

Formation of Cryptatium Species in Solution: Electrochemistry of Bipyridyl-, Bipyrimidyl-, and Bithiazole-Based Cryptates

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As a consequence of our recent success in isolating and characterizing the first crystalline cryptatium species, the redox properties of a series of cryptates have been analyzed in DMF using cyclic voltammetry. A total of eight cryptates, derived from six cryptands, were studied (see structures in the text). These were the Na⁺, Ca²⁺, and La³⁺ cryptates of tris(bipyridyl) (1-Na⁺, 1-Ca²⁺, 1-La³⁺) and the Na⁺ complexes of the other five ligands, 2-6. Except for 6-Na⁺, which exhibited irreversible behavior, and for 2-Na⁺, which, as expected, had only one redox couple, all of the cryptates showed at least three quasi-reversible redox couples. For 1-La³⁺ a total of six cathodic waves were observed. A pronounced effect was observed for the reduction potentials when the central metal cation of the cryptate was changed. Thus for 1-Na⁺ the first reduction potential occurs at -2.40 V (vs ferrocene/ferrocenium, Fc/Fc⁺), while the corresponding value for 1-La³⁺ is -1.76 V. On the other hand, for all of the Na⁺ cryptates, the redox potential of each of the individual substituent groups (bipyridyl, bithiazole, dimethylbipyrimidine) was approximately independent of the other substituents present in the molecule, although the reduction state of the complex affected these potentials. For example, the reduction potential for the bithiazole group was the same for the sodium complexes of 2 and 3 and almost the same for the first reduction of 4-Na⁺. Similarly, the reduction of the two bipyridyls of 3 and 5 occurred at the same potentials as those observed for the second and third reductions of 1-Na⁺. All of the reported redox processes correspond to ligand-centered orbitals, not to those of the metals, a result consistent with the spatially-isolated orbital theory which is accepted for bipyridyl complexes of Ru²⁺.

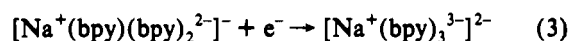
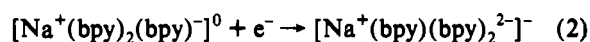
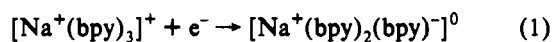
Introduction

Redox properties of some cryptate complexes were reported as early as 1976.² These studies were mainly directed at probing the redox properties of the cryptated metal ions, in an effort to understand the perturbation caused by the presence of the ligands. Cryptands such as [2.2.2] and [2.2.1] were found to cause negatively shifted potentials for the reduction of alkali and alkaline earth cryptated cations.³ The increased difficulty of reduction was found to correlate well with the stability of the corresponding cryptate, a result consistent with a model where ligand binding inhibits electron transfer to the metal center.³ There was only one unexpected and very striking example of drastically modified electrochemical behavior of a cation caused by cryptation by [2.2.2]. The redox couple investigated was that for Eu³⁺/Eu²⁺, and the observation was that the process was much more electrochemically reversible when it took place inside of the cryptand cavity, compared to that in an aqueous solution.⁴ The interpretation was that the cryptand cavity, due to its size, provided an unusually large stabilization of 370 mV for the Eu²⁺ state relative to that of Eu³⁺.⁴

However, the study of the redox properties of the very extensive and diverse family of cryptands and cryptates has been limited to those of the most basic systems such as [2.2.2] and [2.2.1], and these have focused exclusively on the properties of the cryptated metal cations, not on the redox properties of the ligands themselves. There are many cryptands and cryptates which contain redox-

active groups such as bipyridyl, but these have not been studied by electrochemistry before. There has been only one report related to the redox properties of one of the more elaborate cryptates, the sodium cryptate of 1.⁵ In that particular case the redox properties of the ligand, and not those of the cryptated cation, were investigated.⁵

Three quasi-reversible redox waves were observed for 1-Na⁺ in DMF using cyclic voltammetry.⁵ The potentials, $E_{1/2}$, referenced to Fc/Fc⁺ are -2.40, -2.51, and -2.68 V. These correspond to the successive reductions of the three bipyridyl groups of 1-Na⁺, leading to the overall formation of a dianionic complex, eqs 1-3. It was shown⁵ that the one electron reduction



of 1-Na⁺ in acetonitrile led to the precipitation of the neutral complex. If the precipitation was done slowly using an electrocrystallization cell under vacuum, it was possible to generate the neutral complex, which was named a cryptatium in order to capture the essence of its expanded metal character.⁵ It is important to note that none of the reduction waves observed corresponded to a metal-centered orbital. Similarly, in the present work only ligand-based redox processes of the cryptates are investigated.

