

DISSERTATION

SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL
POLYPYRIDINE COMPLEX FULLERENE SALTS

Submitted by

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In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

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COLORADO STATE UNIVERSITY

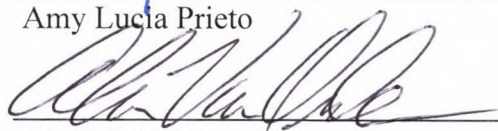
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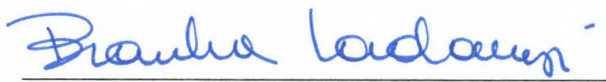
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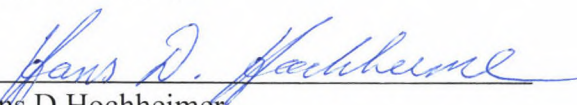
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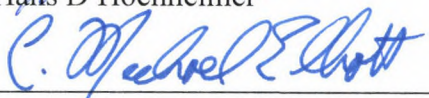
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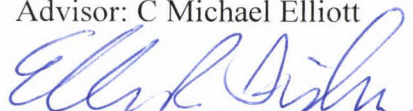
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ABSTRACT OF DISSERTATION

Synthesis and Characterization of Transition Metal Polypyridine Complex

Fullerene Salts

In recent years, ionic fullerene (C_{60}) salts have attracted much attention due to their interesting chemical and physical properties. Transition metal polypyridine complex, most notably, tris (2, 2'-bipyridine)ruthenium-based compounds, $[RuL_3]^{m+}$, have a number of photochemical and electrochemical properties which make them of interest for both fundamental and applied studies. The similarity of electrochemical potentials of $[RuL_3]^{m+}$ and C_{60}^{n-} gives rise to the possibility of a new charge-transfer ionic salts $[RuL_3]^{m+}_n(C_{60}^{n-})_m$. In chapter I, the background of ionic C_{60} salts as well as the motivation of preparing transition metal polypyridine complex C_{60} salts is described in detail. A chart of electrochemical data is generated and used as a guideline to predict the possible stoichiometries of ionic salts throughout the whole research work.

In Chapter II, the synthesis and characterization of three ionic salts using $[Ru(bpy)_3]^{m+}$ ($m = 1, 2$) as cations are fully described. All three salts are semiconducting with the highest conductivity at $\sim 10 \text{ S} \cdot \text{m}^{-1}$. Interesting paramagnetism is reported as well. The detailed discussions based on single crystal

and powder X-ray diffraction studies are useful in better understanding the electronic conduction and magnetism. The physical properties of ionic C_{60} salts can be rationalized based on the crystal packing. In the presence of a bulky cation $Ru(bpy)_3^{m+}$, an expanded crystal lattice is found with weak site-site interactions.

In Chapter III, the ligand substitution effect of $[RuL_3^{m+}]_n(C_{60}^{n-})_m$ is examined. Four ligands: 4, 4'-dimethyl-2, 2'-bipyridine (4DMB), 5, 5'-dimethyl-2, 2'-bipyridine (5DMB), 4, 4'-di-tert-butyl-2, 2'-bipyridine (TBB) and 4, 4', 5, 5'-tetramethyl-2, 2'-bipyridine (TMB) are chosen as the targets. The ligand substitution not only changes the redox potentials of cation $Ru(bpy)_3^{m+}$ but also alters its size. This provides a route for tuning the properties of $[RuL_3^{m+}]_n(C_{60}^{n-})_m$. Electrical and magnetic properties of all compounds as prepared are investigated. The highest conductivity found is also close to $10\ S \cdot m^{-1}$.

In Chapter IV, the effect of substituting ruthenium by chromium in metal complex ionic C_{60} salts is studied. $Cr(bpy)_3^{m+}$ and $Ru(bpy)_3^{m+}$ are very similar in size but of quite different redox potentials. The electrical conductivity of their corresponding ionic salts shows large dependence on the redox potentials.

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CHAPTER I

INTRODUCTION TO IONIC FULLERENE SALTS

Background

Buckminsterfullerene (C_{60}) has attracted extensive attention since its first discovery in 1985.¹ In recent years, great improvement in the production of high purity C_{60} has effectively extended its practical applications over a wide range of scientific fields, including physics, materials chemistry, electrochemistry and organic chemistry, etc.

Many of the special properties that C_{60} exhibits are directly related to its high symmetry.² C_{60} is a closed cage-like hollow molecule composed of twelve hexagons and twenty pentagons with an overall icosahedral symmetry (**Figure 1.1**).² Each carbon atom is trigonally bonded to the other three in a sp^2 -derived bonding configuration.² However, C_{60} has a tendency to avoid double bonds in pentagons which prevents the electrons from delocalizing over the whole cage.^{3,4} The result is that C_{60} behaves much like an electron-deficient alkene and as such readily reacts with electron-rich species.² The electron affinity of C_{60} in the gas phase was measured to be ~ 2.65 eV.⁵ Some important physical constants for C_{60} molecules are listed in **Table 1.1**.

The strong electron-accepting ability of C_{60} allows the addition of up to six electrons into its triply degenerate LUMO orbital and thus forms anions with charges down to -6 (**Figure 1.2**).⁶ This has been demonstrated by observing six reversible reduction peaks of C_{60} in a mixture of acetonitrile/toluene solvent at -10°C (**Figure 1.3**).⁷ The six reductions occur, respectively, at ca. -0.98, -1.37, -1.87, -2.35, -2.85, -3.26 V vs. Fc/Fc^+ .⁸ The relatively even spacing of ca. 0.45 V for the successive reductions is striking, which is a particular feature of fullerenes as reflecting their delocalized LUMOs.⁸

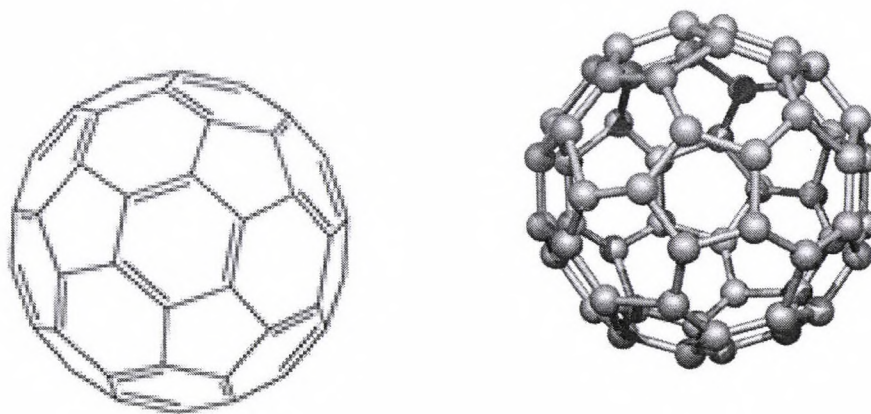


Figure 1.1: Buckminsterfullerene C_{60} molecules.

Table 1.1: Physical constants of C_{60} molecules.²

Quantity	Value
Average C-C distance	1.44 Å
C-C bond length on pentagon	1.46 Å
C-C bond length on hexagon	1.40 Å
C_{60} mean ball diameter	7.10 Å
C_{60} ball outer diameter ^a	10.34 Å
Binding energy per atom	7.40 eV
Electron affinity	2.65 ± 0.05 eV

^a This value for the outer diameter is found by assuming the thickness of the π -electron cloud to be 3.35 Å. In the solid, the C_{60} - C_{60} nearest neighbor distance is 10.02 Å.²

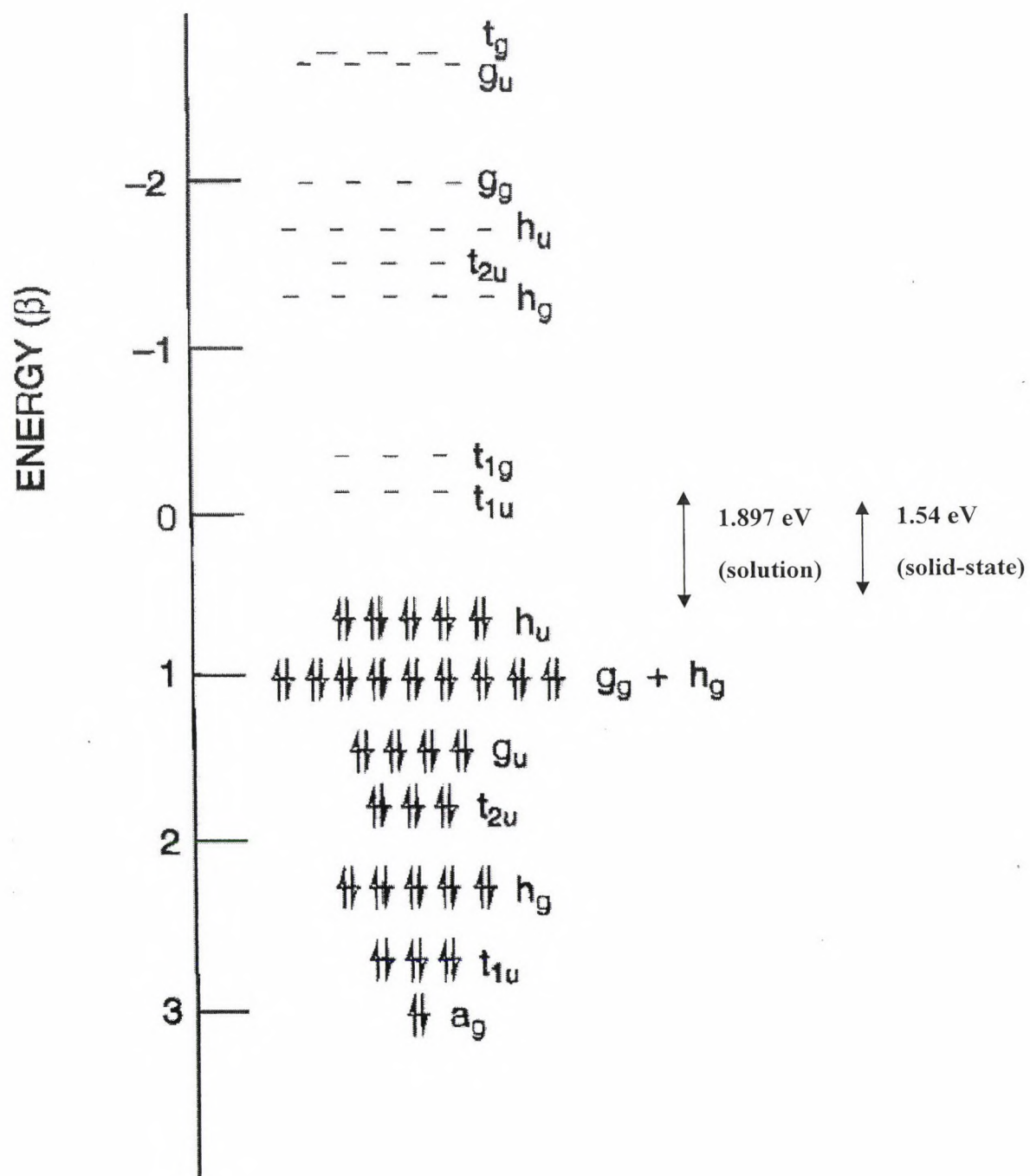


Figure 1.2: Molecular orbital energy diagram for C_{60} . (The graph was obtained from reference 6.)

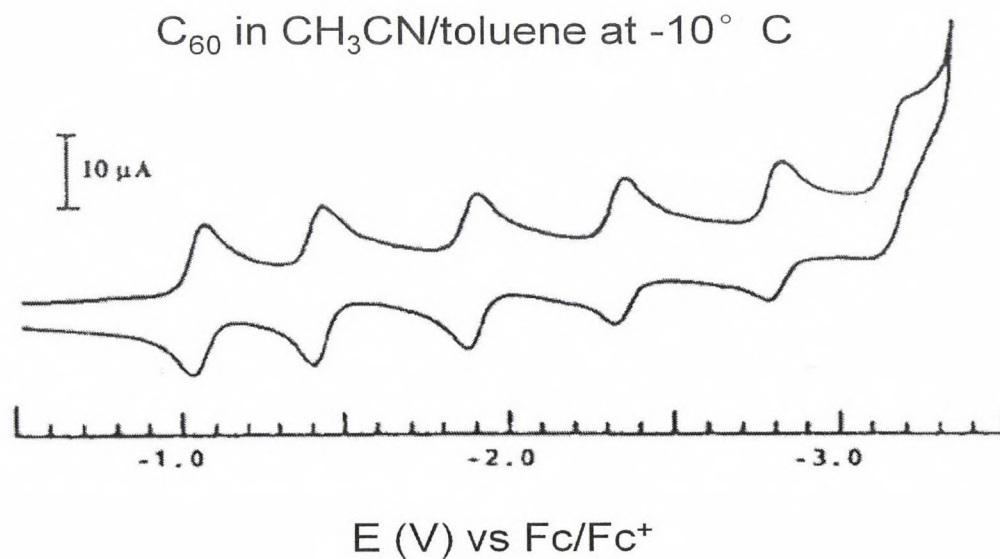


Figure 1.3: Cyclic voltammograms of C_{60} in acetonitrile/toluene at $-10^\circ C$. (The graph was obtained from reference 7.)

