Developments in the Coordination Chemistry of Europium(II)

Joel Garcia[a] and Matthew J. Allen*[a]

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Recent advances in the coordination chemistry of Eu2+ are reviewed. Common synthetic routes for generating discrete Eu2+-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 Eu2+ has led to an upsurge in the utilization of Eu2+-containing complexes in synthetic chemistry, materials science, and medicine.

Introduction

Properties of Eu2+

Among the divalent lanthanides, Eu2+ has the most accessible divalent oxidation state because of its half-filled 4f7 electronic configuration and, consequently, a high stabilization from exchange energy (Figure 1).[1] While Eu2+ is the most accessible of the divalent lanthanides, outside of the solid state it has a propensity to oxidize [Eu⁰(Eu³⁺/Eu²⁺) = −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 Eu²⁺-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]

![Figure 1. Relative reduction potentials for Ln³⁺→Ln²⁺ (V vs. NHE); values from ref.[2]](image)

Despite oxidation and oligomerization, which present obstacles to the preparation and characterization of Eu²⁺-containing complexes, the interesting catalytic, photophysical, and magnetic properties of this ion have spurred a great deal of research. The unique properties of Eu²⁺ are influ-

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 started as an assistant professor of chemistry at Wayne State University, where his group studies the chemistry of lanthanides in aqueous solution.
enced 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 Eu²⁺ 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 Eu²⁺ with V³⁺ of 0.013 m⁻¹ s⁻¹ (1.0 N HClO₄, 25 °C, ionic strength 2.0 M), while the rate constant for the reaction of Cr²⁺ with V³⁺ under the same conditions is 0.85 m⁻¹ s⁻¹.[4] The smaller rate constant observed for Eu²⁺ relative to that for Cr²⁺ 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 Eu²⁺ that stem from the lowest-energy and first-excited-state configurations of 4f² and 4f⁶5d¹, respectively.[5] While the 4f orbitals of Eu²⁺ remain largely unperturbed by the presence of ligands, the energy of the 5d orbitals is influenced readily by ligands. Consequently, the luminescence properties of Eu²⁺ 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 4f⁶5d¹ → 4f⁷ 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→4f transitions are observed, similar to those observed in the Eu³⁺ ion.[5] Beyond the unique luminescence properties of Eu²⁺, the f orbitals are responsible for the interesting magnetic characteristics of this divalent ion that include a high magnetic moment (7.63–8.43 μB) associated with seven unpaired electrons in an 8S⁷/₂ ground-state configuration.[3,9]

In addition to the desirable optical and magnetic properties of Eu²⁺, this ion displays interesting redox chemistry. Divalent lanthanides including Eu²⁺ 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 Eu²⁺-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 Eu²⁺.[12]

**Early Eu²⁺ Complexes**

Discrete Eu²⁺-containing complexes were reported as early as 1964.[13] However, the number of these complexes is small relative to their Eu³⁺ analogues, which form air-stable complexes with most electronegative atoms such as oxygen and nitrogen, partially because Eu³⁺ is a hard Lewis acid. Eu²⁺ is a softer Lewis acid than Eu³⁺ because of its lower charge density; consequently, Eu²⁺-containing complexes often include ligands with relatively soft atoms such as carbon and phosphorus.