No other electrochemical data have been reported for ligand-based redox processes of cryptate systems, but non-cryptate analogues such as tris(bipyridyl) and tris(phenanthrolyl) metal

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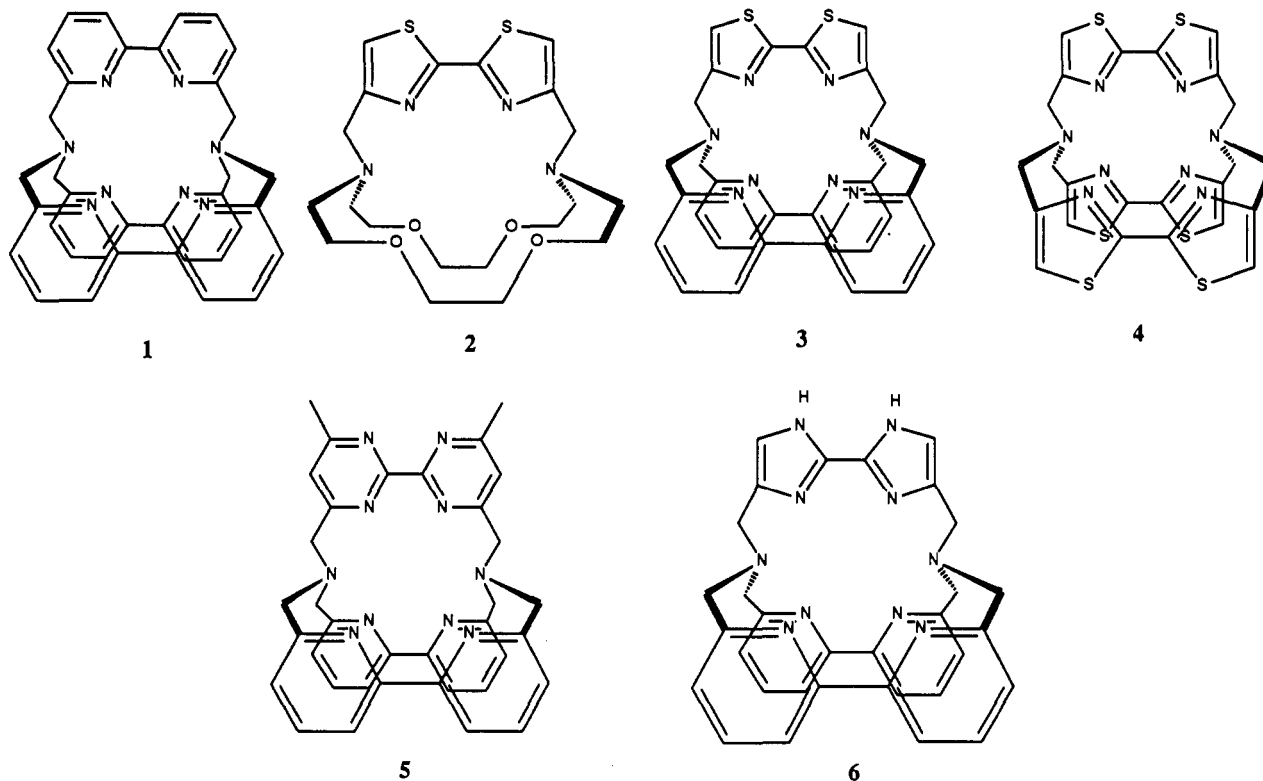
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Chart I



complexes have been extensively studied.⁶⁻¹⁰ Since these are conceptually related to the cryptates presented in this work, the most salient features of their electrochemical behavior are now briefly reviewed. The electrochemical properties of tris(bipyridyl) and tris(phenanthrolyl) complexes of ruthenium, iron, and osmium have been described.⁶⁻¹⁰ Multiple ligand-based electron reductions of these systems lead to the formation of highly anionic complexes.⁶ Six quasi-reversible redox couples have been reported for $[\text{Ru}(\text{bipy})_3]^{2+}$ in DMF at low temperature, while up to ten such processes have been observed for an analogous system with substituted bipyridines ($[\text{Ru}\{4,4'-(\text{CO}_2\text{Et})_2\text{bipy}\}_3]^{2+}$).⁶ All of the observations involving these complexes have been rationalized using the spatially-isolated orbital theory.⁸ This theory assumes that the π orbitals of each of the aromatic ligands are isolated and are thus filled independently as the complex is successively reduced. Thermal activation of the electrons added during the reductions is possible and results in electron hopping rates between the equivalent ligands which can lead to ESR line width effects.⁹ For $[\text{Ru}(\text{bipy})_3]^{2+}$, one-, two-, or three-electron coulometric reduction leads to $S = 1/2$ systems in DMF solution.¹⁰ The first and second electrons are thermally delocalized over the three bipyridyls, as evidenced by the temperature-dependent ESR line widths.⁹ The third electron reduction leads to a thermally localized

