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R&T CODE: 4133032

TECHNICAL REPORT NO. 83

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Transition Metal Chelate-Fulleride Compounds: Electrocrystallization of Semiconducting  
[Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub>

by

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Prepared for publication

in

Inorganic Chemistry

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Ft. Collins, CO 80523

February 22, 1993

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93-04464

98 3 2 126

**REPORT DOCUMENTATION PAGE**

OMB No 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE Feb 1992		3. REPORT TYPE AND DATES COVERED Interim	
4. TITLE AND SUBTITLE Transition Metal Chelate-Fulleride Compounds: Electro-crystallization of Semiconducting (Ru(bpy) <sub>3</sub> )(C <sub>60</sub> ) <sub>2</sub>				5. FUNDING NUMBERS Contract # N00014-82K-0612	
6. AUTHOR(S) C. A. Foss, Jr., D. L. Feldheim, D. R. Lawson, P. K. Dorhout, C. M. Elliott, C. R. Martin and B. A. Parkinson					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dr. Charles R. Martin Department of Chemistry Colorado State University Fort Collins, CO 80523				8. PERFORMING ORGANIZATION REPORT NUMBER  ONR TECHNICAL REPORT # 83	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Two recent breakthroughs in the chemistry of fullerenes have provided the impetus for using fullerenes to prepare novel solid state materials: a method to produce large amounts of C <sub>60</sub> and related materials, and the discovery of superconductivity in fullerides of K, Rb and Cs. The superconducting alkali metal compounds, which appear to contain C <sub>60</sub> <sup>3-</sup> , show a trend toward higher transition temperatures upon increasing the size of the unit cell up to the composition Rb <sub>2</sub> CsC <sub>60</sub> . We thought that the synthesis of new compounds of reduced fullerenes with large cations might produce materials with interesting properties. Transition metal complexes with neutral chelating ligands (e.g. Ru(bpy) <sub>3</sub> <sup>2+</sup> , where bpy = 2,2' bipyridine) seemed like good candidates as cations for C <sub>60</sub> salts. Such complex cations have a rich electrochemistry and photochemistry. Furthermore, the electronic and optical properties can be varied via ligand and metal substitution, providing a route for tuning the properties of the new materials. In addition, these complex cations can have dimensions comparable to the C <sub>60</sub> molecule, perhaps allowing packing of the cations and the fullerene anions into classical ionic structures such as rock salt, CaI <sub>2</sub> or CaF <sub>2</sub> . In this report, we describe our first efforts toward the preparation of such compounds with the synthesis of (Ru(bpy) <sub>3</sub> )(C <sub>60</sub> ) <sub>2</sub> which we find has a surprisingly high electrical conductivity.					
14. SUBJECT TERMS C <sub>60</sub> , Fullerenes, charge transfer salts				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT		
		UNCLASSIFIED			

**Transition Metal Chelate-Fulleride Compounds:  
Electrocrystallization of Semiconducting  
[Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub>**

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Two recent breakthroughs in the chemistry of fullerenes have provided the impetus for using fullerenes to prepare novel solid state materials: a method to produce large amounts of C<sub>60</sub> and related materials (1), and the discovery of superconductivity in fullerides of K, Rb and Cs (2). The superconducting alkali metal compounds, which appear to contain C<sub>60</sub><sup>3-</sup>, show a trend towards higher transition temperatures upon increasing the size of the unit cell up to the composition Rb<sub>2</sub>CsC<sub>60</sub> (3). We thought that the synthesis of new compounds of reduced fullerenes with large cations might produce materials with interesting properties. Transition metal complexes with neutral chelating ligands (e.g. Ru(bpy)<sub>3</sub><sup>2+</sup>, where bpy = 2,2' bipyridine) seemed like good candidates as cations for C<sub>60</sub> salts. Such complex cations have a rich electrochemistry and photochemistry (4). Furthermore, the electronic and optical properties can be varied via ligand and metal substitution (4), providing a route for tuning the properties of the new materials. In addition, these complex cations can have dimensions comparable to the C<sub>60</sub> molecule (5), perhaps allowing packing of the cations and the fullerene anions into classical ionic structures such as rock salt, CaI<sub>2</sub> or CaF<sub>2</sub>. In this report, we describe our first efforts towards the preparation of such compounds with the synthesis of [Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub> which we find has a surprisingly high electrical conductivity.

