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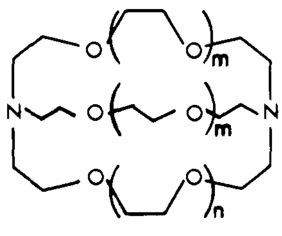
Synthesis and Chemical Properties of Lanthanide Cryptates

Sir:

Several polyoxadiazamacrobicyclic ligands[1] of the type pictured have been found by Lehn and co-workers[2] to encapsulate alkali and alkaline earth cations to form metal cryptate coordination compounds that are extremely stable in aqueous as well as in nonaqueous media. The complexes are found to attain maximum thermodynamic stability when the sizes of the bare metal ions are comparable with the dimensions of the cryptate cavity.[2] Further, the rate constant for dissociation of the divalent $[Ca(2{:}2{:}2)]^{2+}$ cryptate is markedly smaller than that for the monovalent $[Na(2{:}2;2)]^{+}$ cryptate in aqueous solution,[3,4] despite the closeness (near 1 Å) of ionic radius for Ca^{2+} and Na^{+} and the similar thermodynamic stabilities of the two complexes.[2] Such considerations suggested that the encryptation[5] of the tripositive lanthanide ions, whose ionic radii[6] vary in the range of 0.85–1.15 Å, would produce a series of systematically varied, substitutionally inert, yet thermodynamically stable, complexes which could find use in NMR, electrochemistry, synthesis, and medicine. Herein we report the preparation of these novel coordination compounds and discuss a few of their more uncommon chemical properties.



1 m = 1, n = 0 2:2:1

2 m = n = 1 2:2:2

Various nonaqueous solvent syntheses were required to produce analytically pure, crystalline samples.[7] Reaction of stoichiometric quantities of anhydrous $EuCl_3$, for example, with the 2:2:1 ligand **1** in anhydrous organic solvents results in quantitative complex formation. Evaporation and precipitation with ethyl ether gave the crude product, which yielded a white, microcrystalline sample after recrystallization. Analogous procedures were used to prepare the 2:2:1 cryptate trichlorides of tripositive La, Pr, Gd, and Yb. The following analytical determinations for the europium complex are representative. Calcd for $Eu(C_{16}H_{32}N_2O_5)Cl_3$: C, 32.53; H, 5.46; N, 4.74; Eu, 25.72. Found: C, 32.45; H, 5.60; N, 4.92; Eu, 24.73. Formation of the 2:2:2 ligand **2** salts was found to be more facile. The use of lanthanum nitrate yielded $[La(C_{18}H_{36}N_2O_6)](NO_3)_3$. Calcd: C, 30.79; H, 5.13. Found: C, 30.68; H, 5.15. An x-ray crystallographic study of the latter complex is underway.

The Eu(III) and Gd(III) cryptates exhibit remarkable kinetic stability in water and appear to be the first truly substitutionally inert lanthanide complexes.[8] Neutral solutions show no metal hydroxide precipitate even after several days of aging. In strongly basic solution, pH >10, the complexes are stable for hours. Virtually no dissociation of complex is seen even after several days in 0.1 M aqueous perchloric acid, as evidenced by unchanged NMR spectra.[9] This inertness renders the $[Gd(2{:}2{:}1)]^{3+}$ ion useful as a T_1 (shiftless) relaxation reagent[10] for NMR spectroscopy in polar organic solvents or in aqueous solution. For D_2O solutions containing 10% 1,4-dioxane and 40% acetone, successive additions of that cryptate were seen, by using a Varian CFT-20 spectrometer, to reduce the T_1 relaxation times of the acetone CH_3 and CO carbons from 17.6 and 35.4 s, respectively, to 4.9 and 4.8 s at 0.0018 M Gd(III) and to 0.56 and 0.51 s at 0.018 M Gd(III). The relatively inert nature of the cryptate is proven by the exceedingly small (0.2, 1.1 Hz) paramagnetic shifts induced into these resonances, as measured vs. the dioxane signal, even at 0.18 M Gd(III) concentrations. Some very recent, soon to be reported, results of similarly decreased relaxation times from ^{15}N and metal nuclide NMR spectroscopy are even more portentous.