system, for which ESR hyperfine has been resolved at high temperature.¹⁰

We present here electrochemical results for cryptate complexes of the macrobicyclic ligands 1-6.^{11,12} They are in accord with those observed for the tris(bipyridyl)-like complexes and thus consistent with the spatially-isolated redox orbital model. All of the cryptate complexes contained Br^- as the counterion, except for 1- La^{3+} , which contained Cl^- .

Results and Discussion

The cyclic voltammograms of three representative cryptates, 1- Na^+ ,¹¹ 1- Ca^{2+} , and 1- La^{3+} ,¹² are shown in Figure 1. The potentials, $E_{1/2}$, for all of the cryptates studied, and measured from the voltammograms vs Fc/Fc^+ , are given in Table I. A simple inspection of all of the voltammograms shows that the wave pattern observed is very similar for all of the cases studied. Most of them consist of three, evenly spaced and quasi-reversible redox couples, followed, in some cases, by other more distant waves at much more negative potentials. One exception to this behavior is 2- Na^+ , an anticipated result since this complex contains only one reducible ligand, a bithiazole (btz) ring; see Figure 2a. All others contain three reducible groups and exhibit these three consecutive redox waves. The regularity of the wave sequence is best interpreted as the stepwise reduction of each ligand. The pattern is, as discussed in the Introduction, similar to the cases of non-cryptand systems such as $[\text{Ru}(\text{bipy})_3]^{2+}$.⁶⁻¹⁰ This explanation seems plausible since the observed reductions parallel the number and type of ligand units present in the corresponding cryptates (Figure 2). For the Na^+ cryptates the btz groups are reduced commencing at -2.1 V vs Fc/Fc^+ (see entries in Table I for 2- Na^+ , 3- Na^+ , and 4- Na^+ and Figure 2a,b,d); the dimethylbipyrimidine groups are reduced also around -2.1 V,

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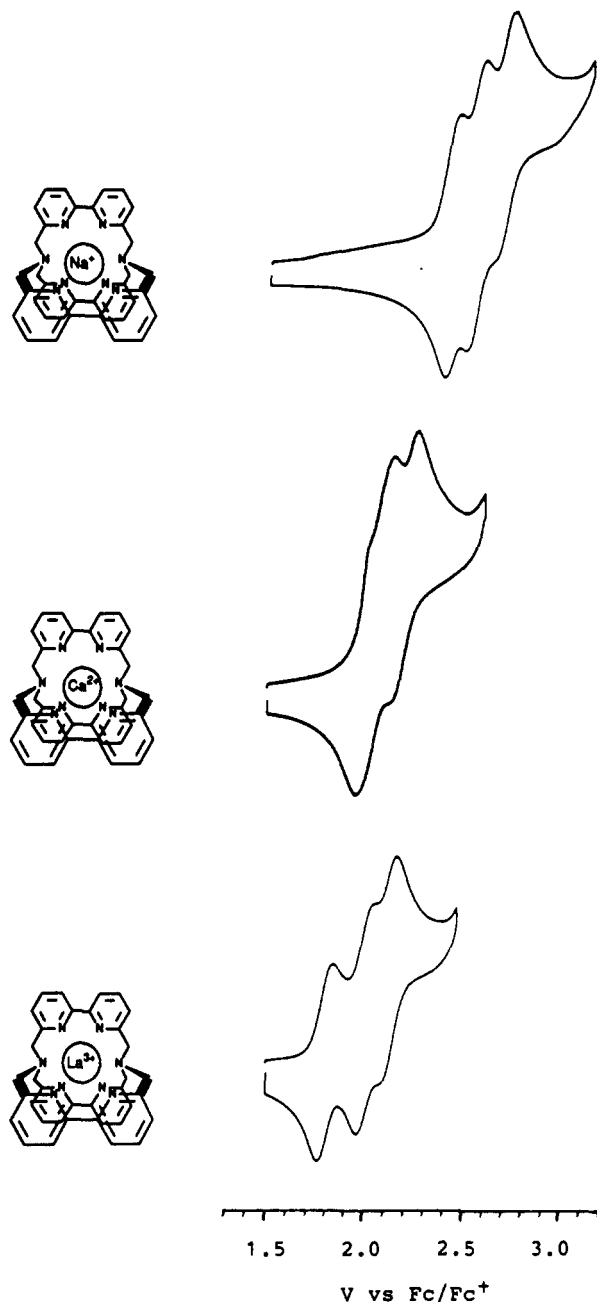


