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Developments in the Coordination Chemistry of Europium(II)

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Abstract

Recent advances in the coordination chemistry of Eu^{2+} are reviewed. Common synthetic routes for generating discrete Eu^{2+} -containing complexes reported since 2000 are summarized, followed by a description of the reactivity of these complexes and their applications in reduction chemistry, polymerization, luminescence, and as contrast agents for magnetic resonance imaging. Rapid development of the coordination chemistry of Eu^{2+} has led to an upsurge in the utilization of Eu^{2+} -containing complexes in synthetic chemistry, materials science, and medicine.

Keywords

Lanthanides; Coordination chemistry; Imaging agents; Luminescence; Polymerization

Introduction

Properties of Eu^{2+}

Among the divalent lanthanides, Eu^{2+} has the most accessible divalent oxidation state because of its half-filled $4f^7$ electronic configuration and, consequently, a high stabilization from exchange energy (Figure 1).^[1] While Eu^{2+} is the most accessible of the divalent lanthanides, outside of the solid state it has a propensity to oxidize [$\text{Eu}^0(\text{Eu}^{3+}/\text{Eu}^{2+}) = -0.35$ V vs. the normal hydrogen electrode (NHE)],^[2] which necessitates handling under an inert atmosphere. Four decades ago, there were only a few discrete Eu^{2+} -containing complexes reported. Most of these complexes were halides, chalcogenides, and organometallic compounds that are generally insoluble in organic solvents such as tetrahydrofuran (THF) because of the formation of extended structures.^[3]

Despite oxidation and oligomerization, which present obstacles to the preparation and characterization of Eu^{2+} -containing complexes, the interesting catalytic, photophysical, and magnetic properties of this ion have spurred a great deal of research. The unique properties of Eu^{2+} are influenced largely by the spacing of the energy levels of the $4f$ and $5d$ orbitals and the reducing properties of the ion.

The f orbitals make the electronic properties of Eu^{2+} unique in comparison to those of elements in the d block. For example, using spectroscopic techniques, Adin and Sykes demonstrated that electron transfer from f orbitals is more difficult than that from d orbitals.^[4] They observed a rate constant for the reaction of Eu^{2+} with V^{3+} of $0.013 \text{ M}^{-1}\text{s}^{-1}$ ($1.0 \times 10^{-3} \text{ M HClO}_4$, 25°C , ionic strength 2.0 M), while the rate constant for the reaction of Cr^{2+} with V^{3+} under the same conditions is $0.85 \text{ M}^{-1}\text{s}^{-1}$.^[4] The smaller rate constant observed

for Eu^{2+} relative to that for Cr^{2+} can be attributed to the shielding of the valence 4f orbitals from the environment by the electrons in the fully occupied 5s and 5p orbitals. An additional influence of the f orbitals is exemplified by the photophysical properties of Eu^{2+} that stem from the lowest-energy and first-excited-state configurations of $4f^7$ and $4f^65d^1$, respectively.^[5] While the 4f orbitals of Eu^{2+} remain largely unperturbed by the presence of ligands, the energy of the 5d orbitals is influenced readily by ligands. Consequently, the luminescence properties of Eu^{2+} can be tuned by using coordination chemistry, and the characteristic emission properties of this divalent ion include a broad emission band (390–580 nm)^[6] and a short radiative lifetime (ca. 1 μs) that are attributed to the Laporte-allowed $4f^65d^1 \rightarrow 4f^7$ transitions.^[5] In addition to these allowed transitions, sharp emission bands, which appear between 354 and 376 nm^[7,8] and have longer radiative emission lifetimes (ca. 1 ms) that correspond to the Laporte-forbidden $4f \rightarrow 4f$ transitions are observed, similar to those observed in the Eu^{3+} ion.^[5] Beyond the unique luminescence properties of Eu^{2+} , the f orbitals are responsible for the interesting magnetic characteristics of this divalent ion that include a high magnetic moment (7.63–8.43 μ_B) associated with seven unpaired electrons in an $^8S_{7/2}$ ground-state configuration.^[3,9]

In addition to the desirable optical and magnetic properties of Eu^{2+} , this ion displays interesting redox chemistry. Divalent lanthanides including Eu^{2+} act as one-electron reductants, and detailed discussions of the reductive chemistry of divalent lanthanides were published by Evans in 2000 and 2002.^[2,10] Since then, research efforts have been directed toward developing Eu^{2+} -containing species that act as multielectron reductants in synthetic chemistry.^[11] Additionally, there is interest in studying the influence of ligands on the redox properties of Eu^{2+} .^[12]

Early Eu^{2+} Complexes

Discrete Eu^{2+} -containing complexes were reported as early as 1964.^[13] However, the number of these complexes is small relative to their Eu^{3+} analogues, which form air-stable complexes with most electronegative atoms such as oxygen and nitrogen, partially because Eu^{3+} is a hard Lewis acid. Eu^{2+} is a softer Lewis acid than Eu^{3+} because of its lower charge density; consequently, Eu^{2+} -containing complexes often include ligands with relatively soft atoms such as carbon and phosphorus.

Among the first discrete Eu^{2+} -containing complexes prepared was the metallocene-like complex Cp_2Eu , where Cp is cyclopentadiene. This complex did not garner much interest because of its insolubility in polar organic solvents such as THF.^[14] This insolubility was ascribed to a polymerization that can be prevented with the use of bulkier ligands.^[9,14,15] Templeton and co-workers were able to isolate crystals from THF or toluene of Cp^*_2Eu (**1**) in which Cp^* is methyl-substituted Cp (Figure 2).^[9] Evans and co-workers investigated the bond characteristics and the electronic spin–spin paramagnetic relaxation rate of Eu in $\text{Cp}^*_2\text{Eu}(\text{THF})$ (**2**) and $\text{Cp}^*_2\text{Eu}(\text{THF})(\text{Et}_2\text{O})$ (**3**). The Eu–ligand bonds of **2** and **3** are ionic in character as indicated by the isomer shifts of these complexes: ^{151}Eu Mössbauer spectroscopy, a technique used to study the oxidation state and the local environment of Eu in the solid state, provides the information that the shifts of **2** and **3** are not different from those of ionic Eu^{2+} halide complexes.^[16] Moreover, the data obtained from the spherical relaxation model fits of the ^{151}Eu Mössbauer spectra of **2**, **3**, and $[\text{Cp}^*\text{Eu}(\text{THF})_2(\mu\text{-I})_2]$ (**4**) in the solid state indicate that the Eu–Eu distances affect the electronic spin–spin paramagnetic relaxation of these complexes: longer Eu–Eu distances lead to slower spin–spin relaxation rates.^[16] In addition to Cp^* , the sterically demanding ligand bis(trimethylsilyl)amide, $[\{(\text{CH}_3)_3\text{Si}\}_2\text{N}]^-$, was used as a precursor in preparing Eu^{2+} complexes. The six-coordinate complex $[\{(\text{CH}_3)_3\text{Si}\}_2\text{N}]_2\text{Eu}(\text{CH}_3\text{OCH}_2\text{CH}_2\text{-OCH}_3)_2$ (**5**) and the four-coordinate complex $[\{(\text{CH}_3)_3\text{Si}\}_2\text{-N}]_2\text{Eu}(\text{bpy})$ (**6**), where bpy is 2,2'-

bipyridine, are both soluble in THF, pentane, toluene, and 1,2-dimethoxyethane (DME).^[3] In general, the problem of insolubility in hydrocarbons is addressed by using sterically demanding ligands to increase hydrophobicity and to prevent the formation of coordination polymers.^[9,14,15]

Phosphane complexes of Eu^{2+} have been investigated since the early 1980s and display unique structural and electronic properties.^[17–19] In some cases, phosphorus-containing ligands form dative bonds with Eu^{2+} in the presence of oxygen-containing bases.^[20] Templeton and co-workers reported the synthesis of phosphane complexes of Eu^{2+} : in their procedure, $\text{NaEu}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_3$ was prepared from EuI_2 and $\text{NaN}[\text{Si}(\text{CH}_3)_3]_2$ in diethyl ether, and the relatively weak donor ligand $[\text{N}(\text{Si}(\text{CH}_3)_3)_2]^-$ was displaced by a phosphorus-containing ligand such as 1,2-bis(dimethyl-phosphanyl)ethane (DMPE) to give a complex with an empirical formula of $\text{Eu}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_2(\text{DMPE})_{1.5}$.^[19] Another Eu^{2+} -containing phosphane complex was reported by the same group with Cp^* in place of $[\text{N}(\text{Si}(\text{CH}_3)_3)_2]^-$. The resulting complex, $\text{EuCp}^*_2(\text{DMPE})$ (**7**), was not soluble in noncoordinating solvents, potentially because of the role of DMPE in bridging complexes to form coordination polymers. To reduce the potential for aggregation, ethylene-bridged DMPE was replaced with methylene-bridged 1,2-bis(dimethylphosphanyl)methane (DMPM).^[21] As a result, complex $\text{EuCp}^*_2(\text{DMPM})$ (**8**) was isolated, but analogous complexes with monodentate phosphanes such as $\text{P}(\text{CH}_3)_3$ or $\text{P}(n\text{Bu})_3$ were not reported, likely because the steric bulk of these phosphanes prevented the formation of a coordinatively saturated metal ion.^[21] Another Eu^{2+} -containing phosphane complex was reported by Rabe and coworkers.^[18] Their four-coordinate, homoleptic Eu^{2+} -containing phosphane complex $\text{Eu}[\{\mu\text{-P}(t\text{Bu})_2\}_2\text{-Li}(\text{THF})_2]$ (**9**) assumes a heavily distorted tetrahedral geometry. The oxidation state of Eu in the complex was confirmed by ^{151}Eu Mössbauer spectroscopy with an isomer shift of -11.7 mms^{-1} as opposed to isomer shifts of $0\text{--}1 \text{ mms}^{-1}$ for compounds that contain Eu^{3+} (Figure 3).^[18] One interesting feature of this complex is that an alkali ion, Li^+ , interacts with the phosphorus in $\text{P}(t\text{Bu})_2$ and the oxygen in THF in a similar way to the structure of complex $\text{NaEu}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_3$, where Na^+ interacts with the nitrogen atom of $[\text{N}(\text{Si}(\text{CH}_3)_3)_2]^-$.^[15,18] Also, an agostic interaction between Eu^{2+} and the *tert*-butyl groups in $\text{P}(t\text{Bu})_2$ was observed in **9**.^[18] The authors postulated that this interaction is driven by the tendency of the metal to form a coordinatively saturated environment and also by crystal packing forces because this interaction is only observed in the solid state.^[15,18]

