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A SERIES OF F-ELEMENT CHELATORS; DIAZA CROWN ETHERS

FUNCTIONALIZED WITH CATECHOLATE BINDING SUBSTITUENTS.

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One step Mannich synthesis from commercially avilable starting materials





Lanthanide catecholate/semiquinone coordination chemistry

Dedicated to Prof. William J. Evans for his inspirational and creative contributions to f-element redox chemistry.

ABSTRACT

Reported here is the preparation of azacrown ethers functionalized with catechol groups. The synthetic approach was (1st) novel in that it made use of the Mannich

reaction and (2nd) valuable in that it provided an improved synthesis (in terms of practical deployment) of the known N,N'-bis(2,3-dihydroxybenzyl)-4,13-diaza-18-crown-6, *H₄ChaCha*. Moreover, it demonstrated potential application of the synthetic method for accommodating a wide range of catecholate functionalities by using the synthetic strategy to prepare N,N'-bis(2,3-dihydroxy-5-*tert*-butylbenzyl)-4,13-diaza-18-crown-6 (*H₄*Bu₂ChaCha*) for the first time. These *H₄ChaCha* and *H₄*Bu₂ChaCha* macrocycles offer exciting opportunity to expand redox chemistry for the *f*-elements. As "proof-of-principle," we isolated the unusual tetrameric cluster [La₂(*^tBuChaCha*)₂]₂ from reactions between *H₄*Bu₂ChaCha* and La[N(SiMe₃)₂]₃. Characterization of [La₂(*^tBuChaCha*)₂]₂ by elemental analysis, single crystal X-ray diffraction, IR, and UV-vis-NIR spectroscopy suggested that the combination of La³⁺ and *H₄*Bu₂ChaCha* provided access to one-electron oxidation chemistry within redox potential windows that were amenable to mild reaction conditions.

INTRODUCTION

Since the initial discovery by *PEDERSEN* and colleagues (1967),[1] crown ethers and their derivatives (e.g. azacrowns[2]) have emerged as one of the most fundamentally important classes of chelating agents. For instance, crown ethers find broad use[3] in radioisotope chelation,[4] ion transport,[5] and actinide decorporation.[6] Perhaps, the most attractive component associated with crown and azacrown ethers is the versatility at which functional groups can be tethered from the rings to create "lariat" crown ethers. This diversity allows chelating properties to be tuned for highly specific functionality. For example, equipping acetate side-arms to the

1,4,7,10-tetraazacyclododecane macrocycle generates one of the best lanthanide(III) chelators known, namely 1,4,7,10-tetraazacyclododecane-N,N',N'','''-tetraacetic acid (DOTA).[7, 8] In addition, attaching chromogenic[9, 10] and redox non-innocent pendant arms[11] opens exciting avenues of research across the periodic table.

Herein, we have contributed to the voluminous collection of lariat azacrown ethers[12, 13] by reporting the preparation of catechol-functionalized macrocycles *via* the Mannich reaction. Previously, *HOSSEINI ET. AL.* prepared a catechol functionalized diaza-18-crown-6 ether, N,N'bis(2,3-dihydroxybenzyl)-4,13-diaza-18-crown-6 (*H*₄*ChaCha*) (Scheme 1),[14] and explored *H*₄*ChaCha*'s reactivity as a ditopic binding moiety for boron and alkali metals.[14, 15] Contributed here, is a simplification of that *H*₄*ChaCha* synthesis. Compatibility of the revised process with *tert*-butyl ('Bu) substituted catecholate functional groups was additionally explored. The experiments were successful and N,N'-bis(2,3-dihydroxy-5-*tert*-butylbenzyl)-4,13-diaza-18crown-6 (*H*₄^{*t*}*Bu*₂*ChaCha*) was isolated for the first time. While more experimentation is required to define generality for this synthetic method, it seems possible that our approach has potential to accommodate a wide range of catecholate functionalities necessary for fine tuning metal binding properties and ligand solubilities.

The bis-catechol azacrown ethers reported here offer exciting opportunities for expanding redox chemistry for the *f*-elements. Consider the transformative impact that catechol redox behavior has had on transition metal chemistry.[16-23] The catecholate ligand has been heavily studied because of its ability to support two reversible oxidation reactions within redox potential windows that are amenable to mild reaction conditions. The first electron transfer accessible to catecholate (Cat²⁻) forms a semiquinone (SQ¹⁻) and the second a quinone (Q; Scheme 2).[23] With the exception of a few examples (particularly by *RAYMOND ET. AL.*),[6, 24, 25] *f*-element

catecholate chemistry has lagged in comparison to the *d*-block elements, in part, because *f*element catecholate coordination chemistry can be difficult to control.[26] Lanthanides and actinides have large coordination numbers, complicated hydrolysis behavior, and propensity to be bridged by catecholates.[26] Hence, *f*-element catecholate reaction products tend to be oligomeric, insoluble, or difficult to characterize. Tethering catecholates to crown – or azacrown – ethers offers opportunities to chelate the *f*-element cation and limit uncontrollable oligomerization reactions. As testament, additionally contributed here is a prototypical reaction chemistry of the bis-catechol azacrown ethers with La^{3+} . These efforts resulted in reproducible formation of an intriguing *f*-element dioxolene cluster, specifically $[La_2({}^tBuChaCha)_2]_2$, which is reported for the first time.

RESULTS AND DISCUSSION

Synthesis of H_4 ChaCha-2HCl. Two synthetic routes were developed to the H_4 ChaCha 2HCl macrocycle. Both synthetic methods employed relatively benign reagents, required simple chemical-handling manipulations, and were tolerant of exposure to air and moisture. Our foray into the synthetic process was inspired by the published synthetic methodology used to synthesize H_4 ChaCha previously.[14] That original published 5-step synthetic route started from commercially available 2,3-dihydroxybenzaldehyde to give the protected catechol-azacrown ether that was subsequently deprotected with H_2 /Pd.[14] Motivated by the significant difficulty we had with reproducing several key steps, in particular the bromination with PBr₃, efforts were made to find an alternative synthesis. The 1st revision (Scheme 3) represented marginal improvement. It was slightly less technically challenging and provided H_4 ChaCha 2HCl in acceptable yields from commercially available reagents; the

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previous synthesis was reported to proceed in 53% overall yield (5 steps) while our route could be carried out in 26% overall yield (5 steps). Despite the lower yield, our approach avoided the PBr₃ reaction and was initially our preferred method for making H_4 ChaCha 2HCl.

revised procedure, protecting both alcohol substituents Our began by of dihydroxybenzaldehyde with the common tert-butyldimethyl silyl group using the wellestablished method originally reported by COREY and coworkers (STEP A; Scheme 3).[27] Subsequently (STEP B), the aldehyde was reduced to the benzyl alcohol with sodium borohydride (NaBH₄) in cold methanol. Then (STEP C) the alcohol was converted to a chloride using trichlorotriazine (TCT)/DMF.[28] The resulting Int-1c was attached to the diaza-18-crown-6 backbone in STEP D in a S_N2-reaction. However, this benzylic substitution represented the lowest yielding step in the synthetic procedure (40%), likely due to the formation of an unidentified red impurity that precipitated at low temperature. With Int-1d in hand, acidic conditions (HCl/MeOH) were used to de-protect the alcohol substituents (STEP E), and $H_4ChaCha 2HCl$ was isolated as a pale beige crystalline powder.