Although the Eu(III) cryptates do tend to act as aqueous lanthanide shift reagents, the effect of encryptation upon the electrochemical behavior of the Eu(III)/Eu(II) redox couple is more remarkable, as illustrated by the cyclic voltammograms

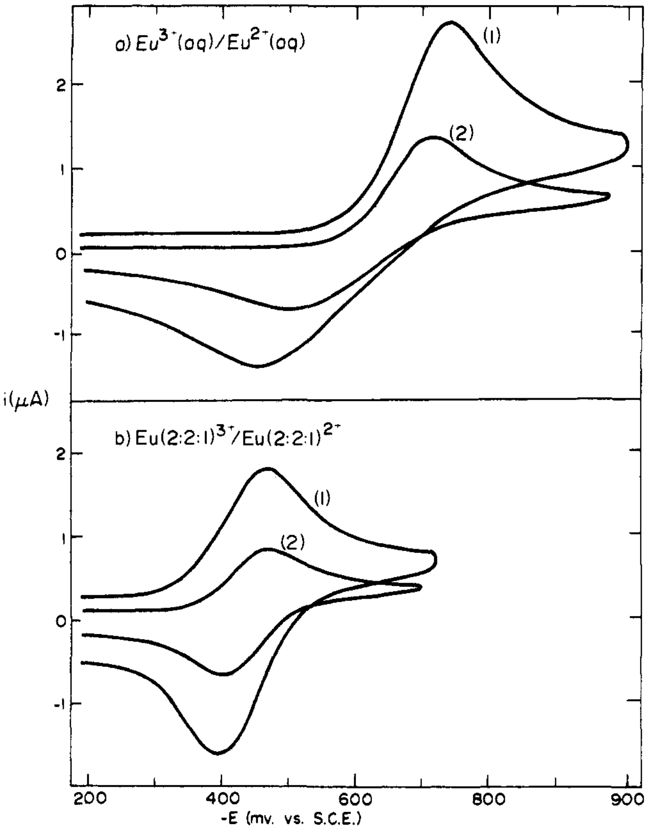


Figure 1. Cathodic-anodic cyclic voltammograms of (a) 0.4 mM Eu^{3+}(aq) in 0.5 M $NaClO_4$ at pH 2 and (b) 0.35 mM $[Eu(2{:}2{:}1)]^{3+}$ cryptate in 0.5 M $NaClO_4$ at pH 7. Electrode area = 0.032 cm^2. Sweep rates: (1) 200 mV s^{-1}; (2) 50 mV s^{-1}.

recorded in Figure 1. Sample waves observed for the reduction and subsequent reoxidation of aquated Eu^{3+} ions in acidified 0.5 M $NaClO_4$ at a hanging mercury drop electrode are shown in Figure 1 (a). Results are acid independent in the range of pH 1-4. The large and sweep rate dependent potential separation between the cathodic and anodic peaks arises from the irreversibility (i.e., slow heterogeneous electron transfer rates) of this couple.[11] In contrast, the corresponding cyclic voltammograms shown in Figure 1 (b) for $[Eu(2{:}2{:}1)]Cl_3$ in 0.5 M $NaClO_4$ exhibit symmetrical peaks with a much smaller, sweep rate independent separation of 65 mV, which is close to the 57-mV value expected for electrochemically reversible redox couples at room temperature.[12] A sizable (>100 fold) catalysis of the Eu(III)/Eu(II) heterogeneous exchange reaction by encryptation is therefore indicated. Cryptate peak potentials were found to be pH independent in the range of pH 1-9 and were unchanged by the substitution of $[(C_2H_5)_4N]ClO_4$ for $NaClO_4$ at a given ionic strength. Taken together, these data provide strong evidence for the electrochemical and chemical reversibility of the $[Eu(2{:}2{:}1)]^{3+}/[Eu(2{:}2{:}1)]^{2+}$ couple and furthermore indicate that both species maintain their chemical integrity on the time scale of these measurements.

The differences in the voltammetric behavior between aquated and encryptated europium ions is useful for following the kinetics of the slow aquation of $[Eu(2{:}2{:}1)]^{3+}$. Thus, at pH <5, Eu^{3+}(aq) is eventually formed as seen by the appearance of the normal, irreversible cyclic voltammograms and by the corresponding decrease in the magnitude of the cryptate peaks. Aquation rate constants, k_{aq}, for that Eu(III) species are measured to be slow, but pH dependent, being near 2×10^{-4} s^{-1} at pH 12, 3×10^{-7} s^{-1} at pH 7, and 1×10^{-6} s^{-1} at pH 0 (for ionic strength of $\mu \sim 1$). For the $[Eu(2{:}2{:}1)]^{2+}$ ion prepared by exhaustive cathodic electrolysis of the tripositive ion at a mercury pool electrode, markedly increased aquation rates (e.g., 2×10^{-4} s^{-1} at pH 5) are observed.

