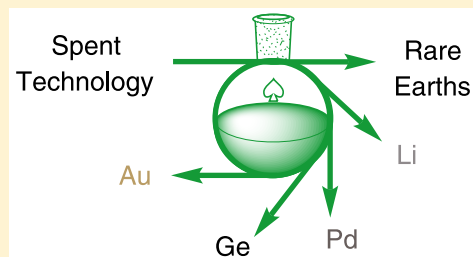


Sustainable Inorganic Chemistry: Metal Separations for Recycling

Joshua J. M. Nelson¹ and Eric J. Schelter^{1*}

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104, United States

ABSTRACT: Inorganic materials are critical components of clean energy technology. For example, rare earths are key for the function of electric car batteries and in permanent magnets used in wind turbines, and palladium helps to reduce harmful exhaust in automotive three-way catalysts. Many of the critical elements for these materials are of low abundance in the earth's crust, found in few places globally, and/or require energy- and resource-intensive purification. By comparison, many of these elements are concentrated in waste electrical and electronic equipment, which represents an attractive secondary resource. Inorganic chemists are ideally positioned to develop new chemistry and greener processes that are more efficient and use less hazardous reagents to separate high-value metals from waste electronics. The purpose of this Viewpoint is to highlight recent discoveries in fundamental inorganic chemistry that can contribute to new recycling technologies for gold, lithium, palladium, germanium, and rare earths, especially using simple approaches in solid–liquid extraction. Such fundamental studies are expected to help close metal supply chain loops and create circular economies.



INTRODUCTION

The study of green and/or sustainable chemistry is motivated by the need to support society with chemical processes that minimize waste and environmental damage. Green chemistry is a guide to the development of technology and processes that are safe to human health, benign to the environment, and minimize waste.¹ Green chemistry has often been identified with organic chemistry, for example, in the use of nontoxic and sustainably sourced solvents or reagents that improve process chemistry.^{1,2} What are the opportunities for inorganic chemistry in the field of green chemistry? A central focus in recent years has been in renewable energy science using inorganic materials. Another answer has been in the development of nonprecious metal catalysts. However, sustainable practices encompass the whole of the chemical enterprise, and there are numerous opportunities for fundamental inorganic chemistry in the development of improved industrial practices.

Industry values green chemistry because industrial chemists recognize how greener processes impact their companies' bottom lines, contribute to positive models in corporate ethics, and deliver value on customers' needs. An emerging area of sustainable chemistry is the development of *circular economies*, that is, the ability to efficiently and inexpensively process spent consumer materials back into raw materials for recycling.³ Separation and purification of raw materials are estimated to consume ~15% of global energy use.⁴ Of central interest here are materials containing essential metals that are expensive or otherwise energy-intensive to purify from their primary ores, such as gold, lithium, palladium, germanium, and rare earths. These elements were chosen because of their widespread or growing use in technology, concerns over continued supplies, and difficulty in their separations from mixtures. These separations problems are fundamentally different from mining

chemistries because the postconsumer "ore" comprises different chemical constituents.

On April 10, 2017, Apple Computer released their 2017 *Environmental Responsibility Report*.⁵ The company pledged to end mining and use 100% recycled materials in their products. Apple's pledge reflects a growing interest among technology companies and governments of major global economies to reduce the environmental burden of raw materials and create closed-loop supply chains for manufacturing. Incremental progress toward this goal can be made through engineering (e.g., disassembly of spent products). To achieve the grand challenges of a circular economy, new and improved separations chemistries of high-value metals, including rare earths, gold, indium, tantalum, and others, are essential. The key chemical questions here are the pursuit of selectivity for the purification of one metal over others from complex mixtures. There is a clear need for transformative, fundamentally new approaches in inorganic chemistry that address this grand challenge of metals recycling.

In the following Viewpoint, we examine a collection of related studies from the recent literature where fundamental inorganic chemistry is brought to bear for improved metal separations. Key here is the fundamental nature of the work: we highlight the fact that inorganic chemistry, motivated by goals in sustainability, provides a platform for the development of fundamental chemistry that addresses emerging problems and potentially creates new opportunities for industry. We also discuss more traditional "green" aspects of these processes with focus on the use of less toxic reagents and less wasteful, more efficient chemistry and highlight some aspects where these works might

Received: July 16, 2018

Published: January 7, 2019

be improved. This Viewpoint is not intended as a comprehensive review of metals separations chemistry applied to recycling but instead connects fundamental inorganic chemistry to problems in separations and recycling. We hope that, by examining and featuring the systems described below, others will similarly be inspired to consider new ways in which fundamental coordination chemistry can address critical problems in global sustainability.

GOLD

Electronic waste is a primary target for creating circular economies for metals. Among these, gold is an excellent target metal in terms of environmental, energy, and resource savings for recycling, compared to mining.⁶ The concentration of gold in mobile-phone waste is estimated to be up to ~70 times that of primary mining ores.⁷ Other notable metals in mobile-phone waste include copper, silver, palladium, iron, and rare earths.^{7,8} Gold is also an important target in terms of environmental impact. Distributed, small-scale gold mining typically relies upon cyanide salts and mercury amalgamation to process ores.^{9,10} This “artisanal” gold mining waste is accumulated in tailings ponds, resulting in mercury contamination of the water and soil, a significant health hazard for nearby communities.^{10–12}

In a 2016 breakthrough, the group of Prof. Jason Love reported the simple primary amide $\text{H}_2\text{NC}(\text{O})\text{CH}_2\text{CH}(\text{Me})\text{CH}_2\text{tBu}$ (**1**; Figure 1a).¹¹ In single-metal experiments, they

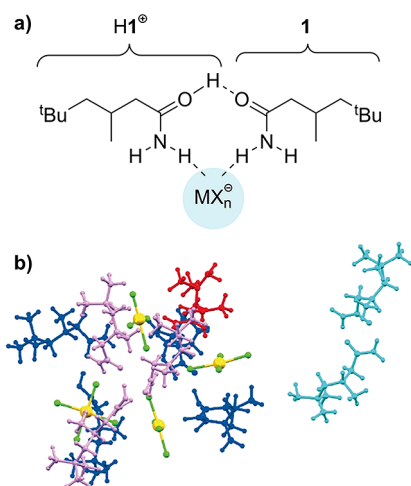


Figure 1. (a) Receptor H1_2^+ used for the extraction of $[\text{AuCl}_4]^-$ (b) MD calculations on the 10:4 **1**/H $[\text{AuCl}_4]$ system displayed several amide-bridged entities, including $[(\text{H1})(\text{AuCl}_4)_2]^-$ (red), $[(\text{H1}_2)(\text{AuCl}_4)_2]^-$ (dark blue), $[(\text{H1}_3)(\text{AuCl}_4)_2]^-$ (magenta), and $(\text{1})_2$ (cyan). Adapted with permission from ref 11. Copyright 2016 Wiley-VCH.

found that **1** was capable of extracting >90% gold from 2 M HCl into toluene. Compared to ~55% extraction of antimony(V) and <5% extraction of iron(III), palladium(II), platinum(IV), and copper(II), this represents a significant selectivity for gold over other metals. This selectivity was tested through extractions from realistic mobile-phone waste mixtures in which the concentration of gold is significantly less than that of the other metals present. These experiments were successful at extracting 82% gold, with just 6.4% iron and 2.7% tin. Notably copper was not extracted into the organic phase even though it was 2000 times more concentrated than gold in the starting mixture. This selectivity shows improvement over the commercial reagents

methyl isobutyl ketone (MIBK) and diethylene glycol butyl ether (DBC), which extracted large quantities of the other metals in addition to gold. The gold could be easily back-extracted (up to 88%) into an aqueous phase by the addition of water to the organic phase, another improvement over MIBK and DBC—both of which require additional reagents to remove gold from the organic phase.

The organic-phase structure of **1** with gold was probed to gain an understanding of the species being extracted from aqueous solutions. Solutions of **1** in toluene were contacted with solutions of varying AuCl_4^- concentration in 6 M HCl. Slope analysis of the gold content in the organic phase revealed a 1:1 Au ratio of 2.5–3:1. This suggested that the simple ion pair H1AuCl_4 was not the extracted species. Karl–Fischer titrations of the organic phase revealed a constant water content regardless of the quantity of gold extracted and discounted micellar species formation. Positive-ion electrospray ionization mass spectrometry (ESI-MS) in CH_3CN revealed the dominant gold-containing species to be of the form $[(\text{H1})_{n+1}(\text{AuCl}_4)_n]^+$ ($n = 1–4$). Density functional theory (DFT) was used to support this speciation. The protonated dimer $(\text{H1}_2)^+$ was found to be ~20 kcal mol^{-1} more stable than the monomer $(\text{H1})^+$ and formed ion pairs in which $[(\text{H1}_2)(\text{AuCl}_4)]$ was energetically favored over $[(\text{H1})(\text{AuCl}_4)]$. Hydrogen bonding by $(\text{H1}_2)^+$ and $(\text{H1})^+$ through the O–H and N–H groups bridged the AuCl_4^- anions and imparted stability, making clustering observed by ESI-MS thermodynamically favorable. Molecular dynamics (MD) calculations with 10:4 **1**/ AuCl_4^- resulted in a supramolecular cluster (Figure 1b). The results of those calculations showed that the AuCl_4^- anions were bridged by the amide functional groups of the $(\text{H1})^+$, $(\text{H1}_2)^+$, and $(\text{H1}_3)^+$ moieties, resulting in well-separated AuCl_4^- anions free of any intermolecular Au–Cl interaction. These combined results suggested that gold is extracted from the organic phase in clusters formed by hydrogen-bonded amide **1**.