Table 1.2: Physical constants for crystalline C_{60} , K_3C_{60} and $TDAE \cdot C_{60}$ in solid state.^{2,9}

Compound	Crystalline Phase	Lattice Constant (Å)	C_{60} - C_{60} distances (Å)
C_{60}	face-centered cubic	14.17	10.02
K_3C_{60}	face-centered cubic	14.24	10.06
$TDAE \cdot C_{60}$	monoclinic C	$a = 15.807$ $b = 12.785$ $c = 9.859$	9.98 (along c axis) 10.26 (along a - b plane)

Ionic Fullerene Salts

In the presence of a strong reducing agent, C_{60} can be readily reduced to C_{60}^{n-} ($n = 1\sim6$) and thus a charge-transfer ionic salt is formed. “Fulleride” has been commonly used as a generic name for negatively charge fullerene. Upon reduction, except for the increased electron density on C_{60} , the original buckyball cage stays almost intact without any bond breakage.² This allows C_{60}^{n-} to remain most of the properties of unreduced C_{60} .²

Among a number of ionic C_{60} salts reported previously, there are mainly three types of reducing agents used to transfer charge onto C_{60} s. The first type is a metal reducing agent, for example, alkali-metal or alkaline-earth metal.^{2,8} The second type includes coordination and organometallic compounds, for example, $Cr^{II}(TPP)$ (TPP = tetraphenylporphyrin)¹⁰ and Cp^*_2Co (decamethylcobaltocene)¹¹. Lastly, some organic molecules, like amines and thiols, etc., have been successfully used as selective reducing agents as well.⁸ All of those ionic C_{60} salts exhibit interesting physical properties. The two most famous ones are the superconducting tris-alkali-metal doped fullerides and the molecular ferromagnet $TDAE^{+}C_{60}^{-}$. {TDAE = [tetrakis(dimethylamino)ethylene]}

The M_3C_{60} or $M_xM'_{3-x}C_{60}$ (where $x = 1, 2, 3$) alkali metal-doped fulleride (M, M' are different alkali metals) have attracted a great deal of attention since the relatively high critical temperature ($T_c = 18K$) of K_3C_{60} was observed.⁶ This work was soon followed by observations of superconductivity with even higher critical temperatures in Rb_3C_6 ($T_c = 29K$), in Rb_2CsC_{60} ($T_c = 31K$), in $RbCs_2C_{60}$ ($T_c = 33K$), and in Cs_3C_{60} under pressure ($T_c = 40K$).² In alkali-metal doped fullerides, the resulting cations, required for charge neutrality, reside in the interstitial voids of the C_{60} lattice (**Figure 1.4**), and most M_3C_{60}

crystals retain the pristine face-centered cubic lattice of C_{60} .² The exceptional ball-ball interaction is believed to be the basis of superconductivity.¹² As the size of cation increased, a larger lattice expansion was observed along with higher T_c .²

$TDAE^{+}C_{60}^{-}$ is well known as an organic magnet by its ferromagnetism with a high Curie temperature of 16.1 K.¹³ The relatively large TDAE molecule effectively changed the f.c.c. structure of C_{60} to monoclinic C (**Figure 1.4**).⁹ As indicated in **Table 1.2**, the C_{60} - C_{60} intermolecular distance in $TDAE^{+}C_{60}^{-}$ is reduced along c axis as compared to C_{60} and K_3C_{60} . The ferromagnetic ordering is believed to be mainly attributed to the ball-ball close contact.^{2,13}

Obviously, the size and shape of the reducing agent are critical to the crystal structure which has a substantial effect on the physical properties of ionic C_{60} salts. If a larger cation also participates in the crystal packing, the ball-ball contact is very likely to be broken and thus interesting properties might arise. It is therefore of fundamental interest to study discrete fulleride ions and to explore the nature of weaker or less extended interactions between them.

Transition Metal Polypyridine C_{60} Salts

Ruthenium and chromium polypyridine complexes seem to be promising candidates as the electron donors to form ionic fullerene salts. In solution, the first four reductions of C_{60} occur precisely in the potential region where Ru/Cr polypyridine complexes are reduced. Consequently, it should be possible to prepare fulleride salts of the general form: $[ML_3^{m+}]_n(C_{60}^{n-})_m$ where M is Ru or Cr, L is bipyridine (substituted or

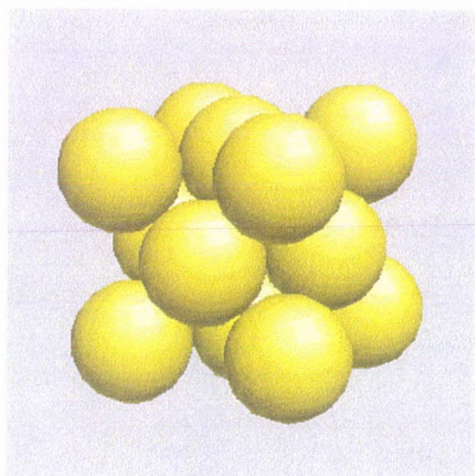
unsubstituted); $m+ = +1, +2$; and $n- = -1, -2, -3$. In addition, since these complex cations are roughly spherical with dimensions comparable to C_{60} , very different structures from those alkali metal doped fulleride will necessary result. Both Ru/Cr polypyridine complexes and C_{60} are rich in electrochemistry and photoelectrochemistry. By incorporating them into ionic salts, interesting properties might be found.

Besides the well-known superconducting properties of alkali-metal doped fulleride (M_3C_{60}), they also exhibit metallic conductivity at room temperature.^{2,6} The conduction is thought to occur by charge transfer through weak overlap of wave functions on adjacent C_{60} molecules.⁶ In ionic salts $[ML_3^{m+}]_n(C_{60}^{n-})_m$, both cations and anions are redox active and therefore novel electronic materials could result since both C_{60}^{n-} and ML_3^{m+} can participate in the electron conduction. The conducting ability of $[Ru(bpy)_3]^{1+}$ and $[Ru(bpy)_3]^0$ has been demonstrated before and especially, $[Ru(bpy)_3]^0$ shows $\sigma = 15 \text{ S} \cdot \text{m}^{-1}$ at 25°C .¹⁴⁻²⁰ In **Figure 1.5**, a simplified molecular orbital of $[Ru(bpy)_3]^{2+}$ is shown. By adding electrons to the π^* orbital originating from the ligand, $[Ru(bpy)_3]^{1+}$ and $[Ru(bpy)_3]^0$ can be readily formed. Both species have unpaired electrons. When forming corresponding ionic C_{60} salts, they will contribute to the magnetic properties as well.

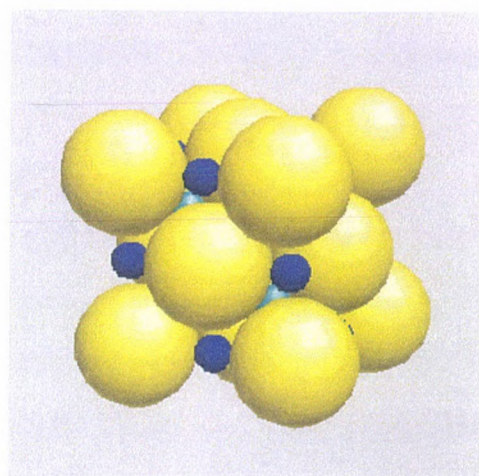
Based on the luxury of tuning the properties of metal complexes by ligand or metal substitution, a systematic study for a new type of solid-state materials $[ML_3^{m+}]_n(C_{60}^{n-})_m$ is allowed. There are several variables we can change, like cation/anion charge, cation size, and the relative cation/anion redox potentials. Electrochemical data in the format presented in **Chart 1.1** was used as a guideline for predicting possible accessible stoichiometries. Because of the solubility difference of C_{60} and metal complexes, their redox potentials were first measured in different electrolytes and then

calibrated by the Fc/Fc^+ couple. The first three half-wave redox potentials of C_{60} in acetonitrile/toluene were found to be -0.51, -0.88 and -1.38 V vs. SSCE. The detailed electrochemical data of other metal complexes vs. SSCE is illustrated in the following chapter II-IV. In **Chart 1.1**, along the x-axis is the potential. Each horizontal line except the bottom one for C_{60} corresponds to a different metal complex indicated on the left-hand side. The vertical marks indicate each respective $E_{1/2}$. The color bars indicate the charge borne by the dominant redox form of the complex within the potential range. **Chart 1.1** is useful in establishing what oxidation states of C_{60} are compatible in solution with what metal-complex oxidation states. In solid-state phase, different redox potentials should be found because there will be more interactions between ions. However, the difference is believed to be modest. This idea is supported by previous studies on a wide array of disordered polymers based on $[\text{M}(\text{bpy})_3]^{m+}$. The redox sites within these polymers and their corresponding monomers have very similar redox properties.²¹⁻²⁴ Even in the ordered crystalline $[\text{M}(\text{bpy})_3]^{m+}$ solids, no strong and long-rang interactions were found as well.^{25,26} Furthermore, in solid $[\text{ML}_3^{m+}]_n(\text{C}_{60}^{n-})_m$, since both cation and anion are bulky with similar size, a crystalline structure with almost discrete C_{60} sites is very likely to be formed. The direct C_{60} - C_{60} interactions will be much weaker than in pure f.c.c. solid C_{60} . The diminished interaction could produce a more solution-like redox behavior. Therefore, the redox potentials of $[\text{ML}_3^{m+}]_n(\text{C}_{60}^{n-})_m$ in solution and in solid-state phase should be at least similar. The effectiveness of **Chart 1.1** as a guideline has been demonstrated by the fact that most of the predicted ionic salts have been actually synthesized through our research work. In the latter chapters, the synthesis and

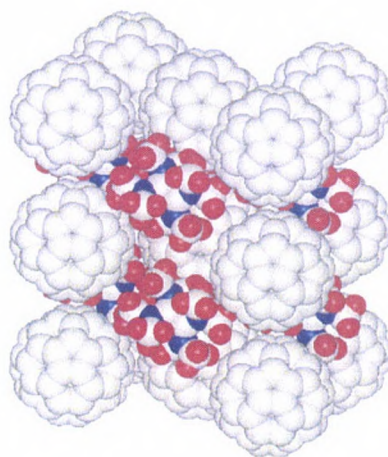
characterization of ruthenium or chromium polypyridine complex fullerides are fully described.



(A)



(B)



(C)

Figure 1.4: Crystal packing of (A) C₆₀ (ref.²⁷) (B) K₃C₆₀ (ref.²⁷) (C) TDAE·C₆₀ (ref.²⁸) [These graphs are attributed to reference 27 and reference 28.]