In addition to the softer C- and P-containing ligands, polyoxadiazamacrobicyclic ligands (cryptands) form stable complexes (cryptates) of Eu^{2+} (complexes **10–13**), which were first reported in the late 1970s. Cryptands are used to encapsulate Eu^{2+} to oxidatively stabilize this ion and enable studies of the luminescence properties of Eu^{2+} . Gansow and co-workers demonstrated the oxidative stabilization of Eu^{2+} , by using cyclic voltammetry, when the ion is bound by cryptands.^[22] This stabilization was attributed to a good fit of the Eu^{2+} ion into the cryptand cavity,^[22] and the thermodynamic stability constants ($\log K$) for some Eu^{2+} -containing cryptates were reported by Burns and Baes to be $10.2\text{--}13.0$.^[23] Besides the thermodynamic properties of these compounds, these Eu^{2+} -containing cryptates are substitutionally inert towards the Na^+ , Ba^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , and tetraethylammonium cations.^[24,25] Beyond stabilizing the Eu^{2+} ion thermodynamically and kinetically, cryptands also exclude a large number of solvent molecules from the inner sphere of the ion. This solvent exclusion is important because coordinated solvent molecules quench the luminescence of Eu^{2+} , thus this ion does not exhibit strong luminescence in aqueous solution at room temperature when not chelated.^[26]

In the 1990s, Eu^{2+} complexes with a wide variety of ligands were synthesized. Shore and co-workers reported Eu^{2+} -containing borohydrides $(\text{NH}_3)_x\text{Eu}(\text{B}_{10}\text{H}_{14})$,

$(\text{CH}_3\text{CN})_2\text{Eu}(\text{BH}_4)_2$, and $(\text{C}_5\text{H}_5\text{N})_{1.8}\text{Eu}(\text{BH}_4)_2$ as precursors for preparing metal borides.^[20,27] However, all complexes that contain borohydrides are unstable as solids and tend to decompose to produce *closo*- $[\text{B}_{10}\text{H}_{10}]^{2-}$.^[20] The conversion from Eu^{2+} borohydrides to Eu^{2+} borides was performed successfully at high temperatures ($> 200^\circ\text{C}$) under vacuum to obtain the stable boride phase EuB_6 .^[27] Although Eu^{2+} -containing complexes with borohydrides as ligands were successfully synthesized, the coordination modes of Eu^{2+} in these complexes were not fully explored because of the lack of X-ray crystallographic data. In addition to Eu^{2+} borohydrides, Eu^{2+} selenolates and tellurolates were also prepared. For example, $\text{Eu}[\text{ESi}\{\text{Si}(\text{CH}_3)_3\}_3]_2(\text{TMEDA})_2$ (**14**) and $[\text{Eu}\{\text{ESi}\{\text{Si}(\text{CH}_3)_3\}_3\}_2(\text{DMPE})_2]_2(\mu\text{-DMPE})$ (**15**) were reported by Arnold and co-workers; in these compounds TMEDA is $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ and E is Se or Te.^[28] The crystal structure of **15** reveals a seven-coordinate Eu^{2+} ion that is bridged by DMPE to form a dimeric complex that was not observed for the TMEDA-containing complex. The difference in coordination chemistry of the two complexes was attributed to the larger covalent radius of P relative to N and, consequently, a less crowded metal center in complex **15**.^[28]

The seminal studies of the coordination chemistry of Eu^{2+} from the 1960s through the 1990s built a foundation for the design of new ligands that will be driven by the functions of the resulting Eu^{2+} -containing complexes. While Eu^{2+} -containing clusters and polymers are reported in the literature,^[29–33] these compounds are not described in this review, because the focus of this review is recent advances in the coordination chemistry of discrete Eu^{2+} complexes. Synthetic strategies reported in the 21st century are presented, followed by a description of the reactivity and applications of the resulting Eu^{2+} -containing complexes.

Synthesis of Recent Eu^{2+} -Containing Complexes

The rapid increase in the reports on Eu^{2+} -containing complexes over the last two decades has resulted in the publication of several synthetic pathways to prepare these complexes (Scheme 1). These methods fall into three categories regarding the europium-based starting materials used: (1) metallic europium; (2) europium(III) salts including halides, triflates, oxides, or nitrates; (3) europium(II) halides. This section is organized on the basis of these three types of starting materials: oxidation of Eu metal, reduction of Eu^{3+} , and metathesis of Eu^{2+} .

Oxidation of Eu^0

Oxidation of Eu metal can be accomplished by activation of Eu^0 with Hg, iodine, or liquid ammonia, by redox trans-metallation, or by pseudo-Grignard-compound formation. It is crucial to perform this type of synthesis under an inert atmosphere, because Eu metal will oxidize uncontrollably in air to produce mixtures of Eu^{2+} - and Eu^{3+} -containing complexes.

Syntheses of Eu^{2+} complexes from Eu^0 often require activation. Mercury, which activates Eu^0 through amalgamation, was used to prepare the homoleptic and tetranuclear Eu^{2+} complex $\text{Eu}_4[(t\text{Bu})_2\text{pz}]_8$ (**16**) in which $(t\text{Bu})_2\text{pz}$ is 3,5-di-*tert*-butylpyrazolate (Figure 4).^[34] Structural elucidation of linear complex **16** revealed different coordination modes (η^2 , μ - η^5 : η^2 , and μ - η^2 : η^2) of the pyrazolate groups to Eu^{2+} . The outer Eu^{2+} ions are bonded in a η^2 fashion by the two terminal pyrazolate groups; a μ - η^5 : η^2 coordination mode is observed for the four pyrazolate groups that bridge the inner and outer Eu^{2+} ions; and a μ - η^2 : η^2 binding mode is exhibited by the two pyrazolate groups that bridge the two inner Eu^{2+} centers.^[34]

An alternative to Hg as an activating agent is iodine, which was reported to be crucial in the preparation of several lanthanide-based complexes including the dimeric $[\text{Eu}(\text{Odip})(\mu\text{-Odip})(\text{THF})_2]_2$ (**17**) in which Odip is 2,6-diisopropylphenolate.^[35] In addition to mercury and

iodine, dissolution in liquid ammonia can be used in the activation of Eu^0 . Such is the case in the preparation of Eu^{2+} -containing alkoxide $\text{Eu}[\text{OC}_6\text{H}_3\text{-2,6-(tBu)}_2]_2(\text{THF})_3 \cdot 0.75\text{C}_7\text{H}_8$ (**18**) and aryloxides $[\text{Eu}_4(\mu\text{-OC}_{10}\text{H}_7)_6(\text{OC}_{10}\text{H}_7)_2(\text{THF})_{10}] \cdot 2\text{THF}$ (**19**) and $\text{Eu}(\text{OC}_6\text{H}_4\text{OCH}_3)_2$ (**20**).^[36–38] Activation of Eu^0 by using liquid ammonia was also employed for the synthesis of $[\text{Eu}_2\{(\text{tBu})_2\text{pz}\}_4(\text{THF})_2]$, which is characterized by centrosymmetric Eu^{2+} centers bonded in $\mu\text{-}\eta^2\text{:}\eta^5$ and η^2 modes by the bridging and terminal pyrazolate ligands, respectively.^[39] These coordination modes can also be found in pyrazolate-based Eu^{2+} complex **16** and demonstrate the ability of pyrazolate ligands to coordinatively saturate Eu^{2+} . Liquid ammonia was also used in the one-pot synthesis of an organohydroborate complex of Eu^{2+} , $[(\text{THF})_4\text{Eu}\text{-}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2]$ (**21**), which features an agostic interaction between Eu^{2+} and a hydrogen atom in one of the hydroborate ligands. Structural and IR spectroscopic data suggest the presence of agostic interactions in solution and in the solid state, and these interactions may have influenced the *cis* arrangement of the hydroborate ligands in the octahedral complex.^[40]