After initially isolating $H_4ChaCha 2HCl$, and with dissatisfaction in the time consuming multi-step procedure, a more time efficient synthetic route was developed (Scheme 4). This 2nd procedure was based upon the Mannich condensation, which enabled $H_4ChaCha 2HCl$ to be prepared in three – relatively short – synthetic steps and with no tedious workup or chromatography. Moreover, the Mannich condensation approach enabled $H_4ChaCha 2HCl$ to be prepared in a 33% overall yield from commercially available and inexpensive catechol. While the overall yield was not an improvement in comparison to the original procedure,[14] our new synthesis was advantageous based on chemical throughput and in terms of application. For example, our procedure did not require any refined synthetic technique and avoided particularly

air or moisture sensitive reagents. It was additionally attractive because it could be carried out on the gram scale with minimal effort in one eight-hour day.

Similar to the synthesis described in Scheme 3, the Mannich-based procedure involved protecting the alcohol substituents of catechol with the common *tert*-butyldimethyl silyl group (STEP A; Scheme 4).[27] However, the Mannich-based method differed in that only one of the alcohol substituents was protected, not two. Mono-protection was key for STEP B, where the Mannich reaction was used to affix Int-2b to the diaza-18-crown-6 (Kryptofix 22) reagent. The success of STEP B seemed to rely on the presence of a single ionizable proton, as all of our attempts to use unprotected catechol directly resulted in an intractable dark mixture of byproducts. We speculate that the bulky tert-butyl silyl (TBS) protecting group directed substitution for the Mannich reaction exclusively to the ortho-position of the catechol ring and inhibited undesired catechol based oligomerization/polymerization reactions. Int-2b was easily de-protected using a mixture of HCl and MeOH, and H₄ChaCha 2HCl was isolated in highyield and purity. Regardless of the method used to prepare $H_4ChaCha \cdot 2HCl$, we found it important to isolate the macrocycle as the HCl salt. In this form, the $H_4ChaCha$ molecule was protected against oxidative degradation and could be stored in our laboratory for long periods of time (>6 months) on the benchtop with no detectable decomposition (¹H NMR shows no impurities) beyond a slight darkening in color.

Synthesis of $H_4^t Bu_2 ChaCha$. Motivated by the success in preparing $H_4 ChaCha 2HCl$, attempts were made to prepare a derivative that had improved solubility in organic solvents. As such, efforts were made to prepare the ^tBu-substituted analogue. Using similar methodology described in Scheme 5, it was observed that $H_4^t Bu_2 ChaCha$ could be prepared in a single step

from commercially available starting materials: diaza-18-crown-6 (Kryptofix-22), 4-*tert*butylcatechol, and paraformaldehyde. This reaction proceeded directly to $H_4^{t}Bu_2ChaCha$ via the Mannich condensation reaction,[29] which surprisingly formed only the N,N'-bis(2,3-dihydroxy-5-tert-butylbenzyl)-4,13-diaza-18-crown-6 isomer. Additionally, unlike the syntheses for $H_4ChaCha 2HCl$ (the one reported previously[14] and the two described herein) protection of the alcohol substituents on the catecholate functional groups was not required to achieve synthetic success. Finally, this reaction showed greatly improved yield relative to the synthesis of $H_4ChaCha 2HCl$, at 84%. The relative ease with which $H_4ChaCha 2HCl$ and $H_4^{t}BuChaCha$ were prepared was consistent with previous reports that used Mannich condensations to prepare substituted lariat crown ethers.[13, 29]

Comparisons of H₄ChaCha–2HCI with H₄^tBu₂ChaCha. The isolation of H₄ChaCha– 2HCl and H₄^tBu₂ChaCha represent a new family of readily accessible aza-crown-ethers functionalized with catechol groups. The subtle differences in catechol substitution imparted substantial differences in solubility, such that H₄ChaCha-2HCl was soluble in polar solvents, like H₂O, acetonitrile, methanol, and DMSO. Meanwhile, H₄^tBu₂ChaCha favored less polar solvents. It readily dissolved in chloroform and ethyl acetate, had slight solubility in toluene and tetrahydrofuran, and was insoluble in H₂O.

The ¹H NMR spectra from both $H_4ChaCha-2HCl$ and $H_4^tBuChaCha$ were easily interpreted, as both compounds were diamagnetic. The spectra were additionally simplified by fast (on the NMR time scale) fluxional and rotational processes, which rendered equatorial and axial protons as single peaks. As shown in Figure 1, the spectrum from $H_4ChaCha-2HCl$ contained five resonances. There were a series of poorly resolved peaks associated with the azacrown backbone. A singlet from the benzylic protons was present at 4.49 ppm, and two similarly poorly resolved peaks associated with the aromatic rings were seen at 7.0 and 6.9 ppm. A similar spectrum was obtained for $H_4^{I}Bu_2ChaCha$ (Figure 1). Subtle differences associated with the benzyl resonance were observed, such that the benzyl peak from $H_4^{I}Bu_2ChaCha$ was shifted slightly downfield at 3.80 ppm in comparison to $H_4ChaCha-2HCl$. This was likely associated with the nitrogen atoms in $H_4ChaCha-2HCl$ being protonated while the amines were basic in $H_4^{I}Bu_2ChaCha$. Additionally, the $H_4^{I}Bu_2ChaCha$ spectrum was dominated by a large peak (18H) at 1.25 ppm attributable to the *tert*-butyl substituents on the catechol groups. Interestingly, features seen in the spectrum of $H_4ChaCha-2HCl$ were substantially broadened relative to $H_4^{I}Bu_2ChaCha$. Perhaps the steric crowding from the large *tert*-butyl substituents or stronger catechol-amine hydrogen bonding limited fluxional processes in $H_4^{I}Bu_2ChaCha$ and provided a more rigid solution-phase structure, which (in turn) accounted for the sharper resonances.

Structure of $H_4^t Bu_2 ChaCha$. Single crystals of $H_4^t Bu_2 ChaCha$ readily formed by slow evaporation of ethanolic solutions (Figure 2). The X-ray diffraction data was best modeled in the *P*-1 space group and the structure was consistent with the ¹H NMR results, showing methylene bridged catechols tethered from each amine. The 18-membered ring orientation of the diaza-18crown-6 macrocycle was analogous to the "chair" confirmation of cyclohexane. Each amine group was pyramidal and had catechol groups occupying the equatorial ring position (not axial). The C–C, C–O, and C–N distances for the diaza-18-crown-6 macrocycle were consistent with single bonds and averaged 1.502(7), 1.426(4), and 1.467(5), respectively (error reported as the standard deviations from the mean, 1 σ). This orientation placed the catechol groups on opposite sides of the macrocycle, providing a geometry that minimized destabilizing steric interactions. Interestingly, each catechol groups had one -OH substituent oriented toward the diaza-18-crown-6 macrocyclic ring, likely reflecting intramolecular hydrogen bonding with the amine. The bond distances were consistent with the formulation of neutral catechols, showing C–C (catechol ring) double bonds and C–OH (catechol substituent) single bonds, averaging 1.392(9) and 1.37(1), respectively. Hence, the structural results and diamagnetic behavior of the $H_4^{t}BuChaCha$ suggested that no unexpected oxidation occurred during the synthesis. Thus, the $H_4^{t}BuChaCha$ compound was best described as containing two catechol (not semiquinone or quinone) groups.