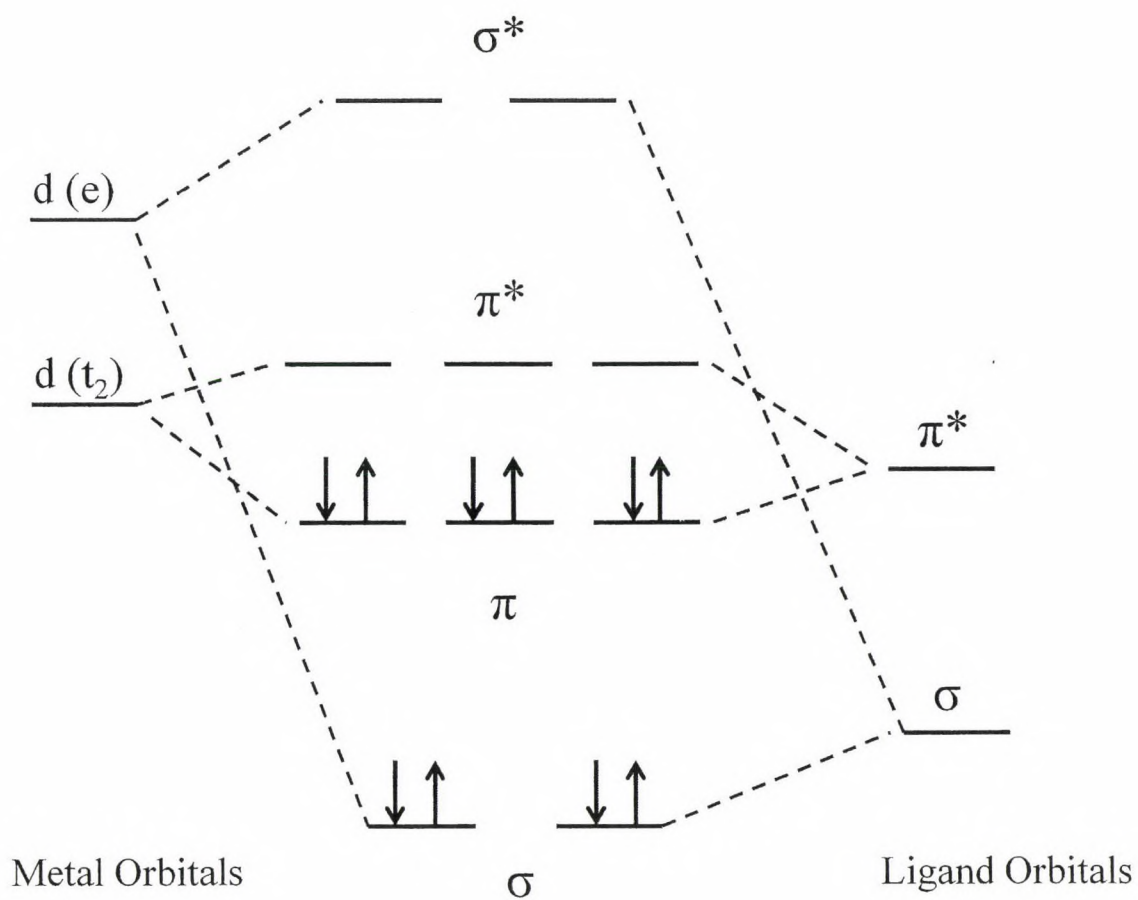
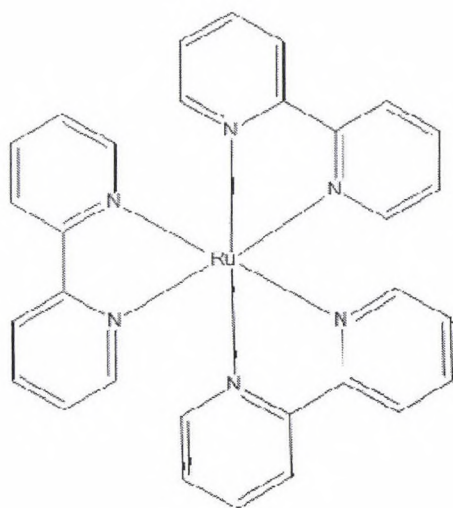


Figure 1.5: A simplified MO of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex in O_h symmetry.

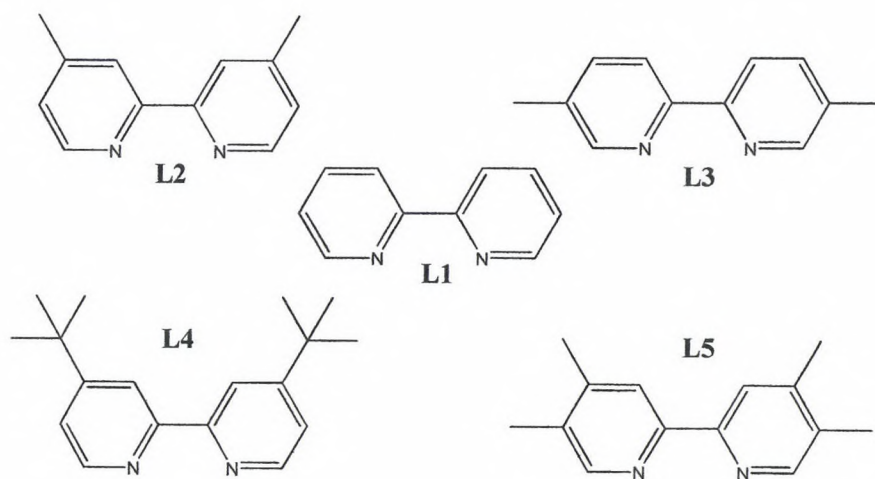
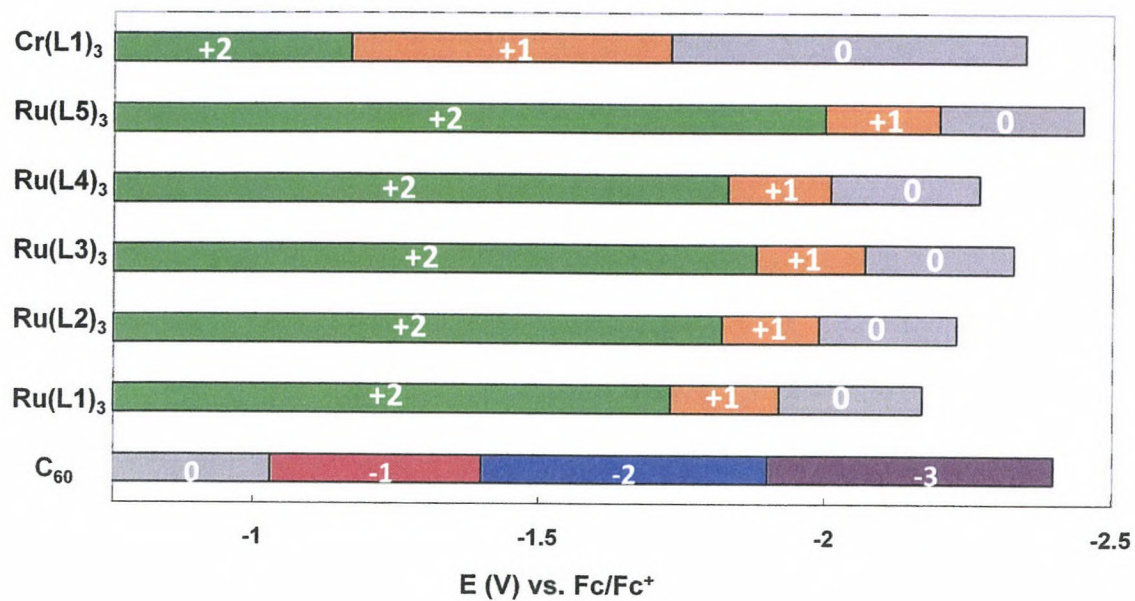


Chart 1.1: Electrochemical data of C₆₀ and metal complexes.

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CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF TRIS (2, 2'-BIPYRIDINE)

RUTHENIUM COMPLEX FULLERENE SALTS

Introduction

In superconducting alkali-metal doped C_{60} and ferromagnetic $TDAE^{+\bullet}C_{60}^{\bullet-}$, cations are basically redox-inert.¹ Synthesis of new ionic C_{60} salts containing larger and redox-active cations can potentially produce new solid-state materials with interesting new physical properties. $[Ru(bpy)_3]^{m+}$ is a potential candidate for such materials because of its rich electrochemistry and its comparable dimension to the C_{60} molecule.¹⁻⁴

As shown in **Figure 2.1**, there is significant overlap in the potential regions where $[Ru(bpy)_3]^{m+}$ and C_{60}^{n-} each is redox active; thus the feasibility of generating ionic salts with a general composition $[Ru(bpy)_3]^{m+}_n(C_{60}^{n-})_m$ exists. The presence of large cations can effectively break the ball-to-ball close contact between C_{60} s and perhaps allow the formation of classical ionic structures such as rock salt.^{1,2,5} Besides the alteration of structure, since both cations and anions are redox active relative to, for example, alkali-doped C_{60} where only the anions can exchange electrons, the possibility arises for novel electronic and magnetic properties for the ionic salts.^{6,7} Semiconducting $[Ru(bpy)_3]^{2+}(C_{60}^{1-})_2$ has been successfully synthesized by Foss et al.² This material was reported to have a two-probe conductivity of $1.0 \text{ S} \cdot \text{m}^{-1}$ at 25°C .² However, neither structural information nor magnetic properties were reported.² The previous study gave rise to a demand for in-depth study of this new series of solid-state materials.

In this chapter, we present our work on synthesizing and characterizing three tris (2, 2'-bipyridine) ruthenium C_{60} ionic salts predicted from **Figure 2.1**. They are $[Ru(bpy)_3]^{1+}_2(C_{60}^{2-})$, $[Ru(bpy)_3]^{2+}(C_{60}^{2-})$, and $[Ru(bpy)_3]^{2+}(C_{60}^{1-})_2$, respectively.

Compared with the electrocrystallization method reported in literature,² a much simpler chemical method was utilized. The reaction sequence was carried out as described in **Scheme 2.1**. UV-vis-NIR, XPS, and elemental analyses were applied to characterize the compounds. Their electronic, magnetic as well as structural properties are also investigated and discussed in detail.

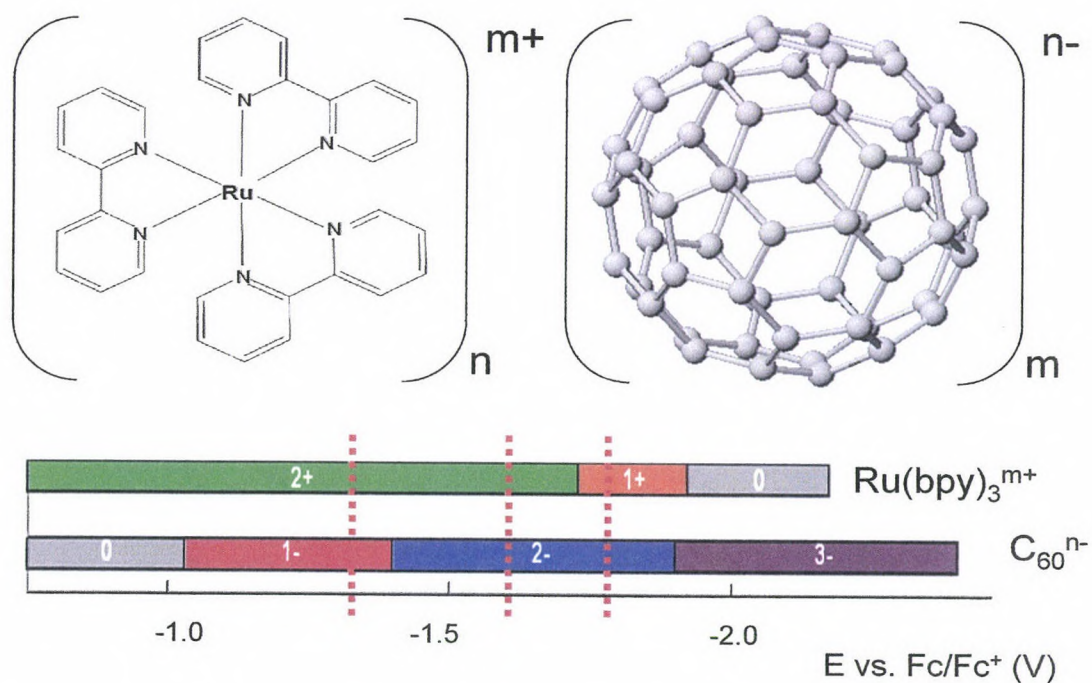
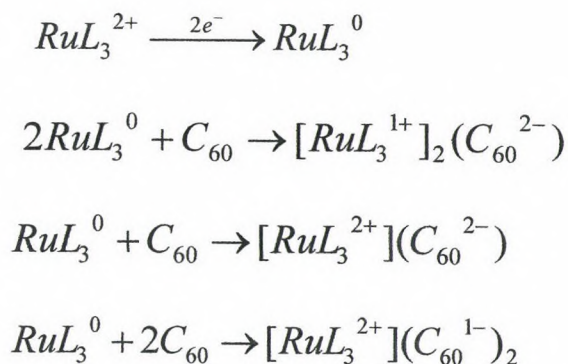


Figure 2.1: Reductive potential regions of $[\text{Ru}(\text{bpy})_3]^{m+}$ and C_{60}^{n-} referenced to ferrocene/ferrocenium redox couple.



Scheme 2.1: Chemical synthesis of ruthenium metal complex C_{60} ionic salts. L represents 2, 2'-bipyridine ligand.

Experimental

Materials

C₆₀ (≥ 99.5 % purity) was purchased from Term-USA. 2, 2'-bipyridine was supplied by Alfa Aesar. Ammonium hexafluorophosphate (Elf Atochem) and tetra-n-butylammonium hexafluorophosphate (electrochemical grade, Sigma Aldrich) were used as received. Benzonitrile (99 %, Aldrich) was dried over sodium metal for 12 hrs and distilled under reduced pressure. Dry deoxygenated acetonitrile, N, N'-dimethylformamide (DMF) and toluene were obtained from Pure-Solv solvent purification system. All solvents were stored in an inert atmosphere glove box and were purged with N₂ gas prior to each use.

[Ru(bpy)₃](PF₆)₂

A modified literature procedure was used.⁸ Ru(DMSO)₄Cl₂⁹ (400 mg, 0.826 mmol) and 2, 2'-bipyridine (400 mg, 2.56 mmol) were combined in 30 mL ethylene glycol and 8 mL 1:1 CH₃OH:H₂O. The mixture was refluxed for 2 hours in 100 °C oil bath producing a clear red solution. An aqueous solution of NH₄PF₆ (300 mg, 1.84 mmol) was added to the cooled solution whereupon a reddish orange precipitate immediately formed. After filtration, the solids were washed with H₂O and then EtOH. Recrystallization from EtOH/acetone yielded red/orange crystals. The final yield is 600 mg, 85 %.