In the preparation of Eu^{2+} complexes through redox transmetallation, mercury- and tin-based complexes are sometimes used as oxidants, and activating agents such as Hg are used to improve the yields of this type of synthesis. The preparation of the (perfluoroaryl)europium(II) complex $\text{Eu}(\text{C}_6\text{F}_5)_2(\text{OC}_4\text{H}_8)_5$ (**22**) entails the oxidation of Eu^0 by using bis(pentafluorophenyl)mercury, $\text{Hg}(\text{C}_6\text{F}_5)_2$, in THF. Complex **22**, characterized by a pentagonal bipyramidal geometry with axial C_6F_5 groups and five THF molecules in the equatorial position, has relatively long Eu–C bonds (2.82 Å); this is likely due to the inductive electron-withdrawing effect of the fluorine substituents of the two phenyl groups.^[41] The same oxidant, $\text{Hg}(\text{C}_6\text{F}_5)_2$, was used to prepare the homoleptic and dinuclear $\{\text{Eu}(\text{iPr}_2\text{pz})_2\text{-}(\text{iPr}_2\text{pzH})_2\}_2$ (**23**) in which iPr_2pz is 3,5-diisopropylpyrazolate. An X-ray crystal structure of pyrazolato Eu^{2+} complex **23** shows a different coordination mode ($\mu\text{-}\eta^5\text{:}\eta^1$) to Eu^{2+} by the bridging 3,5-diisopropylpyrazolate centers. This coordination mode of the bridging pyrazolate groups in addition to the η^1 binding mode of the terminal pyrazolate groups was ascribed to intramolecular hydrogen binding.^[42] It is worth noting that redox transmetallation reactions carried out in nonpolar solvents including toluene (for example, in the preparation of complex **23**) can produce homoleptic Eu^{2+} complexes. In addition to complexes **22** and **23**, $\text{Hg}(\text{C}_6\text{F}_5)_2$ was used as oxidant in the preparation of Eu^{2+} -containing complexes with tri-azanides as ligands $[\text{Dmp}(\text{Tph})\text{N}_3\text{EuC}_6\text{F}_5]$ (**24**) and $[\text{Eu}\{\text{N}_3\text{Dmp}(\text{Tph})\}_2]$ (**25**) in which Dmp is 2,6-[2,4,6-(CH_3)₃ C_6H_2]₂ C_6H_3 and Tph is 2-(2,4,6- $\text{iPr}_3\text{C}_6\text{H}_2$) C_6H_4 . Of particular note are the coordination modes of the ter-phenyl and biphenyl groups in complexes **24** and **25** that exhibit π -arene–Eu interactions with Eu–C distances of 3.088–3.233 and 3.011–3.311 Å in complex **24** and **25**, respectively. In complex **24**, both the mesityl ring of the terphenyl group and the triisopropylphenyl ring of the biphenyl moiety show an η^5 interaction with the metal, whereas in complex **25**, the mesityl rings of terphenyl groups exhibit η^5 and η^3 binding modes. The assignment of hapticity was based on the shortest metal–centroid separation or the smallest angle between the M–centroid vector and the normal of the arene plane.^[43,44]

When $\text{Hg}(\text{SCN})_2$ was used as oxidant, $[\text{Eu}(\text{NCS})_2\text{-}(\text{DME})_3]$ (**26**) was obtained from redox transmetallation with Eu^0 in DME, and bimetallic $[\text{Eu}(\text{NCS})_2(\text{THF})_4]_2$ (**27**) was obtained when THF was used as solvent. The crystal structure of the eight-coordinate **26** shows configurational isomers, and the relative amount of each isomer is dependent on temperature. Racemic mixtures in a single crystal can be obtained at lower temperature (5 °C), while a mixture of enantiomerically pure Λ (left-hand) or Δ (right-hand) products was observed in a single crystal at room temperature.^[45] The coordination environment in **27** features two bridging thiocyanate ligands and terminal THF molecules, adapting a distorted pentagonal bipyramidal geometry at each Eu^{2+} center.

Besides mercury-based oxidants, trialkyltin(IV) compounds were explored for redox transmetallation with Eu^0 . Either the trivalent $[\text{Eu}^{3+}(\text{Ph}_2\text{pz})_3(\text{DME})_2] \cdot 2\text{DME}$ (**28**) or the divalent *cis*- $[\text{Eu}^{2+}(\text{Ph}_2\text{pz})_2(\text{DME})_2]$ (**29**) can be made from the reaction of $\text{Sn}(\text{CH}_3)_3(\text{Ph}_2\text{pz})$, where Ph_2pz is 3,5-diphenylpyrazolate, with Eu^0 in DME by changing the amount of excess Eu^0 .^[46,47]

In contrast to redox transmetallation, the route toward the formation of a pseudo-Grignard compound has been successful in preparing Eu^{2+} complexes even without the use of Hg, iodine, or ammonia. Thiolate-containing complex $\text{Eu}(\text{SAr}^*)_2(\text{THF})_{0.5}$ (**30**), in which Ar^* is 2,6-[2,4,6-(*i*Pr) $_3\text{C}_6\text{H}_2$] $_2\text{C}_6\text{H}_3$, was prepared from Eu^0 , Ar^*SH , and 2-iodobenzotrifluoride.^[48] This thiolate complex is characterized by η^6 - π interactions of Eu^{2+} with two *o*-2,4,6-triisopropylphenyl rings of the terphenyl groups, as evidenced by IR spectroscopy and X-ray crystallography.^[48] Another example of a Eu^{2+} -containing complex that shows η^1 - π interactions with Eu^{2+} and was prepared from europium metal is $\text{Eu}(\text{Dpp})(\text{THF})_2$ (**31**), where Dpp is 2,6- $\text{Ph}_2\text{C}_6\text{H}_3$. Complex **31** was synthesized from Eu^0 and DppI in THF and exhibits a distorted tetrahedral geometry with two aryl ligands and two THF molecules.^[49]

While the oxidation of Eu^0 through activation of the metal surface, redox transmetallation, and formation of pseudo-Grignard compounds is used to prepare homo-metallic Eu^{2+} complexes, charge-separated and neutral heterobimetallic Eu^{2+} -containing complexes can also be synthesized from Eu^0 . Treatment of Eu^0 and another rare earth metal (Y^0 , Nd^0 , or Ho^0) with 2,6-diphenylphenol (OHdpp) at elevated temperature (190 °C) in the presence of Hg yielded charge-separated complexes $[\text{Eu}_2(\text{Oddp})_3][\text{Y}(\text{Oddp})_4]$ (**32**), $[\text{Eu}_2(\text{Oddp})_3][\text{Nd}(\text{Oddp})_4]$ (**33**), and $[\text{Eu}_2(\text{Oddp})_3][\text{Ho}(\text{Oddp})_4]$ (**34**). The Eu^{2+} centers in $[\text{Eu}_2(\text{Oddp})_3]^+$ are bridged by aryloxy ligands and have coordination modes of $\eta^4:\eta^2:\eta^1$ and $\eta^1:\eta^6:\eta^3$ with π -arene-Eu interactions.^[50] In contrast to the charge-separated complexes, heterobimetallic complexes $[\text{CaEu}(\text{Oddp})_4]$ (**35**), $[\text{SrEu}(\text{Oddp})_4]$ (**36**), and $[\text{BaEu}(\text{Oddp})_4]$ (**37**) were produced upon reaction of Eu^0 and an alkaline-earth metal (Ca^0 , Sr^0 , or Ba^0) with OHdpp at high temperatures (210–235 °C). However, when Eu^0 was treated with HODpp in the presence of MODpp ($\text{M} = \text{Na}^0$, K^0 , and Li^0) at elevated temperature (210 °C), heterobimetallic Eu^{2+} -containing complexes $[\text{NaEu}(\text{Oddp})_3] \cdot \text{PhCH}_3$ (**38**) and $[\text{KEu}(\text{Oddp})_3] \cdot 2.5\text{PhCH}_3$ (**39**) and the mixed-valent complex $[\text{Eu}_2(\text{Oddp})_3][\text{Eu}(\text{Oddp})_4]$ (**40**) were obtained. These heterobimetallic complexes also show π -arene-Eu interactions that coordinatively saturate Eu^{2+} . The coordination mode of the Eu^{2+} center is similar in **35** and **36** ($\eta^2:\eta^3$), while a different binding mode was observed in **37** ($\eta^3:\eta^5$). The coordination modes in the Eu^{2+} -containing complexes with alkaline metals are $\eta^4:\eta^2:\eta^1$ (complex **38**) and $\eta^3:\eta^1:\eta^1$ (complex **39**) and are similar to that of $[\text{Eu}_2(\text{Oddp})_3]^+$ in charge-separated complexes **32–34**.^[51] Structural data for the $[\text{Eu}_2(\text{Oddp})_3]^+$ unit in **40** depict aryloxides binding in $\eta^1:\eta^4:\eta^2$ and $\eta^3:\eta^2:\eta^3$ fashions.^[51] Purification of charge-separated or heterobimetallic complexes requires solvent extraction to remove the unreacted metal and homometallic coproducts.^[50,51]

Despite the propensity of Eu metal to undergo uncontrolled oxidation to both Eu^{2+} and Eu^{3+} , the use of Eu metal can produce modest to excellent yields (23–96%) in the preparation of Eu^{2+} -containing complexes. Also, activating Eu^0 with Hg has been shown to increase the yield of the desired Eu^{2+} complexes.