Among the first discrete Eu²⁺-containing complexes prepared was the metallocene-like complex Cp₂Eu, 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 Cp*₂Eu(THF) (2) and Cp*₂Eu(THF)(Et₂O) (3). The Eu–ligand bonds of 2 and 3 are ionic in character as indicated by the isomer shifts of these complexes: [15] 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 Eu²⁺ halide complexes.[16] Moreover, the data obtained from the spherical relaxation model fits of the [12] Eu Mössbauer spectra of 2, 3, and [Cp*₂Eu(THF)(µ-I)] (4) in a solvent (alkane) induced 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, [(CH₃)₃Si]₂[N]⁻, was used as a precursor in preparing Eu²⁺ complexes. The six-coordinate complex [(CH₃)₃Si]₂[N]Eu(CH₃OCH₂CH₂-OCH₃)₂ (5) and the four-coordinate complex [(CH₃)₃Si]₂[N]₂Eu(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 Eu²⁺ 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 Eu²⁺ in the presence of oxygen-containing bases.[20] Templeton and co-workers reported the synthesis of phosphane complexes of Eu²⁺ in their procedure, NaEu[N(Si(CH₃)₃)₂]₃ was prepared from Eu₂ and Na[N(Si(CH₃)₃)₂] in diethyl ether, and the relatively weak donor ligand [N(Si(CH₃)₃)₂]⁻ was displaced by a phosphorus-containing ligand such as 1,2-bis(dimethylphosphanyl)ethane (DMPE) to give a complex with an empirical formula of Eu[N(Si(CH₃)₃)₂]₂(DMPE)₁.⁵⁻.[19] Another Eu²⁺-containing phosphane complex was reported by the same group with Cp* in place of [N(Si(CH₃)₃)₂]⁻. The resulting complex, EuCp*₂(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(methylphosphanyl)methane (DMPM).[21] As a result, complex EuCp*₂(DMMP) (8) was isolated, but analogous complexes with monodentate phosphanes such as P(CH₃)₃...
or P(nBu)₃ were not reported, likely because the steric bulk of these phosphanes prevented the formation of a coordinatively saturated metal ion.[21] Another Eu²⁺-containing phosphane complex was reported by Rabe and co-workers.[18] Their four-coordinate, homoleptic Eu²⁺-containing phosphane complex Eu[µ-P(tBu)₂]₂-Li(THF)]₂ (9) assumes a heavily distorted tetrahedral geometry. The oxidation state of Eu in the complex was confirmed by ¹⁵¹Eu Mössbauer spectroscopy with an isomer shift of −11.7 mm s⁻¹ as opposed to isomer shifts of 0–1 mm s⁻¹ for compounds that contain Eu³⁺ (Figure 3).[18] One interesting feature of this complex is that an alkali ion, Li⁺, interacts with the phosphorus in P(tBu)₂ and the oxygen in THF in a similar way to the structure of complex NaEu[N{Si(CH₃)₃}]₂, where Na⁺ interacts with the nitrogen atom of [N{Si(CH₃)₃}]⁻.[15,18] Also, an agostic interaction between Eu²⁺ and the tert-butyl groups in P(tBu)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
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$^{2+}$.