Figure 1. Cyclic voltammograms for the complexes 1-Na^+ , 1-Ca^{2+} , and 1-La^{3+} . The potential axis is referenced to the Fc/Fc^+ couple. All voltammograms were recorded in DMF-TBAPF₆ (0.1 M) at a sweep rate of 100 mV/s, using a glassy-carbon working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode.

the biimidazoles around -2.4 V, and the bipyridines at -2.4 V. The observations for all of the cryptates are thus consistent with the spatially-isolated redox orbital theory used to account for the behavior of non-cryptand ligand-metal complexes. One may note that the individual redox-active units are covalently linked in the present cryptands, yet they behave similarly to the cases where the ligands are held in the complex via their interactions with the central metal ion.

An interesting aspect of the observed results is the independence of the potential values for each of the substituent groups, regardless of the other groups present in the ligand. Similar behavior has been previously observed and reported for a variety of transition metal complexes with pyridyl-type ligands.⁷ This behavior is illustrated by the cyclic voltammograms presented in Figure 2. For example, the potential for the reduction of btz in 2-Na^+ (-2.15 V) is essentially identical to that in 3-Na^+ (-2.14 V), even though the latter contains two bipyridyl (bpy) groups instead of

the polyether chains (Figure 2a,b). Although slightly lower, the value for the redox potential of the btz group in 4-Na^+ (-2.08 V) is also very close to these two cases (Figure 2d). When only bpy's are present in the ligand, as in 1-Na^+ , the first reduction is much more negative (-2.40 V, Figure 2c), but the second and third (-2.51 and -2.68 V, respectively) match closely the corresponding ones for 3-Na^+ (-2.44 and -2.64 V), which also contains two bipyridyl groups. This pattern is also matched by 5-Na^+ , whose second and third redox processes are assigned to the two bipyridyls in the complex (at -2.48 and -2.63 V, respectively). Serendipitously, the redox potential for the dimethylbipyrimidine group in 5-Na^+ (-2.15 V) is essentially identical to that for the btz group.

Some of these results are presented in graphical form in Figure 3. These plots were constructed from the corresponding cathodic potentials only, not from the $E_{1/2}$ values, in order to be able to include the corresponding numbers for the fourth electron reduction, which, in all cases, was chemically irreversible. The potential values versus the charged state of the complex are presented for 1-Na^+ , 3-Na^+ , 4-Na^+ , and 5-Na^+ . Notice the almost perfectly linear correlation observed for the three experimentally observed potential values of 4-Na^+ . It is interesting to note that even though this was the easiest complex to reduce in this group, it was the only one for which it was not experimentally possible to detect a fourth cathodic wave. Another reasonably linear correlation is observed for the four waves detected for 1-Na^+ . The latter four are negatively shifted by about 0.3 V relative to those for 4-Na^+ , but the slope of the line is almost identical. The behavior of 3-Na^+ is a composite of these two. The initial potential is almost coincident with that for 4-Na^+ , but the second and third waves are very close to the corresponding ones for 1-Na^+ , as described in the previous paragraph. This is indicative of the high degree of independence of these substituent groups, at least in terms of their redox energies. One can also see from Figure 3 that complex 5-Na^+ follows the behavior of the second and third waves of 1-Na^+ , while its initial wave potential, although closer to that for 4-Na^+ , is not coincident with any of the other three complexes represented in this graph. Interestingly, a fourth wave was also observed for all of the complexes, except for 4-Na^+ , which however is initially the easiest to reduce.¹ Furthermore, the most positive fourth wave was exhibited by 1-Na^+ , which is initially the most difficult to reduce. These observations indicate that formation of the anion radical of the btz group is much more energetically favorable than the corresponding reduction to form the bpy anion radical. On the other hand, formation of the dianion must be much more unfavorable for btz, to the point where a fourth wave was not detected down to ~ -3 V vs Fc/Fc^+ . This is consistent with its smaller size compared with bpy and thus the consequent increase in charge density that would result. The fact that the fourth wave is so much more negative for 3-Na^+ than for 1-Na^+ is probably indicative of extensive electron delocalization for these multianionic species. If charge and spin densities were to be largely localized even for the multianionic species, then it would have been anticipated that 3-Na^+ should have exhibited a fourth reduction at a very comparable potential to that observed for 1-Na^+ . The fact that it is so much more positive for 1-Na^+ must reflect a large stabilization arising from delocalization. Such stabilization is not possible for 3-Na^+ if btz dianion formation is energetically disfavored.