The Love group’s easily synthesized, primary amide was shown to be highly efficient and selective for the biphasic extraction of gold from mixtures of dissolved metals derived from mobile-phone waste. Solution-state characterization and computational results both demonstrated aggregation through hydrogen bonding to form clusters that were evidently extracted into the organic phase. This study of selectivity for gold extraction was strongly identified with the concepts of spontaneous assembly and metallosupramolecular chemistry.^{12,13} The Love group findings are directly transferrable to current separations technology, namely, countercurrent solvent extraction. However, this work does not explain the selectivity of the primary amide, **1**, for gold over other metals and suggests that there may be other factors to consider for metal extraction performance. Understanding the other factors will promote a rational chemical design for the improvement of such a system.

The Stoddart group first reported using host–guest interactions between macrocycles such as cyclodextrin (CD) and alkali metal haloaurate salts in 2013. With this strategy, recognition of metal complexes, rather than simple cations, is examined. Upon combination of KAuBr_4 with α -CD in aqueous media, the Stoddart group reported precipitation.¹⁴ When Br^- is replaced with Cl^- , or α -CD with β -CD or γ -CD under identical conditions, precipitation was not observed. These results prompted investigation into the structural features that promoted cocrystallization of $\alpha\text{-CD}\cdot\text{K}\cdot\text{Br}$.¹⁵ The notation here refers to $\text{CD}\cdot\text{alkali metal cation}\cdot\text{tetrahaloaurate anion}$. X-ray analysis of single crystals revealed a dimer of α -CD 2° faces,

which encapsulated the $[\text{K}(\text{OH}_2)_6]^+$ ion (Figure 2b). The 1° face of this dimer was coordinated to the AuBr_4^- ion with

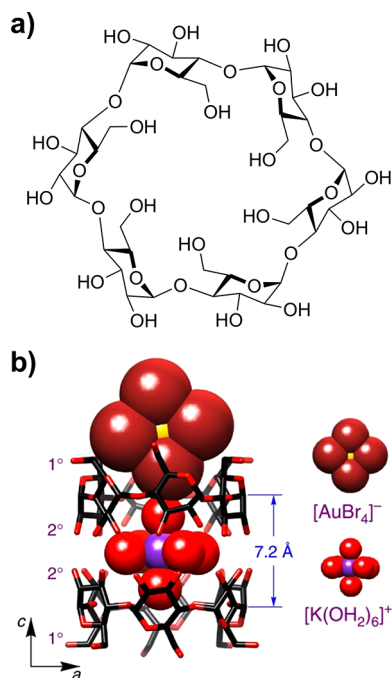


Figure 2. (a) α -CD. (b) Side-on view showing the orientation of the primary and secondary faces of the α -CD rings. Adapted with permission from ref 14. Copyright 2013 Springer Nature.

extensive $\text{C}-\text{H}\cdots\text{Br}-\text{Au}$ hydrogen bonding, as well as evidence for $\text{O}-\text{H}\cdots\text{Br}-\text{Au}$ hydrogen bonds with the water molecules solvating the K^+ ion. These dimers were stacked in a head-to-head fashion to yield a one-dimensional chain in the supramolecular structure with a nanowire of alternating $[\text{K}(\text{OH}_2)_6]^+$ and $[\text{AuBr}_4]^-$ ions. The secondary coordination spheres of each ion were effectively saturated by α -CD (Figure 3a). Multiple chains evidently assembled in a cable-like fashion through intermolecular H-bonding between α -CD moieties. SEM and TEM images of solids obtained from precipitation revealed crystalline needles with high aspect ratios, which suggested the mechanism of self-assembly began with dimeric subunits forming 1-D chains followed by aggregation into larger crystals.

Upon replacement of Br^- with Cl^- , the orientation of the AuX_4^- ion was maintained in the crystal structure, but the $\text{O}-\text{H}\cdots\text{X}-\text{Au}$ hydrogen-bonding interactions with water molecules

solvating the K^+ ion were lost. The decreased $\text{Au}-\text{Cl}$ bond length, compared to $\text{Au}-\text{Br}$, increased the $\text{O}-\text{H}\cdots\text{X}-\text{Au}$ distance enough to prevent the hydrogen bond from forming and resulted in significantly different first- and second-sphere coordination environments for the K^+ ion (Figure 3a). This resulted in the K^+ ion being readily accessible by solvent molecules, evidently maintaining the α -K-Cl aggregate in solution. The subtle change from Br^- to Cl^- highlights the effect that the ligand can have on not only first-sphere but second-sphere coordination of ions, thereby influencing the formation of cocrystallized materials.

Increasing the size of the CD ring by one sugar unit also yielded dimeric structures in the β -CD system, although the K^+ and AuX_4^- ions were coordinatively unsaturated (Figure 3a). Increasing the ring size to γ -CD eliminated any interactions of K^+ ions with the CD ring and oriented the AuX_4^- anion parallel to the CD ring. These structures increased solvent accessibility to both ionic species and the CD rings and prevented spontaneous coprecipitation. Similarly, the identity of the alkali-metal cation was found to affect this process. Coprecipitation from aqueous solutions was observed for K^+ , Rb^+ , and Cs^+ with α -CD and AuBr_4^- in 78%, 41%, and 68% yields, respectively.¹⁵ Combinations involving Na^+ , β -CD, γ -CD, and AuCl_4^- did not induce any precipitation. Examination of the coprecipitated structures revealed the formation of a 2D metal–organic network with Rb^+ and a 3D metal–organic scaffold with Cs^+ compared with the 1D nanowire with K^+ (Figure 3b). These other structural motifs lead to stable solids but have decreased yields of coprecipitates, presumably because of less efficient ion and α -CD packing. Together, these results further highlight the unique fit of KAuBr_4 with α -CD and the influence of first- and second-sphere coordination environments on the properties of metal complexes.

Cocrystallization of KAuBr_4 with α -CD can selectively recover 78% of the gold-containing material from a mixture in the presence of other square-planar transition-metal salts in which the initial ratio of $\text{Au}:\text{Pt}:\text{Pd}$ was $\sim 1:0.7:1$. Less than 3% of the other MX_4^{2-} ($\text{M} = \text{Pd}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}$) precipitated under these conditions as well. The subtle differences in the $\text{M}-\text{L}$ bonding character of $\text{M} = \text{Pd}$ or Pt compared to $\text{M} = \text{Au}$ result in different first- and second-sphere coordination environments that do not spontaneously self-assemble to precipitate from solution. Following precipitation, the gold salt can then be reduced to eliminate Au^0 and recover α -CD, which can be recycled into the gold separation process, along with the filtrate containing impurities and residual gold. In application to red and

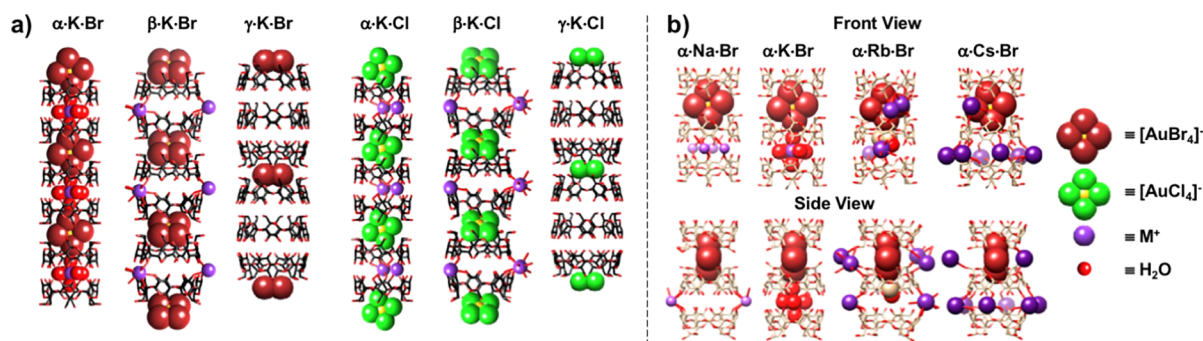
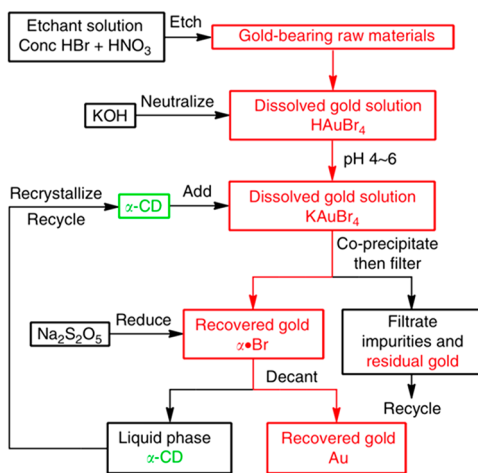


Figure 3. (a) Front view of single-crystal superstructures of KAuBr_4 and KAuCl_4 with α -CD, β -CD, and γ -CD. (b) Front and side views of single-crystal superstructures of α -Na-Br, α -K-Br, α -Rb-Br, and α -Cs-Br. Adapted with permission from ref 14. Copyright 2013 Springer Nature. Adapted with permission from ref 15. Copyright 2016 American Chemical Society.

yellow gold alloy scraps, which can contain silver, copper, and zinc, metallic gold was recovered in 89% yield with 97% purity and 92% yield with 95% purity, respectively.

