	E_{cathodic} (mV)	E_x (mV)
$[\text{Bu}_4\text{N}][1\text{-OH}_2]$	CH_2Cl_2 (TFE)	+125 (+465)	+30 (+380)	+78 (+422)
$[\text{Bu}_4\text{N}][1]^b$	CH_2Cl_2	+395	--- ^c	irr. ^d
$[\text{Bu}_4\text{N}][2\text{-OH}_2]$	CH_2Cl_2 (TFE)	+95 (+450)	-40 (+335)	+28 (+392)
$[\text{Bu}_4\text{N}][2]^b$	CH_2Cl_2	+335	+230	+282
Ca_2_2	TFE	multiple ^e	+405 ^f	irr. ^d
Sr_2_2	TFE	multiple ^e	+385 ^f	irr. ^d
Ba_2_2	TFE	multiple ^e	+370 ^f	irr. ^d

^a Scan rate = 100 mV/s with $[\text{Bu}_4\text{N}][\text{PF}_6]$ as the supporting electrolyte. All values vs. Fc/Fc^+ . See Figure 4 for electrochemical traces. ^b Features of aqua complexes consistently appear as minor impurities, likely arising from adventitious H_2O in the experimental setup. ^c The return oxidation wave of $[\text{Bu}_4\text{N}][1]$ is not discernible. ^d Electrochemically irreversible, but cycling current does not result in changes to the voltammogram (chemically reversible). ^e Multiple oxidation events. ^f Position of final (lowest-potential) reduction wave.

$[\text{Bu}_4\text{N}][2]$ and $[\text{Bu}_4\text{N}][2\text{-OH}_2]$ are clearly distinguishable by their electronic absorption profiles in CH_2Cl_2 (Figure 5), most notably by the presence of a transition of the anhydrous species at 414 nm that is absent in the hydrated species, providing a benchmark for assessing the coordination number of the cobalt ions in the members of the M_2_2 series in solution. As described above, Ca_2_2 , Sr_2_2 , and Ba_2_2 are all soluble in TFE but are insoluble in CH_2Cl_2 . Consistent with our electrochemical studies, dissolution of $[\text{Bu}_4\text{N}][2]$ in TFE furnishes an absorption spectrum that is indistinguishable from the absorption spectrum of $[\text{Bu}_4\text{N}][2\text{-OH}_2]$ in TFE, suggesting that $[\text{Bu}_4\text{N}][2]$ is binding either residual water from the TFE or TFE itself in the fifth coordination site of Co^{II} . However, the positions of the peaks of $[\text{Bu}_4\text{N}][2\text{-OH}_2]$ are nearly solvent independent (no solvatochromism), giving us confidence in our ability to distinguish between the spectra of four- and five-coordinate Co^{II} species in both CH_2Cl_2 and TFE. All three soluble members of the M_2_2 series give nearly identical electronic absorption spectra in TFE, and these spectra clearly align with the spectrum of $[\text{Bu}_4\text{N}][2]$ in CH_2Cl_2 , including the presence of a transition around 400 nm, indicating that four-coordinate Co^{II} centers are present in each sandwich complex even though no efforts were made to dry

the TFE and the samples were prepared open to air. Given our inability to obtain spectra of $[\text{Bu}_4\text{N}][\mathbf{2}]$ in TFE, the presence of four-coordinate Co^{II} ions in the members of the $\mathbf{M2}_2$ series indicates that $[\mathbf{2}]^-$ binds preferentially to the Group II ions examined instead of water, and that these interactions between $[\mathbf{2}]^-$ and M^{2+} prevent H_2O or TFE coordination at Co^{II} . Furthermore, the positions of the d-d bands are largely unaffected by the identity of the counteranion ($[\text{Bu}_4\text{N}]^+$, Ca^{2+} , Sr^{2+} , or Ba^{2+}), even though the electrochemical properties of $[\mathbf{2}]^-$ are affected by the identity of the counteranion (Figure 4 and Table 2). Taken together, the electrochemical and electronic absorption data reveal that $\mathbf{M2}_2$ species are not ionized in solution, but retain four coordinate Co^{II} ions and interactions between the Group II ions and $[\mathbf{2}]^-$ even in wet TFE.