**Scheme 1.** Synthetic methods for obtaining Eu$^{2+}$-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.

Oxidation of Eu$^{0}$

Oxidation of Eu metal can be accomplished by activation of Eu$^{0}$ with Hg, iodine, or liquid ammonia, by redox metatllation, 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 homoletic and tetrameric Eu$^{2+}$ complex Eu$_4$[(Bu)$_2$pz]$_8$ (16) in which (Bu)$_2$pz is 3,5-di-tert-butylpyrazolate (Figure 4).[^134^] Structural elucidation of linear complex 16 revealed different coordination modes ($\eta^2$, $\mu$-$\eta^2$: $\eta^2$, and $\mu$-$\eta^2$: $\eta^2$) of the pyrazolate groups to Eu$^{2+}$. The outer Eu$^{2+}$ ions are bonded in a $\eta^2$ fashion by the two terminal pyrazolate groups; a $\mu$-$\eta^2$: $\eta^2$ coordination mode is observed for the four pyrazolate groups that bridge the inner and outer Eu$^{2+}$ ions; and a $\mu$-$\eta^2$: $\eta^2$ 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 sev-
eral lanthanide-based complexes including the dimeric \([\text{Eu(Odip)}(\mu\text{-Odip})(\text{THF})_2]_2\) (17) in which Odip is 2,6-di-isopropylphenolate\(^{[35]}\). In addition to mercury and iodine, dissolution in liquid ammonia can be used in the activation of \(\text{Eu}^0\). Such is the case in the preparation of \(\text{Eu}^{2+}\)-containing alkoxide \(\text{Eu}[\text{OC}_6\text{H}_3-2,6-(\text{tBu})_2]\_2(\text{THF})_2\cdot0.75\text{C}_7\text{H}_8\) (18) and aryloxides \(\text{Eu}_4(\mu\text{-OC}_{10}\text{H}_7)_6(\text{OC}_{10}\text{H}_7)_2(\text{THF})_{10}\cdot2\text{THF}\) (19) and \(\text{Eu}(\text{OC}_6\text{H}_4\text{OCH}_3)\_2\) (20).\(^{[36–38]}\) Activation of \(\text{Eu}^0\) by using liquid ammonia was also employed for the synthesis of \([\text{Eu}_2]\{(\text{tBu})_2\text{pz}\}_2(\text{THF})_2\], which is characterized by centrosymmetric \(\text{Eu}^{2+}\) centers bonded in \(\mu\eta^2:\eta^5\) and \(\eta^2\) modes by the bridging and terminal pyrazolate ligands, respectively.\(^{[39]}\) These coordination modes can also be found in pyrazolate-based \(\text{Eu}^{2+}\) complex 16 and demonstrate the ability of pyrazolate ligands to coordinatively saturate \(\text{Eu}^{2+}\). Liquid ammonia was also used in the one-pot synthesis of an organohydroborate complex of \(\text{Eu}^{2+}\), \([\text{THF}]_4\text{Eu-}\{\mu\text{-H}\}_2\text{BC}_{6}\text{H}_4[1,2]\) (21), which features an agostic interaction between \(\text{Eu}^{2+}\) 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 influ-
enced 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 Eu(C\(_6\)F\(_5\)\(_2\))(OC\(_6\)H\(_5\))\(_3\) \((22)\) entails the oxidation of Eu\(^0\) by using bis(pentafluorophenyl)mercury, Hg(C\(_6\)F\(_5\)\(_2\))\(_2\) in THF. Complex \(22\), characterized by a pentagonal bipyramidal geometry with axial C\(_6\)F\(_5\) 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 fluorene substituents of the two phenyl groups.\(^{[41]}\) The same oxidant, Hg(C\(_6\)F\(_5\)\(_2\))\(_2\), was used to prepare the homoleptic and dinuclear [Eu(Pr\(_2\)pz\(_2\)-\((iPr\(_2\)pz)\(_2\))\(_2\) \((23)\) in which Pr\(_2\)pz is 3,5-diisopropylpyrazolate. An X-ray crystal structure of pyrazolato Eu\(^{2+}\) complex \(23\) shows a different coordination mode (\(\mu_6\eta^1\pi^1\eta^1\)) to Eu\(^{2+}\) by the bridging 3,5-diisopropylpyrazolate centers. This coordination mode of the bridging pyrazolate groups in addition to the \(\eta^1\) binding mode of the terminal pyrazolate groups was ascribed to intramolecular hydrogen bonding.\(^{[42]}\) 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 \(23\), Hg(C\(_6\)F\(_5\)\(_2\))\(_2\) was used as oxidant in the preparation of Eu\(^{2+}\)-containing complexes with triazanides as ligands [Dmp(Tph)\(_3\)]\(_2\)Eu(C\(_6\)F\(_5\)\(_2\)) \((24)\) and [Eu\(_2\)]\(_2\)Dmp(Tph)\(_3\)] \((25)\) in which Dmp is 2,6-(2,4,6-(CH\(_3\))\(_3\))C\(_6\)H\(_3\) and Tph is 2-(2,4,6-(iPr\(_2\)C\(_6\)H\(_5\))\(_2\))C\(_6\)H\(_3\). Of particular note are the coordination modes of the terphenyl and biphenyl groups in complexes \(24\) and \(25\) that exhibit \(\pi\)-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 \(\eta^2\) interaction with the metal, whereas in complex \(25\), the mesityl rings of terphenyl groups exhibit \(\eta^1\) and \(\pi^1\) binding modes. The assignment of hapticity was based on the shortest metal–centroid separation or the smallest angle between the M–centroid vectors and the normal of the arene plane.\(^{[43,44]}\)