The selective precipitation results highlight the key role of both first- and second-sphere interactions for the coprecipitation of α -K-Br. The Stoddart group has shown that AuBr_4^- has second-sphere interactions between the Br^- anions and the hydroxide protons of the α -CD ring to anchor the square-planar complex within the aperture. The larger sizes of the β -CD and γ -CD rings do not align as precisely. The hexaquo K^+ ion also has second-sphere interactions with the CD ring, which encapsulated the hydrated ion between two α -CD rings. There is an additional interaction between the aqua ligand and Br^- of AuBr_4^- , which helps to tether the salt through the α -CD ring. These interactions were not as prevalent in the other permutations containing β -CD, γ -CD, Cl^- , other alkali-metal cations, or other transition metals and failed to yield substantial precipitates. The mechanism of crystallization for the efficiently packed α -K-Br was also probed, which further highlighted the second-sphere interactions, causing the initial assembly, followed by aggregation into the larger superstructures. This process avoids the use of highly toxic reagents such as cyanide and mercury. The process also decreases the overall quantity of solvent required and uses a sustainably sourced agent to accomplish the separation of gold from mixtures containing other metals. While this method avoids the use of toxic reagents, such as cyanide and mercury utilized in artisanal gold mining, the etchant solution used here to dissolve metallic gold consists of HBr mixed with HNO_3 (Scheme 1), a highly corrosive

Scheme 1. Gold Recovery Process Flow Diagram^a



^aRed arrows indicate the flow direction of the gold recovery. Reproduced with permission from ref 14. Copyright 2013 Springer Nature. The gold-bearing raw materials could be waste electronic devices as well as crushed ores.

mixture requiring precautions while handling.¹⁴ Cycladex has made progress toward milder dissolution strategies that can also regenerate their lixiviate through oxidation of Br^- with H_2O_2 but still requires the use of HBr.¹⁷ Another drawback is the cost of α -CD, which is ~ 30 times the cost of β -CD (Acros Organics: α -CD, \$868.75 per 100 g; β -CD, \$154.10 per 500 g). However, this limitation has not stopped the technology from being implemented in collaboration with an established gold mining company.¹⁶

The Smith group has also investigated host–guest interactions between macrocyclic receptors and square-planar precious metals: gold, palladium, platinum, and halide salts.¹⁸ In 2018, they reported a system that featured amide N–H protons oriented inward toward the cavity of the macrocycle to engage in hydrogen-bonding interactions with the halides and π -donating arenes that engaged the metal center (Figure 4).

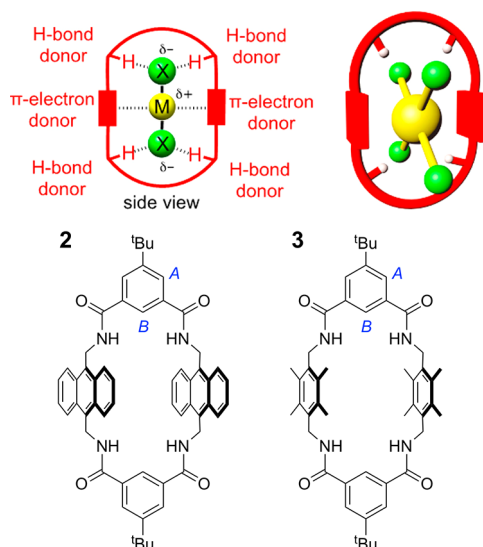


Figure 4. (Top) Conceptual design of a macrocyclic receptor for square-planar MX_4^{n-} anions. (Bottom) Two macrocycles used in this study. Reproduced with permission from ref 18. Copyright 2018 American Chemical Society.

Mixing receptor 2 with a HAuX_4 ($\text{X} = \text{Cl}, \text{Br}$) solution results in the immediate formation of a precipitate. Single-crystal X-ray analysis of the solid indicated a host–guest complex, with the gold complex sandwiched between the anthracene moieties and the halide atoms forming weak hydrogen-bonding interactions with the amide protons (Figure 5a). Notably, 2 does not require significant conformational changes to encapsulate the AuX_4^- anions. The solution-state speciation was probed using ^1H NMR studies with the tetrabutylammonium (TBA) cation to solubilize the complexes. Titration of TBACl , TBAuCl_4 , or TBAuBr_4 into a CDCl_3 solution of 2 resulted in a downfield shift of the amide N–H protons, as well as the phenyl proton pointing toward the cavity, B. Fits of the data yielded a 1:1 binding model consistent with the solid-state structure and guest affinities (K_a) of 923, 187, and 90 M^{-1} for AuCl_4^- , AuBr_4^- , and Cl^- , respectively. To improve the affinity and selectivity of the macrocyclic receptor, the anthracene moiety was replaced with 2,3,5,6-tetramethylbenzene (durene) to yield receptor 3 (Figure 4). DFT calculations of 2 and 3 indicated that the electrostatic potential of the center of the arene in 3 is more negative than that in 2, supposing a stronger interaction for 3 with metal centers. The periphery of the arene of 3 is more positive than that of 2, which was expected to improve interactions with the halides.

The crystal structure of 3-AuCl_4^- (Figure 5b) was isostructural with 2-AuCl_4^- (Figure 5a). ^1H NMR titration experiments in CDCl_3 performed with 3 and TBACl , TBAuCl_4 , or TBAuBr_4 again resulted in a 1:1 binding model. The K_a values for AuCl_4^- and AuBr_4^- each increased by a factor of 10 (7.8×10^4 and $2.5 \times 10^3 \text{ M}^{-1}$, respectively), but the value for Cl^- decreased by a factor of 4 (24 M^{-1}), showing

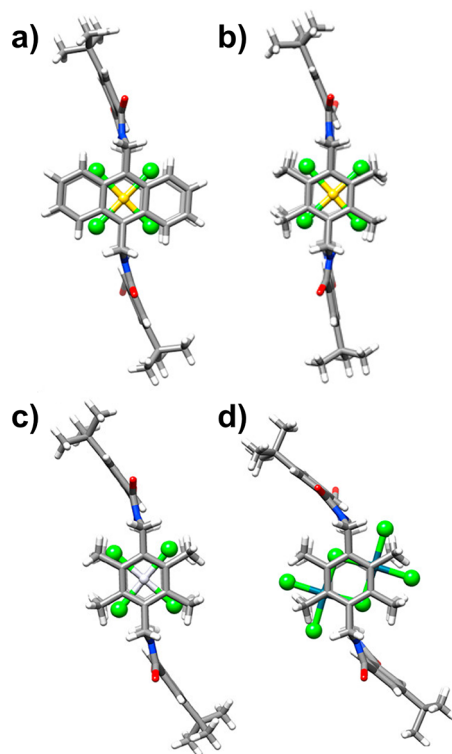


Figure 5. X-ray crystal structures of (a) 2-AuCl_4^- , (b) 3-AuCl_4^- , (c) 3-PtCl_4^- , and (d) $3\text{-Pd}_2\text{Cl}_6^{2-}$. Adapted with permission from ref 18. Copyright 2018 American Chemical Society.

improved selectivity for AuX_4^- over the metal-free halide anion. The interactions of **3** with PtCl_4^{2-} and PdCl_4^{2-} were also examined in the solid and solution states. 3-PtCl_4^{2-} (Figure 5c) was found to be isostructural with 3-AuCl_4^- (Figure 5b), except with two counteranions. However, the binding constant, K_a , was found to be just 20 M^{-1} for PtCl_4^{2-} , which is 3 orders of magnitude less than that of AuCl_4^- . This observation was attributed to a lower electrophilicity of PtCl_4^{2-} , compared to AuCl_4^- , which resulted in a weaker interaction with the π -donating durene moiety. Crystallization of PdCl_4^{2-} with **3** resulted in the isolation of $3\text{-Pd}_2\text{Cl}_6^{2-}$ (Figure 5d). The additional interaction of the Cl^- ligands in the palladate dimer with the positive electrostatic potential regions of the durene rings provided stability to the supramolecular structure and resulted in a relatively high K_a for PdCl_4^{2-} of $3.8 \times 10^3\text{ M}^{-1}$ despite the relatively smaller $\pi\text{-M}$ interactions than those in the AuCl_4^- adduct.

Taken together, these results highlight the importance of interactions with both the metal center and its halide ligands for stabilizing the complex within the macrocyclic receptor and maximizing association. Tuning the electronic properties of the π donor was shown to improve the affinity of the receptor for AuX_4^- 10-fold and decrease the affinity for Cl^- 4-fold. The electrostatic potential around the periphery of the receptor also significantly influenced interactions with the halide ligands. While the Smith group has not yet applied these differences in association constants to precious metal separations chemistry, this work suggests that it will be possible to preferentially bind gold over palladium and platinum and isolate gold through either precipitation of a solid or transfer into an organic solvent in a liquid–liquid extraction system. The design of the system appears to be highly tunable, which should allow for the development of macrocyclic receptors for specific metals.

LITHIUM

Lithium is critical for commercial interest because of its importance in modern battery technology.¹⁹ Projections estimate the need for a minimum of doubling production in the coming decades to meet growing demands,²⁰ and the lack of supplier diversity has led to price spikes.²¹ Lithium is found globally in brines and in pegmatite or spodumene ores and requires purification for commercial use. For example, processing of lithium-containing ores requires chlorination, a leaching process, formation of lithium carbonate, and subsequent separation of carbonate salts.²² Waste for lithium production is accumulated in tailings ponds. Such waste could be reduced using selective extractants without the need for significant pretreatment of ores or brines. Significant research has been done in this area, including the investigation of crown ethers with and without side chains, acidic extractants, and solvating extractants (see refs 22 and 23 for recent reviews). These works have probed the mechanism of extraction, synergistic effects with multiple extractants, and binding constants. However, selectivity for Li^+ compared to other alkali metals, as well as alkaline-earth metals, remains an important challenge.