of hydration of $\mathbf{M2}_2$ and $\mathbf{Ca1}_2$ on the identity of both the redox-inert metal ion and the ligand (aryl- vs. alkylsulfonamide). Both $\mathbf{Ca2}_2$ and $\mathbf{Sr2}_2$ contain essentially all four-coordinate Co^{II} ions in dried TFE, whereas both $\mathbf{Ba2}_2$ and $\mathbf{Ca1}_2$ contain both four- and five-coordinate Co^{II} ions in dried TFE. The extent of hydration in the $\mathbf{M2}_2$ series is strongly dependent on the nature of M, where hydration of $\mathbf{Ca2}_2$ is most difficult (half of the Co^{II} ions are five-coordinate when 209 equivalents of H_2O are added), followed by hydration of $\mathbf{Sr2}_2$ (half of the Co^{II} ions are five-coordinate when 116 equivalents of H_2O are added), and $\mathbf{Ba2}_2$ is already a mixture of four- and five-coordinate Co^{II} species in the absence of added H_2O , consistent with Ca^{2+} having the strongest interaction with the sulfonyl oxygens and Ba^{2+} having the weakest. While the extent of hydration is dependent on the identity of the redox-inert metal ion in the $\mathbf{M2}_2$ series, the starkest difference in hydration is derived from changing the ligand from an arylsulfonamide ligand in $\mathbf{Ca1}_2$ ($[\text{Ts}_3\text{tren}]^{3-}$) to an alkylsulfonamide ligand in $\mathbf{Ca2}_2$ ($[\text{Bus}_3\text{tren}]^{3-}$), where hydration of $\mathbf{Ca1}_2$ occurs much more readily than hydration of $\mathbf{Ca2}_2$. This is consistent with the solid-state behaviour of members of the $\mathbf{M1}_2$ and $\mathbf{M2}_2$ series, where isostructural members of the $\mathbf{M2}_2$ series were accessible for $\text{M} = \text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} and Ba^{2+} , whereas with $[\mathbf{1}]^-$ anions, the only accessible sandwich compound was $\mathbf{Ca1}_2$. The relative ease of hydration of $\mathbf{Ca1}_2$ and $\mathbf{Ca2}_2$ is also a clear indication that the alkylsulfonyl oxygens are more electron rich than arylsulfonyl oxygens, and accordingly bind Ca^{2+} more tightly. Taken together, the solid-state, solution-phase, and redox behaviour of Co^{II} ions in complexes of $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$ reveal that $[\text{Bus}_3\text{tren}]^{3-}$ is a significantly improved ligand for interactions with second-sphere redox-inert metal ions than $[\text{Ts}_3\text{tren}]^{3-}$.

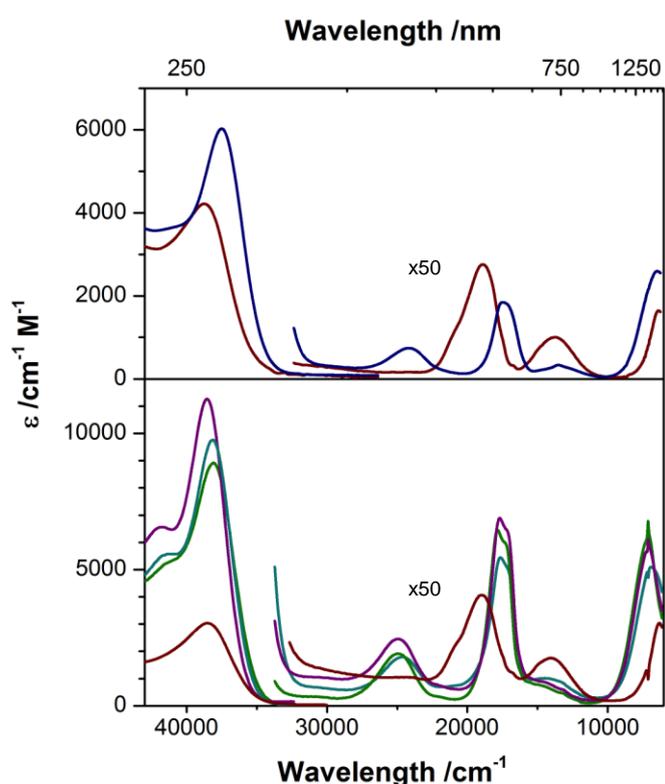


Figure 5. Electronic absorption spectra of $[\text{Bu}_4\text{N}][\mathbf{2}]$ (—) and $[\text{Bu}_4\text{N}][\mathbf{2-OH}_2]$ (—) in CH_2Cl_2 (top); and $[\text{Bu}_4\text{N}][\mathbf{2-OH}_2]$ (—) $\mathbf{Ca2}_2$ (—), $\mathbf{Sr2}_2$ (—), and $\mathbf{Ba2}_2$ (—) in TFE.