When Hg(SCN)\(_2\) was used as oxidant, [Eu(NCS)\(_2\)]\(_2\)(DME)\(_3\) \((26)\) was obtained from redox transmetallation with Eu\(^0\) in DME, and bimetallic [Eu(NCS)\(_2\)](THF)\(_2\)] \((27)\) was obtained when THF was used as solvent. The crystal structure of the eight-coordinate complex \(26\) 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 A (left-hand) or A (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, trialkylvin(IV) compounds were explored for redox transmetallation with Eu\(^0\). Either the trivalent [Eu\(_3+i\)\((P\(_3\)h\(_2\)pz)\(_2\))(DME)\(_3\)] \((28)\) or the divalent \(\text{cis-}[\text{Eu}^{2+}(\text{P}h\(_3\)pz)\(_2\)](\text{DME})\(_2\) \((29)\) can be made from the reaction of Sn(CH\(_3\))\(_3\)(Ph\(_3\)pz), where Ph\(_3\)pz 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 Eu(SAr\(_*\))\(_2\)(THF)\(_3\) \((30)\), in which Ar\(_*\) is 2,6-[2,4,6-(iPr\(_2\)C\(_6\)H\(_5\))\(_2\)]C\(_6\)H\(_3\), was prepared from Eu\(^0\), Ar\(_*\)SH, and 2-iodobenzotrifluoride.\(^{[48]}\) This thiolate complex is characterized by \(\eta^6\pi\) interactions of Eu\(^{2+}\) with two o-2,4,6-trisoproplyphenyl 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 \(\eta^1\pi\) interactions with Eu\(^{2+}\) and was prepared from europium metal is Eu(Dpp)(THF) \((31)\), where Dpp is 2,6-Ph\(_2\)C\(_6\)H\(_3\). Complex \(31\) was synthesized from Eu\(^0\) and Dpp 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 heterometalic Eu\(^{2+}\) complexes, charge-separated and neutral heterobimetallic Eu\(^{2+}\)-containing complexes can also be synthesized from Eu\(^+\). Treatment of Eu\(^+\) and another rare earth metal (Y\(^3+\), Nd\(^3+\), or Ho\(^3+\)) with 2,6-diphenylphenol (OHdpp) at elevated temperature (190 °C) in the presence of Hg yielded charge-separated complexes [Eu\(_2\)O(ddpp)\(_4\)]\(_2\), [Y(Oddp)\(_2\)] \((32)\), [Eu\(_2\)O(ddpp)\(_2\)][Nd(Oddp)\(_4\)] \((33)\), and [Eu\(_2\)O(ddpp)]\(_2\)[Ho(Oddp)\(_4\)] \((34)\). The Eu\(^{2+}\) centers in [Eu\(_2\)O(ddpp)\(_4\)]\(_2\) are bridged by aryloxide ligands and have coordination modes of \(\eta^1\pi^2\eta^1\eta^1\) and \(\eta^1\eta^1\eta^1\eta^1\) with \(\pi\)-arene–Eu interactions.\(^{[50]}\) In contrast to the charge-separated complexes, heterobimetallic complexes [CaEu(Oddp)\(_4\)] \((35)\), [SrEu(Oddp)\(_4\)] \((36)\), and [BaEu(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 Mo(dpp) \((M = \text{Na}^0, \text{K}^0, \text{Li}^0)\) at elevated temperature (210 °C), heterobimetallic Eu\(^{2+}\)-containing complexes [NaEu(Oddp)\(_2\)]\(_3\)PhCH\(_3\) \((38)\) and [KEu(Oddp)\(_2\)]\(_2\) 2.5PhCH\(_3\) \((39)\) and the mixed-valent complex [Eu\(_2\)O(ddpp)\(_4\)]\(_2\) \((40)\) were obtained. These heterobimetallic complexes also show \(\pi\)-arene–Eu interactions that coordinatively saturate Eu\(^{2+}\). The coordination mode of the Eu\(^{2+}\) center is similar in \(35\) and \(36\) \((\eta^1\pi^2\eta^1\eta^1)\), while a different binding mode was observed in \(37\) \((\eta^1\eta^1\eta^1\eta^1)\). The coordination modes in the Eu\(^{2+}\)-containing complexes with alkaline metals are \(\eta^1\pi^2\eta^1\eta^1\) (complex \(38)\) and \(\eta^1\eta^1\eta^1\eta^1\) (complex \(39)\) and are similar to that of [Eu\(_3\)O(ddpp)\(_4\)]\(_2\) in charge-separated complexes \(32\)–34.\(^{[51]}\) Structural data for the [Eu\(_3\)O(ddpp)\(_4\)]\(_2\) unit in \(40\) depict aryloxide binding in \(\eta^1\pi^2\pi^2\) and \(\eta^3\pi^3\eta^1\) fashions.\(^{[51]}\) Purification of charge-separated or heterobimetallic complexes requires solvent.
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$^{3+}$ 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 alkyllides, amidoalaboranes, crown ethers, and cryptands.$^{[55–58]}$ An example of a Eu$^{3+}$-containing complex that was prepared from Eu$^{3+}$ chlorides with a reducing species is the dinuclear, distorted pentagonal bipyramidal complex $[\text{Eu}(\text{H}_{2}\text{BN-(CH$_3$)$_2$}B\text{H}_4)_2](\text{THF})_2]_2$ (41), which was obtained by using $N,N$-dimethylaminodiborane 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 $[\text{LEu}(\text{HMPA})_2](\text{THF})_4$ (42), in which L is 2,2'-methylene bis(6-tert-butyl-4-methylphenoxo) and HMPA is hexamethyldiphosphoramide tripeptide. 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$_2$O$_5$ was reduced electrochemically in the synthesis of the Eu$^{2+}$ complex of benzo-18-crown-6 and of tricyanolanilime.$^{[55,56]}$ 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$^{3+}$ 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 [Eu$_2$-(Ap$^*py)_2]_1$(THF)]$^{[48]}$, where Ap$^*py$ is deprotonated 6-methylpyridin-2-yl-[6-(2,4,6-trisopropylphenyl)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 [Eu[PhC-\{NSi(CH$_3$)$_3$\}(2,6-(iPr)$_2$NC$_6$H$_3$)$_2$](THF)$_2$]$_2$ (50),$^{[61]}$ an Eu$^{2+}$ complex with olefin-substituted cyclopentadienyl ligands $[[\text{C}_5(\text{CH}_3)_3\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Eu}(\text{THF})]]$, which was obtained by using $N$,$N$-dimethylaminodiborane 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 $[\text{LEu}(\text{HMPA})_2](\text{THF})_4$ (42), in which L is 2,2'-methylene bis(6-tert-butyl-4-methylphenoxo) and HMPA is hexamethyldiphosphoramide tripeptide. 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$_2$O$_5$ was reduced electrochemically in the synthesis of the Eu$^{2+}$ complex of benzo-18-crown-6 and of tricyanolanilime.$^{[55,56]}$ 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.
Developments in the Coordination Chemistry of Europium(II)