[Ru(bpy)₃]⁰

Controlled-potential electrolytic reduction^{3,10} was performed on [Ru(bpy)₃](PF₆)₂ in an inert atmosphere box to produce [Ru(bpy)₃]⁰. A three compartment bulk electrolysis

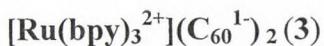
cell was used with Pt as counter electrode, Pt mesh as working electrode (W.E.) and Ag/Ag⁺ 0.1M in DMSO as reference electrode. The supporting electrolyte was 100 mM TBAPF₆ in CH₃CN. Prior to electrolysis, cyclic voltammetry was performed to determine the appropriate potential for reduction. For the specific reference electrode used, the maximum equilibrium concentration of [Ru(bpy)₃]⁰ was obtained at -1.90 V. The W.E. was held at this potential until the measured coulombs passed matched the calculated value for the two-electron reduction of [Ru(bpy)₃](PF₆)₂. The [Ru(bpy)₃]⁰ has limited solubility in acetonitrile and precipitated as a violet/black solid where it was collected from the Pt mesh electrode and washed with a few pipettes of fresh acetonitrile to remove excess supporting electrolyte. The washed solid was then dried by passing glove box atmosphere over the solids with a vacuum suction. The oxidation state of the product was confirmed by UV-visible spectroscopy comparison with literature spectrum.⁶

[Ru(bpy)₃]¹⁺]₂(C₆₀²⁻) (1)

All manipulation was carried out in an inert atmosphere box. [Ru(bpy)₃]⁰ (40 mg, 0.070 mmol) was mixed with C₆₀ (25.3 mg, 0.035 mmol) in 10 mL benzonitrile. The solution turned to reddish brown over 24 hours of stirring and then 30 minutes of ultrasonication at ambient temperature. Toluene (20 mL) was added in to precipitate more solid. The solid was filtered, washed with toluene and then hexane and dried under vacuum.

[Ru(bpy)₃]²⁺](C₆₀²⁻) (2)

The compound was prepared the same way as **1** except a 1:1 molar ratio of [Ru(bpy)₃]⁰:C₆₀ was used. The solution showed a sienna color.



Procedure used was the same as that for **1** except molar ratio of $[\text{Ru}(\text{bpy})_3]^0:\text{C}_{60}$ was changed to 1:2. The solids dissolved in benzonitrile showed a goldenrod color.

Results and Discussion

UV-vis-NIR Spectroscopy

To evaluate the composition of prepared solids, visible/near IR spectra were measured on a Cary 500 UV-VIS-NIR spectrophotometer in a 1 mm air-tight quartz cell. Solvent background correction was done for all samples. According to literature,^{6,11} the red curve (**2**) in **Figure 2.2** indicates the only fullerene anion present is C_{60}^{2-} while absorption at 422 nm, 458 nm is due to $[\text{Ru}(\text{bpy})_3]^{2+}$. Similarly, the green curve (**1**) demonstrated $\text{Ru}(\text{bpy})_3^{1+}$ and C_{60}^{2-} . The black curve (**3**) shows the evidence for $[\text{Ru}(\text{bpy})_3]^{2+}$ and C_{60}^{1-} .

Molar Ratio Calculation

In order to obtain the extinction coefficients of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{1+}$ in benzonitrile, spectroelectrochemistry was performed by utilizing a home-made optically transparent thin layer electrode (OTTLE) cell with a path length of 40 μm (**Figure 2.3**). A solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ in benzonitrile with known concentration along with supporting electrolyte TBAPF₆/benzonitrile was transferred into the working compartment of the OTTLE containing the Au minigrid working electrode located in a HP 8452A diode array spectrophotometer. As electrolysis proceeded, the absorption

spectrum was monitored at the same time. For $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\lambda_{\text{max}} = 452 \text{ nm}$), $\epsilon \text{ (M}^{-1}\text{cm}^{-1}\text{)}$ was calculated to be 17,200, and for $[\text{Ru}(\text{bpy})_3]^{1+}$ ($\lambda = 520 \text{ nm}$), $\epsilon \text{ (M}^{-1}\text{cm}^{-1}\text{)}$ was 16,700. Combining this data with extinction coefficient values of $\text{C}_{60}^{\text{n-}}$ from literature,¹¹ the molar ratio between cation and anion in each compound prepared can be calculated. The results are listed in **Table 2.1**. The calculated molar ratios match within $\pm 10\%$ of the expected values.

X-ray Photoelectron Spectroscopy

From **Figure 2.4**, the presence of only trace amount of phosphorus and fluorine were detected by X-ray photoelectron spectroscopy which indicates that no significant amount of PF_6^- anion is incorporated into the ionic material. Combining with the molar ratio calculation result, the prepared fullerides **1**, **2**, **3** were deemed pure enough for further characterization.

Elemental Analysis

To further demonstrate the compositions and purity, elemental analysis was done. The results are listed in **Table 2.2**. The deviation was found out to be within $\pm 0.4 \%$ between the calculated C-H-N percentages and the experimental values for compound **1** and **3**, which indicates that acceptable purity was found in these two compounds and formulas $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60})$ and $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$ are appropriate for **1** and **3**, respectively.

However, relatively larger deviations were found in the case of compound **2**. To best fit the experimental values, $[\text{Ru}(\text{bpy})_3]_{1.07}(\text{C}_{60}) \cdot 1.84(\text{C}_7\text{H}_5\text{N})$ was derived. The excess 7 % $\text{Ru}(\text{bpy})_3$ species is speculated to originate mainly from the excess $[\text{Ru}(\text{bpy})_3]^0$ in the stoichiometric synthesis. Since the equilibrium potential of

$[\text{Ru}(\text{bpy})_3]^{2+}(\text{C}_{60}^{2-})$ lies between $[\text{Ru}(\text{bpy})_3]^{1+}_2(\text{C}_{60}^{2-})$ and $[\text{Ru}(\text{bpy})_3]^{2+}(\text{C}_{60}^{1-})_2$, any excess of $[\text{Ru}(\text{bpy})_3]^0$ or C_{60} added will result in the formation of either of the two above compounds. Because C_{60}^{2-} and C_{60}^{1-} are quite distinguishable in the UV-vis-NIR spectrum, if any excess C_{60} present, the formation of C_{60}^{1-} can be easily identified. However, when $[\text{Ru}(\text{bpy})_3]^0$ is added in excess, it will be hard to know it by UV-vis-NIR because the resulting $[\text{Ru}(\text{bpy})_3]^{1+}$ has very similar absorption peaks as $[\text{Ru}(\text{bpy})_3]^{2+}$. It was noticed that the unstable pressure and atmosphere of glove box induced some random fluctuation to the readings of balance used for mass measurement. Especially when the experiment was done on a small scale (< 20 mg) because of the solubility concern, the error bar on the measured amount can be magnified. Although this can also happen to compound **1** and **3**, the excess $[\text{Ru}(\text{bpy})_3]^0$ for **1** or excess C_{60} for **3** can be removed easily by washing the solid with toluene. But for $[\text{Ru}(\text{bpy})_3]_{1.07}(\text{C}_{60})$, the similar solubility of $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60})$ and $[\text{Ru}(\text{bpy})_3](\text{C}_{60})$ in most organic solvents make it hard to separate them and obtain the pure powder form of $[\text{Ru}(\text{bpy})_3](\text{C}_{60})$. However, the single crystals of these two compounds have been grown in different solvent systems. (See next section) Therefore, it might be possible to separate them as single crystals based on their different morphology.

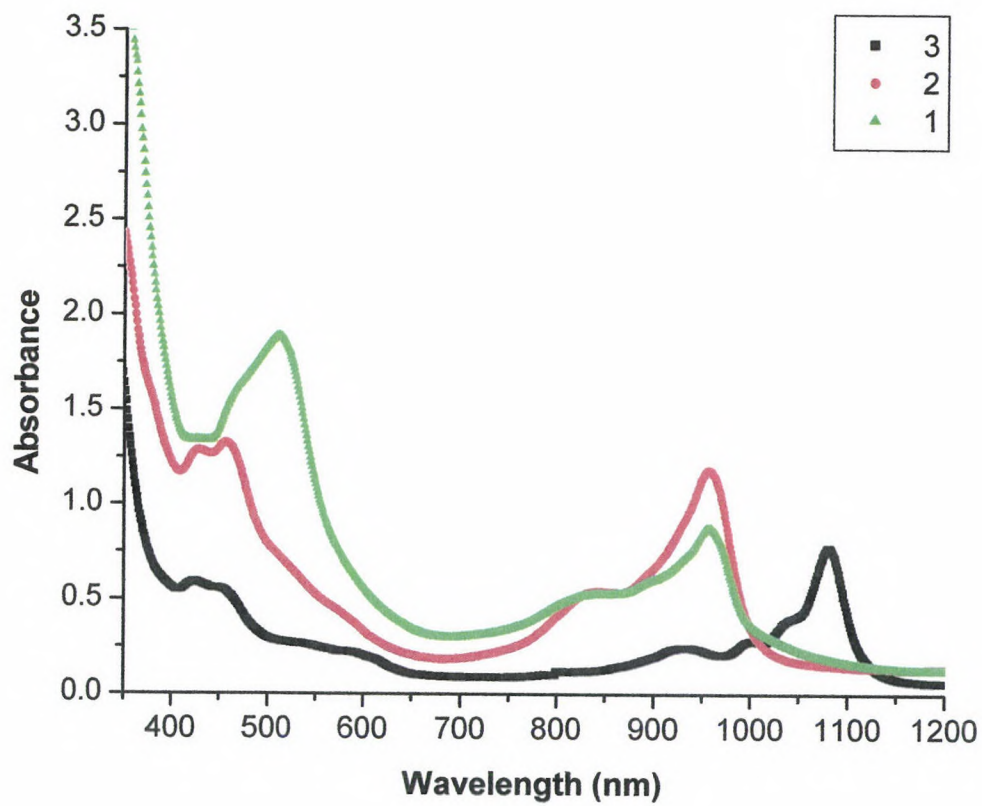


Figure 2.2: Absorption spectrum of compound 1(▲), 2 (◆) and 3 (■) in benzonitrile.

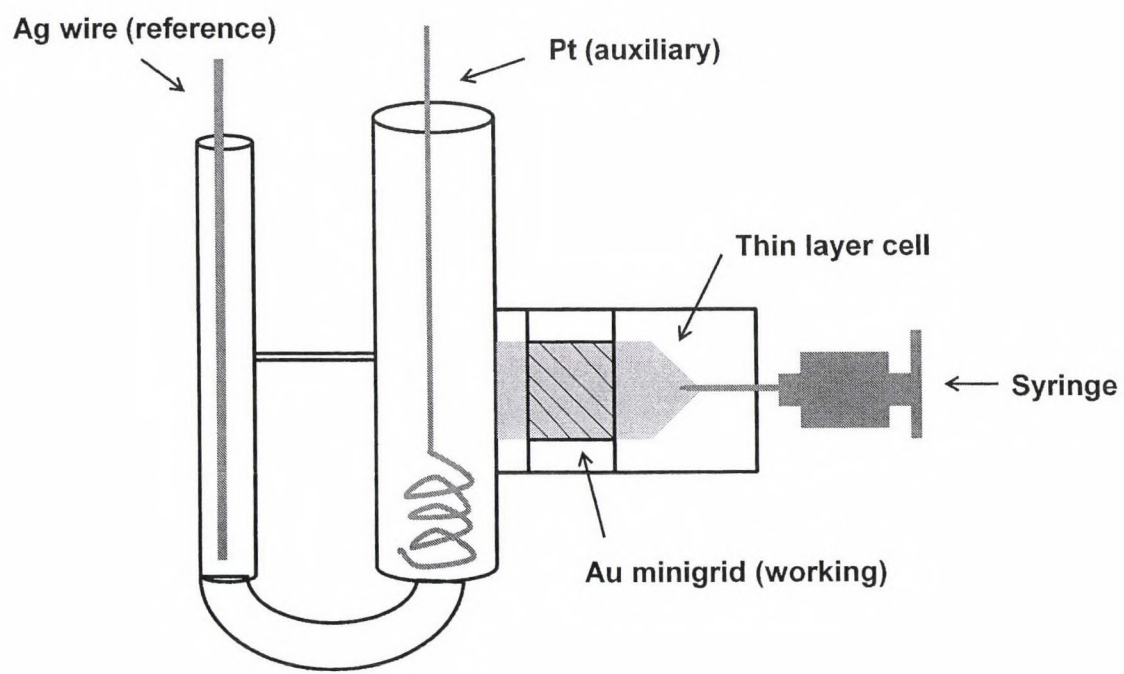


Figure 2.3: Schematic design of OTTLE cell.

Table 2.1: Calculated molar ratio between cation and anion in each fulleride.

* The stoichiometry of $[\text{Ru}(\text{bpy})_3]^{m+}$ was calculated assuming the value of C_{60}^{n-} to be 1.0.