We have used electrocrystallization as one route to prepare [Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub>. In dichloromethane, the half-wave potential for the one-electron reduction of Ru(bpy)<sub>3</sub><sup>2+</sup> is ca. 300 mV negative of the C<sub>60</sub><sup>1-/2-</sup> wave and 700 mV negative of the C<sub>60</sub><sup>0/1-</sup> wave. Therefore, it is possible to produce either C<sub>60</sub><sup>1-</sup> or C<sub>60</sub><sup>2-</sup> at the electrode surface without reducing the ruthenium complex. Since the dielectric constant of dichloromethane is small ( $\epsilon_s = 8.93$  [10]), we find that Ru(bpy)<sub>3</sub><sup>2+</sup> ion pairs with electrogenerated C<sub>60</sub><sup>1-</sup> and [Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub> crystallizes on the electrode surface.

This process is evident in the cyclic voltammograms (11) shown in Figures 1 and 2. In both cases the solution was saturated with  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  and was 0.45 mM in  $\text{C}_{60}$ . Figure 1 shows the first cyclic voltammetric scan where the potential was swept past the first  $\text{C}_{60}$  reduction wave (A) and into the second reduction wave (B). On the anodic sweep there is cross-over consistent with an increase in active electrode surface area, and the waves corresponding to  $\text{C}_{60}^{2-}$  (C) and  $\text{C}_{60}^{1-}$  (D) oxidation are sharp and characteristic of stripping processes (12). The origin of the small shoulder at -1.05 V (E) is currently unknown.

Figure 2 shows the first four voltammetric scans in a more restricted potential range. The scan was started at the foot of the first reduction wave of  $\text{C}_{60}$  and continued into the second reduction wave. The anodic sweep does not reach potentials sufficiently positive to re-oxidize  $\text{C}_{60}^{1-}$ . After such continual voltage scans a black crystalline deposit is visible on the electrode surface.

To obtain larger amounts of material required for conductivity and spectroscopic measurements, crystals were grown at a Pt mesh electrode held at -1.1 V for periods between four and six days. In this deposition regime black crystalline needles could be observed growing out from the surface after ca. 12 hours (13). Figure 3 shows a scanning electron micrograph of the  $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$  crystals obtained on a Pt electrode after only 13 minutes in the potential hold (-1.1 V) regime (14). The absence of sample charging suggests that the crystals are conductive. We are currently optimizing the electrolysis procedure to grow crystals of sufficient quality for X-ray structure determination.

The composition of the deposited material was evaluated by dissolving it in benzonitrile and taking a visible/near-infrared spectrum of the resulting solution. The near-IR spectra show that the only fullerene anion present is  $\text{C}_{60}^{1-}$  (15). Also, from the known extinction coefficients for  $\text{C}_{60}^{1-}$  ( $\lambda_{\text{max}}=1078$  nm) (15) and  $\text{Ru}(\text{bpy})_3^{2+}$  ( $\lambda_{\text{max}}=452$  nm) (16), we calculate a 1:2.0 ( $\pm 0.2$ )

[Ru (bpy)<sub>3</sub><sup>2+</sup>]: [C<sub>60</sub><sup>1-</sup>] stoichiometry. In addition, X-ray fluorescence measurements did not detect the presence of phosphorus or chlorine in the solid material, indicating that the anion PF<sub>6</sub><sup>-</sup> and dichloromethane solvent are not incorporated into the material (14).

Conductivity measurements were conducted on compressed powder samples using a two-point probe method and a cell designed in these laboratories (17). At 25 °C the specific conductivity,  $\sigma$  of the [Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub> was found to be 0.01  $\Omega^{-1} \text{ cm}^{-1}$ . The temperature dependence of the conductivity is shown as an Arrhenius plot in Figure 4. A linear relationship is observed over the entire temperature range measured. The increase in  $\sigma$  with temperature is typical for semiconductors. The activation energy was found to be  $15.1 \pm 0.1 \text{ kJ mol}^{-1}$  (0.15 eV). This value is similar to those found in single crystal alkali metal - TCNQ systems (18). No photoconductivity was observed when the sample was illuminated with white light.

We speculate that the high conductivity is related to electronic overlap between the two ions composing the black solid. We postulate that this overlap involves donation of electron density from the C<sub>60</sub><sup>1-</sup> to the ligand orbitals in the Ru(bpy)<sub>3</sub><sup>2+</sup> ( $\Delta E^{\circ} \approx 0.7 \text{ V}$ ). However, further speculation on the nature of the conductivity and the electronic structure of such transition metal chelate - fulleride materials will have to await future measurements of their structure and properties.