The mean potential between the cathodic and anodic peaks in Figure 1 (b), −435 mV vs. SCE, can be approximately identified with the formal potential, E_f, for the $[Eu(2{:}2{:}1)]^{3+}/[Eu(2{:}2{:}1)]^{2+}$ couple. In contrast, E_f for $Eu^{3+}(aq)/Eu^{2+}(aq)$ has been determined to be −625 mV vs. SCE in 0.5 M $NaClO_4$.[11] This positive shift of E_f upon encryptation, ΔE_f = 190 mV, is equal to $(2.303\ RT/F)(\log K_{II} - \log K_{III})$ where K_{II} and K_{III} are the stability constants for the formation of the Eu(II) and Eu(III) cryptates, respectively, leading to the result that $(\log K_{II} - \log K_{III}) = 3.2$. Two related Eu(III) cryptates,[13] $[Eu(2_B{:}2{:}1{:})]^{3+}$ and $[Eu(2{:}2{:}2)]^{3+}$, have also been prepared and electrochemically characterized and yield similarly reversible cyclic voltammograms with even less negative values of E_f, −370 and −225 mV, which provide values of $(\log K_{II} - \log K_{III})$ of 4.3 and 6.8, respectively. A part of the explanation for the remarkably larger stabilities for Eu(II) vs. Eu(III) cryptates may be found in the significant expansion (~0.15 Å) of the europium ionic radius[6] upon reduction to the +2 state, yielding a better fit within the cryptate cavities. Another important factor may be the considerably greater desolvation that is required for encryptation of the more extensively aquated Eu^{3+} ion.

A further surprising property of the Eu^{3+} cryptates is their strong tendency to complex small anions. In the presence of fluoride or hydroxide anions, for example, cyclic voltammograms for $[Eu(2{:}2{:}1)]^{3+}$ are shifted without change of shape to markedly more negative potentials, and increasingly so when anion concentration is increased. By combining electrochemical data with that obtained from fluoride titration at a fluoride specific ion electrode, anion association with $[Eu(2{:}2{:}1)]^{3+}$ to form complexes containing both one or two ligands was detected, although no such ion association was found for $[Eu(2{:}2{:}1)]^{2+}$. Cumulative stability constants were found to be 3×10^4 M^{-1} and 3×10^6 M^{-2}, respectively, at an ionic strength $\mu = 0.5$. These values are comparable with the corresponding stability constants for the association of *aquated* Eu^{3+} with fluoride, 2.5×10^3 M^{-1} and 3×10^6 M^{-2}, respectively,[14] at $\mu = 0.5$. Similar behavior was found with the hydroxide ion. It is likely that these anions are present between the cryptate strands where they are able to closely approach the Eu(III) center and, because of their small size and negative charge, are able to compete effectively with water for those "coordination" sites.

A considerable effort is underway in our laboratories to more fully elucidate these unusual chemical properties and to exploit their various chemical applications.

Acknowledgments. The authors gratefully acknowledge research support from the Research Corporation (M.J.W.) and the National Science Foundation (O.A.G.), Grant GP-40875.

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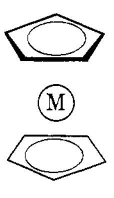
Unusual Electron-Transfer Processes Involving Electron-Rich and Electron-Deficient Metallocenes

Sir:

We wish to report measurements which establish that highly electron-deficient or electron-rich metallocene ((η_5-$C_5H_5)_2M$ or Cp_2M) ions can be generated by electrochemical methods. Although these ions are generally very reactive, cyclic voltammetry (CV) data allow us to draw inferences concerning structural changes involved in the electron-transfer reactions. Included in our discoveries are a 21-electron metallocene (Cp_2Ni^-), which appears to be the most electron-rich metallocene yet detected, the anions of vanadocene (Cp_2V) and chromocene (Cp_2Cr), and a vanadocene cation in which the Cp rings are apparently coplanar.

Working under high-vacuum conditions with an electrochemical cell to be described in a subsequent publication,[1] we have performed electrochemical experiments (CV, dc polarography, coulometry) on the bis(cyclopentadienyl) complexes of V, Cr, and Ni (**1**, $z = 0$). Remarkably, in spite of the obvious



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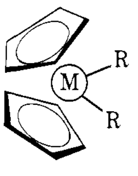

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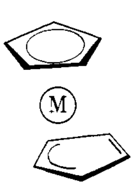

3

importance of oxidation/reduction process in the reactivity (and catalytic properties) of d^2 to d^4 metallocenes,[2-4] no electrochemical studies on neutral Cp_2Cr or Cp_2V have been reported.[5-7] This situation may well have arisen because of the difficulty of handling dilute solutions of these pyrophoric materials, for the redox processes of more air-stable metallocenes such as Cp_2Fe, Cp_2Co^+, and Cp_2Ni have received a great deal of attention.[8]