The Sessler group aims to improve lithium purification through the use of ion-pair receptors. In 2016, they reported a hemispherand-strapped calix[4]pyrrole ligand, **4**, which features a binding pocket for lithium and hydrogen-bond donors to interact with anions (Figure 6a).²⁴ Crystallization of **4** in the

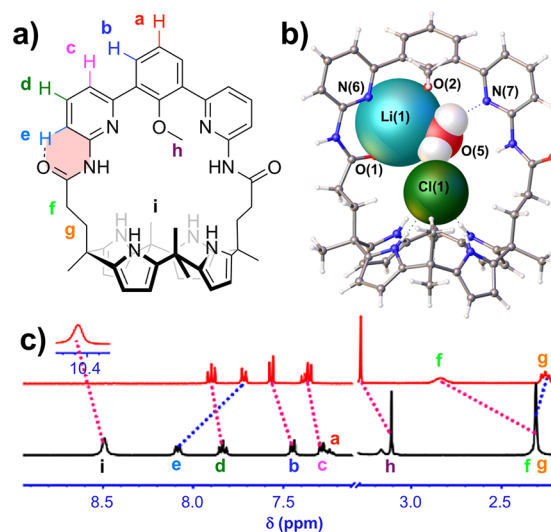


Figure 6. (a) **4**. (b) Crystal structure of $4\cdot\text{LiCl}$. (c) Partial ^1H NMR spectrum of **4** (black trace) and **4** with LiCl (red trace) in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$ (9:1, v/v). Adapted with permission from ref 24. Copyright 2016 American Chemical Society.

presence of LiCl resulted in the targeted coordination complex. The Li^+ cation is coordinated by the pyridine nitrogen atoms and methoxy oxygen atom of the hemispherand strap as well as solvent molecules (Figure 6b). The Cl^- anion is also bound through interactions with N-H protons of the calix[4]pyrrole portion of the ligand.

Evidence for the binding of LiCl to **4** in solution was provided by ^1H NMR spectroscopy (Figure 6c). The most significant changes in the spectrum arose from conformational changes. Upon reception of the ion pair, one of the pyridine C-H protons, *e*, was shifted significantly downfield, which was likely

due to a loss in hydrogen bonding with the carbonyl oxygen atom because it changed its orientation to coordinate the Li^+ cation (Figure 6a, highlighted in pink). Consistent with the ligand conformation change is the shift of the two sets of methylene protons, *f* and *g*, which are rotated to accommodate for carbonyl binding to Li^+ . The pyrrole N–H resonances, *i*, were shifted downfield, suggestive of interactions with the chloride anion. These changes in the NMR spectrum were indicative of both Li^+ and Cl^- being bound by the ligand, consistent with the solid-state structure of $4\cdot\text{LiCl}$.

Importantly, combinations of other alkali-metal salts (NaCl , KCl , and RbCl) with **4** did not result in any appreciable changes to the ^1H NMR spectrum in 9:1 $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{OD}$, suggesting that neither metal nor chloride is bound. The addition of LiClO_4 to **4** resulted in an NMR spectrum consistent with bound Li^+ because of shifts in the resonances associated with the two methylene regions, pyridine C–H, and methoxy protons. This spectrum lacked any significant changes in the pyrrole N–H protons to indicate that the anion is bound. Together, these results point to the importance of the cation for binding of the salt. The selectivity of **4** for LiCl over other alkali metals was probed with DFT. The binding energies of putative hydrate complexes, as well as anhydrous complexes, were calculated for LiCl , NaCl , and KCl , with the results summarized in Table 1. In

Table 1. DFT-Calculated Binding Energies of **4** with Alkali-Metal Salts^a

salt	calculated binding energy (kcal mol^{-1})	
	hydrate	anhydrous
LiCl	–244.27	–220.49
NaCl	–217.44	–198.06
KCl	–188.65	–174.65
LiBr	–236.72	
LiNO_2	–237.91	
LiNO_3	–230.24	

^aAdapted with permission from ref 24. Copyright 2016 American Chemical Society.

both the hydrated and anhydrous complexes, formation of the LiCl complex is favored by $>22 \text{ kcal mol}^{-1}$ over other MCl complexes. The Sessler group also calculated the binding energies for LiBr , LiNO_2 , and LiNO_3 , which were also shown to bind both cation and anion to examine the impact of the anion on ion-pair complexation. The binding energies for the LiX salts fell within 15 kcal mol^{-1} of each other, which is a negligible range compared to the difference in the binding energies between alkali metals.

The Sessler group then probed the competency of this system as an extractant. The addition of microcrystalline LiNO_2 to a solution of **4** in CD_2Cl_2 resulted in a ^1H NMR spectrum consistent with the binding of the ion pair, whereas exposure to NaNO_2 and KNO_2 failed to produce any changes in the spectrum of **4**. The subsequent addition of LiNO_2 to either of these mixtures resulted in a ^1H NMR spectrum consistent with the ligand bound to LiNO_2 in the absence of other metals, showing the selectivity for LiNO_2 over the other metals as a solid–liquid extractant. Similar experiments were performed with the alkali-metal salts dissolved in D_2O and **4** in CDCl_3 . The ^1H NMR spectrum of the organic portion after exposure to MNO_2 in D_2O was again consistent with binding only LiNO_2 and shows the selectivity of **4** for LiNO_2 when performing as a liquid–liquid extractant from aqueous into organic media.

Receptor **4** is a functional liquid–liquid extractant of LiNO_2 , but it fails to extract LiCl from an aqueous phase. The Sessler group hypothesized that this performance was due to water coordinating the Li^+ cation, as observed, for example, in the solid-state structure (Figure 6b). The hydration of the Li^+ cation prevented the salt's transfer to the organic phase. In 2018, the group reported two new receptors **5** and **6** (Figure 7a,b) that

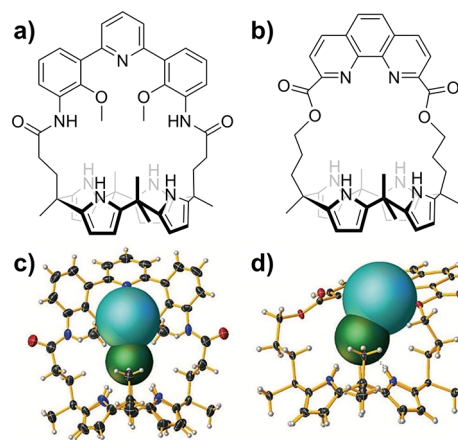


Figure 7. (a) Receptor **5**. (b) Receptor **6**. (c) Crystal structure of $5\cdot\text{LiCl}$. (d) Crystal structure of $6\cdot\text{LiCl}$. Adapted with permission from ref 25. Copyright 2018 Wiley-VCH.

were designed to have smaller binding pockets.²⁵ This new design resulted in decreased Li–Cl distances in $5\cdot\text{LiCl}$ and $6\cdot\text{LiCl}$, consistent with direct contact between the Li^+ and Cl^- ions, with Li^+ cations that were free of coordinated water molecules (Figure 7c,d). Notably, with decreasing binding pocket size there is increased extrusion of the Li^+ cation from the binding pocket. Larger cations could fail to fit into the binding pocket entirely, and this suggests that **6** would selectively bind LiCl over other alkali-metal chloride salts.

Exposure of **6** in CDCl_3 to solid LiCl for 24 h resulted in a ^1H NMR spectrum consistent with both cation and anion binding. Extended exposure of **6** in CDCl_3 for up to 2 weeks to NaCl or KCl failed to induce any changes in the ^1H NMR spectrum, suggesting that neither metal nor chloride is bound. Similar experiments were performed with **6** in CDCl_3 exposed to the alkali-metal salts in D_2O . The resulting ^1H NMR spectra revealed changes consistent with selective salt binding for LiCl , with no evidence for binding of NaCl or KCl . This observation suggests that **6** could be used as a liquid–liquid extractant selective for LiCl over other salts, although **6** was not tested in this application. To test its performance as a solid–liquid extractant, **6** (3 mM in CHCl_3) was layered over a 1:1 solid mixture of NaCl and KCl with 200 ppm LiCl for 48 h. After back-extraction of the organic phase with 0.2 M H_2SO_4 , the Sessler group found 38% loading of **6** with LiCl and only trace NaCl and KCl , demonstrating the selectivity for LiCl extraction into solution from solid mixtures.

In their 2016 report, the Sessler group had shown that the identity of the cation strongly influenced the binding of ion pairs to **4**. Only Li^+ salts are bound by **4** in solution, in part because of its lower binding energy compared with other alkali-metal cations, which have been shown to not bind in solution. This observation was supported by competition studies in which LiX salts were selectively bound in the presence of other alkali metals. The Sessler group has also probed the mechanism of ion-

pair recognition and demonstrated the importance of the Li^+ ion binding before, or at least concurrent with, the anion binding in order to have anion recognition by **4**. This system has also been shown to be functional as solid–liquid and liquid–liquid extractants for LiNO_2 with selectivity over other alkali-metal salts. Using their understanding of the fundamental chemistry of **4** with alkali-metal salts, the Sessler group was able to rationally design a new generation of receptors **5** and **6** to selectively extract LiCl from solid and aqueous phases, even in the presence of excess NaCl and KCl .

