Reducing supermolecules to "pseudo-atoms" and anions: Cryptatium species and C60

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Abstract

As part of our continued interest in the redox properties of macrocyclic and macrobicyclic ligands and their corresponding metal cation complexes, we have recorded the electrochemistry of several cryptands and their cryptates, along with those for the carbon clusters C_{60} and C_{70}. The electrochemistry of C_{60} and C_{70} at low temperature has yielded the first observation of the corresponding hexaanionic forms, C_{60}^{6-} and C_{70}^{6-}. These multiple reductions appear to be chemically and electrochemically reversible under the conditions used, so the method has been employed to generate and detect C_{60}^{2-} by ESR spectroscopy. The cryptands and cryptates studied also exhibit multiple ligand-based redox processes and, in some cases, the reduction products are isolated as crystalline materials. The crystal structure of one of these materials, the first **CRYPTATIUM** species, has been reported. This species is a neutral, expanded-metal type intramolecular ion pair. On a closely related topic, formation of a novel crystalline material from the reductive electrocrystallization of $[Ru(bpy)_3]Cl_2$ is reported here for the first time. The latter material is assumed to be $[Ru(bpy)_3]^{0}$.

INTRODUCTION

Our initial interest in the electrochemistry of macrocyclic and macrobicyclic ligands and their corresponding metal cation complexes derived from a desire to couple the redox processes to the complexation equilibria (ref. 1). The plan was to use the generation of negative charge on the ligand via reduction (of its nitrobenzene or anthraquinone substituent, whichever was the redox antenna) as a vehicle for intramolecular ion pairing with the bound and positively charged cation (ref. 2). Such a design resulted in the syntheses of novel ligands capable of redox-switched enhanced cation binding (ref. 1,2) and enhanced transport across lipophilic environments (ref. 3). Thus, our initial interest in macrocyclic and macrobicyclic electrochemistry stemmed mainly from a desire to impart novel functional properties to these ligands by making them better cation binders and transporters via the redox switch.

More recently, our interest in the electrochemical properties of similar macrocycles, macrobicycles, and even of carbon clusters has been directed by the possibility of manipulating and transforming them into novel materials with unique properties. An example which has captured our interest, as well as that of the rest of the scientific world, is C_{60} (ref. 4). This molecule, along with the many other members of the fullerene family, exhibits very rich redox chemistry (ref. 5). While its mono, di, tetra, penta, and hexaanionic forms are not conducting in the solid state, its trianionic form, prepared with a variety of reducing metals, is superconducting in many cases (ref. 6). These reduced forms of C_{60} are the molecular materials with the highest superconducting T_C's presently known. The wide variety of superconductors made with C_{60} offers a solid experimental base to help theoreticians elucidate the intricate details of this still poorly understood phenomenon. More importantly to us, the redox chemistry of C_{60} is obviously crucial to the understanding of these novel materials. Our contribution in the area of fullerene electrochemistry and preliminary ESR spectroscopy is presented here.

Just as reduction of C_{60} to its trianion (by selected metals) transforms it into a superconductor, reduction of other macrocycles, macrobicycles, and their complexes is expected to result in the formation of novel materials with unique properties. Thus the connection between these two seemingly unrelated topics of our research interest. This was the premise behind the redox studies performed with macrobicyclic

cryptands and cryptates which incorporate redox active ligands, such as bipyridine (ref. 7). The concept was to reduce a positively-charged cation cryptate to its neutral form, to result in the formation of a neutral pseudo-atom or expanded metal atom, as represented in scheme 1. Such a species, called a