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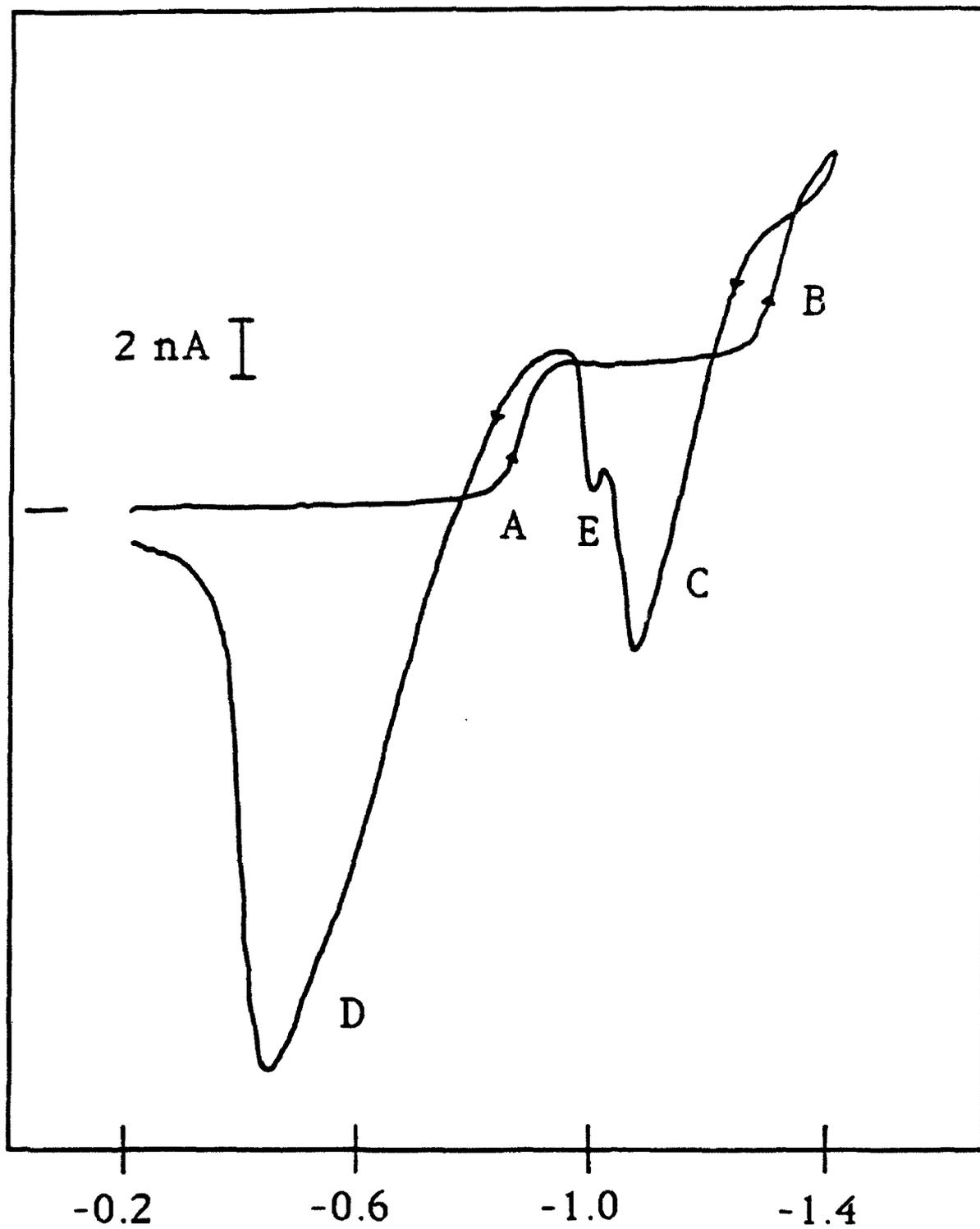
## Figure Captions

**Figure 1.** Cyclic voltammogram of 0.45 mM C<sub>60</sub> in dichloromethane saturated with [Ru(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (first scan). Scan rate 20 mV sec<sup>-1</sup>. Pt electrode diameter 125 μm. Potentials measured against Ag/Ag<sup>+</sup> 0.10 M in DMSO.