Reduction of Eu^{3+}

The reduction of Eu^{3+} by either a ligand that is also a reductant or by chemical or electrochemical methods is more common than the oxidation of Eu metal. Eu^{3+} halides, triflates, oxides, or nitrates are typically used as the precursors for the preparation of Eu^{2+} -

containing complexes with a variety of ligands including aryloxides, amino-diboranates, crown ethers, and cryptands.^[25,52–58] An example of a Eu^{2+} -containing complex that was prepared from Eu^{3+} chlorides with a reducing species is the dinuclear, distorted pentagonal bipyramidal complex $[\text{Eu}\{\text{H}_3\text{BN}-(\text{CH}_3)_2\text{BH}_3\}_2(\text{THF})_2]_2$ (**41**), which was obtained by using *N,N*-dimethylaminodiboranate as the reductant (Figure 5).^[52] However, the preparation of **41** produced mixtures of divalent and trivalent species.^[52] In contrast, only divalent species were obtained when EuI_2 was used as a precursor instead of EuCl_3 .^[52] Qi and co-workers used Eu^{3+} chlorides as starting materials and a Na–K alloy as reductant to prepare $[\text{LEu}(\text{HMPA})_2]_2(\text{THF})_4$ (**42**), in which L is 2,2'-methylene bis(6-*tert*-butyl-4-methylphenoxo) and HMPA is hexamethylphosphoric triamide. Complex **42** is characterized by two phenolate moieties bridging two Eu^{2+} atoms.^[53] Each Eu^{2+} in **42** adopts a distorted trigonal bipyramidal geometry and a slightly asymmetric bridging mode of the phenolate ligand. This asymmetry is also observed in the bond length of Eu–O: the axial Eu–O bond (2.44 Å) is shorter than the equatorial Eu–O bond (2.52 Å).^[53] Also, the variation of the Eu–O–C angles in **42** have been associated with the existence of agostic interactions in this coordinatively unsaturated complex.^[53] In addition to the use of Na–K alloy as a noncoordinating reductant in the preparation of Eu^{2+} -containing complexes, Zn was used as reductant in the synthesis of complexes **10** and Eu^{2+} –18-crown-6 (**43**) from Eu^{3+} triflate.^[54] The reduction of Eu^{3+} by Zn in the presence of 18-crown-6 or [2.2.2]cryptand was monitored by using the absorption bands at 250 and 330 nm, which were assigned to the Eu^{2+} species.^[54] Additionally, Eu^{3+} oxides serve as starting materials for preparing Eu^{2+} -containing complexes by electrochemical reduction. For example, Eu_2O_3 was reduced electrochemically in the syntheses of the Eu^{2+} complex of benzo-18-crown-6 and of triethanolamine.^[55,56] With the strategy of reducing Eu^{3+} , our laboratory prepared several Eu^{2+} -containing cryptates: **10, 11**, and **44–47**.^[57] In general, the advantage of using the reduction approach is that the metal source is air-stable, so the problem of surface oxidation is avoided. Nevertheless, the possibility of incomplete reduction of Eu^{3+} can limit the yield and purity of the desired Eu^{2+} -containing complexes.

Metathesis of Eu^{2+} Complexes

While the other synthetic methods involve redox reactions to obtain Eu^{2+} , the metathesis approach makes use of Eu^{2+} halides and alkali-metal-containing ligands as precursors to generate the desired Eu^{2+} -containing complex. The metathesis reaction has been successful in preparing several Eu^{2+} -containing complexes including the bimetallic $[\text{Eu}_2(\text{Ap}^*\text{py})_3\text{I}(\text{THF})]$ (**48**), where Ap^*py is deprotonated 6-methylpyridin-2-yl-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine,^[59] a monometallic Eu^{2+} -containing *trans*-*N,N'*-dimethyl-*meso*-octaethylporphyrinogen complex (**49**),^[60] a Eu^{2+} -containing benzamidinate complex $[\text{Eu}\{\text{PhC}-\{\text{NSi}(\text{CH}_3)_3\}\{2,6-(i\text{Pr})_2\text{NC}_6\text{H}_3\}\}_2(\text{THF})_2]$ (**50**),^[61] a Eu^{2+} complex with olefin-substituted cyclopentadienyl ligands $[\{\text{C}_5(\text{CH}_3)_4\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}=\text{CH}_2\}_2\text{Eu}]$ (**51**),^[62] bis(diphosphanyl-amido) complex $[\{(\text{Ph}_2\text{P})_2\text{N}\}_2\text{Eu}(\text{THF})_3]$ (**52**),^[63] a Eu^{2+} complex containing bis(phosphinimino)methanide ligands $[\{(\text{CH}_3)_3\text{SiNPPH}_2\}_2\text{CH}\}\text{EuI}(\text{THF})_2]$ (**53**),^[64] an aminotroponimate complex of composition $[\{(\text{Pr})_2\text{ATI}\}-\text{Eu}\{\text{N}\{\text{Si}(\text{CH}_3)_2\}\}(\text{THF})_2]$ (**54**), where $(\text{Pr})_2\text{ATI}$ is *N*-isopropyl-2-(isopropylamino)troponimate,^[65] and a monometallic, heteroleptic complex $[(\text{DIP}_2\text{pyr})\text{Eu}(\text{THF})_3]$ (**55**), where DIP_2pyr is 2,5-bis[*(N*-2,6-diisopropylphenyl)iminomethyl]pyrrolyl (Figure 6).^[66] Complexes **48–55** were prepared by the metathesis reaction of $[\text{EuI}_2(\text{THF})_x]$, where labile THF, iodine, or both are displaced by the desired ligand. Complex **50** exhibits *cisoid* and *transoid* isomers with respect to the position of coordinated THF.^[61] The bidentate diphosphanyl-amides, $(\text{Ph}_2\text{P})_2\text{N}^-$, in complex **52** are η^2 coordinated to the Eu^{2+} center through the phosphorus and nitrogen atoms. The structure of the bimetallic Eu^{2+} -containing complex **53** displays the tridentate bis(phosphinimino)methanide ligands bound to Eu^{2+} through two nitrogen atoms and a methine carbon atom. Two of these ligands are coordinated to a Eu^{2+} center to form a

six-membered metallacycle with a twist boat conformation.^[64] When complex **53** was treated with $\text{K}\{\text{CH}(\text{PPh}_2\text{NSi}(\text{CH}_3)_2)\}$, the six-coordinate amido Eu^{2+} -containing complex $[\{\{(\text{CH}_3)_3\text{-SiNPPH}_2\}_2\text{CH}\}\text{Eu}\{(\text{Ph}_2\text{P})_2\text{N}\}(\text{THF})]$ (**56**) was obtained. As observed in **53**, the methine carbon atom was coordinated to Eu^{2+} in **56**, and the reported Eu–C (methine carbon) bond lengths were 2.945 Å and 2.878 Å for complexes **53** and **56**, respectively.^[64] In contrast to **53**, in which iodine bridged two Eu^{2+} centers, complex **56** is monometallic; a nonbridging iodine atom and THF occupy the axial positions and the tridentate $(\text{DIP}_2\text{pyr})^-$ ligand is bound to Eu^{2+} through its three nitrogen atoms to afford a distorted pentagonal pyramidal complex. As an alternative to the metathesis reaction of $[\text{EuI}_2(\text{THF})_x]$ in preparing Eu^{2+} -containing complexes, we used the commercially available EuI_2 to prepare cryptates **10**, **11**, and **57–59**.^[25,58] A similar europium halide salt was used to generate four-coordinate $[\text{Eu}\{(\text{ArN})_2\text{CN}(\text{iPr})_2\}_2]$ (**60**), where Ar is 2,6-diisopropylphenyl.^[67] Roesky and co-workers used a bimetallic Eu^{2+} -containing complex $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Eu}(\text{THF})(\mu\text{-I})_2]$ and NaBPh_4 as precursors to prepare $[\{\text{CH}(\text{PPh}_2\text{NSi}(\text{CH}_3)_3)_2\}\text{Eu}(\text{THF})_3]\text{BPh}_4$ (**61**).^[68] The resulting complex was used to prepare other Eu^{2+} -containing complexes by metathesis of the labile borate ligand.^[68] Another example of a borate-containing Eu^{2+} complex, $[\text{Cp}^*(\mu\text{-}\eta^6\text{:}\eta^1\text{-Ph})_2\text{-EuBPh}_2]$ (**62**), was prepared from $[\text{Eu}(\text{Cp}^*)_2]$ in the presence of $[\text{Et}_3\text{NH}][\text{BPh}_4]$. The structural motif of complex **62** features one coordinated Cp^* and two of the phenyl rings of BPh_4^- ligand in a $\mu\text{-}\eta^6\text{:}\eta^1$ binding mode, with the ligands in a pyramidal geometry around the coordination sphere of Eu^{2+} . While density functional theory (DFT) calculations predict a trigonal planar shape for complex **62**, the large size of Eu^{2+} prefers intermolecular packing over intramolecular packing in the solid state, and agostic interactions may also have contributed to this deviation of geometry.^[69] In general, with the metathesis approach of preparing Eu^{2+} -containing complexes, the presence of other oxidation states of Eu is not a problem as long as synthesis is performed under an inert atmosphere. The success of this third approach of metathesis relies on the completeness of the displacement of the alkali metal or a practical method of purification to remove byproduct salts. Steric limitations introduced by the incoming ligand may pose a problem in preparing the target Eu^{2+} complex.