Synthesis of [La₂('Bu₂ChaCha)₂]₂. The reaction of $H_1Bu_2ChaCha$ with tris(bis trimethylsilyl)amide lanthanum(III), La[N(SiMe₃)₂]₃ in dry tetrahydrofuran, generated green solutions from which green solids were isolated (Scheme 6). This observation was intriguing, given that most complexes containing diamagnetic La^{III} are weakly colored (off white or yellow). Attempts to characterize this product using NMR spectroscopy were unsuccessful because the spectra were complicated and difficult to interpret. Elemental analysis of the non-crystalline green powder suggested that the identity of the product was La('Bu₂ChaCha). The one-to-one La³⁺-to-'Bu₂ChaCha ratio was consistent with single crystal X-ray diffraction studies carried out on blue single crystals obtained by vapor diffusion of diethyl ether into toluene solutions. The X-ray diffraction experiment revealed the crystalline product as tetrameric [La₂('Bu₂ChaCha)₂]₂ (Figure 3). Formulation of the [La₂('Bu₂ChaCha)₂]₂ reaction product helped explain the complicated NMR data. For one, if the [La₂('Bu₂ChaCha)₂]₂ structure was retained in solution, protons associated with the macrocycles, the arene rings, and potentially the methylene bridges on the side-arms would likely be inequivalent. Assigning proton resonances to the >200 protons associated with this cluster is indeed daunting. Moreover, dissociation reactions to form dimers

and monomers or association reactions that increase oligomerization would additionally complicate the NMR spectra.

Although the diffraction from these crystals was weak, it was of sufficient quality to determine connectivity. The model of the diffraction patters showed that $[La_2({}^{t}Bu_2ChaCha)_2]_2$ was best described as containing two lanthanum dimers. These dimers were related to each other by a C_2 rotational axis. Hence the coordination environment for the left lanthanum dimer in Figure 4 was equivalent to the right dimer. Each dimer was swaddled by a single $H_4^{t}Bu_2ChaCha$ ligand that folded around the La₂ unit. These dimers were bridged by two $H_4^{t}Bu_2ChaCha$ ligands that were essentially unfolded, and contained no metal atom within the diaza crown ether pocket. For each swaddling ${}^{t}BuChaCha$ ligand, there were four oxygen atoms associated with the dioxolene groups. Two oxygen atoms bridged two La³⁺ cations in a μ^2 -fashion, one bound only one La³⁺ metal, and one was terminal. For the each of the unfolded ${}^{t}BuChaCha$ ligands, two oxygen atoms were bridging and two bound only a single La³⁺ cation (no terminal oxygens).

While tempting to evaluate bond distances within this structure, we refrain, as the 0.0679 R-value (wR2 = 0.2108; Table S-1) was quite high. As a result, the structural data could not be used to reliably distinguish catecholate functional groups from singly protonated catecholates (HCat¹⁻), semiquinones (SQ¹⁻), or quinones (Q) within the $[La_2({}^{t}Bu_2ChaCha)_2]_2$ cluster. To provide a neutral cluster, four reasonable dioxolene scenarios existed (Scheme 7). Because the cluster contained four La³⁺ cations (which gave a +12 metal charge) and had four ${}^{t}BuChaCha$ ligands (which contained eight dioxolene groups), it was possible that four of the eight catecholates were singly protonated giving four $H^{t}BuChaCha^{3-}$ ligands (4 Cat²⁻ and 4 HCat¹⁻). Equally likely was the case where two catecholates had been singly protonated while two catecholates underwent a single electron oxidation to form two semiquinones (4 Cat²⁻, 2 HCat¹⁻).

and 2 SQ¹⁻). It was also possible that four single electron oxidation reactions occurred. In this situation, each ${}^{t}Bu_{2}ChaCha$ chelate would contain one catecholate and one semiquinone (4 Cat²⁻ and 4 SQ¹⁻). Finally, two catecholate groups could have undergone two 2e¹⁻ oxidation reactions to form two quinones. In this last case two ${}^{t}Bu_{2}ChaCha$ ligands would contain only catecholates, meanwhile two would contain a catecholate and a quinone functional group (6 Cat²⁻ and 2 Q). To characterize which possible scenarios were most likely, a series of spectroscopic experiments were conducted, as follows.

It is well established that UV-vis spectroscopy provides a fingerprint for identifying catecholate oxidation products, specifically semiquinones and quinones.[30] For instance, catecholates have absorption bands in the UV (>30,000 cm⁻¹; <333 nm), quinones in the blue (approximately 20,000 to 25,000 cm⁻¹; 500 to 400 nm), and semiguinones in the red to NIR (~12,000 to 20,000 cm⁻¹; ~833 to 500 nm).[30] Spectra from [La₂(^tBu₂ChaCha)₂]₂ showed a strong absorbance at high energy (>20,000 cm⁻¹, 500 nm; Figure 4), which was consistent with the presence of catecholate functional groups. In addition to this large peak, and at lower energy, was a less-intense transition that began at 20,000 cm⁻¹, terminated around 12,000 cm⁻¹ (833 to 625 nm), and was centered near 16,000 cm⁻¹ (625 nm). It was this low energy feature that was responsible for the product's green color. Moreover, this absorption band provided unique insight into the fate of $H_4^t Bu_2 ChaCha$ during the reaction with La[N(SiMe_3)_2]_3. The absorption near 16,000 cm⁻¹ provided strong evidence that some degree of oxidation of the catechol moieties has occurred during the reaction. Note, however, that the measured extinction coefficient was rather low (~20 M⁻¹cm⁻¹), suggesting that complete conversion to the semiquinone had not occurred, as semiquinones typically contain extinction coefficients in the range of ~500-1000 M⁻¹cm⁻¹. This supports the notion that only a few of the catecholate groups

were converted to semiquinones during the formation of $[La_2({}^tBu_2ChaCha)_2]_2$; however, one cannot rule out the possibility that the spectral signature has alternative origins nor can the possibility of dissociation (or further oligomerization) of the tetramer to form a mixture of complicated species in solution be ignored.

The absence of intense absorbances in the blue spectral region (20,000 to 25,000 cm⁻¹; 500 to 400 nm) suggested that two electron oxidation reactions to form quinones had not occurred. However, there was a weak peak near 23,000 cm⁻¹. To eliminate the possibility that this subtle feature was associated with quinone formation, FT-IR spectra were taken (Figure 5). Quinones exhibit characteristic stretching frequencies in the infrared spectral region at ~1650 cm⁻¹.[31] In the spectrum from $[La_2({}^{t}Bu_2ChaCha)_2]_2$ there was clearly no feature that could be correlated with quinone functionalities. Combined with the UV-vis data, these results provided evidence that new product, $[La_2({}^{t}Bu_2ChaCha)_2]_2$, contained a mixture of only catecholates and semiquinones side-arms. Given that the La[N(SiMe_3)_2]_3 reaction with $H_4{}^{t}Bu_2ChaCha$ was carried out with rigorous exclusion of air and moisture, the best description of $[La_2({}^{t}Bu_2ChaCha)_2]_2$ was having 4 Cat²⁻ and 4 SQ¹⁻ ligands; although, at this time the possibility of catecholate protonation cannot be exclusively ruled out. Hence, the 4 Cat²⁻, 2 HCat¹⁻, and 2 SQ¹⁻ scenario was equally reasonable.

OUTLOOK

Many recent advances have revealed extraordinary reaction chemistry when strongly Lewis acidic *f*-block elements are paired with redox active ligands.[32-41] Among the many researchers contributing to this area is *Prof. WILLIAM J. EVANS*, to whom this special addition is dedicated. *EVANS* has been a leader in bringing reduction chemistry to the entire *f*-block.[42-51]

The isolation of $[La_2({}^{t}Bu_2ChaCha)_2]_2$ is well within the spirit of *EVANS*' innovative achievements. For example, these results demonstrated that the unique redox properties associated with $H_4^{t}Bu_2ChaCha$ offers new opportunities in electron transfer for lanthanides and actinides. Our approach, inspired by *EVANS*, used catecholate substituents tethered to an azacrown ether, in an attempt to bring oxidation chemistry (not reduction chemistry) to the "primarily" redox inactive *f*-elements metals.