Figure 6. Structures of Eu²⁺-containing complexes 48–62, which were obtained from the metathesis of Eu³⁺-containing complexes.

bridged two Eu²⁺ centers, complex 56 is monometallic; a nonbridging iodine atom and THF occupy the axial positions and the tridentate (DIP₂pyr)⁻ ligand is bound to Eu²⁺ through its three nitrogen atoms to afford a distorted pentagonal pyramidal complex. As an alternative to the metathesis reaction of [EuI₂(THF)ₓ] in preparing Eu²⁺-containing complexes, we used the commercially available EuI₂ to prepare cryptates 10, 11, and 57–59. A similar europium halide salt was used to generate four-coordinate [Eu{(ArN)₂CN(iPr)₂}]₂ (60), where Ar is 2,6-diisopropylphenyl. Roesky and co-workers used a bimetallic Eu²⁺-containing complex [{CH(PPh₂NSiMe₃)₂}Eu(THF)(μ-I)]₂ and NaBPh₄ as precursors to prepare [{CH{PPh₂NSi-(CH₃)₃}₂}Eu(THF)₃]BPh₄ (61). The resulting complex was used to prepare other Eu²⁺-containing complexes by metathesis of the labile borate ligand. Another example of a borate-containing Eu²⁺ complex, [Cp*{(μ-η⁴:η¹-Ph)₂}-EuBPh₂] (62), was prepared from {Eu(Cp*)₂} in the presence of [Et₃NH][BPh₄]. The structural motif of complex 62 features one coordinated Cp* and two of the phenyl rings of BPh₂⁻ ligand in a μ-η⁴:η¹ binding mode, with the ligands in a pyramidal geometry around the coordination sphere of Eu²⁺. While density functional theory (DFT) calculations predict a trigonal planar shape for complex 62, the large size of Eu²⁺ prefers intermolecular packing over intramolecular packing in the solid state, and agostic interactions may also have contributed to this deviation of geometry.

In general, with the metathesis approach of preparing Eu²⁺-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 Eu²⁺ 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 Eu²⁺-containing complexes presented in this section demonstrate the rich coordination chemistry of Eu²⁺. Differences in the coordination environment in Eu²⁺-containing complexes can be attributed to steric and electronic effects of the coordinated ligands as well as the size and electronic properties of Eu²⁺, which are responsible, in part, for the agostic interactions observed in some Eu²⁺ complexes.

The development of other Eu²⁺-containing complexes with use of other divalent lanthanides in generating complexes with Ln²⁺–Ga⁺ or Ln²⁺–Al⁺ (Ln = Sm, Eu, Yb, or Tm) bonds is an active area of research.