Although electrochemical processes more cathodic than the third reduction are detected for several of these systems, most are chemically irreversible (Table I). 1-La^{3+} was the only complex for which a total of six cathodic waves were clearly resolved and for which some degree of chemical reversibility was observed for the last three voltammetric waves. Nevertheless, notice that the values reported in Table I for the last three reduction processes of 1-La^{3+} are based only on cathodic waves, not on $E_{1/2}$ values.

Table I. Potential Values for the Cryptates Studied, Referenced to Fc/Fc⁺,^a Where Values in Parentheses Correspond to Peak-to-Peak Potential Differences for Each Pair

compd	$E_{1/2}^1$	$E_{1/2}^2$	$E_{1/2}^3$	$E_{1/2}^4$	$E_{1/2}^5$	$E_{1/2}^6$
1-Na ⁺ Br ⁻	-2.40 (80)	-2.51 (90)	-2.68 (110)	-2.94 ^b		
1-Ca ²⁺ (Br ⁻) ₂	-1.98 (96)	-2.14 ^b	-2.18 (138)	-2.77 ^b		
1-La ³⁺ (Cl ⁻) ₃	-1.76 (80)	-1.97 (80)	-2.09 (70)	-2.57 ^b	-2.80 ^b	-3.09 ^b
2-Na ⁺ (Br ⁻)	-2.15 (90)					
3-Na ⁺ (Br ⁻)	-2.14 (80)	-2.44 (100)	-2.64 (90)	-3.32 ^b		
4-Na ⁺ (Br ⁻)	-2.08 (90)	-2.19 (120)	-2.35 (100)			
5-Na ⁺ (Br ⁻)	-2.15 (190)	-2.48 (90)	-2.63 (140)	-3.02 ^b		
6-Na ⁺ (Br ⁻)	-2.36 ^b	-2.52 ^c (140)	c	-3.06 ^b	-3.38 ^b	

^a The average peak-to-peak separation for the Fc/Fc⁺ couple was 0.12 V. ^b Reported value is based only on the cathodic wave. ^c Cathodic wave is very broad and clearly includes more than one process.

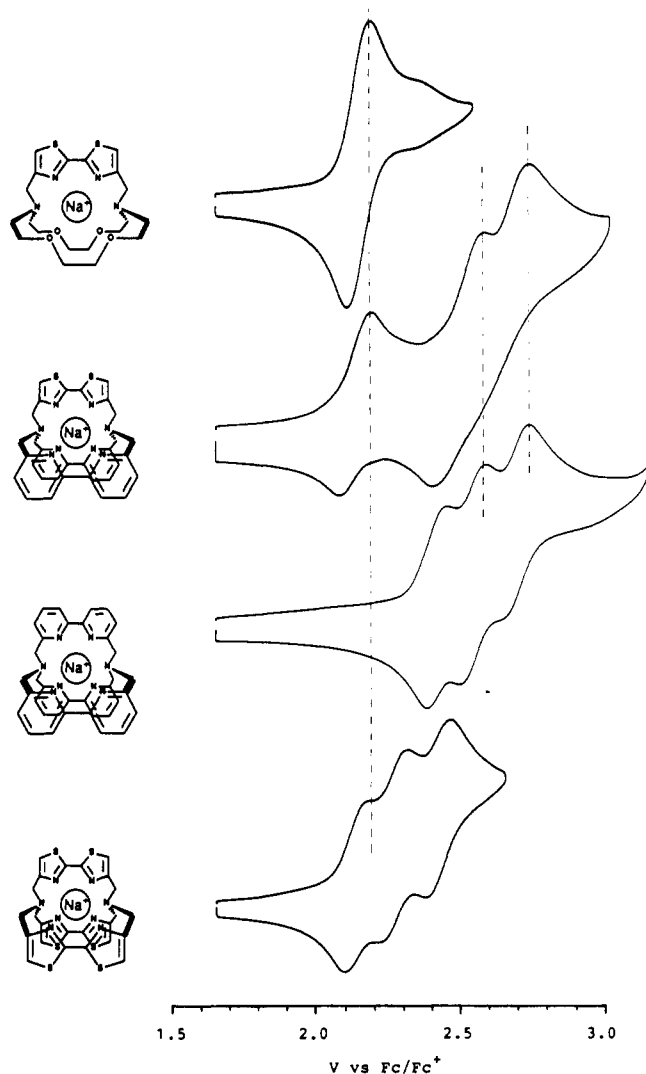


Figure 2. Cyclic voltammograms for the complexes (from top to bottom) (a) 2-Na⁺, (b) 3-Na⁺, (c) 1-Na⁺, and (d) 4-Na⁺. Conditions were the same as those used for Figure 1.