Each of the three synthetic methods described here have distinct advantages and limitations, and each route must be carefully considered when choosing a method to synthesize a new complex. In addition, structural studies of the recently synthesized Eu^{2+} -containing complexes presented in this section demonstrate the rich coordination chemistry of Eu^{2+} . Differences in the coordination environment in Eu^{2+} -containing complexes can be attributed to steric and electronic effects of the coordinated ligands as well as the size and electronic properties of Eu^{2+} , which are responsible, in part, for the agostic interactions observed in some Eu^{2+} complexes.

The development of other Eu^{2+} -containing complexes with use of other divalent lanthanides in generating complexes with $\text{Ln}^{2+}\text{-Ga}^+$ or $\text{Ln}^{2+}\text{-Al}^+$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}, \text{or Tm}$) bonds is an active area of research.^[70–72] The applications of these compounds as reductants are currently being explored.^[70]

Applications of Eu^{2+} -Containing Complexes

The growing interest in Eu^{2+} -containing complexes stems from their unique catalytic, photophysical, and magnetic properties. The remainder of this review describes the use of Eu^{2+} -containing complexes in four different applications.

Reductants

Eu^{2+} is a one-electron reductant for many systems. However, it was reported that a bimetallic Sm^{2+} -containing complex has the potential to be a two-electron reductant per

molecule.^[73] This discovery led to the pursuit of divalent lanthanide species, including Eu^{2+} -containing complexes, that could act as multielectron reductants. This active area of research is important in establishing a more complete understanding in the reduction chemistry of Eu^{2+} . Lee and co-workers reported Eu^{2+} -containing complex **50** that serves as a one-electron reductant to diphenyldichalcogenide PhSeSePh to produce $[\text{Eu}\{\text{PhC}\{\text{NSi}(\text{CH}_3)_3\}\{2,6-(i\text{Pr})_2\text{-NC}_6\text{H}_3\}\}_2(\mu\text{-SePh}_2)]_2$ (**63**), in which the two Eu^{3+} centers are bridged by diphenyl diselenides (Figure 7).^[61] Each Eu^{3+} ion in **63** assumes a distorted octahedral geometry and is coordinated by two η^2 -bound benzamidinate ligands. However, when the same Eu^{2+} -containing bisamidinate complex was allowed to react with diphenyl ditellurides and iodine, both reactions were unsuccessful, indicating that the reducing strength of Eu^{2+} was not sufficient to reduce diphenylditellurides and iodine.^[61] Also, in the case of the macrocyclic ligand system *trans*-*N,N'*-dimethyl-*meso*-octa-ethylporphyrinogen, the Eu^{2+} -containing complex cannot reduce *tert*-butyl-1,4-diazabuta-1,3-diene (*t*Bu-DAB).^[60] However, the analogous Sm^{2+} complex forms a bimetallic complex when reacted with *t*Bu-DAB.^[60] The formation of the bimetallic Sm^{3+} complex bridged by the reduced $[\text{tBu-DAB}]^{2-}$ is driven by the reducing power of Sm^{2+} towards *t*Bu-DAB, but the steric constraints due to the bulky *tert*-butyl moieties makes this reaction reversible.^[60] Because Eu^{2+} has a more positive $\text{Ln}^{2+}/\text{Ln}^{3+}$ oxidation potential (-0.35 V vs. NHE) than Sm^{2+} (-1.55 V vs. NHE), the driving force to form an analogous bimetallic Eu^{3+} complex is hindered, presumably because the reducing strength of Eu^{2+} is not sufficient to reduce *t*Bu-DAB. These examples of controlled redox potential could be useful in selective reductions during multistep syntheses and for developing the first Eu^{2+} -containing complex that could act as multielectron reductant.

An important factor that can control the reducing properties of Eu^{2+} is the nature of the ligands. As an example, the reaction with $\text{Cp}^*_2\text{Eu}(\text{OEt}_2)$ with C_6F_5 -substituted diazabutadiene (DADC_6F_5)⁻ led to the oxidation of Eu^{2+} and formation of the radical anion (DADC_6F_5)^{•-}.^[74] The presence of Eu^{3+} in the resulting complex was demonstrated by crystallographic data, magnetic susceptibility measurements, and IR spectroscopy. The electron-withdrawing characteristic of the C_6F_5 moiety and its proximity to the metal center is likely the cause of the facile oxidation of Eu^{2+} . On the other hand, neither oxidation of Eu^{2+} nor formation of radical anion was observed when *tert*-butyl-substituted diazabutadiene was used.^[74] In general, the diazabutadienyl ligand can have rich redox chemistry when coupled with Eu^{2+} if this ligand is modified by using substituents of different electronic properties.

Polymerization Initiators

As discussed in the previous section, ligands can influence the rich reduction chemistry of Eu^{2+} , and the resulting complex can play an important role in several applications including polymer chemistry. In the preparation of polymers, Eu^{2+} -containing complexes can act as electron-transfer agents to initiate several polymerization processes. An example of this application is the activity of several Eu^{2+} -containing complexes that contain indenyl ligands in the initiation of the polymerization of methyl methacrylate (MMA) and ϵ -caprolactone.^[11,12]

Methyl Methacrylate Polymerization

Eu^{2+} -containing complexes **64–73**, which contain functionalized indenyl ligands are used in the polymerization of MMA (Figure 8).^[11,75–77] The activity of these complexes in polymerizations and the stereochemistries of the resulting polymers are dependent on temperature and solvent (Figure 7). High activity is observed at low temperatures (-30 to -60 °C for complexes **64** and **65**; 0 to -60 °C for complexes **66–69**, **72**, and **73**; -30 to -45 °C for complexes **70** and **71**), and these complexes have solvent-dependent activities.

Complexes **64**, **65**, and **72** have high activities when THF or dimethoxyethane is used as solvent instead of toluene. Complex **66** has high activity in dimethoxyethane, THF, and toluene; **67** shows good activity in THF; and complexes **68**, **69**, and **73** have high activity in dimethoxyethane. The molecular weights of the resulting MMA polymers are high (up to 443 kDa) at low temperatures, which indicates that chain propagation is favored at low temperatures.^[11,75–77] The mechanism of MMA polymerization was postulated to be initiated through reductive dimerization of MMA by electron transfer from Eu^{2+} , which results in the formation of Eu^{3+} enolates.^[11,75–77] Propagation did not go through an insertion mechanism, because the indenyl ligand was not detected on the polymer chains by ^1H NMR spectroscopy.^[11,76]

The stereochemistry of the MMA polymers was determined by ^1H NMR spectroscopy. The majority of the MMA polymers produced by using Eu^{2+} -containing functionalized indenyl complexes **64**, **65**, **72**, and **73** as initiators is syndiotactic.^[11,77] However, when complexes **66–68** were used in dimethoxyethane or THF, a 1:1:1 ratio of isotactic, syndiotactic, and atactic polymers was obtained. However, predominantly syndiotactic polymers were obtained when using **66** in toluene, and a decrease in the ratio of syndiotactic to isotactic polymers was observed with **70** when the solvent was changed from THF or dimethoxyethane to toluene, which suggests that a solvent effect influences the stereochemistry of these polymers. The presence of several tacticities in the synthesized polymers was attributed to the *rac/meso* interconversion, which is favored by solvents including THF and dimethoxyethane.^[77] While the stereochemistry of the polymers showed dependency on the solvent used, it is still unclear whether this stereoregularity is influenced by the nature of the initiator, specifically by the metal or ligands. A similar study that uses different initiators (for example, different divalent lanthanide metal ions or a ligand system other than indene compounds) could answer this question.

Ring-Opening Polymerization of ϵ -Caprolactone

Eu^{2+} -containing complexes **74–79**, which contain indenyl, fluorenyl, and iminopyrrolyl ligands, showed catalytic activity in the ring-opening polymerization of ϵ -caprolactone.^[12,78–80] With these catalysts, high activity is observed at high temperatures (0 to 30 °C for complexes **75** and **76**; –30 to 60 °C for complex **74**; 0 to 60 °C for complex **77**; and 30 to 60 °C for complexes **78** and **79**), and the activities of these complexes depend on the solvent. Complexes **77–79** have high activities when THF or toluene is the solvent; complex **74** exhibits high activity in dimethoxyethane, THF, and toluene, and **75** and **76** show good activity in toluene. Furthermore, the steric bulk of the substituents in the ligands may have an effect on the activity of the complexes and the molecular weights of the resulting polymers. When the silyl substituent in the furfuryl- or tetrahydrofurfuryl-functionalized indenyl ligands of complexes **75** and **76** was absent, the two complexes were not active. However, it is not clear what the role of the silyl substituent is in the polymerization process.^[78] The use of more sterically bulky ligands in **79** relative to the ligands in **78** has been implicated to affect the chain propagation process, thus affecting the molecular weights of the polymers.^[80] Wang and co-workers proposed that the polymerization of ϵ -caprolactone is initiated by the formation of Eu^{3+} -containing alkoxyl radical species formed from the oxidation of the Eu^{2+} metal center (Scheme 2).^[12] The alkoxyl radical species is believed to take a second Eu^{2+} -containing complex and produce a bimetallic Eu^{3+} -containing complex that is bridged by the opened caprolactone.^[12] Subsequently, chain propagation occurs when subsequent molecules of ϵ -caprolactone are added to the Eu^{3+} complex by a coordination–insertion process.^[12]