Contributed herein is the first step to achieve this goal. We report an improved synthetic procedures for H₄ChaCha-2HCl, whose solubility properties offer opportunity to access reactions in polar solvents. Additionally contributed is the preparation and characterization of $H_4'Bu_2ChaCha$ for the first time, which represented a hydrocarbon soluble analogue of the $H_4ChaCha-2HCl$ macrocycle. Isolation of $[La_2(^tBu_2ChaCha)_2]_2$, further demonstrated, as "proof-of-principle," that $H_4^t Bu_2 ChaCha$ was capable of binding metals and forming novel dioxolene complexes. The isolation of $[La_2(^{t}Bu_2ChaCha)_2]_2$ is additionally exciting as it was formed from an unusual oxidation reaction. Characterization of [La₂(^tBuChaCha)₂]₂ by UV-vis spectroscopy showed that the complex contained both catecolate and semiquinone functional groups. The UV-vis data further suggested that there were no quinone functional groups present, a claim substantiated by the IR-spectra. As such [La2(^tBuChaCha)2]2 represents a rare example of an *f*-element semiquinone complex. The first two examples were prepared by prepared by GATTESCHI and coworkers: a monometalic gadolinium tris(pyrazolyl)borate-semiquinone complex^[52] and its analogous dimer.^[53] The only other reported examples of lanthanide semiquinone complexes - of that we are aware - involved the reduction of benzoquinone by either strongly reducing Ln(II) complexes[54, 55] or Ln metals.[56] Overall, our results demonstrated that oxidation chemistry under mild reaction conditions could be accessed by La^{3+}

and $H_4^{t}BuChaCha$. With the synthetic procedure that provided high-purity $[La_2({}^{t}Bu_2ChaCha)_2]_2$ in hand, we are currently defining the electronic properties of this unusual lanthanum cluster. Our goal is to unambiguously characterize the ability of $[La_2({}^{t}Bu_2ChaCha)_2]_2$ to access catecholate vs. semiquinone vs. quinone functionality. In addition, we have commenced exploration of $H_4ChaCha-2HCl$ and $H_4^{t}Bu_2ChaCha$ as *f*-element oxidants, chelators, molecular magnets, and in terms of chromogenic detection of low concentrations of metal ions.

EXPERIMENTAL

General Considerations. The catechol (Acros), imidazole, 4-tert-butylcatechol (Alfa-Aesar), 4,13-diaza-18-crown-6 (kryptofix 22, EMD Millipore), tert-butyldimethylsilyl chloride (Sigma-Aldrich), magnesium sulfate (Sigma-Aldrich), tris[N,N-bis(trimethylsilyl)amide] lanthanum(III) (Alfa Aesar), imidazole (Sigma-Aldrich), and paraformaldehyde (Sigma-Aldrich) reagents were obtained from commercial sources and used as received. Solvents (DMF, Et₂O, MeOH, toluene, tetrahydrofuran, and acetonitrile) were obtained commercially (HPLC grade) and stored over molecular sieves (3 Å; 24 h) prior to use. Solvents for use in an argon glovebox (tetrahydrofuran, toluene, and pentane) were purchased at the anhydrous grade and stored over molecular sieves (3 Å). All H₂O used in the following experiments were purified by means of a Millipore Milli-Q system (18 M Ω). Elemental analyses (C, H, N) were performed by Midwest Microlab Inc., Indianapolis, IN *via* combustion analysis. The NMR experiments were conducted using a Bruker Avance 400 MHz NMR and processed with MestReNova v10. All NMR spectra were referenced to either TMS or residual solvent peaks. Samples for UV-Visible-NIR spectroscopy were made as tetrahydrofuran solutions (8.5 mM) in an inert atmosphere glovebox and loaded into screw top quartz cuvettes (Starna cells). Spectra were collected on a Cary 6000i with a constant bandwidth

setting of 1 nm. FT-IR spectra were collected on a Thermo Scientific Nicolet iS5 spectrometer with an diamond ATR accessory.

Synthetic Route 1 to N,N'-Bis(2,3-dihydroxybenzyl)-4,13-Diaza-18-Crown-6 Dihydrochloride Monohydrate (H₄ChaCha-2HCl).

2,3-Bis(tert-Butyldimethylsilyl Ether)Benzaldehyde (Int-1a).

The first intermediate in Scheme 3 was prepared on the benchtop without exclusion of air and moisture by adding dry dimethyl formaldehyde (DMF; 25 mL) to a round bottom flask (50 mL) charged with 2,3-dihydroxybenzaldehyde (1.00 g; 7.24 mmol) and imidazole (1.97 g; 28.96 mmol). The mixture was stirred at room temperature until the solids dissolved (~5 minutes). Then, tert-butyldimethylsilyl chloride (2.29 g; 15.20 mmol) was added in one portion and the solution was stirred under argon. After one hour, the room temperature solution was transferred to a separatory funnel and diethyl ether (Et₂O; 20 mL) and water (H₂O; 20 mL) were added and the mixture shaken. The aqueous layer (bottom) was discarded, the organic layer (top) washed with brine (3 x 20 mL), and the organic layer dried with magnesium sulfate, MgSO₄. The solvent was removed under reduced pressure using rotary evaporation leaving a colorless oil. Slight heating of this oil (30 °C) under vacuum for 24 h ensures removal of any silyl ether byproducts, and Int-1a was isolated as a pale yellow oil (2.26 g; 6.16 mmol; 85% crude yield). ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 10.39 (d, J = 0.8 Hz, 1H), 7.42 (dd, J = 7.8, 1.7 Hz, 1H), 7.10 (dd, J = 7.9, 1.7 Hz, 1H), 6.92 (td, J = 7.8, 0.8 Hz, 1H), 1.05 (s, 9H), 0.99 (s, 9H), 0.25 (s, 6H),0.17 (s, 6H). Please note that in the exposing the crude mixture for shorter times to vacuum does not remove all of the DMF and bis(tert-butyldimethylsilyl)ether contaminants. However, these

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byproducts do not affect any subsequent synthetic steps and the crude product can be carried through the synthetic steps described below without further purification.

2,3-Bis(tert-Butyldimethylsilyl ether)Benzyl Alcohol (Int-1b).

The second intermediate described in Scheme 3 was prepared on the benchtop without exclusion of air and moisture by charging a round bottom flask (100 mL) with *Int–1a*, (2.26 g; 6.16 mmol) dissolved in methanol (MeOH; 25 mL). This solution was cooled using an ice-water bath. Then, four equivalents of solid sodium borohydride (NaBH₄; 0.206 g; 5.45 mmol) was added slowly (30 s). The flask was equipped with a glass stopper and its contents stirred (3 h; 0 °C \rightarrow room temp). Subsequently, the solution was transferred to a separatory funnel, and diethyl ether (Et₂O; 20 mL) and water (H₂O; 20 mL) that had been saturated with ammonium chloride, NH₄Cl, were added slowly, taking care to relieve any pressure buildup. The aqueous layer (bottom) was discarded, the organic layer (top) was washed with water saturated with NH₄Cl (2 x 20 mL), and the organic layer dried with magnesium sulfate, MgSO₄. The solvent was removed under reduced pressure using rotary evaporation (1 h) and *Int–1b* was isolated as a colorless oil (1.95 g; 5.29 mmol) in 86% yield. ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 6.95 (dd, *J* = 7.2, 2.1 Hz, 1H), 6.86 – 6.78 (m, 2H), 4.67 (s, 2H), 1.02 (s, 9H), 0.96 (s, 9H), 0.22 (s, 6H), 0.17 (s, 6H).

2,3-Bis(tert-Butyldimethylsilyl Ether)Benzyl Chloride (Int-1c).