Compound	Cation present in solution	Anion present in solution	Theoretical molar ratio	Calculated molar ratio *
1	$[\text{Ru}(\text{bpy})_3]^{2+}$	C_{60}^{2-}	2:1	2.0 ($\pm$ 0.2) : 1:0
2	$[\text{Ru}(\text{bpy})_3]^{1+}$	C_{60}^{2-}	1:1	1.0 ($\pm$ 0.1) : 1.0
3	$[\text{Ru}(\text{bpy})_3]^{2+}$	C_{60}^{1-}	1:2	0.50 ($\pm$ 0.05) : 1.00

Table 2.2: Results of elemental analysis for compound **1**, **2**, and **3**.

Elements	1 $[\text{Ru}(\text{bpy})_3]^{1+}_2(\text{C}_{60}^{2-})$		2 $[\text{Ru}(\text{bpy})_3]^{2+}(\text{C}_{60}^{2-})$		3 $[\text{Ru}(\text{bpy})_3]^{1+}(\text{C}_{60}^{1-})_2$	
	Calculated (%)	Found (%)	Calculated (%)	Found (%)	Calculated (%)	Found (%)
C	77.50	77.22	83.78	82.58	89.60	89.20
H	2.58	2.61	1.86	2.29	1.19	1.17
N	9.04	8.89	6.51	7.63	4.18	4.58

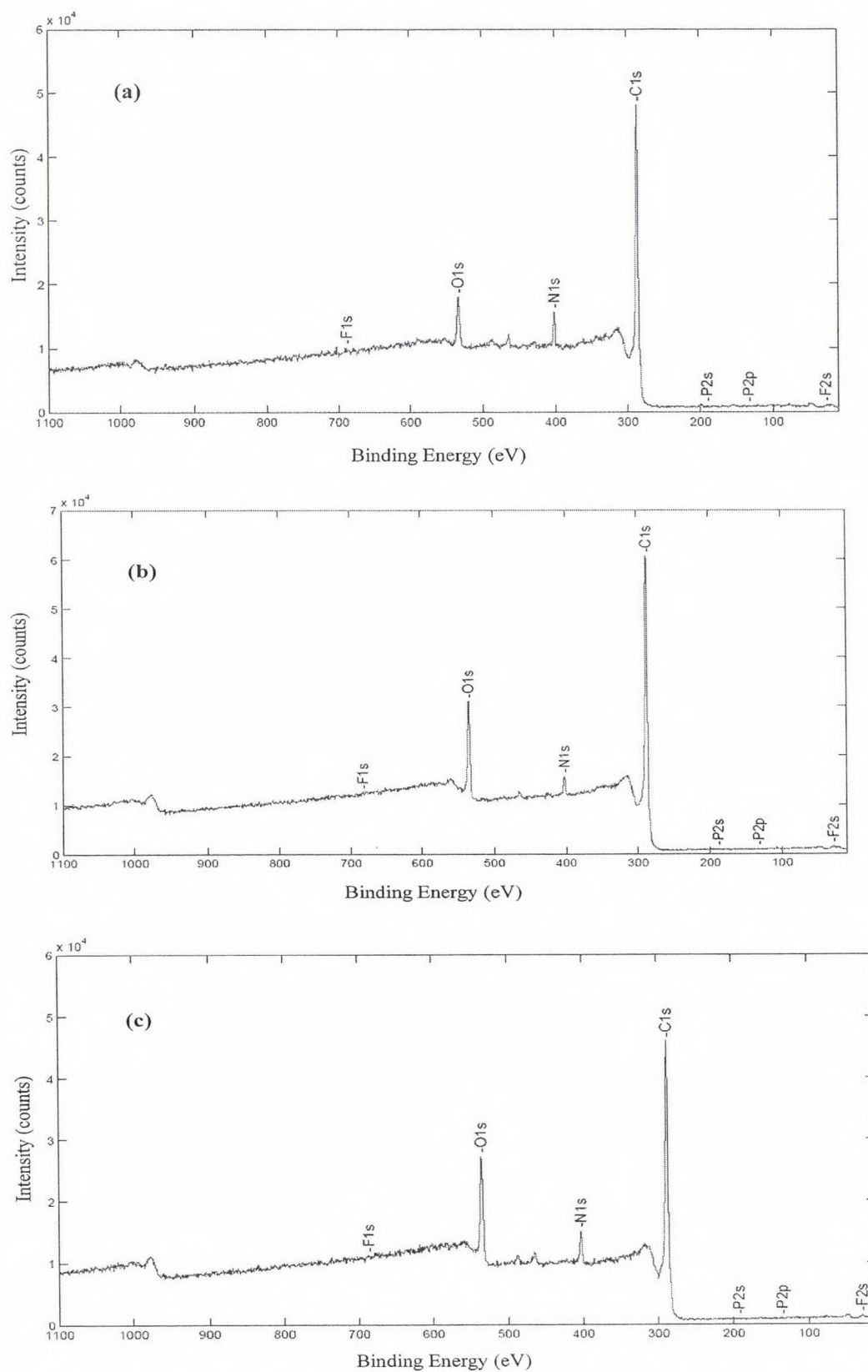


Figure 2.4: XPS survey spectra for oxidized fullerides 1(a), 2 (b), 3 (c)

X-ray Crystal Structure Determinations of **1** and **2**

Single crystals of $[\text{Ru}(\text{bpy})_3]^{1+}_2(\text{C}_{60}^{2-})$ (**1'**) suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of benzene into DMF at room temperature. Single crystals of $[\text{Ru}(\text{bpy})_3]^{2+}(\text{C}_{60}^{2-})$ (**2'**) were grown by slow diffusion of toluene into benzonitrile at room temperature. The crystals were coated in Paratone oil prior to removal from inert atmosphere box, then glued to glass fibers, and mounted on a Bruker Kappa Apex 2 CCD diffractometer under N_2 stream. Data for crystal **1'** and **2'** were collected using graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71703 \text{ \AA}$) at 120 K and 100 K, respectively. Absorption correction was performed with Apex 2 software package. The structures were solved using the SHELXTL software package.¹² Details of crystal data and structure refinements for **1'** and **2'** are summarized in **Table 2.3**.

Patterson method was applied for solving crystal structure of **2'**. The space group of **2'** was determined to be centrosymmetric $C2/c$. The $[\text{Ru}(\text{bpy})_3]^{2+}$ sits on a 2-fold rotation axis thus only 1.5 bpy ligands show up in the asymmetric unit. The C_{60} species also sit on the 2-fold rotation axis. A whole benzonitrile ($\text{C}_6\text{H}_5\text{CN}$) molecule sits on a general position which is clearly seen in **Figure 2.5**. A toluene molecule sits on an inversion center, so the methyl group is disordered over 2 sites and was refined isotropically at 50 % occupancy. However, another toluene molecule which sits on a 2-fold axis appears to be much more disordered. The thermal parameters for the latter toluene molecule were refined isotropically, and no H atoms were included for this badly disordered toluene ($\text{C}_{57}\sim\text{C}_{62}$). H atoms were calculated for all other C atoms, and the thermal parameters were set to be 1.2 times that of the attached carbon atoms except for 1.5 times that of the disordered methyl group on the first toluene. The solvent disorder resulted in the deviant

short intermolecular contact between C₅₆ and C₆₁. Overall, R_I value was found out to be 5.48 % and wR_2 was 15.3 %.

In crystal **2'**, the mean values of 6-6 and 6-5 bonds in C₆₀²⁻ were found to be 1.396(5) Å and 1.449(5) Å. As compared to neutral C₆₀ ($a_6 = 1.40$ Å, $a_5 = 1.46$ Å), the 6-5 bond in particular is significantly shorter in C₆₀²⁻. The diameter of C₆₀²⁻ anion was evaluated by measuring the distance of the two oppositely located carbon atoms. The longest diameter was measured to be 7.120 Å and the shortest one was 7.030 Å. Thus, the ellipsoidal deviation is ~ 0.090 Å, which is almost 3.6 times that for the parent C₆₀ (0.025 Å). The addition of two electrons onto C₆₀ greatly increased the distortion.

The single crystal **1'** was block-shaped with brownish red color. Unfortunately, its diffraction quality was poorer than that of single crystal **2'**. There existed some disorder in the reduced C₆₀. Also, much worse solvent disorder was observed. SQUEEZE program was applied to circumvent the solvent problem. The crystal structure was refined as centrosymmetric $R\bar{3}c$ with acceptable R_I (8.12 %) and wR_2 (22 %) values. The asymmetric unit of crystal **1'** is shown in **Figure 2.6**. While it is probably inappropriate to make a detailed discussion about the bond length and angles in C₆₀ of crystal **1'** due to the disorder, the crystal packing and interionic distances are still reliable.

The crystal packing of **1'** and **2'** projected on bc plane is shown in **Figure 2.7**. It is obvious that in crystal **2'**, ions are well separated from each other. The nearest center-to-center distances of C₆₀•••C₆₀ and Ru(bpy)₃•••Ru(bpy)₃ are both 10.914 Å while the distance of Ru(bpy)₃•••C₆₀ is shorter at 9.308 Å. The shortest carbon-to-carbon contact between [Ru(bpy)₃]²⁺ and C₆₀²⁻ is 3.557 Å. In crystal **1'**, the C₆₀s are even farther apart.

The nearest center-to-center distance is now 13.906 Å. However, much shorter distances of Ru(bpy)₃•••Ru(bpy)₃ (8.119 Å) and Ru(bpy)₃•••C₆₀ (8.836 Å) were observed. The shortest carbon-to-carbon contact between [Ru(bpy)₃]¹⁺ and C₆₀²⁻ is 3.418 Å. Comparing with K₃C₆₀ [C₆₀•••C₆₀ = 10.06 Å, C₆₀(C) •••C₆₀(C) = 3.01 Å], both crystals have C₆₀²⁻ well separated. However, in crystal **1'**, there is possible close contact between [Ru(bpy)₃]¹⁺ cations. The different interionic distances within crystal **1'** and **2'** potentially affect their electronic and magnetic properties, which will be discussed more in detail later.

X-ray Powder Diffraction

Since no diffraction quality single crystals were successfully obtained for compound **3** due to its poor solubility in most organic solvents, X-ray powder diffraction was conducted to investigate its crystallinity. Because compound **3** is very sensitive to air, a solution mixture composed of 2:5 mineral oil/hexane was used to coat the solid sample prior to XRD analysis. It has been demonstrated that this coating can prevent the sample from being oxidized for up to 2 hours. XRD measurements were performed using a Bruker D-8 discover diffractometer using Cu K_α radiation ($E = 8041.3$ eV). The diffraction pattern indicates that compound **3** does show some crystallinity. The cell was determined to be monoclinic P and refinement of observed seven reflections gave the cell parameters as $a = 13.088$ Å, $b = 15.145$ Å, $c = 9.554$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 104.84^\circ$ and $V = 1830.57$ Å³. Considering the mean ball diameter of C₆₀ is 7.10 Å, these cell parameters indicate that at least along c axis, there might exist some van der Waals close contact between C₆₀s.

In order to obtain more reliable results, more measurements need to be done. But before that, a better method for coating the sample has to be developed in order to prevent air oxidation of sample during the long-time measurements.