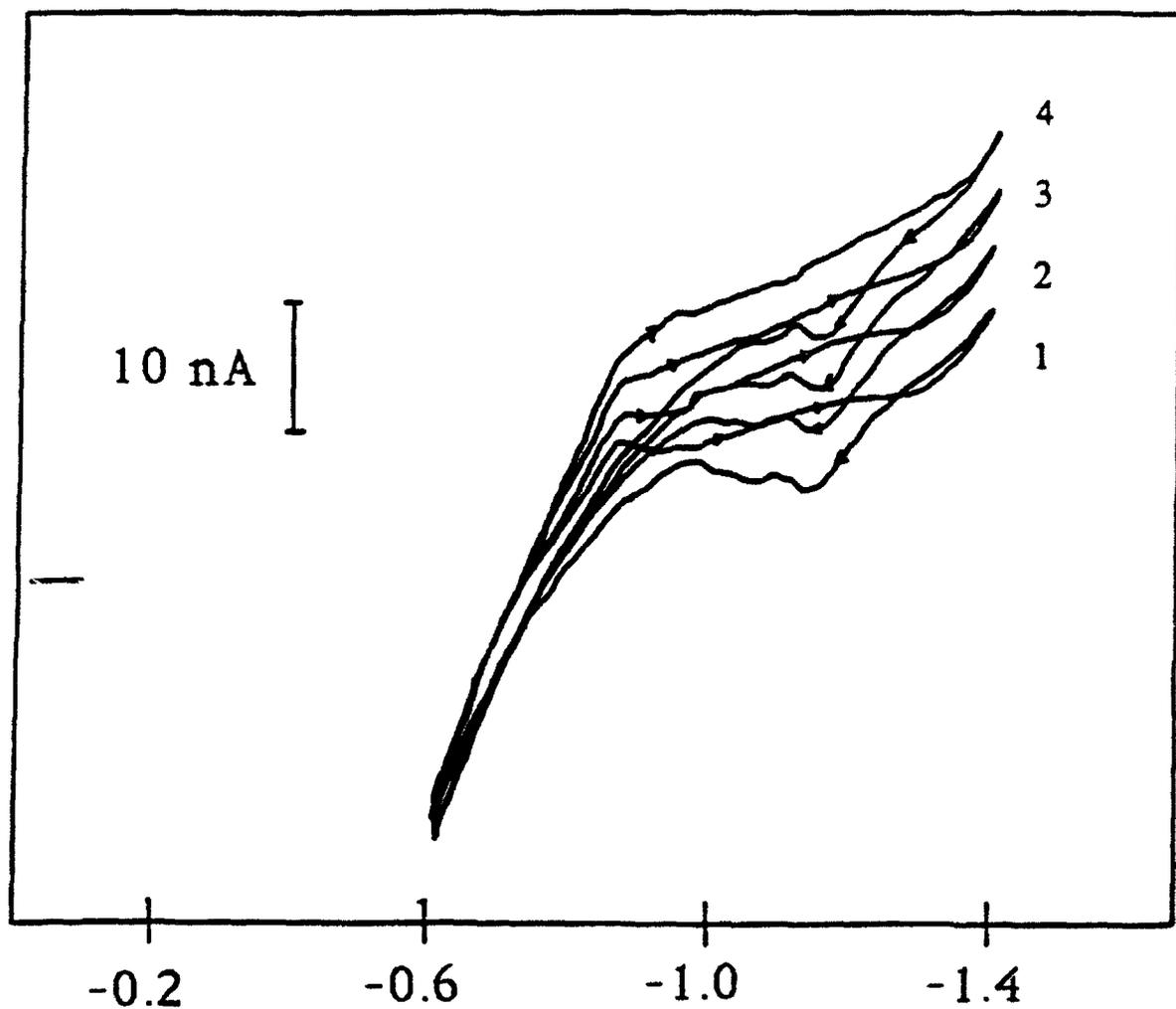
**Figure 2.** Cyclic voltammograms showing successive growth of surface deposit. Conditions as given in Figure 1.

**Figure 3.** Scanning electron microscope image of [Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub> crystals formed on Pt electrode after 13 minutes of electrolysis. Scale bar 10 μm. Magnification 4580X. Accelerating voltage 30 kV. Sample was not metal coated prior to imaging.

**Figure 4.** Temperature dependence (1/T) of conductivity (ln σ) of [Ru(bpy)<sub>3</sub>](C<sub>60</sub>)<sub>2</sub> solid. Temperature range 266.4 K to 308 K. (Inset: inclusion of points at 195 K and 83 K).



Volts vs Ag/Ag+ (0.10M in DMSO)



Volts vs Ag/Ag+ (0.10M in DMSO)



10  $\mu\text{m}$