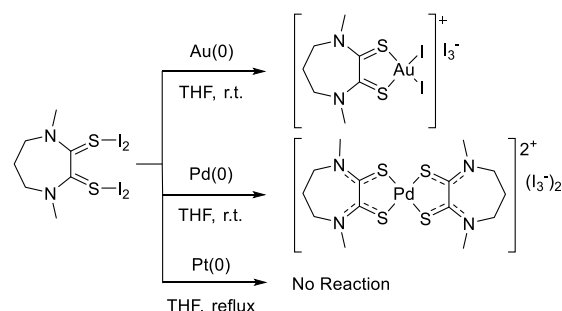
Industrial production of lithium requires substantial pretreatment of the lithium source prior to its isolation. The Sessler group's process is compatible either with hard rock, e.g., pegmatite or spodumene ores, as a solid–liquid extractant or with brines as a liquid–liquid extractant, requiring no pretreatment. The lithium salt can evidently be extracted from the ligand into an aqueous phase to allow for recycling of the ligand.²⁶ A challenge for this system is its low synthetic yield for receptors **4**–**6**, but a further demonstration of selective purification will undoubtedly motivate improved receptor syntheses. The extraction solvents also exhibit undesirable toxicities—especially problematic for chloroform with its high vapor pressure—and would ideally be replaced with more benign solvents.

PALLADIUM

Palladium plays a critical role in the function of automotive three-way catalysts (TWCs), which reduce the emission of pollutants including carbon monoxide, hydrocarbons, and NO_x .³¹ Industrial purification of palladium involves the dissolution of ores, followed by the separation of nonprecious metals, separation of other precious metals (silver and gold), and then separation of individual platinum group metals (PGMs).²⁷ In addition to the laborious purification process, palladium has low natural abundance and is found to be concentrated in a few locations globally.²⁸ Recycling of this PGM is thus an attractive target to avoid the depletion of natural resources, as well as to decrease waste associated with mining. Significant work has been done to investigate the extraction of palladium from high-level liquid waste from processing nuclear fuel (see ref 29 for a recent review). Most efforts in this work use additives featuring soft donors to extract palladium from an acidic aqueous phase into an organic phase. While effective, these processes generally require the metal to be present in a dissolved state. Selective dissolution of palladium from solid mixtures would be a more direct and efficient route to recovery of this metal.

The Deplano group first approached the question of selective palladium leaching in 1998 through the use of $\text{Me}_2\text{dazdt}_2\cdot 2\text{I}_2$, a bis(diiodine) adduct of a cyclic dithiooxamide, which is a water- and oxygen-stable compound.³⁰ This compound is capable of dissolving Au^0 under mild conditions to form $[\text{Au}(\text{Me}_2\text{dazdt}_2)(\text{I}_2)_2](\text{I}_3)^-$ (Scheme 2), a complex that is also stable to air. In 2005, this methodology was applied to the dissolution of Pd^0 , which formed the square-planar complex $[\text{Pd}(\text{Me}_2\text{dazdt}_2)_2](\text{I}_3)_2$.³¹ Interestingly, $\text{Me}_2\text{dazdt}_2\cdot 2\text{I}_2$ exhibited no reactivity toward platinum and rhodium, metals commonly found with palladium in TWCs, even under refluxing conditions. This separation system was shown to be competent for the leaching of >90% palladium from mixtures containing just 0.5–3.0 wt % of the metal from model TWC systems, which is typical palladium loading in commercial technologies.³² This approach significantly outperforms I^- – I_2^- treatment systems for recycling TWCs, which recover only 11% palladium,³³ and industrial pyrometallurgical chlorination, which recovers just 12% of the

Scheme 2. Reactivity of $\text{Me}_2\text{dazdt}_2\cdot 2\text{I}_2$ with Au^0 , Pd^0 , and Pt^0 ^a

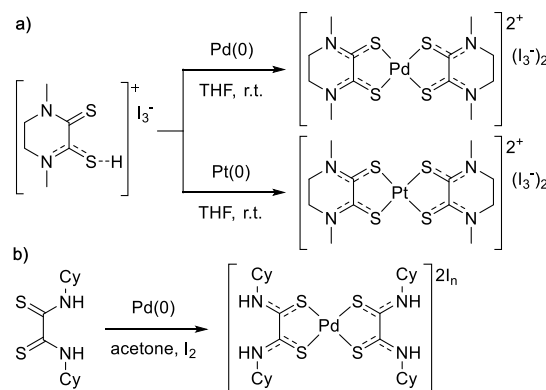


^aAdapted with permission from ref 35. Copyright 2008 Elsevier.

metal.³⁴ $\text{Me}_2\text{dazdt}_2\cdot 2\text{I}_2$ can dissolve PdO as well, which is commonly found in spent TWCs. Thermal treatment of the recovered square-planar complexes allows for the easy isolation of Pd^0 as a raw material for new TWCs.

While $\text{Me}_2\text{dazdt}_2\cdot 2\text{I}_2$ is not capable of dissolving Pt^0 , decreasing from a seven- to a six-membered ring in the backbone results in a protonated triiodide salt ($[\text{Me}_2\text{pipdtH}]\text{I}_3$) capable of dissolving both Pd^0 and Pt^0 (Scheme 3a).^{36,37}

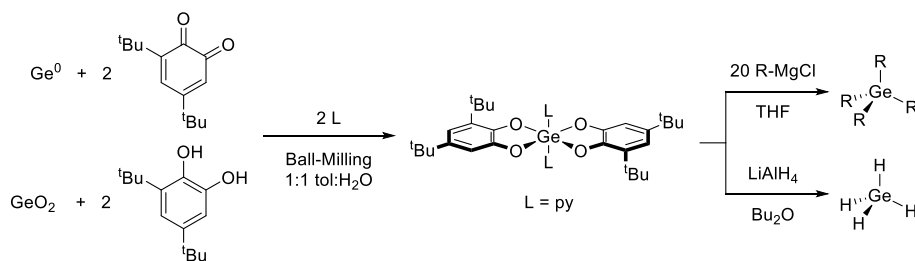
Scheme 3. (a) Reactivity of $[\text{Me}_2\text{pipdtH}]\text{I}_3$ with Pd^0 and Pt^0 and (b) Reactivity of CyDTO with I_2 and Pd^0 ^a



^aAdapted with permission from ref 35. Copyright 2008 Elsevier. Adapted with permission from ref 39. Copyright 2017 Royal Society of Chemistry.

Evidently, the structural difference of a methylene group altered the ligand's electronic properties. The difference in the properties was borne out in the iodine adducts, where the nature of the $\text{S}-\text{I}_n$ interaction altered the bonding of I_2 .³⁸ The sulfur atoms of $\text{Me}_2\text{dazdt}_2$ donated into the I_2 σ^* orbital to elongate, but not break, the $\text{I}-\text{I}$ bond, where Me_2pipdt donates more strongly to form I_3^- .³⁵ The resulting electronic and chemical properties of the latter system is then capable of performing the oxidative dissolution of Pt^0 in addition to Pd^0 .

In 2017, the Wilton-Ely group expanded the Deplano group's work to incorporate acyclic dithiooxamides, which are cheaper than cyclic systems in addition to being easily prepared and functionalized.^{39,40} This work focused on the cyclohexyl-substituted dithiooxamide: Cy_2DTO (Scheme 3b). The targeted complex $[\text{Pd}(\text{Cy}_2\text{DTO})_2](\text{I}_n)_2$ was prepared by exposing Pd^0 to the ligand in the presence of iodine without any prior generation of an iodine adduct. Although not explicitly mentioned, this pathway presumably does not dissolve Pt^0 and

Scheme 4. Solid-State Synthesis of L_2Ge^{IV} Catecholates and Solution-State Formation of Organogermanes and Germane^a

^aAdapted with permission from ref 47. Copyright 2017 American Academy for the Advancement of Science.

retains the selectivity for Pd^0 . As synthesized, this complex was shown to catalyze the regioselective oxidative C–H functionalization of benzo[*h*]quinolone and 8-methylquinoline, well-studied reactions for benchmarking the palladium catalyst performance,^{41,42} in a short period of time (<5 h) in moderate-to-excellent yields with low catalytic loadings of 1–2 mol %. This result demonstrates the ability to directly valorize waste palladium from spent TWCs into functional catalysts for organic transformations.

The design of the combined Deplano and Wilton-Ely systems incorporates inexpensive, commercially available materials to generate the ligand under mild conditions and subsequent metalation under equally mild conditions. This process allows for facile palladium recovery from solid secondary sources either as a raw material for use in new TWCs or directly as a catalyst in the laboratory.

■ GERMANIUM

Germanium metal (Ge^0) is a critical component of electronic and optical devices but predominantly occurs in minerals as germanium oxide.⁴³ Industrially, Ge-containing ores are treated with HCl or Cl_2 , and the resulting chloride salt is separated from $ZnCl_2$ using distillation, an energy intensive process.^{44,45} $GeCl_4$ is then converted to GeH_4 , a toxic gas often requiring purification because of the formation of digermane as a side product, for vapor deposition as Ge^0 .⁴³ This process is also energy-intensive, uses toxic and corrosive chemicals, and involves volatile intermediates. A low-energy and mild recycling process to recover the purified metal from end-of-life technology is therefore an attractive target.