The third intermediate in Scheme 3 was prepared on the benchtop without exclusion of air and moisture by adding trichlorotriazine (1.07 g; 5.82 mmol) to a round bottom flask (50 mL) charged with DMF (5 mL) that had been slightly heated (30 °C). The mixture was stirred (2 h) and solids that precipitated were occasionally broken up with a glass stirring rod.

Dichloromethane (CH₂Cl₂; 25 mL) was added followed by a solution of *Int–1b* (1.95 g; 5.29 mmol) that had been dissolved in CH₂Cl₂ (5 mL). The reaction was monitored by NMR spectroscopy and diethyl ether (Et₂O; 30 mL) was added when the starting material was consumed (~3 h). This caused a yellow solid to precipitate. The mixture was filtered through Celite and the filter cake was washed with Et₂O (2 x 10 mL). The filtrate was transferred to a separatory funnel. The aqueous layer (bottom) was discarded, the organic layer (top) was washed with brine (1 x 30 mL), and the organic layer dried with magnesium sulfate, MgSO₄. The solvent was removed by rotary evaporation and *Int–1c* was isolated as a yellow oil (1.64 g; 4.23 mmol) in 80% yield. ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 6.95 (dd, *J* = 7.2, 2.1 Hz, 1H), 6.87 – 6.77 (m, 2H), 4.67 (s, 2H), 1.02 (s, 9H), 0.96 (s, 9H), 0.22 (s, 6H), 0.17 (s, 6H). If desired, minor impurities can be removed by silica gel chromatography (10% Et₂O:hexanes). However, we found it more convenient to carry the crude product through the following steps without further purification.

N,N'-[2,3-Bis(tert-Butyldimethyl Silyl Ether)Benzyl]-4,13-Diaza-18-Crown-6 (Int– 1d).

The fourth intermediate shown in Scheme 3 was prepared on the benchtop without exclusion of air and moisture by combining 4,13-diaza-18-crown-6 (Kryptofix 22, 501 mg; 1.91 mmol) and N,N-diisopropylethylamine (920 uL; 5.29 mmol) with anhydrous acetonitrile (MeCN; 25 mL) in a round bottom flask (50 mL) equipped with a magnetic stirrer. To this solution, *Int–1c* (1.64 g; 4.23 mmol), also dissolved in anhydrous MeCN (10 mL), was added. The mixture was heated to reflux under argon. After 3 h, the resulting mixture was cooled to room temperature and white crystals precipitated over 12 hours. *Note: cooling the mother liquor below room temperature*

causes precipitation of a red impurity that is difficult to remove. The white solid was collected by vacuum filtration, recrystallized from hot cyclohexane and washed with water and acetonitrile. After drying the solids under vacuum (overnight), *Int–1d* was isolated as a white crystalline solid (684 mg; 0.71 mmol; 37% yield). ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 7.09 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.78 (t, *J* = 7.8 Hz, 2H), 6.72 (dd, *J* = 8.0, 1.8 Hz, 2H), 3.66 (s, 4H), 3.59 (s, 8H), 2.79 (d, *J* = 5.8 Hz, 4H), 1.02 (s, 18H), 0.94 (s, 18H), 0.20 (s, 12H), 0.12 (s, 12H).

N,N'-Bis(2,3-dihydroxybenzyl)-4,13-Diaza-18-Crown-6 Monohydrate (H₄ChaCha-2HCl) From Int–1d.

Dihydrochloride

The *H*₄*ChaCha*–2*HCl* product was prepared from *Int–1d* (Scheme 3) on the benchtop without exclusion of air and moisture by adding hydrochloric acid (1 mL; 12 M) to a scintillation vial that contained a stirred solution of *Int–1d* (684 mg; 0.71 mmol) dissolved in methanol (MeOH; 10 mL). After gently heating the solution (40 °C; 3 h) under air, the solvent was removed by rotary evaporation. The resulting sticky colorless oil was exposed to vacuum (40 °C; 24 h), which enabled *H*₄*ChaCha-2HCl* to be isolated as a fluffy beige hygroscopic powder (418 mg; 0.70 mmol; ~99% yield). ¹H NMR (400 MHz, D₂O: 4.79 ppm) δ 7.02 (2H, m), 6.92 (4H, m), 4.49 (4H, s), 3.87 (8H, br s), 3.53 (18H, m). Anal. Calcd for C₂₆H₄₂Cl₂N₂O₉: C, 52.26; H, 7.09; N, 4.69. Found: C, 52.01; H, 7.01; N, 4.87.

Synthetic Route 2 to N,N'-Bis(2,3-dihydroxybenzyl)-4,13-Diaza-18-Crown-6 Dihydrochloride Monohydrate (H_4 ChaCha-2HCl) via Mannich condensation.

2-(tert-Butyldimethylsilyl Ether)phenol (Int-2a).

The first intermediate in Scheme 4 was prepared on the benchtop without exclusion of air and moisture by adding catechol (5.00 g; 45.4 mmol) to a round bottom flask (50 mL) containing cold DMF (0° C, 25 mL) and was stirred until the catechol was fully dissolved (~5 min). Imidazole (6.49 g; 95.3 mmol) and then tert-butyldimethylsilyl chloride (6.84 g; 45.4 mmol) were added, and stirring was continued (3 h; 0 °C \rightarrow room temp). The reaction was quenched with water (20 mL), stirred (5 min) and the cloudy mixture was transferred to a separatory funnel with the assistance of Et₂O (30 mL). The aqueous layer was separated and discarded. The organic layer was washed with water (25 mL x 3), then brine (25 mL x 1), and dried with sodium sulfate. The solution was filtered through a pad of silica gel, and solvent was removed by rotary evaporation. The product was isolated in 79% crude yield (8.04 g; 35.9 mmol). ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 7.02 (dd, J = 7.9, 1.7 Hz, 1H), 6.92 (m, 2H), 6.81 (td, J = 7.7, 1.7 Hz, 1H), 5.60 (s, 1H), 1.09 (s, 9H), 0.34 (s, 6H). ¹³C NMR (101 MHz, CDCl₃: 77.2 ppm) δ 147.26, 142.33, 122.13, 119.94, 117.85, 114.91, 25.69, 18.14, -4.39. Although vacuum distillation improves purity, the compound can be used in subsequent synthetic steps without further purification.

N,N'-[2-hydroxy-3-(tert-Butyldimethylsilyl Ether)]-4,13-Diaza-18-Crown-6 (Int-2b).

The second intermediate in Scheme 4 was prepared on the benchtop without exclusion of air and moisture by combining kryptofix-22 (1.5 g; 5.72 mmol), paraformaldehyde (435 mg; 14.5 mmol), and *Int–2a* (2.82 g; 12.6 mmol) in a round bottom flask (100 mL) charged with toluene (50 mL) and equipped with an air-cooled condenser. The cloudy mixture was stirred (40 $^{\circ}$ C; overnight) and the solids dissolved generating a clear and colorless solution. The solvent was

removed by rotary evaporation leaving a colorless oil. After 3 h at room temperature, a white solid precipitated from the oil. The oil was removed with repeated cold (-10 °C) hexane washes (10 mL x 3, warm hexane or excess washes will reduce yield) and the white solid was isolated by vacuum filtration. Drying the product under reduced pressure provided *Int–2b* in 42% yield (1.75 g; 2.38 mmol). ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 6.77 (dd, J = 7.2, 2.2 Hz, 2H), 6.64 – 6.56 (m, 4H), 3.77 (s, 4H), 3.66 (t, J = 5.5 Hz, 8H), 3.62 (s, 8H), 2.84 (t, J = 5.5 Hz, 8H), 1.01 (s, 18H), 0.20 (s, 12H). ¹³C NMR (101 MHz, CDCl₃: 77.2 ppm) δ 149.17, 143.76, 123.38, 121.55, 120.54, 118.39, 70.87, 69.15, 58.39, 53.43, 25.83, 18.49, -4.48. This crude product was of sufficient purity to be carried on in subsequent synthetic steps.