Scheme 1
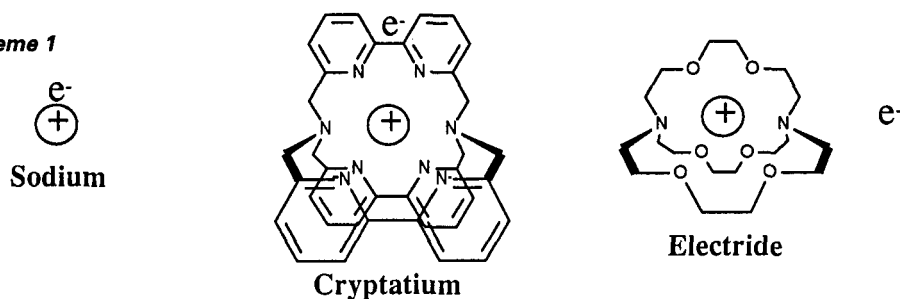
CRYPTATIUM in order to capture its cryptate origin and its neutral metal character, has been isolated for the case where the metal cation is Na⁺ and the ligand is the tris-bpy cryptand depicted in the scheme (ref. 7). The crystal structure for this species has been solved and it clearly showed that the unpaired electron is localized in one of the three bipy groups present (ref. 7). This was evident from the fact that there was a C_2 axis of symmetry present which bisected the py-py bond of only one of the three bipy's and passed through the central Na⁺. Furthermore, that particular bipy was almost perfectly coplanar (dihedral angle of only 0.7°) while the other two had dihedral angles of 16°. Due to its conceptual relation to the electrides (ref. 8), where the electron is expelled completely from the cryptate complex, the latter is also represented in the scheme. Although most of the properties of this cryptatium still remain to be explored, several other cryptates have been analyzed in solution using electrochemical techniques. Some of their results are presented here.

Finally, in a related development, reductive electrocrystallization of [Ru(bpy)₃]Cl₂ has been recently found to yield very dark blue crystals. Such an unprecedented result is reported here for the first time in preliminary form.

RESULTS AND DISCUSSION

C₆₀ electrochemistry and ESR spectroscopy

Our initial cyclic and differential pulse voltammetric (CV and DPV) results for C_{60} and C_{70} at -10° C were reported in a solvent mixture composed of CH_3CN:toluene in a ratio of 1:5.4 by volume, containing $TBAPF_6$ as supporting electrolyte (ref. 9). As noted in ref. 9, all six waves appeared reversible, both chemically and electrochemically, even at scan rates of 100 mV/s (Figure 1).
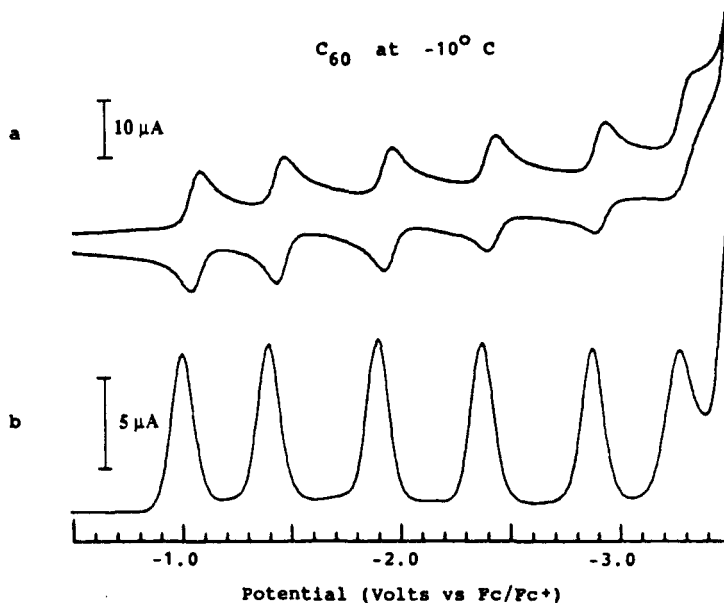

Fig. 1. Electrochemical reduction of C_{60} in CH_3CN/Toluene at -10°C, using a)CV, b) DPV.

Based on these results, we have used the same solvent-electrolyte system described in ref. 9 to generate C_{60}^- and C_{60}^{2-} via bulk electrolysis on a Pt mesh working electrode. All experiments were conducted under high vacuum conditions (10^{-5} mm Hg) as reported in ref. 9 using a BAS-100 Analyzer operating in the bulk electrolysis mode. Reduction was carried out at a potential of -1.15 V for the generation of C_{60}^- and -1.50 V for C_{60}^{2-}, referenced to Fc/Fc$^+$. Integration of the current-time curve yielded a value of 0.98 e$^-$/molecule for the generation of the monoanion and a value of 2.02 e$^-$/molecule for the generation of the dianion at the completion of the electrolysis. These coulometric reduction experiments were performed independently, that is, the dianion was directly prepared from the neutral C_{60}, not from its mono anion. The solution changed from its original violet color to purple-brown (anion), and then to red-brown, which is characteristic of the dianion.