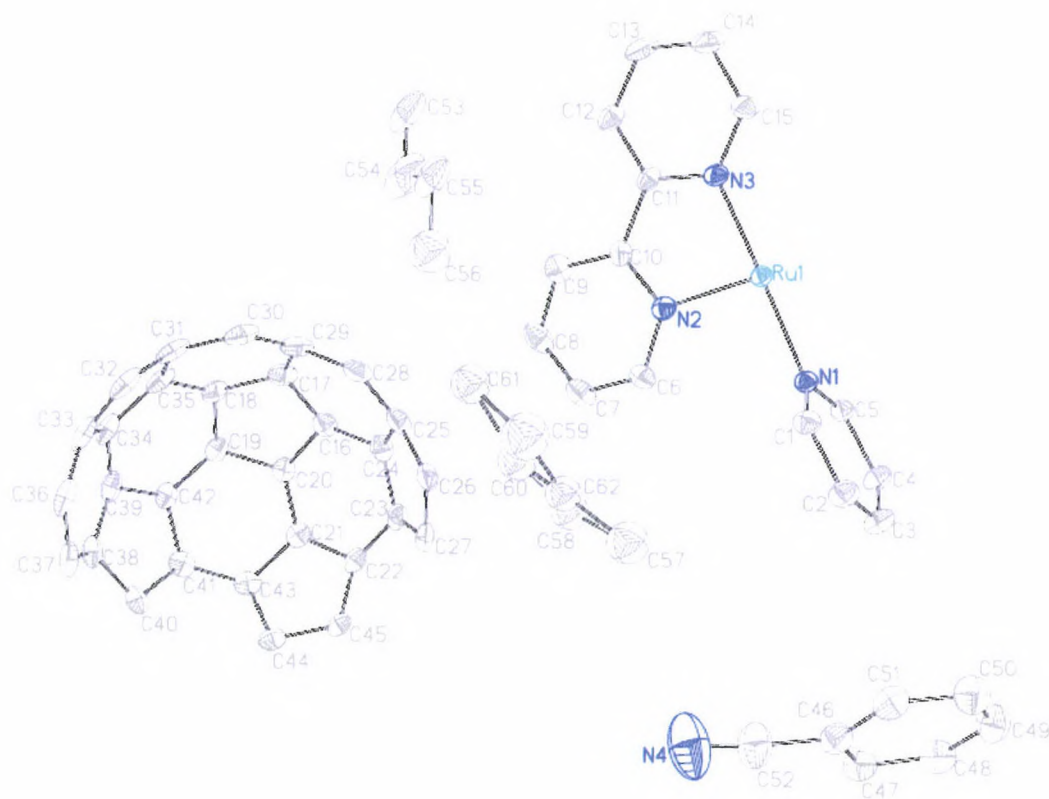


Figure 2.5: Asymmetric unit of Crystal 2'

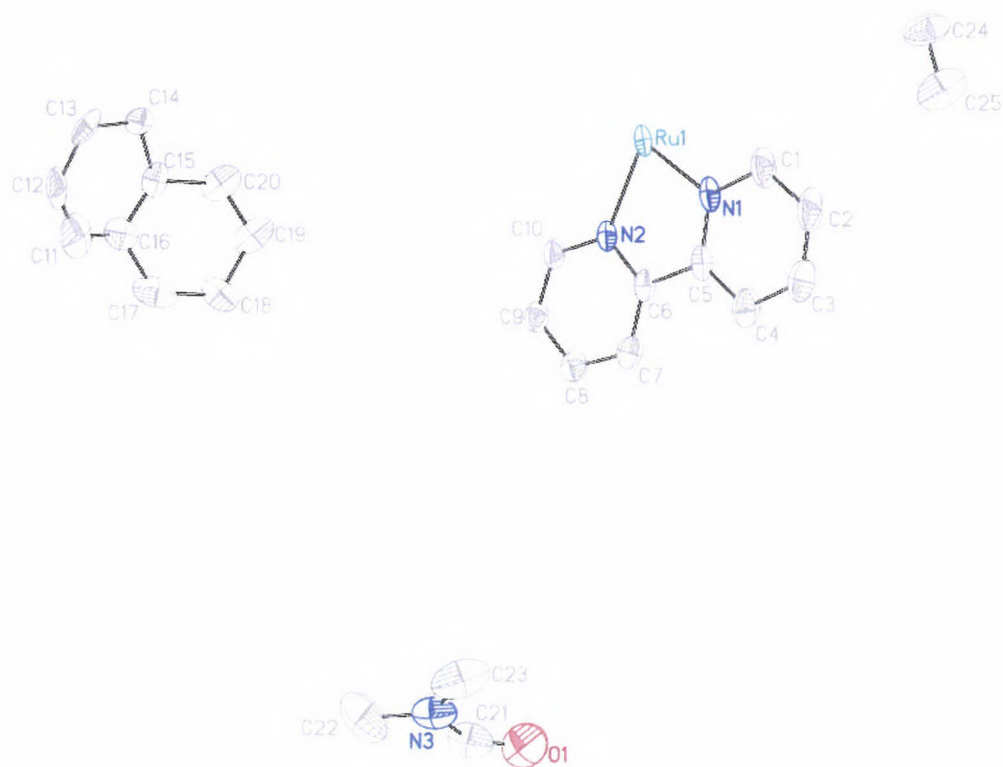


Figure 2.6: Asymmetric unit of crystal **1'**

Table 2.3: Crystallographic data for **1'** and **2'**

	2'	1'
Empirical Formula	C ₁₁₈ H ₄₂ N ₈ Ru	C ₁₅₀ H ₁₀₂ N ₁₈ O ₆ Ru ₂
Structural formula	Ru(bpy) ₃ •(C ₆₀)•(C ₆ H ₅ CN) ₂ •(C ₇ H ₈)•C ₇	[Ru(bpy) ₃] ₂ •(C ₆₀)•(C ₃ H ₇ NO) ₆ •(C ₆ H ₆) ₂
Formula weight (g•mol ⁻¹)	1672.67	2454.64
Crystal size (mm)	0.68 × 0.16 × 0.09	0.28 × 0.26 × 0.25
<i>D_{calc}</i> (g•cm ⁻³)	1.477	1.474
Temperature (K)	100(2)	120(2)
Crystal system	Monoclinic	Trigonal
Space group	<i>C2/c</i>	<i>R3c</i>
<i>a</i> (Å)	10.914(2)	13.9063(2)
<i>b</i> (Å)	40.612(8)	13.9063(2)
<i>c</i> (Å)	17.303(4)	99.067(3)
<i>α</i> (°)	90.00	90.00
<i>β</i> (°)	101.17(3)	90.00
<i>γ</i> (°)	90.00	120.00
<i>V</i> (Å ³)	7524(3)	16591.3(6)
<i>Z</i>	4	6
Unique Reflection	8743	4592
R(int)	0.0357	0.0628
Parameters	561 (0)	267 (0)
<i>F</i> (0 0 0)	3400	7584
2 θ_{max} (°)	56.56	56.56
Resolution (Å)	0.75	0.75
GOOF	1.045	1.092
<i>R</i> _I [F ₀ > 4σ(F ₀)]	0.0548	0.0812
<i>wR</i> ₂	0.1530	0.2200

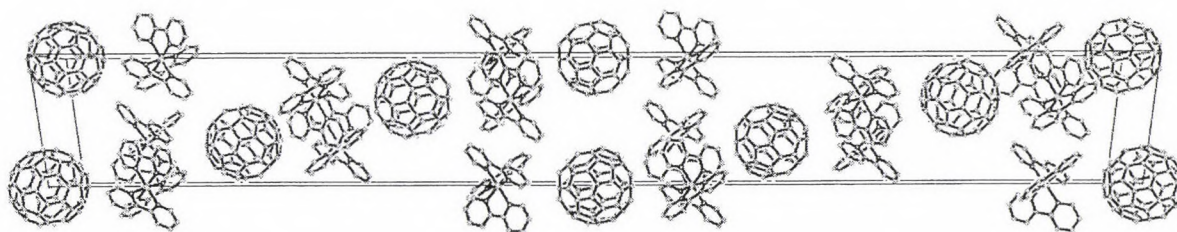
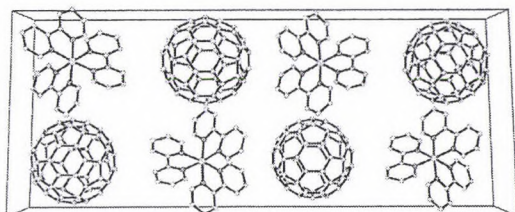


Figure 2.7: Projection of the crystal structures of **2'** (top) and **1'** (bottom) on the *b-c* plane. The solvent molecules were omitted for clarity.

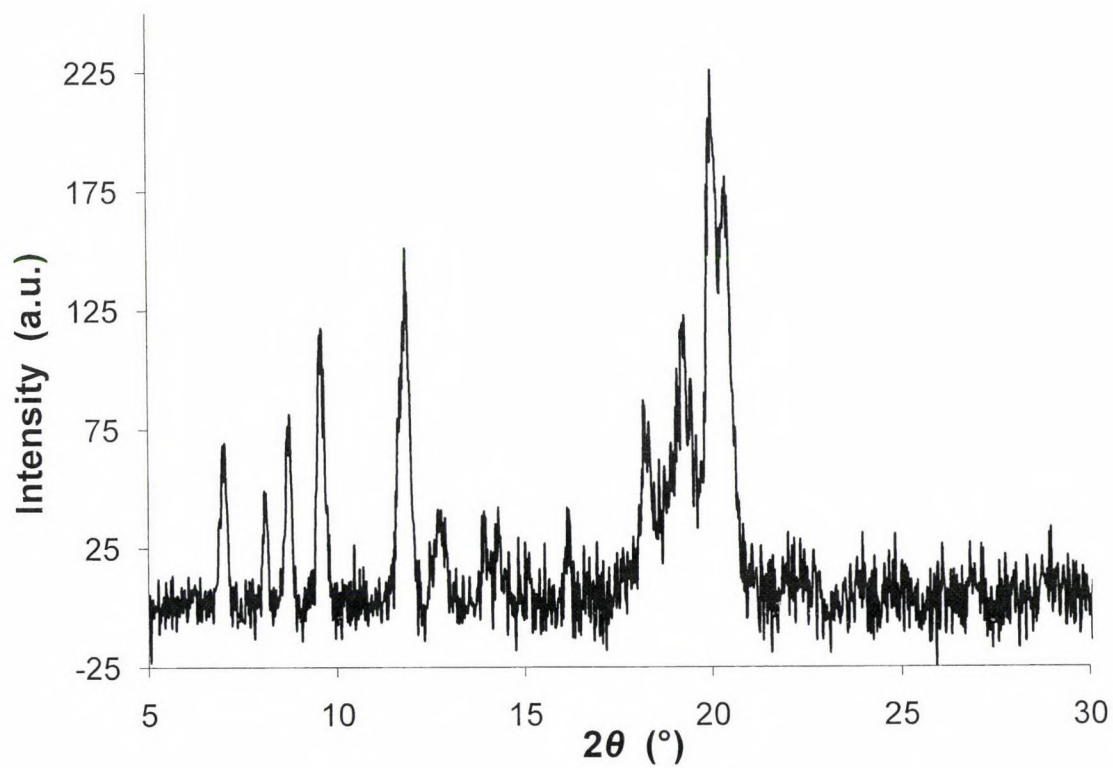


Figure 2.8: Powder diffraction pattern of compound **3** at 293 K.

Four-probe Electrical Conductivity

The dc conductivity was measured using a homemade four-probe design (**Figure 2.9**) on the central section of a circular pellet (radius = 3.5 mm) pressed at room temperature. Four tungsten wires ($d = 75\mu\text{m}$) were lined parallel with equal spacing ($\Delta = 0.77\text{mm} \pm 0.02\text{ mm}$). A knot was tied in each wire and the knots were aligned in parallel. The knot on each tungsten wire was then coated with silver paint and serves as the contact. The apparatus was calibrated with Ba_2Te_3 prior to use. The following equation¹³ was used to calculate the bulk resistivity.

$$\rho = C_s \times t \times R_s$$

R_s represents the sheet resistance which can be directly obtained from the I-V curve measured from the four-probe design. t is the thickness of thin sample sheet. The insulating KBr pellets were made as substrates to support the fragile sample sheets. C_s is the correction factor which depends on the ratio of the diameter of thin sheet to the spacing of probes.¹³ The value of C_s used is 4.17.¹³ When measuring the sheet resistance R_s , standard deviation σ_1 was obtained by multiple measurements with rotating the sample sheet to different positions. The thickness t was obtained by subtracting the thickness of KBr pellet (t_1) from the total thickness (t_2). The standard deviation σ_2 of t is a combination of error bars on t_1 and t_2 . Finally, the standard deviation for bulk resistivity ρ was calculated to be around $\pm (|\sigma_1| + |\sigma_2|)$.

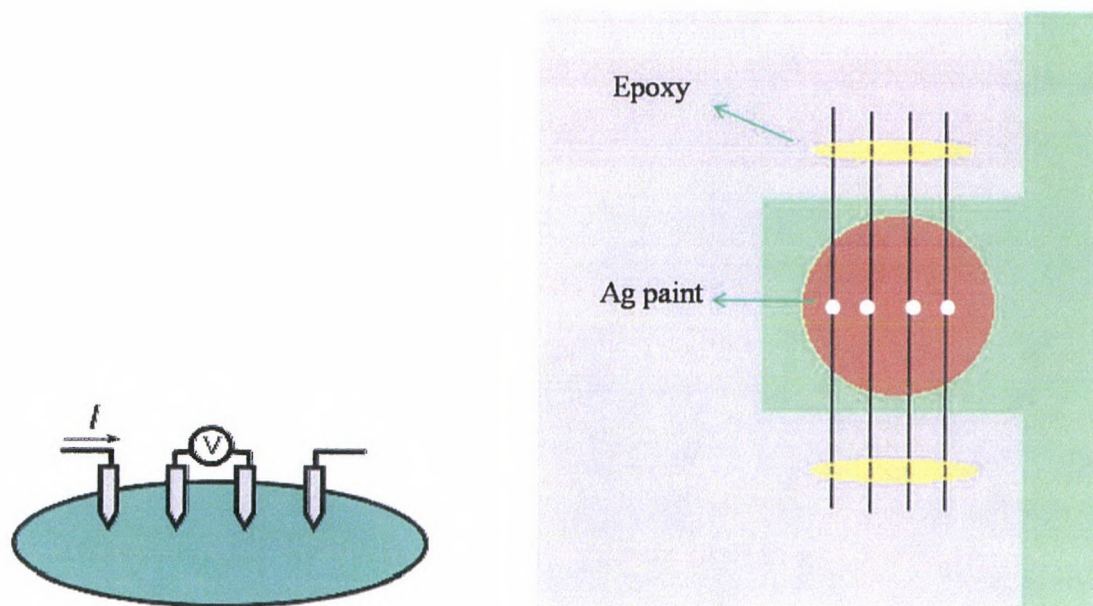


Figure 2.9: (a) The schematic design of four-probe conductivity measurement; (b) The homemade four-point probe apparatus.