N,N'-Bis(2,3-dihydroxybenzyl)-4,13-Diaza-18-Crown-6 Dihydrochloride Monohydrate (H₄ChaCha-2HCl) From Int–2b.

The *H*₄*ChaCha*–2*HCl* product was prepared from *Int*–2*b* (Scheme 4) on the benchtop without exclusion of air and moisture by adding hydrochloric acid (1 mL; 12 M) to a scintillation vial that contained a stirred solution of *Int-2b* (1.75 g; 2.38 mmol) dissolved in methanol (MeOH; 10 mL). After gently heating the solution (40 °C; 3 h) under air, the solvent was removed by rotary evaporation. The resulting sticky colorless oil was dried under vacuum (40 °C; 24 h), which enabled *H*₄*ChaCha-2HCl* to be isolated as a pale beige hygroscopic powder (1.35 g; 2.33 mmol; 98% yield). See above for characterization details.

N,N'-[2,3-Dihydroxy-5-tert-Butylbenzyl]-4,13-Diaza-18-Crown-6 (H₄^tBu₂ChaCha).

The $H_4^t Bu_2 ChaCha$ product was prepared in a single step (Scheme 4) on the benchtop without exclusion of air and moisture by dissolving 4,13-diaza-18-crown-6 (500 mg; 1.9 mmol) and

paraformaldehyde (145 mg; 4.8 mmol) in anhydrous benzene (25 mL) in a round bottom flask (50 mL). To this solution, 4-tert-butylcatechol (790 mg; 4.9 mmol) was added. The solution was roughly degassed by exposure to vacuum followed by argon (3x) and heated at reflux under an argon atmosphere (12 h). Next, the solvent was removed using rotary evaporation. The resulting white solid was ground using a mortar and pestle, washed with diethyl ether, and dried under vacuum (0.1 Torr; 30 °C; 12 h) to give a free-flowing white powder (1.02 g; 1.6 mmol, 84% yield). Single crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of an ethanolic solutions (EtOH) of $H_4^tBu_2ChaCha$. ¹H NMR (400 MHz, CDCl₃: 7.26 ppm) δ 6.90 (t, J = 2.3 Hz, 2H), 6.50 (d, J = 2.3 Hz, 2H), 3.79 (s, 4H), 3.66 (t, J = 5.3 Hz, 8H), 3.61 (s, 8H), 2.81 (t, J = 5.3 Hz, 8H), 1.25 (s, 18H). Anal. Calcd for C₃₄H₅₄N₂O₈: C, 65.99; H, 8.80; N, 4.53. Found: C, 65.83; H, 8.79; N, 4.24.

[La₂(^tBu₂ChaCha)₂]₂

In an argon filled glovebox, tris[N,N-bis(trimethylsilyl)amide] lanthanum(III), La[N(SiMe₃)₂]₃ (367 mg; 0.644 mmol), was dissolved in tetrahydrofuran, THF (10 mL). The colorless solution was added to a vial charged with $H_4^{t}Bu_2ChaCha$ (398 mg; 0.643 mmol). After stirring the mixture overnight, all of the solids dissolved to generate a dark green solution. The solution was filtered through glass wool and the solvent was removed under vacuum to give a sticky green solid. For spectroscopic and analytical analyses this sticky green solid was washed with pentane (3 x 1 mL) and dried at elevated temperature (40 °C) under reduced pressure (~0.1 Torr) to give a free flowing pale green solid (443 mg, 0.146 mmol, 91% yield). For single crystal diffraction studies, aforementioned sticky green solid was dissolved in a minimal amount of dry toluene (~1 mL), gently heated (40 °C), and filtered again through glass wool. Slow diffusion of diethyl

ether, OEt₂, into this solution generated a pale green precipitate (non-crystalline compound) and dark blue block crystals of $[La_2({}^tBuChaCha)_2]_2$ that were suitable for single crystal X-ray Diffraction. Anal. Calcd for $C_{136}H_{204}N_8O_{32}$: C, 54.11; H, 6.81; N, 3.71. Found: C, 53.87; H, 7.07; N, 3.61. UV-vis 14,830 cm⁻¹ (ϵ =18.5). The NMR spectrum was uninterpretable, owing to a very large number of unresolvable peaks.

Crystallographic Studies.

Single crystals of $[La_2(^{t}BuChaCha_2)]_2$ and $H_4tBuChaCha$ were mounted on nylon loops with Paratone-N oil (Hampton Research) and immediately cooled in a cold nitrogen stream on a D8 Bruker QUEST diffractometer. No corrections for crystal decay were necessary. Standard Apex II software was used for determination of the unit cells and data collection control. The intensities of the reflections of a sphere were collected by combining four sets of exposures (frames), which totaled to 1464 frames with an exposure time of 10-60 seconds per frame, depending on the crystal. Apex II software was used for data integration including Lorentz and polarization corrections. Disorder associated with solvent molecules was accounted for by using the SQUEEZE program in PLATON[57]. All of the atoms were refined anisotropically with the acception of a few badly disordered carbon atoms in [La₂(^tBuChaCha₂)]₂. Attempts to model this disorder anisotropically resulted in on going splitting of the carbon atoms. The data was corrected for absorption using redundant reflections using the SADABS program. Structure solution and refinement were performed using SHELX. The hydrogen atoms in H₄tBuChaCha were generated using HFIX function in the SHELXL program. The CIF files used in this manuscript are available through the Cambridge Crystal Data Centre (CCDC 1573878 and 1573879).

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Supporting Information

The CIF file for $[La_2(^tBuChaCha)_2]_2$ and $H_4^tBu_2ChaCha$ are available through the Cambridge Crystal Data Centre (CCDC 1573878 and 1573879).



Scheme 1: The structure of $H_4ChaCha-2HCl$ and $H_4^tBu_2ChaCha$.

Scheme 2: Electron transfer chemistry available to the catecholate ligand.

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Scheme 3: Synthesis of N,N'-[2,3-dihydroxybenzyl]-4,13-diaza-18-crown-6 dihydrochloride (H_4 ChaCha·2HCl) via benzylic substitution of 2,3-bis(*tert*-Butyldimethylsilyl Ether)benzyl chloride (Int-1c) and 4,13-Diaza-18-Crown-6.



Scheme 4: Synthesis of N,N'-[2, 3-dihydroxybenzyl]-4,13-diaza-18-crown-6 dihydrochloride (H_4 ChaCha·2HCl) via Mannich condensation of 2-hydroxy-3-(*tert*-Butyldimethylsilyl Ether) and 4,13-Diaza-18-Crown-6



Scheme 5: Synthesis of N,N'-[2, 3-dihydroxy-5-tert-butylbenzyl]-4,13-diaza-18-crown-6 $(H_4^{\ t}Bu_2ChaCha)$.



Scheme 6: Synthesis of $[La_2(^{t}Bu_2ChaCha)]_2$.



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Scheme 7: A cartoon showing the possible catecholate protonation and oxidation products in the $[La_2({}^tBu_2ChaCha)]_2$ cluster. For clarity, the ^tBu substituents have been omitted and the azacrown ether is represented as solid lines.





Figure 1: ¹H NMR of $H_4ChaCha \cdot 2HCI \cdot H_2O$ in D₂O (blue, bottom) and $H_4^tBu_2ChaCha$ (red, top).