The ESR spectrum for the anion radical is similar to that previously reported (ref. 10). It consists of a very broad line of 87 gauss width superimposed with a very sharp one of 0.97 gauss. The intensity of the sharp line is only 0.25-2% of the intensity of the broad component. The extreme broadness of the ESR line for the anion radical remains unexplained (ref. 10) but seems to be somehow related to the fact that this is the first triply degenerate anion radical ever studied (ref. 10). Previous results with doubly degenerate systems have shown increased linewidths. Since our own results with the anion radical spectrum of C_{60} are essentially identical to those reported by others (ref. 10-13), no spectrum is presented here. On the other hand, results with the dianion are very different from those reported previously, and a corresponding spectrum is presented in Figure 2.

Figure 2 shows two clearly resolved signals, which are separated by approximately 0.4 gauss. These signals are very sharp, and the low field one exhibits a well resolved pattern consisting of seven lines. These lines are very sharp, with an average width around 40 mgauss. The seven line signal reversibly decreases in intensity relative to the high field one as the temperature is decreased, Figure 2. An identical spectrum has been obtained when the electrochemical generation of C_{60}^{2-} was conducted in THF-TBAPF$_6$. Therefore, the procedence of the seven lines is not solvent related.

It is difficult to interpret the two signals, especially the one exhibiting the highly resolved hyperfine structure. Although this is not an interpretation of the observed spectral results, we believe that it may be related to the presence of natural abundance ^{13}C. A quick consideration of natural abundance ^{13}C leads to the conclusion that only 51% of all C_{60} molecules contain exclusively ^{12}C. Thus half of the C_{60} molecules contain at least one ^{13}C atom (34% contain 1 ^{13}C, 11% contain 2, 2.4% contain 3,...). At present it has not been possible to explain all of the resonances observed for the dianion of C_{60}.

One relatively surprising result from the ESR spectrum of C_{60}^{2-} in frozen solution was the observation of a single line down to temperatures near that of liquid nitrogen. It was anticipated that the spectrum would split in the usual manner to yield the corresponding pattern for an axially symmetric triplet state (ref. 14).
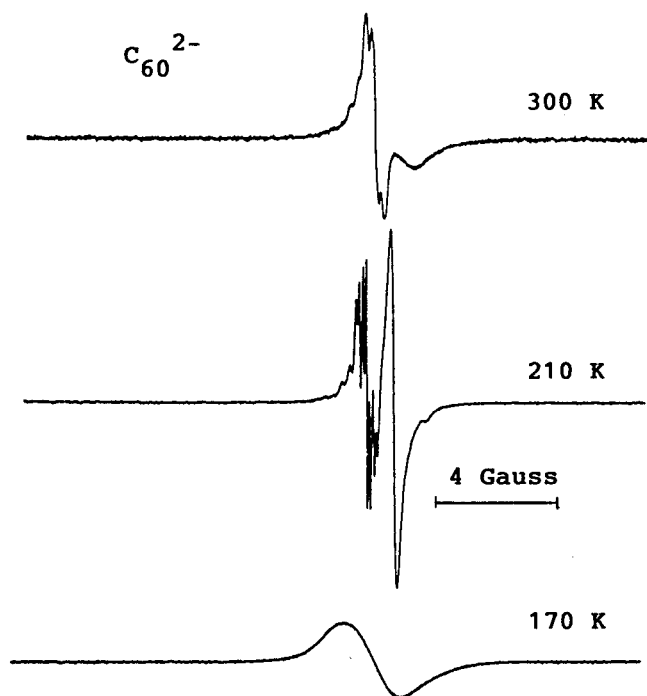

Fig. 2. ESR spectra for C_{60}^{2-} generated electrolytically in CH$_3$CN:Toluene, 1:5.4 v/v.

A Jahn-Teller distortion of C_{60}^- has been predicted theoretically (ref. 15), and has been confirmed by ESR spectroscopy for the optically generated triplet state at 5 K (ref. 16). What seems to be operative is a pseudo-rotation mechanism at temperatures above 5 K which averages out the magnetic axes inequivalency, thus destroying the axial symmetry of the Jahn-Teller distorted molecule (ref. 17). In other words the molecule is indeed spherical on the average on the time scale of the ESR experiment (above 5 K), thus yielding the first triplet state of true high symmetry ever observed. For such a spectrum a single line is predicted since no magnetic anisotropy should result from confinement to a solid lattice (ref. 18). Efforts continue in our laboratory to try to interpret the seven line spectrum observed for C_{60}^{2-}.