Attempts to enhance the chemical reversibility observed for these waves using faster scan rates and/or low temperatures were not fruitful.⁵

Several interesting observations can be made from the results obtained for the complexes of 1. These three complexes are the only ones in the series which offer the potential to analyze the effect of charge on the complex. These three cations have somewhat similar ionic radii with 0.97, 0.99, and 1.045 Å, respectively, for Na⁺, Ca²⁺, and La³⁺. One would anticipate, however, that similarities would be strongest between Na⁺ and Ca²⁺, simply based on their electronic configurations. An attempt was thus made to try to rationalize the electrochemical results obtained on the basis of simple charge differences, assuming that the organic ligand was an essentially rigid structure (a clear

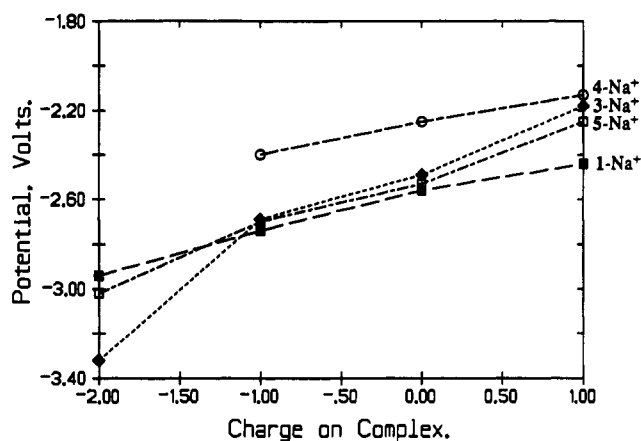


Figure 3. Plot of the cathodic potentials for the complexes 1-Na⁺, 3-Na⁺, 4-Na⁺, and 5-Na⁺ versus the charge on the complex. The lines connect successive reduction peak potentials for each of the complexes.

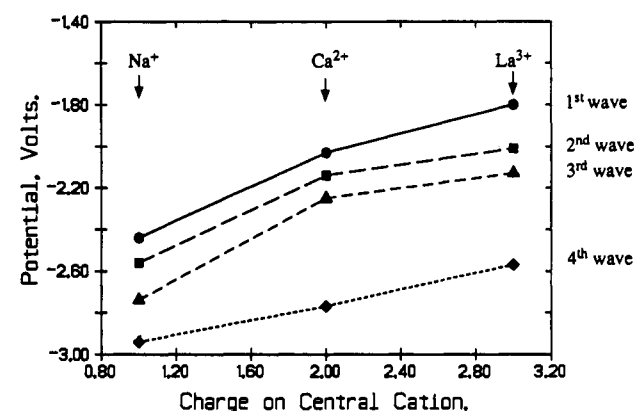


Figure 4. Plot of the cathodic peak potentials for the three complexes of 1, with Na⁺, Ca²⁺, and La³⁺ versus the charge on the central cation. The lines connect the same step reduction in each of the complexes.

oversimplification). Such a model failed, at least partially, but the analyses that resulted provide unanticipated insights about the nature of these systems.

As expected, reduction of the La³⁺ complex is the easiest (first reduction at -1.76 V), while that of the Na⁺ complex is the most difficult (first reduction at -2.40 V), with the one for the Ca²⁺ complex falling in between (at -1.98 V). Figure 4 gives a graphical presentation of the first four cathodic potentials for the complexes of 1 versus the charge on the central cation. Assuming that the complexes are rigid spheres, one would predict that these plots should be linear, simply reflecting the differences in electrostatics predicted from the differences in charge. The plots for the first three cathodic waves are clearly not linear, thus indicating that the model is an oversimplification, while the one for the fourth wave is indeed linear. In order to linearize the results for the first three waves one would have to assume either that the values for the Na⁺ complex were too negative, that those for the Ca²⁺ complex were too positive, or that those for the La³⁺ complex