Catechols can bind to metals through a two-electron oxidation of low-valent metals with *o*-quinone or ligand substitution with higher-valent metals with catechol.⁴⁶ The redox tautomers of catechols were thus attractive reagents to the Lumb group in the complexation of Ge^0 and/or Ge^{IV} .⁴⁷ Ball-milling of germanium powder with 3,5-di-*tert*-butyl-*o*-quinone and pyridine in 1:1 toluene/water yielded *trans*- $Ge(cat)_2(py)_2$ in >80% after recrystallization from the organic phase (Scheme 4). This complex was unambiguously structurally characterized using NMR, single-crystal X-ray analysis, and X-ray absorption spectroscopy. Pyridine could be substituted in this process for other monodentate nitrogen-atom donors to achieve analogous structures. The use of a chelating amine, such as tetramethylethylenediamine (TMEDA), resulted in *cis*- $Ge(cat)_2(TMEDA)$. These complexes were all air-stable, whereas $GeCl_4$ hydrolyzes in the presence of moisture into HCl and GeO_2 . Ball-milling of GeO_2 , the form of germanium present in refining from ZnO, with 3,5-di-*tert*-butylcatechol in conditions identical with those of the oxidative pathway yielded the identical product in >80% yield. In practice, the germanium-

containing product was isolated from unreacted solid ZnO simply by washing with methylene chloride to dissolve the germanium complex.

The catechol ligands were readily substituted to form tetraorganogermanes in yields above 80% with alkyl and aryl Grignard reagents (Scheme 4). As a selected example, reaction with (allyl)MgCl proceeded in near-quantitative yield with good recovery of the catechol. This high selectivity was attributed to a decrease in the steric strain from the bulky catechol ligand to an allyl ligand. This result is in contrast to the analogous reaction starting from $GeCl_4$, where substitution increased the steric bulk around the germanium center as the reaction progressed and resulted in only 45% yield of the desired tetraorganogermane. The effect of sterics on the reaction was probed by substitution of the axial pyridine ligand with the more sterically demanding Et_3N . The reaction with $BuMgCl$ failed to generate $GeBu_4$ but instead yielded a mixture of the di- and tributylgermanium species, with the remaining coordination sites occupied by catechol. This result suggested that increased sterics afforded by Et_3N prevented access to the germanium center for complete substitution to occur.

The Lumb group also examined $Ge(cat)_2(py)_2$ for use as a precursor to GeH_4 , the latter of which is a valuable reagent for vapor deposition of Ge^0 .⁴⁷ The reaction of $Ge(cat)_2(py)_2$ with $LiAlH_4$ at room temperature yielded the exclusive formation of GeH_4 gas as the volatile product by gas chromatography–mass spectrometry. 1H NMR of the solution shows only unreacted $LiAlH_4$, and presumably free catechol, and is free of the presence of oligomeric organogermanes and digermane. Clean formation of GeH_4 likely occurred for the same reason as GeR_4 , where each subsequent substitution proceeded more rapidly as steric strain was released. This sequence reaction prevented the buildup of intermediates, such as digermane, which may oligomerize or form other products instead of fully converting to GeH_4 .

This work demonstrated the utility of the redox-active ligands and liquid-assisted grinding in the synthesis of germanium(IV) catecholates. The ligands selectively reacted with GeO_2 over ZnO from relevant ores and facilitated the initial purification of germanium. The reaction of these complexes with Grignard reagents resulted in the clean formation of organogermanes, which formed through a process that relieved steric strain at the metal cation, with each substitution occurring more rapidly as the metal center became more accessible. The steric profile of the axial nitrogen-donating ligands supported this conclusion, where increasing the bulk from pyridine to triethylamine hindered substitution by the Grignard reagent and resulted in the incomplete substitution of catecholate with the alkyl groups. The clean conversion of $Ge(cat)_2(py)_2$ to germane proceeded with the same mechanism in which subsequent hydride additions were more rapid as steric strain was relieved. This

sequence prevented the buildup of partially substituted germanium-containing species, avoiding unproductive digermane formation.

Ultimately, in this system, the use of highly corrosive reagents, such as HCl and Cl_2 , has been eliminated in favor of the more benign 3,5-di-*tert*-butylcatechol to form air-stable germanium bis(catecholate) complexes in place of the easily hydrolyzed GeCl_4 . Furthermore, the complexes could be formed under mild conditions and isolated using filtration, as opposed to energy-intensive purification by distillation. Last, preparation for vapor deposition yielded clean GeH_4 without any need for subsequent gas purification, a common issue in Ge^0 production. This process could be improved by substitution with a milder hydride source such as NaBH_4 . This substitution would also allow for the use of greener solvents, such as ethyl alcohol, in place of ethereal solvents. Presumably, the catechol can be recovered from the reaction mixture for reuse in the processing of germanium, which would help to minimize any generated waste, although catechol binding to aluminum may complicate its recovery.

■ RARE-EARTH ELEMENTS (REES)

REEs, comprising the lanthanides (La–Lu) scandium and yttrium, are increasingly present in modern technology and are crucial components of wind turbine magnets (neodymium and dysprosium), lighting phosphors (europium and yttrium), and heterogeneous catalysts (lanthanum and cerium).⁴⁸ Industrial processes for rare-earth separations involve many iterations of countercurrent solvent exchange, an energy- and resource-intensive process that could benefit from improvement.⁴⁹ Currently, the People's Republic of China maintains a significant portion of the world reserves of rare-earth oxides and 78% of the mining production of REEs.⁵⁰ With an increasing demand for these elements, especially with the growing clean energy sector, there are concerns over the continued supply of REEs.^{21,28} Less than 1% of REEs in end-of-life technology are recycled, making recycling of these devices an attractive secondary source of these critical elements.⁵¹

Countercurrent solvent extraction is the industry standard for separating mixtures of rare earths in any context and is an important topic of ongoing research. Several research consortia have been developed in recent years to address challenges in rare-earth separation and recycling, such as the European Rare Earth Recycling Network and the Critical Materials Institute in North America. Some of the current research directions in separating rare-earth mixtures from electronic waste include roasting of permanent magnets with hydrogen,⁵² separations with ionic liquids,⁵³ and development of novel extractants.⁵⁴ Separations of REEs from actinides related to the processing of spent nuclear fuel is another active area of research that relies heavily on solvent extraction.⁵⁵ In this section, we focus on a handful of examples of alternative strategies for the separation of REE mixtures from electronic waste.

In 2016, the Emmert group reported a recycling process to separate REEs from end-of-life motors with the goals of an industrially viable process that adheres to the principles of green chemistry.⁵⁶ Starting with nonbonded NdFeB magnets, the Emmert group screened various simple acids for maximal REE dissolution with minimal dissolution of other metals and found HCl and H_2SO_4 to be most effective. Optimization of the acid concentration showed that 4 M $[\text{H}^+]$ is capable of completely dissolving the magnets, while minimizing the acid strength. Increased acid concentrations did not yield any benefit, although high concentrations of H_2SO_4 began to decrease the mass of

REE dissolved, likely through poorly soluble $\text{RE}_2(\text{SO}_4)_3$ formation. HCl (4 M) was also shown to have minimal reactivity with copper and various steel alloys, both common components of motors. The REEs were then selectively precipitated as $\text{RE}_2(\text{C}_2\text{O}_4)_3$ by the addition of solid oxalic acid, with the oxalate complexes isolated by filtration. This is operationally simple to perform and safer than other precipitation methods requiring the addition of base to increase the pH of the solution, which releases significant amounts of heat.

Commercial magnets are often resin- or nickel-coated to increase their stability, necessitating pretreatment to expose the NdFeB surface to the leaching acid. This was accomplished through demagnetization followed with shredding in a hammer-mill. This approach was shown to be scalable to small motors, with potential scalability to industrial sizes (limited in the academic setting to available shredders). The REEs were then precipitated with oxalic acid and isolated using filtration. The Emmert group closed the loop on this process by adding in a pyrohydrolysis step to recycle HCl, which minimized waste and allowed for the recovery of iron/boron oxides (Figure 8).

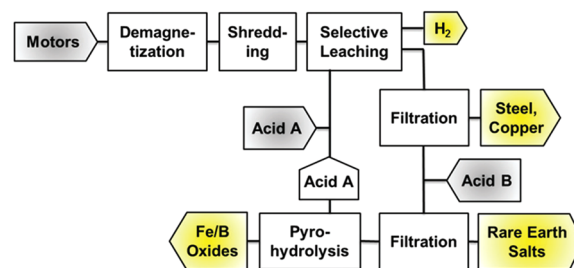
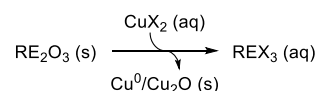


Figure 8. Proposed closed-loop process for the recovery of REEs from end-of-life motors. Gray arrows depict input materials; yellow arrows depict process product materials. Reproduced with permission from ref 56. Copyright 2016 Royal Society of Chemistry.

Researchers from the U.S. Department of Energy Critical Materials Institute have augmented this process. In place of mineral acids to dissolve REEs, their 2018 patent application used aqueous Cu^{II} salts.⁵⁷ It is still relevant though to note the Cu^{II} salts were made under oxidizing conditions with mineral acids. In this oxidative dissolution process, REE salts were formed and $\text{Cu}^0/\text{Cu}_2\text{O}$ were precipitated. The copper by-products were then filtered off with the other undissolved materials, which left a REE-enriched filtrate (Scheme 5). The

Scheme 5. Oxidative Dissolution Pathway Incorporating Cu^{II} Salts



REEs were then precipitated using ammonium oxalate, a process similar to that reported by the Emmert group.⁵⁶ These processes are attractive in their simplicity and consideration of green chemistry ideals. These reports lean toward the direct industrial application of the work, leaving opportunities to probe the fundamental aspects of separations chemistry. However, neither work addresses the separation of individual rare-earth elements from each other, just REEs from other metals and materials.