Cryptate electrochemistry and electrocrystallization

As mentioned in the Introduction, we have studied the electrochemical properties of several cryptate complexes (ref. 7, 19). These cation complexes resemble C_{60} in that they contain an organic "skin" of high symmetry capable of multiple electron reductions with a well defined central cavity where a cation can be bound. Although C_{60} itself does not contain an encapsulated cation in its central cavity, such species have now been prepared and detected (ref. 20), but their quantities are still small. Our interest in these cryptates has thus been related to their capability to form multiple anions and to constitute novel materials, particularly when they are in an overall neutral state (CRYPTATIUM).

The only electrochemistry of these cryptates presently published can be found in ref. 7. Reference 19 corresponds to a full paper containing the electrochemical results for the cryptates of ligands 1-6. All of these have been studied by CV as their corresponding NaBr complexes. In addition, 1 has been studied as the corresponding $CaBr_2$ and $LaCl_3$ complexes (ref. 19). In the interest of brevity, only some highlights of these results are summarized here, particularly for the complexes of 1 (1-Na$^+$, 1-Ca^{2+}, 1-La^{3+}).

Electrochemical reduction of 1-Na$^+$ in DMF-TBAPF$_6$ on a glassy carbon working electrode shows three quasi-reversible waves at -2.40, -2.51, and -2.68 V vs Fc/Fc$^+$ (ref. 7, 19). Scanning the potential to more negative values shows a fourth cathodic wave at -2.94 V, which is irreversible. As expected based on simple electrostatic considerations, reduction of 1-Ca^{2+} is easier than reduction of 1-Na$^+$, and the potentials for the first three waves are observed at -1.98, -2.14, and -2.18 V. The second value, -2.14, corresponds to the cathodic wave only, since it was almost impossible to measure the corresponding anodic wave. Scanning to more negative potentials also resulted in the observation of a fourth cathodic and irreversible wave at -2.77 V. Also as anticipated, 1-La^{3+} was even easier to reduce and exhibited quasi-reversible couples at -1.76, -1.97, and -2.09 V. Scanning to more negative potentials revealed three additional cathodic waves at -2.57, -2.80, and -3.09 V, Figure 3. It is thus possible to observe the
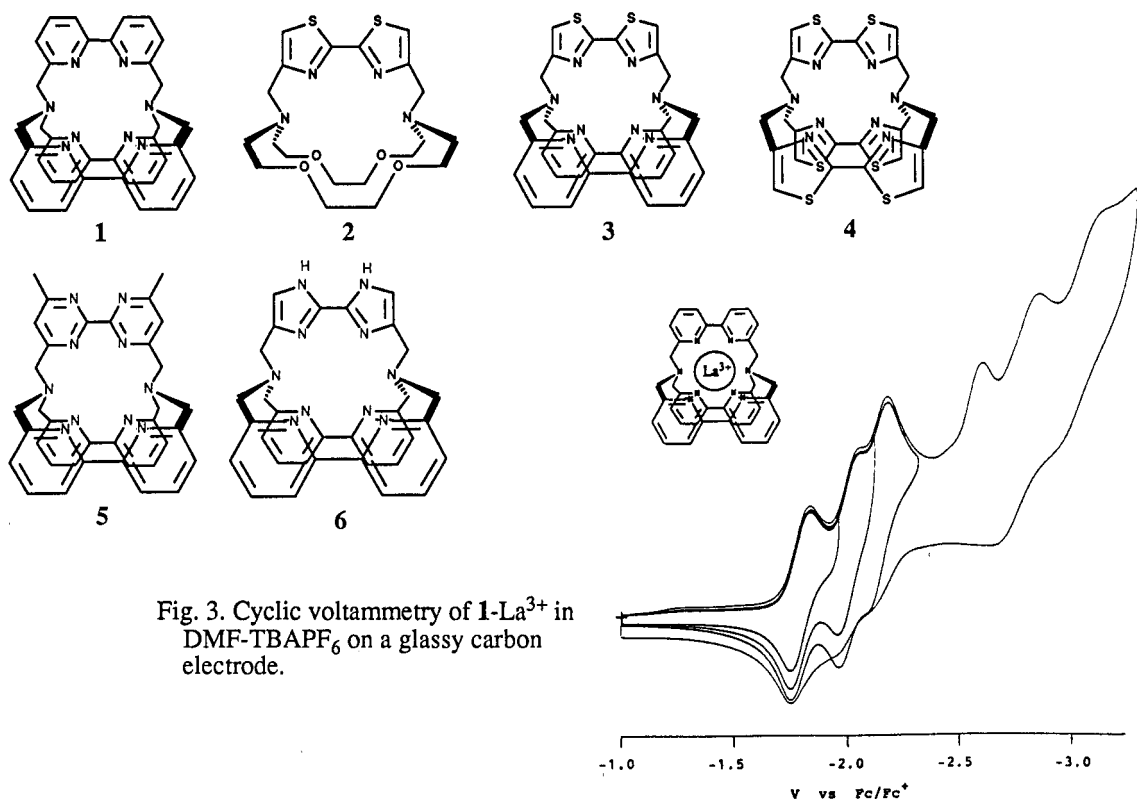