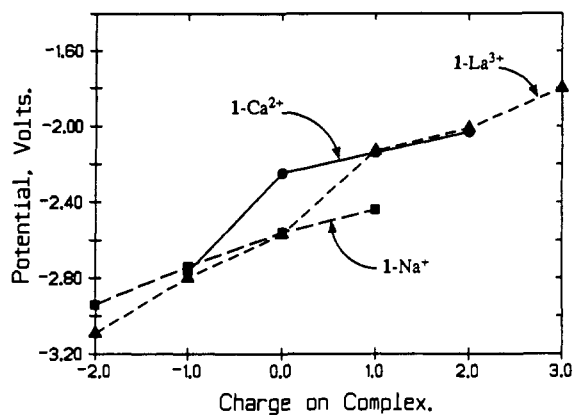


Figure 5. Plot of the cathodic peak potentials for the complexes of **1** with Na^+ , Ca^{2+} , and La^{3+} versus the charge on the complex. The squares, circles, and triangles correspond to the Na^+ , Ca^{2+} , and La^{3+} complexes, respectively.

were too negative. Initially, it would seem reasonable to assume that the Na^+ and Ca^{2+} complexes should follow a more linear correlation, simply based on their almost identical ionic radii and their more similar electronic configurations. But simple inspection of Figure 4 reveals that the behavior exhibited by the Ca^{2+} and La^{3+} complexes is more consistent and very different from that for the Na^+ complex. Notice, for example, that the energy gap between the third and fourth cathodic waves is almost the same for the Ca^{2+} and La^{3+} complexes (0.52 and 0.45 V, respectively) but much smaller for the Na^+ complex (0.20 V). It is also evident that the first reduction of the Ca^{2+} complex occurs at the same potential as the second one of the La^{3+} complex, as expected if both systems behave similarly; vide infra. Thus the conclusion is that the first three reduction waves for the Na^+ complex are the ones occurring at potentials which are too negative, probably indicating that this is, relatively speaking, the most unstable of the three complexes. After the third reduction wave the complexes obey the linear relationship predicted on the basis of simple electrostatic considerations. This must be due to a shielding effect upon completion of a "half-filled" shell, assuming that the hexareduced product corresponds to the filled shell. This leveling effect, which seems to render all species isostructural, is evident when comparing homologous species with equal charge; vide infra.

The data for the electrochemical results of the complexes of **1** can be cast in a different manner in order to provide additional insight. The question one may address is how close are the reduction potentials of species with the same charge? For example, are the electrochemical properties of monoreduced 1-La^{3+} similar to those of 1-Ca^{2+} and those of direduced 1-Ca^{2+} similar or not to those of monoreduced 1-Na^+ , etc.? In order to shed light on these questions the potential values were plotted versus the charge on the complex as shown in Figure 5 (see also Figure 3), thus providing six experimental points for the corresponding cathodic waves observed for 1-La^{3+} and four points for the corresponding ones for the complexes with Na^+ and Ca^{2+} . All potentials fall generally on two sets of approximately parallel straight lines. As previously seen in Figure 3, 1-Na^+ exhibits an approximately linear behavior of the four observed cathodic waves. This is also the case for the first three waves of 1-Ca^{2+} and roughly true for the first three of 1-La^{3+} . It is interesting to note that the first three waves of 1-Ca^{2+} and the first three of 1-La^{3+} all fall on the same line. It is clear that the behavior of the first three waves of 1-Ca^{2+} and 1-La^{3+} corresponds to the filling of the tris-bpy shell of the ligand with one electron per bpy unit. Thereafter, the electrostatic repulsion experienced upon addition of a second electron to a bpy leads to a shift of about 0.5 V to more negative potentials onto another line (fourth wave of 1-Ca^{2+} ; fourth, fifth, and sixth waves of 1-La^{3+}), which is close to the line of the 1-Na^+ potentials. It is difficult to trace the origin of the different behaviors of 1-Ca^{2+} and 1-La^{3+} on one side and of 1-Na^+ on the

other. One may however note that in the crystal structure of $[1\text{-La}^{3+}]\text{Cl}_3$ two chloride anions are bound to the complexed La^{3+} cation.¹³ There are no structural data available for 1-Na^+ , but in the structure of the related cryptate, where the bpy units of **1** are replaced by 1,10-phenanthroline groups, the bromide anion is not linked to the cation.¹⁴ Thus differences in interaction with counterions may affect the redox potentials of the cryptates of **1**. Another factor could be a more or less pronounced twist between the pyridine groups of the bpy units depending on the complexed cation and on its interaction with anions or solvent molecules through the faces of the macrobicyclic system. Electrochemical studies of other related cryptates should help to provide further information on the factors affecting their redox properties.