Because the role of the ligands on the polymerization of MMA and ϵ -caprolactone has yet to be elucidated, several Eu^{2+} complexes, [$\{\eta^5\text{-}\eta^1\text{-}\{1\text{-(CH}_3\text{)}_3\text{Si-3-(C}_5\text{H}_9\text{OCH}_2\text{)-C}_9\text{H}_5\}\}_2\text{Eu}$]

(**80**),^[81] $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_9\text{OCH}_2\text{C}_{13}\text{H}_8)_2\text{Eu}]$ (**81**),^[82] and $[(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_{10}\text{NCH}_2\text{CH}_2\text{C}_{13}\text{H}_8)_2\text{Eu}]$ (**82**),^[82] containing functionalized indenyl and fluorenyl ligands were investigated in terms of their activity towards MMA and ϵ -caprolactone polymerization. The silyl substituent in the indenyl ligands in complex **80** is likely a key factor in the two polymerization processes.^[81] Without the silyl substituent in **80**, no activity was observed under any reaction conditions.^[81] However, high activity was observed with **80** for both MMA and ϵ -caprolactone polymerizations. The effect of the ligand is also evident in the case of complexes **81** and **82**. Complex **81** with *N*-piperidineethyl-functionalized fluorenyl ligands has higher activity in ϵ -caprolactone polymerization than complex **81** with tetrahydro-2*H*-pyranil ligands under the same reaction conditions. However, this ligand effect was not observed on the polymerization of MMA.

In general, Eu^{2+} -containing complexes that have fluorenyl ligands are more effective as catalysts for both MMA and ϵ -caprolactone polymerizations than indenyl ligands with similar substituents. While Eu^{2+} -containing complexes **64–82** initiate the polymerization of MMA or ϵ -caprolactone, it would be useful to investigate the mechanistic role of the different ligands in the initiation. Also, exploration of a broader ligand system would enable an in-depth understanding of how to control better the properties of the synthesized polymers. Although a Eu^{2+} complex has been used in the cyclotrimerization of isocyanates, the scope of the ligands used is still limited.^[83] These ligand-centered studies would expand our understanding of the reduction chemistry of Eu^{2+} and its application to synthetic and polymer chemistry.

Luminescent Complexes

Aside from the rich reduction properties of Eu^{2+} , this ion produces complexes that are luminescent both in solution and in the solid state. Current research efforts are directed towards developing Eu^{2+} -containing complexes that have high luminescence efficiency.

The luminescence of uncomplexed Eu^{2+} and Eu^{3+} in protic solvents is quenched by the O–H oscillators of coordinated solvent molecules.^[84] Thus, macrocyclic ligands including crown ethers and cryptands are used to encapsulate Eu^{2+} for protecting this ion from luminescence quenching by solvent molecules. The luminescence properties of Eu^{2+} -containing crown ethers, azacrown ethers, cryptands, and polymers were reviewed by Adachi and co-workers in 1998.^[6] Since then, efforts have focused on developing luminescent complexes with high quantum yields by introducing functional groups into macrocyclic ethers or by using other ligands that better encapsulate Eu^{2+} .^[85–88] There is also a growing interest in the comparison of spectroscopic properties of Eu^{2+} in the solid state to Eu^{2+} -containing complexes in solution.

A variety of functional groups have been used to study the contribution of antenna effects and conjugated π systems on the luminescence efficiency of Eu^{2+} -containing complexes.^[86–87] Pyridine groups, known for exhibiting an antenna effect in Eu^{3+} -containing complexes, were introduced into 18-crown-6. When bis(pyridino)-18-crown-6 was complexed with Eu^{2+} , the emission of the complex in the solid state was quenched at room temperature, and only a weak emission at 430 nm was observed at 77 K, which is typical for Eu^{2+} -containing crown ethers.^[86] This quenching is likely due to the energy transfer from the excited-state, quasi-5d energy level of Eu^{2+} to the π^* levels of pyridine, and this quenching was not observed when unfunctionalized 18-crown-6 ligand **83** was used.^[86] However, a blue luminescence was observed when benzo-15-crown-5 **84** and benzo-18-crown-6 **85** were used as ligands.^[54,87] The Eu^{2+} -containing complex with benzo-15-crown-5 is characterized by a Eu^{2+} metal center that is sandwiched by two benzo-15-crown-5 ligands.^[86] In the solid state, Eu^{2+} -**85** shows an emission peak that is

similar to that observed in methanol at room temperature. This observation is also true for Eu^{2+} -containing 15-crown-5 compound **Eu-86**. These observations suggest that similar structures exist in the solid state and in solution.^[88] The mean lifetime of the excited state of **Eu-84** at room temperature is 0.65 μs in the solid state and 0.14 μs in methanol (Table 1).^[87] This difference in excited state lifetime is likely due to the additional relaxation processes caused by the methanol O–H oscillators.^[87] Furthermore, a phenyl moiety in the crown ether might contribute to a reduction in the lifetime, because this moiety can rigidify the crown ether and lead to structural changes to make Eu^{2+} more exposed to luminescence quenchers relative to Eu^{2+} bound to unmodified crown ethers.^[6] Also, the cavity size of the crown ether affects the luminescence lifetime of the excited state. Among the three crown ethers studied, the cavity size of **86** is most efficient in reducing the number of coordinating anions or solvent molecules that decrease luminescence lifetime.^[88]

The search for ligands that could provide more complete encapsulation remains an active area of research in investigating the luminescence properties of Eu^{2+} . Along these lines, a nonmacrocyclic ligand, nitrotriacetate $[\text{N}(\text{CH}_2\text{COO})_3]^{3-}$, was tested for its luminescence properties when chelated to Eu^{2+} .^[85] An emission at 483 nm at 77 K was observed for the Eu^{2+} -containing complex with nitro-triacetate in the solid state, and this emission is in the wavelength range observed for Eu^{2+} -containing complexes of crown ethers that contain tertiary amines.^[85] The luminescence lifetime was shorter (< 0.1 μs) relative to those of Eu^{2+} -containing crown ethers.^[85]

In general, macrocyclic ligands with cavity sizes that closely match the ionic radius of Eu^{2+} are the best ligands to insulate Eu^{2+} from solvent-based luminescence quenchers. Rigidifying ligands by adding phenyl groups and the addition of substituents like pyridine lead to a decrease in luminescence emission. These factors should be taken into consideration when designing Eu^{2+} -based luminescent materials.

MRI Contrast Agents

In addition to the reducing and luminescence properties of Eu^{2+} , the magnetic properties of this ion are important in the development of Eu^{2+} -based contrast agents for magnetic resonance imaging (MRI). In the last two decades, research on the properties of Eu^{2+} that are relevant to MRI has been reported. A fast water-exchange rate and a ground state isoelectronic to Gd^{3+} are properties that make Eu^{2+} an excellent candidate for use as a contrast agent for MRI.^[89] This area started when Merbach and co-workers reported the fast water-exchange rate of the Eu^{2+} aqua ion, which is in the order of 10^9 s^{-1} . After detailed mechanistic studies on the water exchange of the Eu^{2+} aqua ion,^[90] investigations of the nuclear and electronic relaxation processes of Eu^{2+} chelated by polyaminopolycarboxylates, commonly used with Gd^{3+} , were performed.^[91] When chelated to diethylenetriamine pentaacetate (DTPA), Eu^{2+} has a water-exchange rate that is three orders of magnitude faster than that of the clinically approved contrast agent $[\text{GdDTPA}]^{2-}$ (**87**) (Figure 9).^[91] In addition to the water-exchange rate, other molecular parameters, including rotational correlation time and electronic spin relaxation time, are important factors that influence the efficiency of contrast agents, known as relaxivity. For example, despite the fast water-exchange of $[\text{EuDTPA}]^{3-}$ (**88**), the reported relaxivity of **88** at 20 MHz is 20% lower than that of **87**, because relaxivity is influenced by fast rotation and by fast electronic spin relaxation.^[91] The same observation was implicated for the higher relaxivity of Eu^{2+} -containing 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate $[\text{Eu-DOTA}]^{2-}$ (4.74 $\text{mM}^{-1} \text{ s}^{-1}$) than that of $[\text{EuDTPA}]^{3-}$ (3.49 $\text{mM}^{-1} \text{ s}^{-1}$) at 20 MHz and 298 K.^[92] Results with other Eu^{2+} -containing complexes indicate that the unfavorable fast electronic spin relaxation rate is not observed with all Eu^{2+} complexes.^[91,93] Tóth and co-workers reported that the electron paramagnetic resonance line widths of **10** are narrower by a factor of 8–10 relative

to those of **88**, which indicates a slower electronic spin relaxation of Eu^{2+} in cryptate **10** relative to that in **88**.^[94] Consequently, the observed electronic spin relaxation for Eu^{2+} -containing cryptates does not limit relaxivity. In addition to slow electronic spin relaxation, this Eu^{2+} -containing cryptate has a fast water-exchange rate (10^8 s^{-1}) and contains two inner-sphere water molecules in a ten-coordinate complex.^[94] These properties are promising because they present an opportunity to develop Eu^{2+} -containing cryptates as effective contrast agents for MRI. A review of the similarities and differences in terms of these molecular parameters for several Eu^{2+} - and Gd^{3+} -containing complexes and their implications on research in MRI contrast agents was written by Merbach and co-workers in 2001.^[93]

While Eu^{2+} has properties that make it a candidate for use as a contrast agent for MRI, its propensity to get oxidized prevents in vivo applications.^[57] We have demonstrated that Eu^{2+} can be oxidatively stabilized by using coordination chemistry principles, including hard–soft acid–base theory, to the extent that it is more oxidatively stable than Fe^{2+} in hemoglobin.^[57] These studies raised the possibility of using Eu^{2+} -containing cryptates for in vivo applications.