Figure 2: Thermal ellipsoid plot of $H_4^t Bu_2 ChaCha$. Thermal ellipsoids set at 50% probability. Hydrogen atoms have been hidden for clarity.



Figure 3: A ball-and-stick representation showing connectivity for $La_4({}^tBu_2ChaCha)_{4.}$ The La^{3+} cations were colored green. To facilitate viewing, dioxolene groups have been completely shaded as red (oxygen) and gray (carbon). Meanwhile, atoms within the diaza-18-crown-6 macrocyclic ring were shaded with cross-hatches (nitrogen, blue; oxygen, red; carbon, gray). Hydrogen atoms and tert-butyl groups have been omitted for clarity.



Figure 4: UV-Vis electronic absorption spectrum of $[La_2(^tBu_2ChaCha_2)]_2$ in THF. The small discontinuity at ~12,500 cm⁻¹ is due to a grating/detector changeover.



Figure 5: Solid-state ATR FT-IR spectra of $H_4^t Bu_2 ChaCha$ (black) and $[La_2({}^tBu_2ChaCha_2)]_2$ (red).

References

[1] C.J. Pedersen, Cyclic polyethers and their complexes with metal salts, J. Am. Chem. Soc. 89 (1967) 7017-7036.

[2] K.E. Krakowiak, J.S. Bradshaw, D.J. Zamecka-Krakowiak, Synthesis of aza-crown ethers, Chem. Rev. 89 (1989) 929-972.

[3] R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, Thermodynamic and Kinetic Data for Macrocycle Interaction with Cations, Anions, and Neutral Molecules, Chem. Rev. 95 (1995) 2529-2586.

[4] W.A. Volkert, T.J. Hoffman, Therapeutic Radiopharmaceuticals, Chem. Rev. 99(9) (1999) 2269-2292.

[5] G.W. Gokel, D.M. Dishong, C.J. Diamond, Lariat ethers. Synthesis and cation binding of macrocyclic polyethers possessing axially disposed secondary donor groups, J. Chem. Soc., Chem. Commun. 1980 (1980) 1053-1054.

[6] A.E.V. Gorden, J. Xu, K.N. Raymond, P. Durbin, Rational Design of Sequestering Agents for Plutonium and Other Actinides, Chem. Rev. 103 (2003) 4207-4282.

[7] J.F. Desreux, Nuclear magnetic resonance spectroscopy of lanthanide complexes with a tetraacetic tetraaza macrocycle. Unusual conformation properties, Inorg. Chem. 19 (1980) 1319-1324.

[8] K. Kumar, C.A. Chang, M.F. Tweedle, Equilibrium and kinetic studies of lanthanide complexes of macrocyclic polyamino carboxylates, Inorg. Chem. 32 (1993) 587-593.

[9] Y. Katayama, R. Fukuda, T. Iwasaki, K. Nita, M. Takagi, Synthesis of chromogenic crown ethers and liquid—liquid extraction of alkaline earth metal ions, Anal. Chim. Acta 204 (1988) 113-125.

[10] Y. Katayama, K. Nita, M. Ueda, H. Nakamura, M. Takagi, K. Ueno, Synthesis of chromogenic crown ethers and liquid-liquid extraction of alkali metal ions, Anal. Chim. Acta 173 (1985) 193-209.

[11] D.A. Gustowski, L. Echegoyen, D.M. Goli, A. Kaifer, R.A. Schultz, G.W. Gokel, Electrochemically switched cation binding in nitrobenzene-substituted, nitrogen-pivot lariat ethers, J. Am. Chem. Soc. 106 (1984) 1633-1635.

[12] G.W. Gokel, Lariat ethers: from simple sidearms to supramolecular systems, Chem. Soc. Rev. 21 (1992) 39-47.

[13] A.H.M. Elwahy, A.A. Abbas, Synthesis of N-pivot lariat ethers, J. Heterocycl. Chem. 45 (2008) 1-65.

[14] E. Graf, M.W. Hosseini, R. Ruppert, Synthesis of macrocyclic ditopic receptors designed for simulataneous binding of alkaline and transition metal cations, Tetrahedron Lett. 35 (1994) 7779-7782.

[15] F. Bockstahl, E. Graf, M.W. Hosseini, D. Suhr, A. De Cian, J. Fischer, Borocryptands : Synthesis and Structural Analysis of a Lithium Borocryptate, Tetrahedron Lett. 38 (1997) 7539-7542.

[16] D.-H. Zhu, M.J. Kappel, K.N. Raymond, Coordination chemistry of lanthanide catecholates, Inorg. Chim. Acta 147 (1988) 115-121.

[17] S.K. Sahoo, M. Baral, B.K. Kanungo, Potentiometric, spectrophotometric, theoretical studies and binding properties of a novel tripodal polycatechol-amine ligand with lanthanide(III) ions, Polyhedron 25 (2006) 722-736.

[18] P. Caravan, T. Hedlund, S. Liu, c.S. Sjoeberg, C. Orvig, Potentiometric, Calorimetric, and Solution NMR Studies of a Tridentate Ligand Which has a Marked Preference for Formation of Bis(ligand) versus Mono(ligand) Lanthanide Complexes and Which Exhibits High Selectivity for Heavier Lanthanides, J. Am. Chem. Soc. 117 (1995) 11230-11238.

[19] A. Bismondo, P. Di Bernardo, R. Portanova, M. Tolazzi, P.L. Zanonato, Complexation of lanthanide(III) with a tripodal polyaza polycatecholate ligand, Polyhedron 21 (2002) 1393-1396.

[20] A. Bismondo, C. Comuzzi, P. Di Bernardo, P. Luigi Zanonato, Complexation of thorium(IV) by tris((2,3-dihydroxybenzylamino)ethyl)amine—a new strong chelating agent, Inorg. Chim. Acta 286 (1999) 103-107.

[21] P.D. Bernardo, P.L. Zanonato, A. Bismondo, A. Melchior, M. Tolazzi, Protonation and lanthanide(III) complexation equilibria of a new tripodal polyaza-polycatechol-amine, Dalton Trans. (2009) 4236-4244.

[22] C.G. Pierpont, Studies on charge distribution and valence tautomerism in transition metal complexes of catecholate and semiquinonate ligands, Coord. Chem. Rev. 216–217 (2001) 99-125.

[23] C.G. Pierpont, R.M. Buchanan, Transition metal complexes of o-benzoquinone, osemiquinone, and catecholate ligands, Coord. Chem. Rev. 38 (1981) 45-87.

[24] T.A. Pham, J. Xu, K.N. Raymond, A Macrocyclic Chelator with Unprecedented Th4+ Affinity, J. Am. Chem. Soc. 136 (2014) 9106-9115.

[25] K.N. Raymond, G.E. Freeman, M.J. Kappel, Actinide-specific complexing agents: Their structural and solution chemistry, Inorg. Chim. Acta 94 (1984) 193-204.

[26] G.E. Freeman, K.N. Raymond, Specific sequestering agents for the actinides. 12. Synthetic and structural chemistry of gadolinium and holmium catecholates, Inorg. Chem. 24 (1985) 1410-1417.

[27] E.J. Corey, A. Venkateswarlu, Protection of hydroxyl groups as tert-butyldimethylsilyl derivatives, J. Am. Chem. Soc. 94 (1972) 6190-6191.

[28] L. De Luca, G. Giacomelli, A. Porcheddu, An Efficient Route to Alkyl Chlorides from Alcohols Using the Complex TCT/DMF, Org. Lett. 4 (2002) 553-555.