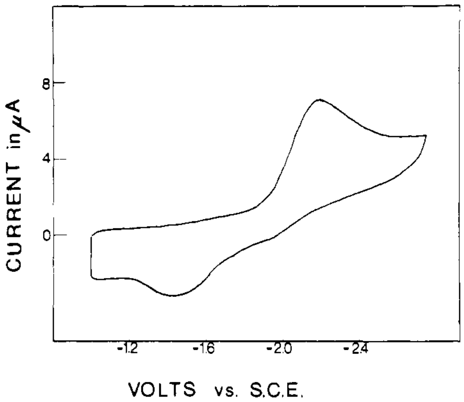

Figure 2. Cyclic voltammogram of the reduction Cp_2Ni in DMF at a platinum electrode, scan rate ~50 V/s.

The electron-transfer reactions of Cp_2Cr appear to be the simplest of the three metals being reported. In either THF or CH_3CN, Cp_2Cr undergoes an electrochemically reversible oxidation to Cp_2Cr^+ and reduction to Cp_2Cr^-, as shown by CV (Figure 1). Salts of the chromocene cation, such as Cp_2CrI, are well known,[9] and the cation probably retains the symmetric coplanar ring structure **1**. The reduction of chromocene is more interesting, for the anion of Cp_2Cr, like all other metallocenes except Co,[8,10,11] has not been previously reported. CV measurements of this reduction show that the anion undergoes follow-up reactions to as yet unspecified products, but the CV peak heights, as well as bulk coulometry measurements, show that a one-electron process is involved in THF.

Cp_2V is reduced just before solvent discharge (ca. −3 V). Polarographic and CV data are consistent with a reversible one-electron change to give the vanadocene anion, a species isoelectronic with Cp_2Cr. The anion is stable enough to be monitored by slow CV, but no bulk electrolyses have been performed as yet.

The electrochemical oxidation of Cp_2V at a platinum electrode allow us to probe the effects of metal oxidation state on the metallocene structure, since the V(III) and V(IV) species derived from Cp_2V, such as Cp_2VX or Cp_2VX_2,[7,12] are believed to have the "bent" structure **2**.[13] Our results confirm that the oxidation of Cp_2V in a relatively inert medium like THF occurs in two discrete steps, yielding first Cp_2V^+ and then Cp_2V^{2+}. The first oxidation, at about −0.7 V, is reversible, and apparently involves no important structural distortions. The second oxidation is irreversible, with an anodic peak potential which is highly dependent on scan rate. The slow electron transfer in the second oxidation is to be expected for a redox process which involves severe structural changes,[14] such as from the planar to the bent structure, **1** → **2**. Presumably,

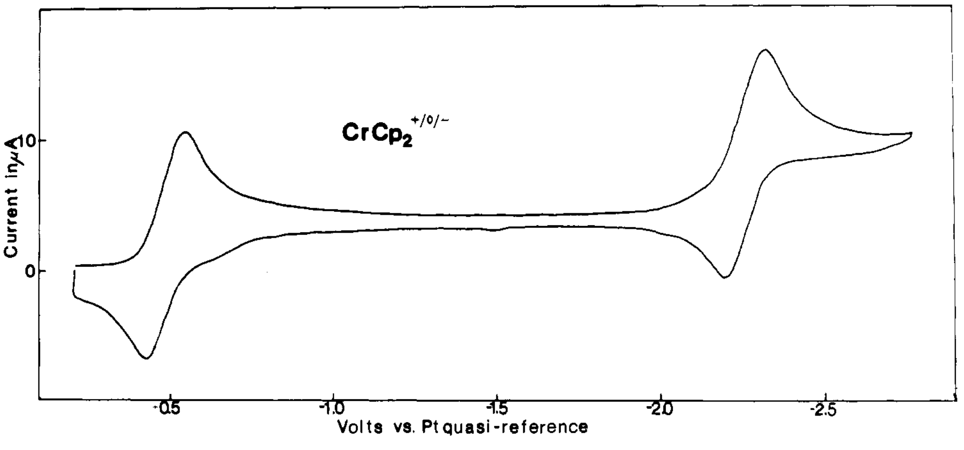

Figure 1. Cyclic voltammogram of Cp_2Cr in THF at a platinum electrode at a scan rate of ~100 mV/s, showing the reversible oxidation to Cp_2Cr^+ and reduction to Cp_2Cr^-.