In an effort to quantify the extent to which the $\mathbf{M2}_2$ and $\mathbf{Ca1}_2$ species remain intact in solutions containing H_2O , we explored the hydration reactivity of the four-coordinate Co^{II} ions in samples of $\mathbf{M2}_2$ and $\mathbf{Ca1}_2$ in dried TFE by titrating H_2O and measuring the change in absorption profile consistent with conversion from four- to five-coordinate Co^{II} (see Supplementary Information for details). Figure 6 shows the decay of four-coordinate Co^{II} upon titration with H_2O , and we have verified that the product in each case corresponds to five-coordinate Co^{II} derived from hydration of the Co^{II} ion. As shown in Figure 6, there is a strong dependence of the extent

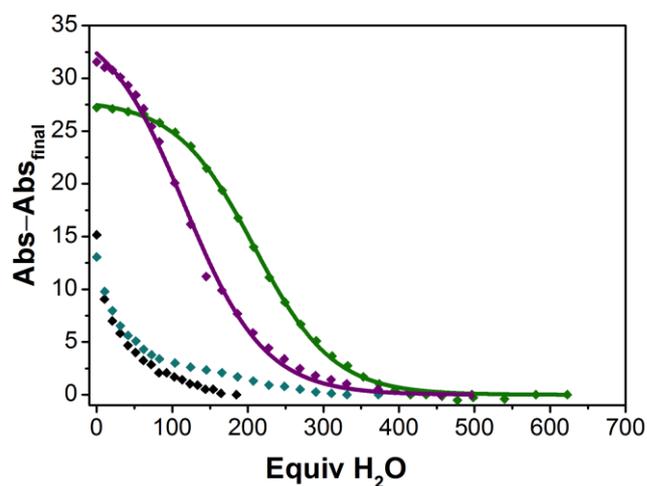


Figure 5. Decay of four-coordinate Co^{II} ions in $\mathbf{Ca2}_2$ (◆), $\mathbf{Sr2}_2$ (◆), $\mathbf{Ba2}_2$ (◆) and $\mathbf{Ca1}_2$ (◆) into five-coordinate Co^{II} in TFE with added water. $\text{Abs} - \text{Abs}_{\text{final}}$ represents the absorption of $\mathbf{Ca2}_2$ at 401 nm, $\mathbf{Sr2}_2$ at 401 nm, $\mathbf{Ba2}_2$ at 406 nm, and $\mathbf{Ca1}_2$ at 406 nm as a function of added equivalents of H_2O , with the final absorption value for each species subtracted from each point. The curves for $\mathbf{Ca2}_2$ and $\mathbf{Sr2}_2$ are fits to the data using

sigmoidal logistic functions (see Supplementary Information for details).

Conclusions

We have detailed the synthesis of novel heterotrimetallic sandwich complexes involving two Co^{II} ions bridged by redox-inert metal ions (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺). These **M2₂** assemblies, which are made readily accessible by the new ligand [Bus₃tren]³⁻, are isostructural across the entire series. Furthermore, electrochemical and electronic absorption studies indicate that **Ca2₂**, **Sr2₂**, and **Ba2₂** retain interactions between the Group II ions and [2]⁻ in solution. The solid-state, solution-phase, and redox behaviour of members of the **M2₂** series compared to related complexes derived from [1]⁻ demonstrates the improved properties of alkylsulfonamide ([Bus₃tren]³⁻) vs. arylsulfonamides ([Ts₃tren]³⁻) ligands for formation of discrete heterotrimetallic sandwich complexes. These results highlight the rational design of complex heterotrimetallic clusters with significant solution integrity, and open the door to the exploration of the effect of Group II ions on substrate reactivity at the open coordination site of Co^{II} in these systems. Our studies into the reactivity of these sandwich species will be published in due course.



Chris Scarborough was born in Orange County, California. He obtained his B.S. in Chemistry in 2003 from the University of California – Irvine and conducted undergraduate research under Gregory Weiss. His graduate studies at the University of Wisconsin under the supervision of Shannon Stahl focused on the development of axially chiral 7-membered N-heterocyclic carbene ligands and their application to palladium catalysis. After

completion of his PhD in 2008, Chris was an Alexander von Humboldt postdoctoral researcher at the Max Planck Institute for Bioinorganic Chemistry under Karl Wieghardt, where he examined the electronic structure of electron-rich metal-bipyridine complexes. In 2011, Chris began his independent career at Emory University where he has developed a research program exploring novel methods of activating O₂ and H₂O₂ for oxidation catalysis.

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Notes and references

‡ Crystallographic data deposited to the Cambridge Structural Database: [Bu₄][1] (1434440), **Ca1₂** (1434437), **Sr1₂(OH)₂** (1434441), **[Ba1₂]₂** (1434432), [Bu₄][2-OH₂] (1434433), [Bu₄][2] (1434434), **Mg2₂** (1434438), **Ca2₂** (1434436), **Sr2₂** (1434439), **Ba2₂** (1434435).

§ Onset of oxidation is used here instead of E_{1/2} because some events are electrochemically irreversible. Each of these electrochemical events may be cycled without changes to the voltammogram, demonstrating chemical reversibility.

§§ **Mg2₂** is not sufficiently soluble for study by CV or electronic absorption spectroscopy.

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