In addition to using modified cryptands as ligands to stabilize Eu^{2+} , we investigated the relaxivity of several Eu^{2+} -containing cryptates **10–11** at different field strengths (1.4, 3, 7, 9.4, and 11.7 T).^[25,58] These cryptates showed higher relaxivity at higher fields (7 and 9.4 T) than at lower fields (1.4 and 3 T), unlike common Gd^{3+} -containing contrast agents.^[25,58] While high relaxivity is a requirement for effective contrast agents, other properties including kinetic stability need to be considered for utility in vivo. We demonstrated that Eu^{2+} -containing cryptates **10** and **11** are stable to transmetallation in the presence of endogenous ions such as Ca^{2+} , Mg^{2+} , and Zn^{2+} ,^[25] and we are currently investigating the thermodynamic stability and toxicity of several other Eu^{2+} -containing cryptates.

Conclusions

The rapid increase in the number of Eu^{2+} -containing complexes reported in the past few decades has paved the way to making these complexes commonplace in coordination chemistry. New information regarding the stability and utility of Eu^{2+} -containing complexes with a variety of ligands has opened new frontiers in lanthanide chemistry. Careful control of ligand properties produces Eu^{2+} -containing complexes that are useful in synthetic, materials, and medicinal applications.

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References

1. Huheey, JE.; Keiter, EA.; Keiter, RL. *Inorganic Chemistry: Principles of Structure & Reactivity*. 4. HarperCollins College Publishers; New York: 1993. p. 601
2. Evans WJ. *Coord Chem Rev.* 2000; 206–207:263–283.
3. Tilley TD, Zalkin A, Andersen RA, Templeton DH. *Inorg Chem.* 1981; 20:551–554.
4. Adin A, Sykes AG. *Nature.* 1966; 209:804–804.
5. Sabbatini N, Ciano M, Dellonte S, Bonazzi A, Bolletta F, Balzani V. *J Phys Chem.* 1984; 88:1534–1537.
6. Jiang J, Higashiyama N, Machida K, Adachi G. *Coord Chem Rev.* 1998; 170:1–29.

7. Hoffman MV. *J Electrochem Soc.* 1971; 118:933–936.
8. Ryan FM, Lehmann W, Feldman DW, Murphy J. *J Electrochem Soc.* 1974; 121:1475–1481.
9. Tilley TD, Andersen RA, Spencer B, Ruben H, Zalkin A, Templeton DH. *Inorg Chem.* 1980; 19:2999–3003.
10. Evans WJ. *J Organomet Chem.* 2002; 652:61–68.
11. Wang S, Zhou S, Sheng E, Xie M, Zhang K, Zheng L, Feng Y, Mao L, Huang Z. *Organometallics.* 2003; 22:3546–3552.
12. Zhou S, Wang S, Sheng E, Zhang L, Yu Z, Xi X, Chen G, Luo W, Li Y. *Eur J Inorg Chem.* 2007:1519–1528.
13. Fischer EO, Fischer H. *Angew Chem.* 1964; 76:52. *Angew Chem Int Ed Engl.* 1964; 3:132–133.
14. Nief F. *Dalton Trans.* 2010; 39:6589–6598. [PubMed: 20631944]
15. Tilley TD, Andersen RA, Zalkin A. *Inorg Chem.* 1984; 23:2271–2276.
16. Williams AF, Grandjean F, Long GJ, Ulibarri TA, Evans WJ. *Inorg Chem.* 1989; 28:4584–4588.
17. Rabe GW, Yap GPA, Rheingold AL. *Inorg Chim Acta.* 1998; 267:309–311.
18. Rabe GW, Yap GPA, Rheingold AL. *Inorg Chem.* 1997; 36:3212–3215. [PubMed: 11669982]
19. Tilley TD, Andersen RA, Zalkin A. *J Am Chem Soc.* 1982; 104:3725–3727.
20. White JP III, Shore SG. *Inorg Chem.* 1992; 31:2756–2761.
21. Tilley TD, Andersen RA, Zalkin A. *Inorg Chem.* 1983; 22:856–859.
22. Gansow OA, Kausar AR, Triplett KM, Weaver MJ, Yee EL. *J Am Chem Soc.* 1977; 99:7087–7089.
23. Burns JH, Baes CF. *Inorg Chem.* 1981; 20:616–619.
24. Yee EL, Gansow OA, Weaver MJ. *J Am Chem Soc.* 1980; 102:2278–2285.
25. Garcia J, Kuda-Wedagedara ANW, Allen MJ. *Eur J Inorg Chem.* 2012:2135–2140. [PubMed: 22639543]
26. Adachi G-Y, Tomokiyo K, Sorita K, Shiokawa J. *J Chem Soc, Chem Commun.* 1980:914–915.
27. White JP III, Deng H, Shore SG. *Inorg Chem.* 1991; 30:2337–2342.
28. Cary DR, Arnold J. *Inorg Chem.* 1994; 33:1791–1796.
29. Maudez W, Meuwly M, Fromm KM. *Chem Eur J.* 2007; 13:8302–8316. [PubMed: 17639546]
30. Ple nik CE, Liu S, Chen X, Meyers EA, Shore SG. *J Am Chem Soc.* 2004; 126:204–213. [PubMed: 14709086]
31. Rybak JC, Müller-Bushbaum K. *Z Anorg Allg Chem.* 2010; 636:126–131.
32. Janicki R, Mondry A, Starynowicz P. *Z Anorg Allg Chem.* 2005; 631:2475–2477.
33. Hou Z, Zhang Y, Nishiura M, Wakatsuki Y. *Organometallics.* 2003; 22:129–135.
34. Deacon GB, Gitlits A, Roesky PW, Bürgstein MR, Lim KC, Skelton BW, White AH. *Chem Eur J.* 2001; 7:127–138. [PubMed: 11205004]
35. Hamidi S, Deacon GB, Junk PC, Neumann P. *Dalton Trans.* 2012; 41:3541–3552. [PubMed: 22315047]
36. Carretas J, Branco J, Marçalo J, Domingos Â, Pires de Matos A. *Polyhedron.* 2003; 22:1425–1429.
37. Carretas J, Branco J, Marçalo J, Isolani P, Domingos A, de Matos AP. *J Alloys Compd.* 2001; 323–324:169–172.
38. Carretas J, Branco J, Marçalo J, Valente N, Waerenborgh JC, Carvalho A, Marques N, Domingos Â, de Matos AP. *J Alloys Compd.* 2004; 374:289–292.
39. Hitzbleck J, O'Brien AY, Deacon GB, Ruhlandt-Senge K. *Inorg Chem.* 2006; 45:10329–10337. [PubMed: 17140242]
40. Chen X, Lim S, Ple nik CE, Liu S, Du B, Meyers EA, Shore SG. *Inorg Chem.* 2004; 43:692–698. [PubMed: 14731031]
41. Forsyth CM, Deacon GB. *Organometallics.* 2000; 19:1205–1207.
42. Hitzbleck J, Deacon GB, Ruhlandt-Senge K. *Eur J Inorg Chem.* 2007:592–601.
43. Hauber SO, Niemeyer M. *Inorg Chem.* 2005; 44:8644–8646. [PubMed: 16296814]
44. Lee HS, Niemeyer M. *Inorg Chem.* 2010; 49:730–735. [PubMed: 20014863]