The exploitation of photochemistry and redox behavior of the lanthanides have been explored during the past 40 years. In

particular, the ability to reduce Eu^{III} to Eu^{II} in solution by irradiation of readily accessible charge transfer bands has been investigated for the separation of europium from mixtures of rare earths.^{58–61} Recently, the Binnemans group reported the optimized photochemical separation of europium from yttrium in red lamp phosphor waste that expanded on the reported methodologies.⁶² In aqueous conditions, EuSO_4 is several orders of magnitude less soluble than $\text{RE}_2(\text{SO}_4)_3$ salts, making the reduction of europium in the presence of sulfates an attractive target for separations chemistry.^{63,64} Under aqueous conditions, $[\text{Eu}(\text{H}_2\text{O})_6]^{3+}$ can be readily reduced to form $[\text{Eu}(\text{H}_2\text{O})_6]^{2+}$ using 188 nm light.⁵⁸ The charge transfer from sulfates to europium can also be induced by irradiation but at lower energy 240 nm light. The reverse oxidation of Eu^{II} back to Eu^{III} can occur by irradiation with 366 nm light. In order to optimize the reduction event, a light source with strong spectral outputs near 190 and 240 nm and weak or no output at 366 nm is ideal. These requirements are realized in low-pressure mercury lamps, which have strong outputs at 185 and 254 nm and a much less intense output around 366 nm.

The transfer of single electrons to the europium center results in the formation of hydroxyl and sulfate radicals, necessitating the presence of radical scavengers to prevent reoxidation of the metal back to Eu^{III} . Common radical scavengers include formic acid and isopropyl alcohol.^{58,59} The use of formic acid resulted in an acidic reaction mixture and favored the oxidation of Eu^{II} to Eu^{III} , which is counterproductive. Isopropyl alcohol did not affect the pH of the reaction mixture, allowing the photochemical reduction of Eu^{III} to proceed smoothly. Furthermore, isopropyl alcohol is less toxic than formic acid and makes it a better choice of radical scavenger.

The concentration of sulfate ions, choice of radical scavenger, operating pH, and light source all contribute to the optimized separation of europium from yttrium in red phosphor waste. Under these conditions, the Binnemans group reported removal of up to 90% europium with a purity of 98.5%, depending on the europium/yttrium ratios. Europium/REE separations chemistry has clearly benefitted through the use of well-established fundamental properties of europium that stand out from the properties of other REEs. An attractive goal in this type of separation scheme would be to vary the system (e.g., ligand choice) to allow access to lower-energy charge-transfer bands that improve the utility of fundamental europium photoredox chemistry in application to europium/REE separations.

CONCLUSIONS AND OUTLOOK

Each of the systems considered in this Viewpoint derives from fundamental inorganic chemistry of the metal of interest. The properties of the complexes were exploited for separations chemistry with typically significantly less energetic cost than current industrial separations. Insights gained through each of these studies potentially contributes to the rational design of novel frameworks tailored for the recycling of valuable materials from end-of-life technology.

There are many opportunities for the application of inorganic chemistry to real-life devices, namely, efficiently extracting and separating each of the critical metals found in mobile phones, such as gold, REEs, lithium,⁸ using chemistry that is complementary. As technology emerges, the list of critical materials will continue to grow and call for new separations chemistry grounded in fundamental inorganic chemistry to create sustainable economies.

AUTHOR INFORMATION

Corresponding Author

*E-mail: schelter@sas.upenn.edu.

ORCID

Joshua J. M. Nelson: 0000-0002-5510-6545

Eric J. Schelter: 0000-0002-8143-6206

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

Biographies



Joshua Nelson received his B.A. degree in chemistry from Boston University (2013) where he performed undergraduate research in Prof. Linda Doerrer's group on 3d metal complexes. In 2016, he joined Prof. Eric Schelter's group as a graduate student at the University of Pennsylvania. His research interests are focused on the separation of rare-earth elements for the recycling of waste electronic devices.



Eric J. Schelter received his Ph.D. degree from Texas A&M University (2004) under the direction of Prof. Kim R. Dunbar. He was subsequently a postdoctoral researcher at Los Alamos National Laboratory (2004–2009) with Drs. Jaqueline Kiplinger, Kevin John, and Joe Thompson. He is currently a Professor of Chemistry at the University of Pennsylvania with a research program spanning lanthanide and actinide coordination chemistry, f-element separations chemistry, lanthanide bioinorganic chemistry, and the photochemistry of f elements. He has received the Harry Gray Award for Creative Work in Inorganic Chemistry by a Young Investigator (2016) and the U.S. EPA Green Chemistry Challenge Award (2017).

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the University of Pennsylvania and the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Separation Science program under Award DE-SC0017259.