Applications of Eu²⁺-Containing Complexes

The growing interest in Eu²⁺-containing complexes stems from their unique catalytic, photophysical, and magnetic properties. The remainder of this review describes the use of Eu²⁺-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 [Eu({PhC{NSi(CH3)3}{2,6-(iPr)2-NC6H3}})}_{2}μ-SePh]_{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+} has a more positive Ln^{2+/3+} oxidation potential than Sm^{2+/3+}.[60] The formation of the radical anion (DADC_{6}F_{5})– is driven by the reducing power of Sm^{2+} towards diphenyldichalcogenide, trans,N,N’-dimethyl-meso-octaethylporphyrinogen, the Eu^{2+}-containing complex cannot reduce tert-butyl-1,4-diazabuta-1,3-diene (tBu-DAB).[60] However, the analogous Sm^{2+} complex forms a bimetallic complex when reacted with tBu-DAB.[60] The formation of the bimetallic Sm^{3+} complex bridged by the reduced tBu-DAB^2− is driven by the reducing power of Sm^{2+} towards tBu-DAB, but the steric constraints due to the bulky tert-butyl moieties makes this reaction reversible.[60]

**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 stereochromies 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 dimethoxymethane 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 dimethoxymethane. 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

Eu²⁺-containing complexes 74–79, which contain indenyl, fluorenyl, and iminopyrrolyl ligands, showed catalytic activity in the ring-opening polymerization of ε-caprolactone. 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 dimethoxymethane, 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. 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. Wang and co-workers proposed that the polymerization of ε-caprolactone is initiated by the formation of Eu³⁺-containing alkoxyl radical species formed from the oxidation of the Eu²⁺ metal center (Scheme 2). The alkoxyl radical species is believed to take a second Eu²⁺-con-
taining complex and produce a bimetallic Eu\(^{3+}\)-containing complex that is bridged by the open 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^2-\eta^2]-1-(CH_3)_2Si-3-(C_4H_9OCH_2)C_6H_4]_2\text{Eu}] (80),\(^{81}\) \([[\eta^2-\eta^2]-C_4H_9OCH_2C_12H_25]_2\text{Eu}] (81),\(^{82}\) and \([[\eta^2-\eta^2]-C_9H_5\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\(\Pi\)-pyranyl 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.\(^{86}\) 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.\(^{84,87}\) 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\(^{2+}\)–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.\(^{86}\) 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, nitrotriacectate \([\text{N(CH}_2\text{COO})_3]^{2–}\), 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 nitrotriacectate 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\(^{3+}\)-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 in 2001.[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]

![Image of complexes 87 and 88](image-url)

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

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 demon-

<table>
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<th>Complex</th>
<th>Maximum emission band (nm) (solid)</th>
<th>Maximum emission band (nm) (methanol)</th>
<th>Luminescence lifetime (μs) (solid)</th>
<th>Luminescence lifetime (μs) (methanol)</th>
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<tr>
<td>Eu(^{2+})–83</td>
<td>ND (r.t.)</td>
<td>411.5 (77 K)</td>
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<td>ND</td>
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<tr>
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<td>417</td>
<td>0.65 (r.t.), 0.59 (77 K)</td>
<td>0.14</td>
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<tr>
<td>Eu(^{2+})–85</td>
<td>425 (r.t.), 430 (77 K)</td>
<td>447</td>
<td>8.34 (r.t.), 8.01 (77 K)</td>
<td>0.028</td>
</tr>
<tr>
<td>Eu(^{2+})–86</td>
<td>433 (r.t.), 417 (77 K)</td>
<td>432</td>
<td>0.922 (r.t.), 0.745 (77 K)</td>
<td>0.800</td>
</tr>
</tbody>
</table>

[a] Legend: r.t. is room temperature, ND is no data available.
strated that Eu²⁺-containing cryptates 10 and 11 are stable to transmutation in the presence of endogenous ions such as Ca²⁺, Mg²⁺, and Zn²⁺, and we are currently investigating the thermodynamic stability and toxicity of several other Eu²⁺-containing cryptates.

Conclusions

The rapid increase in the number of Eu²⁺-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 Eu²⁺-containing complexes with a variety of ligands has opened new frontiers in lanthanide chemistry. Careful control of ligand properties produces Eu²⁺-containing complexes that are useful in synthetic, materials, and medicinal applications.

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