Table 2.4: Electrical conductivities of compounds **1**, **2**, **3** at room temperature and calculated distribution of redox species in solution at room temperature. L represents 2, 2'-bipyridine ligand.

Compound	$\sigma \text{ (S} \cdot \text{m}^{-1} \text{)}$	RuL_3^{2+}	RuL_3^{1+}	RuL_3^0	C_{60}	C_{60}^{1-}	C_{60}^{2-}	C_{60}^{3-}
1	9.5 (± 26%)	0.068	1.900	0.032	0	0	0.964	0.036
2	0.018 (± 13%)	0.998	0.002	0	0	0.002	0.998	0
3	2.0 (± 31%)	1.000	0	0	0.0015	1.997	0.0015	0

The measurements were also repeated several times by using different batch of samples. The average conductivity and the value of standard deviation are listed in **Table 2.4**.

At room temperature, all three compounds show absolute conductivity in the semiconductor range (**Table 2.4**). As the temperature increases, their conductivities increase as well. The order for descending conductivity is **1** > **3** > **2** compound. **1** is about 500 times more conductive than **2**, while **3** is about 100 times more conductive than **2**. Based on the result of elemental analysis, Compounds **1**, **3** correspond to $[\text{Ru}(\text{bpy})_3]_2\text{C}_{60}$ and $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$ respectively, while compound **2** is mainly $[\text{Ru}(\text{bpy})_3]\text{C}_{60}$ with minor amount of possible compound **1** $[\text{Ru}(\text{bpy})_3]_2\text{C}_{60}$ (< 7 %). Because of the relatively high conductivity of compound **1**, the pure form of compound **2** should exhibit conductivity even smaller than $0.018 \text{ S}\cdot\text{m}^{-1}$. Since this does not conflict with the observed trend of conductivity, the following discussion will be based on the assumption that compound **2** is pure with formula $[\text{Ru}(\text{bpy})_3]\text{C}_{60}$.

In the single crystal structures of **1** and **2**, there is only weak site-site interaction since the cations and anions are all well separated from each other. The electronic conductivity is best described by an electron hopping model in this immobilized polyvalent redox system rather than by band structure.^{14,15}

There are two limiting factors for electron hopping efficiency.¹⁶ The first is the relative concentrations of electron hopping sites, which greatly depend on the degree of mixed-valency.¹⁶ Increasing the relative number of electron donor and acceptor increases the probability of charge transport.^{16,17} For $[\text{Ru}(\text{bpy})_3]_n(\text{C}_{60})_m$ compounds, both cation and anion are in principle electroactive. Supposing the respective stoichiometries of

compound **1**, **2** and **3**, distribution of various redox species in solution at equilibrium can be calculated from the Nernst equations and the electroneutrality principle (**Table 2.4**). As an example, the equations used for calculating the distribution of redox species for compound **1** are shown in **Table 2.5**. The calculated equilibrium potentials of compounds in solution turned out to be right in the middle of the overlapped potential region of corresponding cation and anion. For qualitative discussion, disproportionation calculated in solution can serve as a reasonable approximation for the case in solid state but is almost certainly not quantitatively the same. Possible electron hopping pathways are predicted in **Scheme 2.2**. Obviously, among the three, **1** has the highest degree of mixed-valency and the maximum possible electron transfer pathways.

The second important factor in determining the operative electron-hopping pathways is the intersite hopping distance.¹⁶ The overlap of HOMO and LUMO of electron donor and acceptor decreases as the distance increases, which results in a higher activation energy for electron to hop. Therefore, shorter site-site distance generally should result in easier electron hopping. In the single crystal of **2**, $[\text{Ru}(\text{bpy})_3]^{m+}$ and C_{60}^{n-} basically occupy the interchangeable positions in the unit cell (**Figure 2.10**). There are two types of $[\text{Ru}(\text{bpy})_3]^{m+}$ (or C_{60}^{n-}) sites with different surroundings (**Figure 2.11**). Both types represent the shortest electron hopping distance (9.308 Å) between adjacent $[\text{Ru}(\text{bpy})_3]^{m+}$ and C_{60}^{n-} on the *a-c* plane. And the second shortest distance (10.780 Å) is between adjacent $[\text{Ru}(\text{bpy})_3]^{m+}$ and C_{60}^{n-} along the *b* axis. In the single crystal of **1**, three types of $[\text{Ru}(\text{bpy})_3]^{m+}$ sites as well as two types of C_{60}^{n-} sites were found (**Figure 2.12**). The shortest electron hopping distance is 8.119 Å between adjacent $[\text{Ru}(\text{bpy})_3]^{m+}$ sites on the *a-b* plane.

Table 2.5: Equations for calculating disproportionated redox species for compound **1** in solution with the assumption that $[\text{Ru}(\text{bpy})_3]^0$ and C_{60} are mixed in exact 2:1 molar ratio.

$$[\text{RuL}_3^{2+}] + [\text{RuL}_3^{1+}] + [\text{RuL}_3^0] = 2$$

$$[\text{C}_{60}^{1-}] + [\text{C}_{60}^{2-}] + [\text{C}_{60}^{3-}] = 1$$

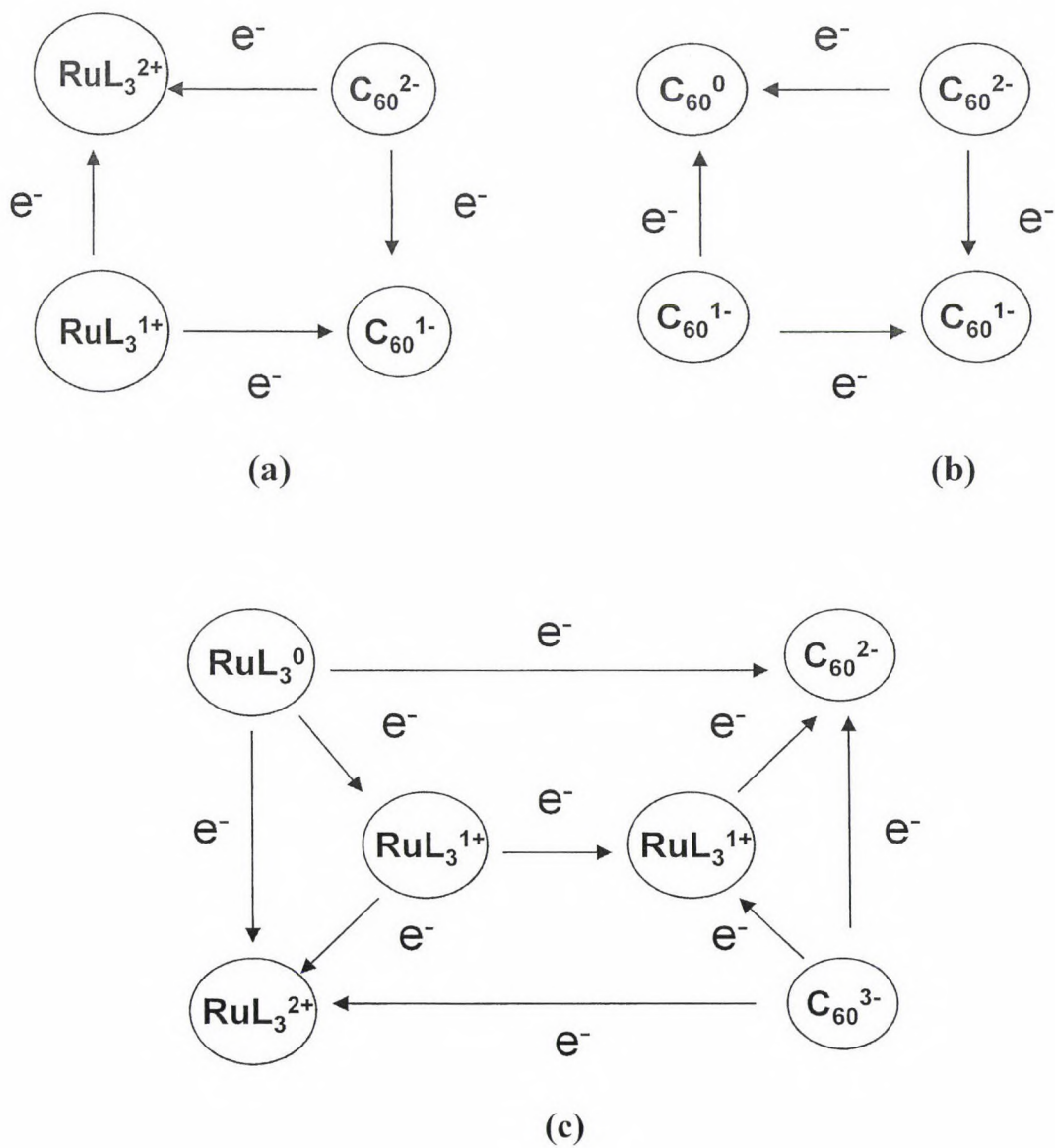
$$2[\text{RuL}_3^{2+}] + [\text{RuL}_3^{1+}] = [\text{C}_{60}^{1-}] + 2[\text{C}_{60}^{2-}] + 3[\text{C}_{60}^{3-}]$$

$$E_{eq.} = E_{+1/+2}^0 - \frac{RT}{F} \ln \frac{[\text{RuL}_3^{1+}]}{[\text{RuL}_3^{2+}]}$$

$$E_{eq.} = E_{0/+1}^0 - \frac{RT}{F} \ln \frac{[\text{RuL}_3^0]}{[\text{RuL}_3^{1+}]}$$

$$E_{eq.} = E_{2-/1-}^0 - \frac{RT}{F} \ln \frac{[\text{C}_{60}^{2-}]}{[\text{C}_{60}^{1-}]}$$

$$E_{eq.} = E_{3-/2-}^0 - \frac{RT}{F} \ln \frac{[\text{C}_{60}^{3-}]}{[\text{C}_{60}^{2-}]}$$



Scheme 2.2: Schematic pictures of possible electron transfer in compound (a) **2** (b) **3** and (c) **1**. L represents 2, 2'-bipyridine ligand.

The second shortest distance turned out to be 8.836 Å between the neighboring $[\text{Ru}(\text{bpy})_3]^{m+}$ and C_{60}^{n-} along the c axis. Apparently, longer intersite distances were found in the single crystal of compound **2** and thus it will be harder for electrons to hop from one site to another as compared to those in the single crystal of compound **1**. The indication from structural information is in accordance with the conductivity results that compound **1** is much more conductive than compound **2**. As for compound **3**, the electron transfers exclusively reside in the C_{60} manifolds while $[\text{Ru}(\text{bpy})_3]^{2+}$ only act a spacer (**Scheme 2.2**). Because the electrons only hop from one C_{60} to another, the C_{60} - C_{60} distances are of more importance for conductivity than other site-site distances. Although no single crystal structure was obtained for **3**, the preliminary result of powder diffraction data indicates a high probability of close contact between C_{60} s at least along the c axis. When the degree of mixed-valency and number of electron-transfer pathways are similar in **2** and **3**, easier electron hopping would most likely happen in **3** because it very possibly has shorter C_{60} - C_{60} distances. This speculation is in accordance with the measured conductivity that **3** is about 100 times more conducting than **2**.

Based on **Scheme 2.2**, all possible electron transfer mechanisms for all three compounds are listed in **Table 2.6**. Combining the conclusions from analyzing intersite distances in compounds **1**, **2** and **3** with their mixed-valency information, the favorable electron hopping pathway can be predicted as follows.

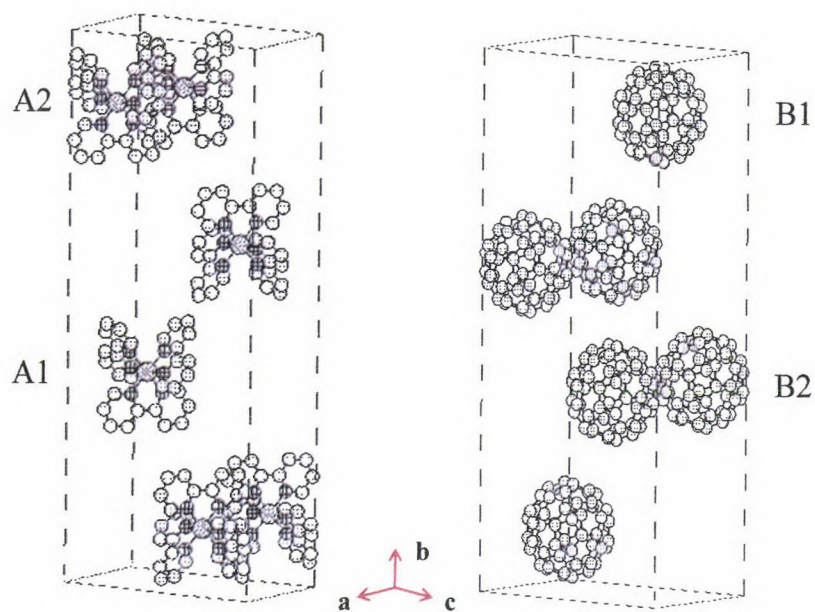


Figure 2.10: In single crystal **2'**, the positions of $[\text{Ru}(\text{bpy})_3]^{\text{m}+}$ (left) and $\text{C}_{60}^{\text{n}-}$ (right) in one unit cell.