REFERENCES

- (1) Anastas, P. T.; Zimmerman, J. B. Peer reviewed: through the 12 principles of green engineering. *Environ. Sci. Technol.* **2003**, *37*, 94A–101A.
- (2) Sheldon, R. A. Organic synthesis – past, present and future. *Chem. Ind.-London* **1992**, 903–906.
- (3) Geissdoerfer, M.; Savaget, P.; Bocken, N. M. P.; Hultink, E. J. The circular economy – a new sustainability paradigm? *J. Cleaner Prod.* **2017**, *143*, 757–768.
- (4) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* **2016**, *532*, 435–437.
- (5) Apple Inc.. *Apple Environmental Responsibility Report*; 2017; pp 1–58.
- (6) Bigum, M.; Brogaard, L.; Christensen, T. H. Metal recovery from high-grade WEEE: a life cycle assessment. *J. Hazard. Mater.* **2012**, *207*–208, 8–14.
- (7) Hagelüken, C.; Corti, C. W. Recycling of gold from electronics: cost-effective use through ‘design for recycling’. *Gold Bulletin* **2010**, *43*, 209–220.
- (8) Müller, A. *The chemistry of the mobile phones Nokia N9500 5230, Nokia 5130 and Sony Ericsson W595*, 2013.026; 2013; pp 1–24.
- (9) Renner, H.; Schlamp, G.; Hollmann, D.; Lüscho, H. M.; Tews, P.; Rothaut, J.; Dermann, K.; Knödler, A.; Hecht, C.; Schlott, M.; Drieselmann, R.; Peter, C.; Schiele, R. *Ullmanns Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; Vol. 17, pp 93–143.
- (10) Esdaile, L. J.; Chalker, J. M. The mercury problem in artisanal and small-scale gold mining. *Chem. - Eur. J.* **2018**, *24*, 6905–6916.
- (11) Doidge, E. D.; Carson, I.; Tasker, P. A.; Ellis, R. J.; Morrison, C. A.; Love, J. B. A simple primary amide for the selective recovery of gold from secondary resources. *Angew. Chem., Int. Ed.* **2016**, *55*, 12436–12439.
- (12) Lanigan, N.; Wang, X. Supramolecular chemistry of metal complexes in solution. *Chem. Commun.* **2013**, *49*, 8133–8144.
- (13) Chifotides, H. T.; Dunbar, K. R. Anion- π interactions in supramolecular architectures. *Acc. Chem. Res.* **2013**, *46*, 894–906.
- (14) Liu, Z.; Frascioni, M.; Lei, J.; Brown, Z. J.; Zhu, Z.; Cao, D.; Iehl, J.; Liu, G.; Fahrenbach, A. C.; Botros, Y. Y.; Farha, O. K.; Hupp, J. T.; Mirkin, C. A.; Fraser Stoddart, J. Selective isolation of gold facilitated by second-sphere coordination with α -cyclodextrin. *Nat. Commun.* **2013**, *4*, 1855–9.
- (15) Liu, Z.; Samanta, A.; Lei, J.; Sun, J.; Wang, Y.; Stoddart, J. F. Cation-dependent gold recovery with α -cyclodextrin facilitated by second-sphere coordination. *J. Am. Chem. Soc.* **2016**, *138*, 11643–11653 Further permissions related to the material excerpted should be directed to the ACS. .
- (16) Cycladex History. <http://cycladex.com/history/> (accessed Aug 30, 2018).
- (17) Pettman, R. B.; Arnold, D. F. Recovery of precious and rare earth metals using cyclodextrin. International Publication Number WO 2017/158561 A1, Sept 21, 2017.
- (18) Liu, W.; Oliver, A. G.; Smith, B. D. Macrocyclic receptor for precious gold, platinum, or palladium coordination complexes. *J. Am. Chem. Soc.* **2018**, *140*, 6810–6813.
- (19) Song, M.-K.; Park, S.; Alamgir, F. M.; Cho, J.; Liu, M. Nanostructured electrodes for lithium-ion and lithium-air batteries: the latest developments, challenges, and perspectives. *Mater. Sci. Eng., R* **2011**, *72*, 203–252.
- (20) Mohr, S. H.; Mudd, G. M.; Giurco, D. Lithium resources and production: critical assessment and global projections. *Minerals* **2012**, *2*, 65–84.
- (21) U. S. Department of Energy. *Critical Materials Strategy*; Washington, DC, 2011; pp 1–196.
- (22) Swain, B. Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: a review. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 2549–2562.
- (23) Swain, B. Recovery and recycling of lithium: a review. *Sep. Purif. Technol.* **2017**, *172*, 388–403.
- (24) He, Q.; Zhang, Z.; Brewster, J. T.; Lynch, V. M.; Kim, S. K.; Sessler, J. L. Hemispherand-strapped calix[4]pyrrole: an ion-pair receptor for the recognition and extraction of lithium nitrite. *J. Am. Chem. Soc.* **2016**, *138*, 9779–9782.
- (25) He, Q.; Williams, N. J.; Oh, J. H.; Lynch, V. M.; Kim, S. K.; Moyer, B. A.; Sessler, J. L. Selective solid-liquid and liquid-liquid extraction of lithium chloride using strapped calix[4]pyrroles. *Angew. Chem., Int. Ed.* **2018**, *57*, 11924–11928.
- (26) He, Q.; Peters, G. M.; Lynch, V. M.; Sessler, J. L. Recognition and extraction of cesium hydroxide and carbonate by using a neutral multitopic ion-pair receptor. *Angew. Chem., Int. Ed.* **2017**, *56*, 13396–13400.
- (27) *Safe Use of Platinum Group Metals in the Workplace*; International Platinum Group Metals Association, 2017; pp 1–10.
- (28) European Commission. *Study on the review of the list of Critical Raw Materials*; 2017; pp 1–93.
- (29) Ruhela, R.; Singh, A. K.; Tomar, B. S.; Hubli, R. C. Separation of palladium from high level liquid waste – a review. *RSC Adv.* **2014**, *4*, 24344–7.
- (30) Bigoli, F.; Angela Pellinghelli, M.; Deplano, P.; Mercuri, M. L.; Pintus, G.; Serpe, A.; Trogu, E. F. A powerful new oxidation agent towards metallic gold powder: *N,N'*-dimethylperhydrodiazepine-2,3-dithione (D) bis(diiodine). Synthesis and X-ray structure of $[\text{AuDI}_2]_3$. *Chem. Commun.* **1998**, *0*, 2351–2352.
- (31) Serpe, A.; Bigoli, F.; Cabras, M. C.; Fornasiero, P.; Graziani, M.; Mercuri, M. L.; Montini, T.; Pilia, L.; Trogu, E. F.; Deplano, P. Pd-dissolution through a mild and effective one-step reaction and its application for Pd-recovery from spent catalytic converters. *Chem. Commun.* **2005**, *38*, 1040–1042.
- (32) Bernal, S.; Blanco, G.; Calvino, J. J.; Gatica, J. M.; Omil, J. A. P.; Pintado, J. M. Characterisation of three-way automotive aftertreatment catalysts and related model systems. *Top. Catal.* **2004**, *28*, 31–45.
- (33) Nakao, Y.; Sone, K. Reversible dissolution/deposition of gold in iodine-iodide-acetonitrile systems. *Chem. Commun.* **1996**, *7*, 897–898.
- (34) Kendall, T. *Platinum 2004* **2004**, 1–60.
- (35) Serpe, A.; Artizzu, F.; Mercuri, M. L.; Pilia, L.; Deplano, P. Charge transfer complexes of dithioamides with dihalogens as powerful reagents in the dissolution of noble metals. *Coord. Chem. Rev.* **2008**, *252* (10–11), 1200–1212.
- (36) Bigoli, F.; Deplano, P.; Mercuri, M. L.; Pellinghelli, M. A.; Pintus, G.; Serpe, A.; Trogu, E. F. *N,N'*-Dimethylpiperazinium-2,3-dithione Triiodide, $[\text{Me}_2\text{Pipdt}]_3\text{I}_3$, as a Powerful New Oxidation Agent toward Metallic Platinum. Synthesis and X-ray Structures of the Reagent and the Product $[\text{Pt}(\text{Me}_2\text{Pipdt})_2](\text{I}_3)_2$. *J. Am. Chem. Soc.* **2001**, *123*, 1788–1789.
- (37) Bigoli, F.; Deplano, P.; Mercuri, M. L.; Pellinghelli, M. A.; Pilia, L.; Pintus, G.; Serpe, A.; Trogu, E. F. Ion pair charge-transfer complexes between anionic and cationic metal-dithiolenes $[\text{M}(\text{II}) = \text{Pd}, \text{Pt}]$. *Inorg. Chem.* **2002**, *41*, 5241–5248.
- (38) Deplano, P.; Ferraro, J. R.; Mercuri, M. L.; Trogu, E. F. Structural and Raman spectroscopic studies as complementary tools in elucidating the nature of the bonding in polyiodides and in donor- I_2 adducts. *Coord. Chem. Rev.* **1999**, *188*, 71–95.
- (39) Jantan, K. A.; Kwok, C. Y.; Chan, K. W.; Marchiò, L.; White, A. J. P.; Deplano, P.; Serpe, A.; Wilton-Ely, J. D. E. T. From recovered metal waste to high-performance palladium catalysts. *Green Chem.* **2017**, *19*, 5846–5853.
- (40) Hurd, R. N.; Mater, G. D. L.; McElheny, G. C.; Turner, R. J.; Wallingford, V. H. Preparation of dithioamide derivatives. *J. Org. Chem.* **1961**, *26*, 3980–3987.

- (41) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300.
- (42) Powers, D. C.; Ritter, T. Bimetallic Pd(III) complexes in palladium-catalysed carbon-heteroatom bond formation. *Nat. Chem.* **2009**, *1*, 302–309.
- (43) Venkatasubramanian, R.; Pickett, R. T.; Timmons, M. L. Epitaxy of germanium using germane in the presence of tetramethylgermanium. *J. Appl. Phys.* **1989**, *66*, 5662–5664.
- (44) Moskalyk, R. R. Review of germanium processing worldwide. *Miner. Eng.* **2004**, *17*, 393–402.
- (45) Torma, A. E.; Jiang, H. Extraction processes for gallium and germanium. *Miner. Process. Extr. Metall. Rev.* **1991**, *7*, 235–258.
- (46) Glavinović, M.; Qi, F.; Katsenis, A. D.; Friščić, T.; Lumb, J.-P. Redox-promoted associative assembly of metal-organic materials. *Chem. Sci.* **2016**, *7*, 707–712.
- (47) Glavinović, M.; Krause, M.; Yang, L.; McLeod, J. A.; Liu, L.; Baines, K. M.; Friščić, T.; Lumb, J.-P. A chlorine-free protocol for processing germanium. *Sci. Adv.* **2017**, *3*, No. e1700149. Copyright The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC), <http://creativecommons.org/licenses/by-nc/4.0/>.
- (48) Charalampides, G.; Vatalis, K. I.; Apostoplos, B.; Ploutarch-Nikolas, B. Rare earth elements: industrial applications and economic dependency of Europe. *Proc. Econ. Financ.* **2015**, *24*, 126–135.
- (49) Gupta, C. K.; Krishnamurthy, N. Extractive metallurgy of rare earths. *Int. Mater. Rev.* **1992**, *37*, 197–248.
- (50) U.S. Geological Survey. *Mineral Commodity Summaries 2018*, Reston, VA, 2018; pp 1–200.
- (51) Binnemans, K.; Jones, P. T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths: a critical review. *J. Cleaner Prod.* **2013**, *51*, 1–22.
- (52) Walton, A.; Yi, H.; Rowson, N. A.; Speight, J. D.; Mann, V. S. J.; Sheridan, R. S.; Bradshaw, A.; Harris, I. R.; Williams, A. J. The use of hydrogen to separate and recycle neodymium-iron-boron-type magnets from electronic waste. *J. Cleaner Prod.* **2015**, *104*, 236–241.
- (53) Riaño, S.; Binnemans, K. Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets. *Green Chem.* **2015**, *17*, 2931–2942.
- (54) Tyumentsev, M. S.; Foreman, M. R. S. J.; Ekberg, C.; Matyskin, A. V.; Retegan, T.; Steenari, B.-M. The solvent extraction of rare earth elements from nitrate media with novel polyamides containing malonamide groups. *Hydrometallurgy* **2016**, *164*, 24–30.
- (55) Veliscek-Carolan, J. Separation of actinides from spent nuclear fuel: a review. *J. Hazard. Mater.* **2016**, *318*, 266–281.
- (56) Bandara, H. M. D.; Field, K. D.; Emmert, M. H. Rare earth recovery from end-of-life motors employing green chemistry design principles. *Green Chem.* **2016**, *18*, 753–759.
- (57) Mudring, A.-V.; Prodius, D.; Nlebedim, C. I. Dissolution and separations of rare earth metals. International Publication Number WO 2018/048464 A1, Mar 15, 2018.
- (58) Donohue, T. Photochemical separation of europium from lanthanide mixtures in aqueous solution. *J. Chem. Phys.* **1977**, *67*, 5402–5404.
- (59) Hirai, T.; Komasa, I. Separation of Eu from Sm/Eu/Gd mixture by photoreductive stripping in solvent extraction process. *Ind. Eng. Chem. Res.* **1995**, *34*, 237–243.
- (60) Tsushima, S.; Nagasaki, S.; Suzuki, A. Photochemical separation and co-precipitation of lanthanides in nitric acid solution. *J. Photochem. Photobiol., A* **1997**, *106*, 57–60.
- (61) de Moraes, C. A.; Ciminelli, V. S. T. *Sep. Sci. Technol.* **2002**, *37*, 3305.
- (62) Van den Bogaert, B.; Havaux, D.; Binnemans, K.; Van Gerven, T. Photochemical recycling of europium from Eu/Y mixtures in red lamp phosphor waste streams. *Green Chem.* **2015**, *17*, 2180–2187.
- (63) Sklyarenko, Y. Divalent europium sulfate. *Zh. Neorganicheskoi Khim.* **1965**, *10*, 647–652.
- (64) *Comprehensive Inorganic Chemistry*, 1st ed.; Bailar, J. C., Emeléus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press, 1973.