45. Bakker JM, Deacon GB, Forsyth CM, Junk PC, Wiecko M. *Eur J Inorg Chem.* 2010;2813–2825.
46. Beaini S, Deacon GB, Hilder M, Junk PC, Turner DR. *Eur J Inorg Chem.* 2006;3434–3441.
47. Beaini S, Deacon GB, Delbridge EE, Junk PC, Skelton BW, White AH. *Eur J Inorg Chem.* 2008;4586–4596.
48. Niemeyer M. *Eur J Inorg Chem.* 2001;1969–1981.
49. Heckmann G, Niemeyer M. *J Am Chem Soc.* 2000; 122:4227–4228.
50. Deacon GB, Junk PC, Moxey GJ, Ruhlandt-Senge K, StPrix C, Zuniga MF. *Chem Eur J.* 2009; 15:5503–5519. [PubMed: 19360834]
51. Deacon GB, Junk PC, Moxey GJ. *Chem Asian J.* 2009; 4:1309–1317. [PubMed: 19585640]
52. Daly SR, Girolami GS. *Inorg Chem.* 2010; 49:4578–4585. [PubMed: 20392118]
53. Bao L, Yingming Y, Mingyu D, Yong Z, Qi S. *J Rare Earths.* 2006; 24:264–267.
54. Shinoda S, Nishioka M, Tsukube H. *J Alloys Compd.* 2009; 488:603–605.
55. Starynowicz P, Bukiety ska K, Gol b S, Ryba-Romanowski W, Sokolnicki J. *Eur J Inorg Chem.* 2002;2344–2347.
56. Starynowicz P. *J Alloys Compd.* 2001; 323–324:159–163.
57. Gamage NDH, Mei Y, Garcia J, Allen MJ. *Angew Chem Int Ed.* 2010; 49:8923–8925.
58. Garcia J, Neelavalli J, Haacke EM, Allen MJ. *Chem Commun.* 2011; 47:12858–12860.
59. Dietel AM, Döring C, Glatz G, Butovskii MV, Tok O, Schappacher FM, Pöttgen R, Kempe R. *Eur J Inorg Chem.* 2009;1051–1059.
60. Dick AKJ, Frey ASP, Gardiner MG, Hilder M, James AN, Junk PC, Powanosorn S, Skelton BW, Wang J, White AH. *J Organomet Chem.* 2010; 695:2761–2767.
61. Yao S, Chan HS, Lam CK, Lee HK. *Inorg Chem.* 2009; 48:9936–9946. [PubMed: 19757783]
62. Evans WJ, Perotti JM, Brady JC, Ziller JW. *J Am Chem Soc.* 2003; 125:5204–5212. [PubMed: 12708873]
63. Roesky PW. *Inorg Chem.* 2006; 45:798–802. [PubMed: 16411716]
64. Panda TK, Zulys A, Gamer MT, Roesky PW. *J Organomet Chem.* 2005; 690:5078–5089.
65. Datta S, Gamer MT, Roesky PW. *Organometallics.* 2008; 27:1207–1213.
66. Jenter J, Gamer MT, Roesky PW. *Organometallics.* 2010; 29:4410–4413.
67. Heitmann D, Jones C, Mills DP, Stasch A. *Dalton Trans.* 2010; 39:1877–1882. [PubMed: 20449435]
68. Wiecko M, Roesky PW. *Organometallics.* 2009; 28:1266–1269.
69. Evans WJ, Walensky JR, Furche F, DiPasquale AG, Rheingold AL. *Organometallics.* 2009; 28:6073–6078.
70. Jones C, Stasch A, Woodul WD. *Chem Commun.* 2009;113–115.
71. Wiecko M, Roesky PW. *Organometallics.* 2007; 26:4846–4848.
72. Gamer MT, Roesky PW, Konchenko SN, Nava P, Ahlrichs R. *Angew Chem.* 2006; 118:4558. *Angew Chem Int Ed.* 2006; 45:4447–4451.
73. Evans WJ, Clark RD, Ansari MA, Ziller JW. *J Am Chem Soc.* 1998; 120:9555–9563.
74. Moore JA, Cowley AH, Gordon JC. *Organometallics.* 2006; 25:5207–5209.
75. Sheng E, Zhou S, Wang S, Yang G, Wu Y, Feng Y, Mao L, Huang Z. *Eur J Inorg Chem.* 2004;2923–2932.
76. Zhang K, Zhang W, Wang S, Sheng E, Yang G, Xie M, Zhou S, Feng Y, Mao L, Huang Z. *Dalton Trans.* 2004;1029–1037. [PubMed: 15252681]
77. Wang S, Feng Y, Mao L, Sheng E, Yang G, Xie M, Wang S, Wei Y, Huang Z. *J Organomet Chem.* 2006; 691:1265–1274.
78. Wu Y, Wang S, Qian C, Sheng E, Xie M, Yang G, Feng Q, Zhang L, Tang X. *J Organomet Chem.* 2005; 690:4139–4149.
79. Miao H, Wang S, Zhou S, Wei Y, Zhou Z, Zhu H, Wu S, Wang H. *Inorg Chim Acta.* 2010; 363:1325–1331.
80. Zhou S, Yin C, Wang H, Zhu X, Yang G, Wang S. *Inorg Chem Commun.* 2011; 14:1196–1200.

81. Wang S, Wang S, Zhou S, Yang G, Luo W, Hu N, Zhou Z, Song HB. *J Organomet Chem.* 2007; 692:2099–2106.
82. Wei Y, Yu Z, Wang S, Zhou S, Yang G, Zhang L, Chen G, Qian H, Fan J. *J Organomet Chem.* 2008; 693:2263–2270.
83. Zhu X, Fan J, Wu Y, Wang S, Zhang L, Yang G, Wei Y, Yin C, Zhu H, Wu S, Zhang H. *Organometallics.* 2009; 28:3882–3888.
84. Kropp JL, Windsor MW. *J Chem Phys.* 1963; 39:2769–2770.
85. Starynowicz P. *Polyhedron.* 2003; 22:2761–2765.
86. Christoffers J, Starynowicz P. *Polyhedron.* 2008; 27:2688–2692.
87. Starynowicz P, Bukiety ska K. *Eur J Inorg Chem.* 2002:1835–1838.
88. Starynowicz P. *Polyhedron.* 2003; 22:337–345.
89. Caravan P, Merbach AE. *Chem Commun.* 1997:2147–2148.
90. Caravan P, Tóth É, Rockenbauer A, Merbach AE. *J Am Chem Soc.* 1999; 121:10403–10409.
91. Seibig S, Tóth É, Merbach AE. *J Am Chem Soc.* 2000; 122:5822–5830.
92. Burai L, Tóth É, Moreau G, Sour A, Scopelliti R, Merbach AE. *Chem Eur J.* 2003; 9:1394–1404. [PubMed: 12645029]
93. Tóth É, Burai L, Merbach AE. *Coord Chem Rev.* 2001; 216–217:363–382.
94. Burai L, Scopelliti R, Tóth É. *Chem Commun.* 2002:2366–2367.

Biographies

Joel Garcia received his B.S. in Chemistry from the University of the Philippines in Diliman in 2004. During his undergraduate years, he studied the electrocatalytic activity of rhenium(I)-containing 2,3-bis(2'-pyridyl)benzoquinoxaline, 2,3-bis(2'-pyridyl)pyrazine and 2,3-bis(2'-pyridyl)quinoxaline complexes under the supervision of Dr. Girlie Sison. He moved to Wayne State University to join the Allen group for his Ph.D. studies and is studying the properties of europium(II)-containing cryptates and their relevance to magnetic resonance imaging.

Matthew J. Allen, received his B.S. in Chemistry from Purdue University in 1998, where he did undergraduate research with Jillian Buriak, and his Ph.D. from the California Institute of Technology in 2004, where he studied gadolinium-containing complexes with Thomas Meade. Matt then moved to the University of Wisconsin–Madison where he was an NIH postdoctoral fellow in the laboratories of Laura Kiessling and Ronald Raines. In 2008, he

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Figure 1. Relative reduction potentials for $\text{Ln}^{3+} \rightarrow \text{Ln}^{2+}$ (V vs. NHE); values from ref.^[2]

Figure 2.
Structures of Eu^{2+} -containing complexes **1–15**.

Figure 3. ^{151}Eu Mössbauer spectrum of **9** at 4.2 K. Reprinted with permission from ref.^[18] Copyright (1997) American Chemical Society.

Figure 4. Structures of Eu^{2+} -containing complexes **16–19**, **21–28**, **30–35**, **38**, and **40**, which were prepared by the oxidation of Eu^0 .

Figure 5.

Structures of Eu²⁺-containing complexes **41–47**, which were synthesized by the reduction of Eu³⁺.

Figure 6.

Structures of Eu^{2+} -containing complexes **48–62**, which were obtained from the metathesis of Eu^{2+} -containing complexes.

Figure 7.
Structure of Eu^{2+} -containing reductant **63**.

Figure 8. Structures of Eu^{2+} -containing complexes **64–82**, which were used as polymerization initiators.

Figure 9.
Structures of complexes **87** and **88**.

Oxidation of Eu metal

or

or

Reduction of Eu³⁺

or

Metathesis of Eu²⁺ complexes **Scheme 1.**

Synthetic methods for obtaining Eu²⁺-containing complexes arranged by source of europium where L is a ligand, N is either Hg or Sn, and M is an alkali metal ion.

Scheme 2.

Proposed mechanism of polymerization of ϵ -caprolactone.^[12] Ind is the indenyl ligand. Adapted with permission from ref.^[12] Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.

Table 1

Luminescence properties of Eu²⁺-containing complexes in methanol solution and in the solid state (room temperature and 77 K).^[6,54,87,88]

Complex	Maximum emission band (nm) (solid)	Maximum emission band (nm) (methanol)	Luminescence lifetime (μs) (solid)	Luminescence lifetime (μs) (methanol)
Eu ²⁺ - 83	ND (r.t. ^[a]), 411.5 (77 K)	ND ^[a]	ND, ND	ND
Eu ²⁺ - 84	422 (r.t.), 427 (77 K)	417	0.65 (r.t.), 0.59 (77 K)	0.14
Eu ²⁺ - 85	425 (r.t.), 430 (77 K)	447	8.34 (r.t.), 8.01 (77 K)	0.028
Eu ²⁺ - 86	433 (r.t.), 417 (77 K)	432	0.922 (r.t.), 0.745 (77 K)	0.800

^[a] Legend: r.t. is room temperature, ND is no data available.