1   2   3   4

5   6

Fig. 3. Cyclic voltammetry of 1-La^{3+} in DMF-TBAPF$_6$ on a glassy carbon electrode.

V vs Fc/Fc$^+$

formation of $[1\text{-La}]^{3-}$ in DMF solution. The observation of these six waves is somewhat reminiscent of the six waves observed for C_{60}, except for the fact that for the latter the waves are more or less equidistant and reversible. For 1-La^{3+}, there is a clear gap between the third and fourth waves, a situation previously seen for a multitude of tris-bipyridyl complexes of a variety of metal ions (ref. 21). Such a gap is the result of electron-electron repulsion resulting from the formation of the first dianionic bpy. The gap, which is 0.52 V for 1-Ca^{2+} and 0.46 V for 1-La^{3+}, is only 0.20 V for 1-Na^{+}. Why there is such a relatively large discrepancy of the gap value between the Ca^{2+} and La^{3+} complexes on the one hand and the Na^{+} complex on the other is presently not well understood. Other related cryptands and cryptates are currently under study in order to try to understand this difference.

From the results of cryptates **2-6**, which are presented in detail in ref. 19, one conclusion has been established. Every group acts electrochemically independently from the others, as has also been found for the bipyridyl complexes of several metal ions (ref. 22). This is a somewhat surprising finding when one considers that these ligands are in fairly close proximity in the cryptand. With non-covalently linked ligands, such as $[Ru(bipy)_3]^{2+}$, this behavior is easier to understand since the ligands are held together via their interaction with the central metal ion.

Future work in this area will be directed to a full characterization of the different reduced states of these cryptates in solution using ESR spectroscopy. Electron hopping rates between the individual ligands as well as their activation energies will be determined via variable temperature ESR experiments. Such experiments are currently underway.

Reductive electrocrystallization of [Ru(bpy)₃]Cl₂

Since the electrochemistry of $[Ru(bipy)_3]^{2+}$ (ref. 21) has been the subject of many studies and is very well understood, we decided to use this system as the non-covalent model for our electrocrystallization experiments. Looking through the literature we found a few places where formation of $[M(bipy)_3]^{0}$ was reported (M=Fe, Ru, Os, ref. 23). Yet the only one that we found which expressly described the material as black and crystalline was ref. 23a, in which M=Fe. As far as we are aware, no attempt to grow single crystals of these materials had ever been reported or even tried. We thus set out to try a reductive electrocrystallization of this complex following the procedures described in detail in ref. 7. Acetonitrile containing 0.1 M TBAPF$_6$ was used as solvent, and the controlled current process was conducted under high vacuum conditions at 7.5 μA. Two Pt wires were used, one as cathode and one as anode.

After several hours at constant current it was possible to see dark black-blue needles growing out of the cathode. These were very thin and grow perpendicular to the electrode surface, pretty much follwing the field lines from the Pt wire. The material is very sensitive to air and must be manipulated under inert atmospheres or under high vacuum.

Preliminary measurements of the properties of this material are encouraging, especially its solid state conductivity, but much awaits to be done. At the present time the only thing that can be safely said is that a new type of material has been found, whose structure and properties may (or may not) show unusual behavior and may parallel that of others such as the CRYPTATIUM described in ref. 7 and maybe C_{60} and some of its anions.

Acknowledgements

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