[29] K.-W. Chi, H.-C. Wei, T. Kottke, R.J. Lagow, A New One-Pot Synthesis of Double-Armed Ionizable Crown Ethers Using the Mannich Reaction, J. Org. Chem. 61 (1996) 5684-5685.

[30] M.D. Stallings, M.M. Morrison, D.T. Sawyer, Redox chemistry of metal-catechol complexes in aprotic media. 1. Electrochemistry of substituted catechols and their oxidation products, Inorg. Chem. 20(8) (1981) 2655-2660.

[31] A.B.P. Lever, P.R. Auburn, E.S. Dodsworth, M.A. Haga, W. Liu, M. Melnik, W.A. Nevin, Bis(dioxolene)(bipyridine)ruthenium redox series, J. Am. Chem. Soc. 110 (1988) 8076-8084.

[32] E.J. Schelter, R. Wu, J.M. Veauthier, E.D. Bauer, C.H. Booth, R.K. Thomson, C.R. Graves, K.D. John, B.L. Scott, J.D. Thompson, D.E. Morris, J.L. Kiplinger, Comparative Study of f-Element Electronic Structure across a Series of Multimetallic Actinide and Lanthanoid-Actinide Complexes Possessing Redox-Active Bridging Ligands, Inorg. Chem. 49 (2010) 1995-2007.

[33] F. Pointillart, B.L. Guennic, O. Maury, S. Golhen, O. Cador, L. Ouahab, Lanthanide Dinuclear Complexes Involving Tetrathiafulvalene-3-pyridine-N-oxide Ligand: Semiconductor Radical Salt, Magnetic, and Photophysical Studies, Inorg. Chem. 52 (2013) 1398-1408.

[34] S.V. Klementyeva, N.P. Gritsan, M.M. Khusniyarov, A. Witt, A.A. Dmitriev, E.A. Suturina, N.D.D. Hill, T.L. Roemmele, M.T. Gamer, R.T. Boeré, P.W. Roesky, A.V. Zibarev, S.N. Konchenko, The First Lanthanide Complexes with a Redox-Active Sulfur Diimide Ligand: Synthesis and Characterization of [LnCp*2(RN=)2S], Ln=Sm, Eu, Yb; R=SiMe3, Chem. Eur. J 23(6) (2017) 1278-1290.

[35] F. Gao, X.-M. Zhang, L. Cui, K. Deng, Q.-D. Zeng, J.-L. Zuo, Tetrathiafulvalene-Supported Triple-Decker Phthalocyaninato Dysprosium(III) Complex: Synthesis, Properties and Surface Assembly, Scientific Reports 4 (2014) srep05928.

[36] Y. Fang, Z. Ou, K.M. Kadish, Electrochemistry of Corroles in Nonaqueous Media, Chem. Rev. 117 (2017) 3377-3419.

[37] H. Fang, B.E. Cole, Y. Qiao, J.A. Bogart, T. Cheisson, B.C. Manor, P.J. Carroll, E.J. Schelter, Electro-kinetic Separation of Rare Earth Elements Using a Redox Active Ligand, Angew. Chem. Int. Ed. 56(43) (2017) 13450-13454.

[38] P.L. Diaconescu, P.L. Arnold, T.A. Baker, D.J. Mindiola, C.C. Cummins, Arene-Bridged Diuranium Complexes: Inverted Sandwiches Supported by δ Backbonding, J. Am. Chem. Soc. 122 (2000) 6108-6109.

[39] S. Demir, M. Nippe, M.I. Gonzalez, J.R. Long, Exchange coupling and magnetic blocking in dilanthanide complexes bridged by the multi-electron redox-active ligand 2,3,5,6-tetra(2-pyridyl)pyrazine, Chemical Science 5 (2014) 4701-4711.

[40] E.J. Coughlin, M. Zeller, S.C. Bart, Neodymium(III) Complexes Capable of Multi-Electron Redox Chemistry, Angew. Chem. Int. Ed. 56(40) (2017) 12142-12145.

[41] C. Camp, V. Guidal, B. Biswas, J. Pécaut, L. Dubois, M. Mazzanti, Multielectron redox chemistry of lanthanide Schiff-base complexes, Chemical Science 3 (2012) 2433-2448.

[42] W.J. Evans, S.A. Kozimor, Expanding the chemistry of U3+ reducing agents, Coord. Chem. Rev. 250 (2006) 911-935.

[43] W.J. Evans, B.L. Davis, Chemistry of Tris(pentamethylcyclopentadienyl) f-Element Complexes, (C5Me5)3M, Chem. Rev. 102 (2002) 2119-2136.

[44] W.J. Evans, Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States, Organometallics 35 (2016) 3088-3100.

[45] W.J. Evans, Advances in f element reductive reactivity as a paradigm for expanding lanthanide and actinide science and technology, J. Alloys Compd. 488 (2009) 493-510.

[46] W.J. Evans, The expansion of divalent organolanthanide reduction chemistry via new molecular divalent complexes and sterically induced reduction reactivity of trivalent complexes, J. Organomet. Chem. 647 (2002) 2-11.

[47] W.J. Evans, Recent advances in f element reduction chemistry, J. Organomet. Chem. 652 (2002) 61-68.

[48] W.J. Evans, Achieving new lanthanide chemistry within the tetracyclopentadienyl cavity formed by two (C5Me5)2Ln moieties, J. Alloys Compd. 192 (1993) 205-210.

[49] W.J. Evans, The organometallic Chemistry of the lanthanide elements in low oxidation states, Polyhedron 6 (1987) 803-835.

[50] W.J. Evans, Synthesis, structure and reactivity of organometallic complexes of Sm(II), Inorg. Chim. Acta 139 (1987) 169-170.

[51] W.J. Evans, Organometallic Lanthanide Chemistry, Adv. Organomet. Chem. 24 (1985) 131-177.

[52] A. Caneschi, A. Dei, D. Gatteschi, L. Sorace, K. Vostrikova, Antiferromagnetic Coupling in a Gadolinium(III) Semiquinonato Complex, Angew. Chem. Int. Ed. 39 (2000) 246-248.

[53] A. Dei, D. Gatteschi, C.A. Massa, L.A. Pardi, S. Poussereau, L. Sorace, Spontaneous Symmetry Breaking in the Formation of a Dinuclear Gadolinium Semiquinonato Complex: Synthesis, High-Field EPR Studies, and Magnetic Properties, Chem. Eur. J 6 (2000) 4580-4586.

[54] N.A. Pushkarevsky, M.A. Ogienko, A.I. Smolentsev, I.N. Novozhilov, A. Witt, M.M. Khusniyarov, V.K. Cherkasov, S.N. Konchenko, Cooperative reduction by Ln2+ and Cp*ions: synthesis and properties of Sm, Eu, and Yb complexes with 3,6-di-tert-butyl-obenzoquinone, Dalton Trans. 45 (2016) 1269-1278.

[55] Â. Domingos, I. Lopes, J.C. Waerenborgh, N. Marques, G.Y. Lin, X.W. Zhang, J. Takats, R. McDonald, A.C. Hillier, A. Sella, M.R.J. Elsegood, V.W. Day, Trapping of Anionic Organic Radicals by (TpMe2)2Ln (Ln = Sm, Eu), Inorg. Chem. 46 (2007) 9415-9424.

[56] D.M. Kuzyaev, D.L. Vorozhtsov, N.O. Druzhkov, M.A. Lopatin, E.V. Baranov, A.V. Cherkasov, G.K. Fukin, G.A. Abakumov, M.N. Bochkarev, 3,5-Di-tert-butyl-o-benzoquinone complexes of lanthanides, J. Organomet. Chem. 698 (2012) 35-41.

[57] A.L. Spek, PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, Acta Crystallogr. C 71(1) (2015) 9-18.

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