The cathodic potential for the monoreduced 1-La^{3+} to form its monopositive product is indeed coincident with that for the unreduced 1-Ca^{2+} to form its monopositive product. Similarly, the reduction wave for direduced 1-La^{3+} (to form the neutral complex) coincides with the one for the monoreduced 1-Ca^{2+} , also to form its corresponding neutral complex. Yet neither one of the latter corresponds to the value observed for the first cathodic wave of 1-Na^+ , which also leads to the formation of a neutral complex. All of these observations are in agreement with the conclusion arrived at in the previous paragraph that the Na^+ complex is the odd one in the series. It is not until their fourth reductions that the 1-La^{3+} and 1-Ca^{2+} have cathodic waves which fall on the line for the 1-Na^+ homologue. Thus reduction of trireduced 1-La^{3+} ($[1\text{-La}]^0$) to its corresponding monoanionic complex ($[1\text{-La}]^-$) occurs at the same potential as the reduction of $[1\text{-Na}]^0$ to $[1\text{-Na}]^-$. The closeness of subsequent waves for both of these complexes continues all the way down to the most negatively measured cathodic waves (the sixth of 1-La^{3+} and the fourth of 1-Na^+), although some deviation is apparent for the most negative values. Also the wave leading to the formation of $[1\text{-Ca}]^{2-}$ coincides with those leading to the formation of $[1\text{-Na}]^{2-}$ and $[1\text{-La}]^{2-}$.

Experimental Section

Reagents. The metal complexes used in the present study were synthesized and purified according to previously published procedures.^{11,12} Electrochemical grade tetrabutylammonium hexafluorophosphate (TBAPF₆) from Fluka Chemical Corp. was recrystallized twice from pure ethanol, pulverized, and dried in a vacuum oven at 125 °C.

HPLC grade *N,N*-dimethylformamide from Aldrich Chemical Co. was dried over metallic sodium and vapor transferred directly into the electrochemical cell from the benzophenone ketyl radical after repeated freeze-pump-thaw degassing cycles at 10^{-5} – 10^{-6} mmHg.

Preparation of the Cryptate 1-CaBr_2 . $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$ (26 mg, 0.11 mmol) was added to a stirred solution of 1-NaBr (50 mg, 0.07 mmol) in CH_3OH (10 mL) at reflux. Heating and stirring was continued for 24 h under a nitrogen atmosphere. Slow evaporation yielded a white microcrystalline product, 47 mg (82%). Mp: 179 °C dec. ¹H NMR (CD_3OD) (δ): 4.21 ($\text{CH}_2\text{-bpy}$); 7.45 (d, $J = 7.2$, 6H); 7.91 (t, $J = 7.7$, 6H); 8.04 (d, $J = 7.4$, 6H). FAB-MS (NBA/ CH_3OH): m/e 695.0 ($[\text{M} + \text{Ca} + \text{Br}]^+$), 613.1 ($[\text{M} + \text{Ca}]^+$), 429.0 ($[(\text{bpy-bpy}) + \text{Ca}]^+$). Anal. Calc for $\text{C}_{36}\text{H}_{30}\text{N}_8 \cdot \text{CaBr}_2 \cdot 4\text{H}_2\text{O}$ (846.63): C, 51.07; H, 4.52; N, 13.23. Found: C, 51.37; H, 4.12; N, 12.99.

Procedure. In general, a 1-mL sample solution containing $(1-2) \times 10^{-3}$ M metal complex and 0.1 M TBAPF₆ was prepared by drying the solid reagents directly in the electrochemical cell at 10^{-5} mmHg and then transferring the solvent directly into it through the vacuum line.

Instrumentation. The electrochemical cell used was designed and constructed in-house in order to perform all the electrochemical studies under high-vacuum conditions. A conventional three-electrode configuration was used, with a 3-mm diameter glassy-carbon disk as the working electrode (from Bioanalytical Systems, Inc.), a platinum counter electrode, and a Ag/AgCl reference electrode.

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Cyclic voltammograms at room temperature were recorded using a Soltec Model VP-64235 X-Y recorder interfaced with a Princeton Applied Research electrochemical system composed of a Model 173 potentiostat/galvanostat, a Model 175 universal programmer, a Model 178 electrometer probe, and a Model 179 digital coulometer.

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