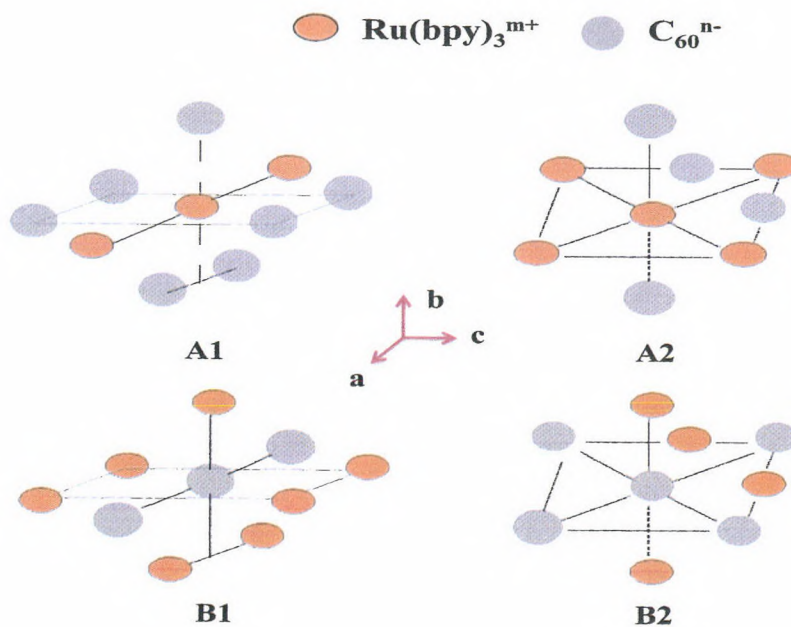


Figure 2.11: The surroundings of two types of $[\text{Ru}(\text{bpy})_3]^{\text{m}+}$ sites (A1, A2) and two types of $\text{C}_{60}^{\text{n}-}$ sites (B1, B2) in single crystal **2'**.

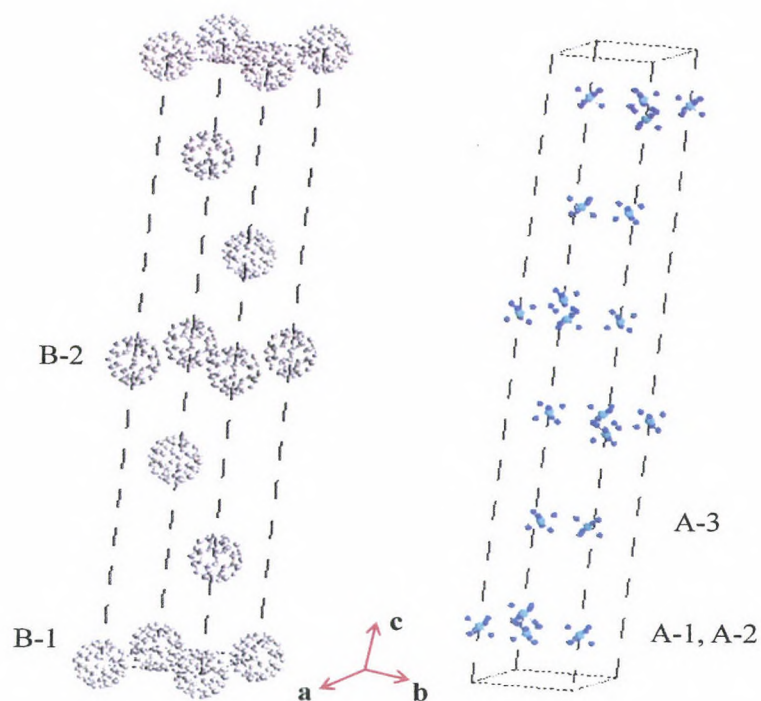


Figure 2.12: In single crystal **1'**, the positions of $[\text{Ru}(\text{bpy})_3]^{\text{m}+}$ and $\text{C}_{60}^{\text{n}-}$ in one unit cell.

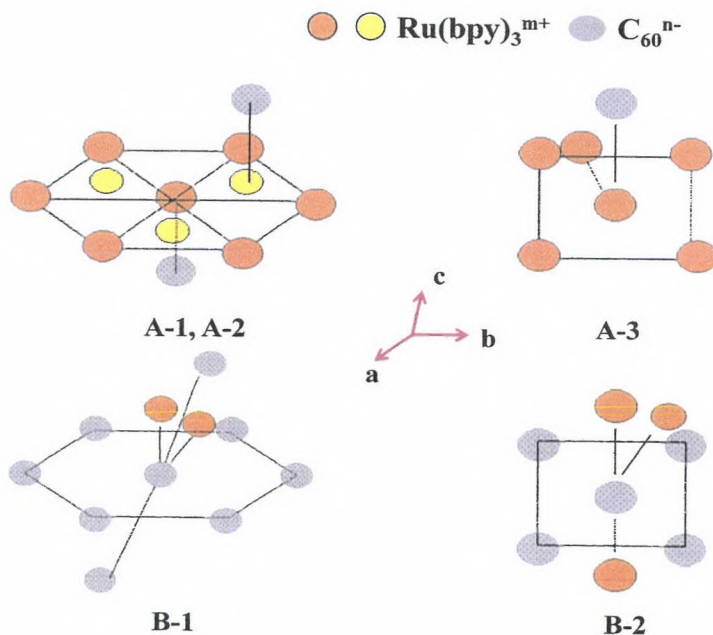
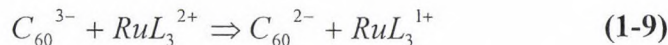
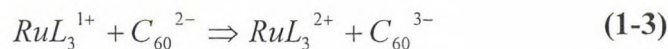
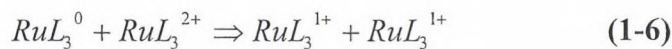
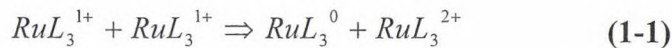


Figure 2.13: The surroundings of three types of $[\text{Ru}(\text{bpy})_3]^{\text{m}+}$ sites (A-1, A-2, A-3) and two types of $\text{C}_{60}^{\text{n}-}$ sites (B-1, B-2) in single crystal **1'**.

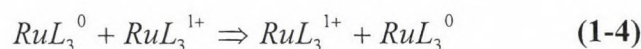
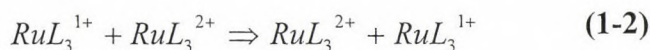
Table 2.6: Prediction of possible electron hopping mechanism in compound **1**, **2** and **3**. L represents 2, 2'-bipyridine ligand.

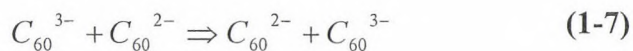
Compound	Possible Mechanism	Favorable (F) or Unfavorable (UF)
1	$RuL_3^{1+} + RuL_3^{1+} \Rightarrow RuL_3^{2+} + RuL_3^0$	(1-1) UF
	$RuL_3^{1+} + RuL_3^{2+} \Rightarrow RuL_3^{2+} + RuL_3^{1+}$	(1-2) F
	$RuL_3^{1+} + C_{60}^{2-} \Rightarrow RuL_3^{2+} + C_{60}^{3-}$	(1-3) UF
	$RuL_3^0 + RuL_3^{1+} \Rightarrow RuL_3^{1+} + RuL_3^0$	(1-4) F
	$RuL_3^0 + C_{60}^{2-} \Rightarrow RuL_3^{1+} + C_{60}^{3-}$	(1-5) F (possible)
	$RuL_3^0 + RuL_3^{2+} \Rightarrow RuL_3^{1+} + RuL_3^{1+}$	(1-6) UF
	$C_{60}^{3-} + C_{60}^{2-} \Rightarrow C_{60}^{2-} + C_{60}^{3-}$	(1-7) F
	$C_{60}^{3-} + RuL_3^{1+} \Rightarrow C_{60}^{2-} + RuL_3^0$	(1-8) F (possible)
	$C_{60}^{3-} + RuL_3^{2+} \Rightarrow C_{60}^{2-} + RuL_3^{1+}$	(1-9) UF
2	$RuL_3^{1+} + RuL_3^{2+} \Rightarrow RuL_3^{2+} + RuL_3^{1+}$	(2-1) F
	$RuL_3^{1+} + C_{60}^{1-} \Rightarrow RuL_3^{2+} + C_{60}^{2-}$	(2-2) UF
	$C_{60}^{3-} + C_{60}^{2-} \Rightarrow C_{60}^{2-} + C_{60}^{3-}$	(2-3) F
	$C_{60}^{2-} + RuL_3^{2+} \Rightarrow C_{60}^{1-} + RuL_3^{1+}$	(2-4) UF
3	$C_{60}^{1-} + C_{60}^0 \Rightarrow C_{60}^0 + C_{60}^{1-}$	(3-1) F
	$C_{60}^{1-} + C_{60}^{1-} \Rightarrow C_{60}^0 + C_{60}^{2-}$	(3-2) UF
	$C_{60}^{2-} + C_{60}^{1-} \Rightarrow C_{60}^{1-} + C_{60}^{2-}$	(3-3) F
	$C_{60}^{2-} + C_{60}^0 \Rightarrow C_{60}^{1-} + C_{60}^{1-}$	(3-4) UF

In compound **1**, there are nine possible electron-transfer mechanisms, which fall into three groups. Group I includes the following four equations.

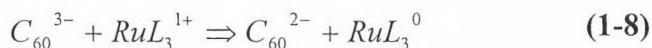
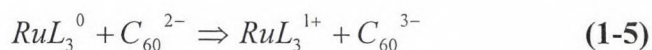


Consider first reaction (1-6), where the relative concentrations calculated from solution redox data of RuL_3^0 , RuL_3^{2+} and RuL_3^{1+} are 0.036, 0.068 and 1.900, respectively (Table 2.4). In order for electron to hop via this mechanism, one RuL_3^0 and one RuL_3^{2+} must happen to sit on the adjacent positions. Considering their small relative concentrations and assuming a random distribution over the solids, the possibility of this electron hop to be a major contribution to the overall conduction would be very small. Therefore, equation (1-6) is not likely to be an important electron hopping mechanism. Reaction (1-9) is also unfavorable for the same reasons. (Concentrations of reactants C_{60}^{3-} and RuL_3^{2+} are only 0.036 and 0.068.) Reactions (1-1) and (1-3) are simply the reverse of (1-6) and (1-9). Although here both reactants have large concentrations, the probability to generate two minor species would be small for thermodynamic reasons. On the whole, the first group of mechanism (1-1), (1-3), (1-6) and (1-9) is considered as “unfavorable” in their contributions to the hopping. In group II, three “favorable” mechanisms for electron transfer were found.



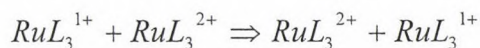
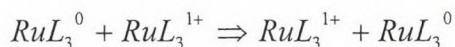


The similarity of all three above equations is that the reactants and products are the same, thus, since the equilibrium constant for each reaction equals 1, the thermodynamic “cost” is zero (Ignoring, of course, any columbic contribution to rearrange charges within the solid). Also, the presence of at least one ion present at high relative concentration in the reactant side greatly increases the probability of electron hopping. Contribution from reactions in the third group (shown below) is less clear.



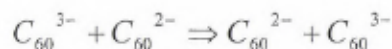
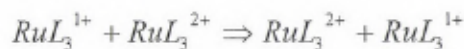
Based on the concentration given in **Table 2.4**, the K_{eq} for (1-5) and (1-8) are calculated to be 2.22 and 0.45 respectively. Also, each reaction involves one reactant that is present at a large relative concentration. Thus, while they are not thermoneutral processes, their contribution to the overall conduction mechanism cannot be discounted.

Combining the above discussion with the site-site distribution information obtained from X-ray diffraction of compound **1**, the most preferable electron hopping mechanisms can be predicted as follows with hopping distance 8.119 Å along the *a-b* plane.

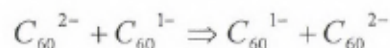
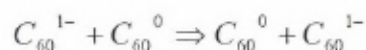


The same protocol was followed to figure out the favorable and unfavorable electron hopping mechanisms in **2** and **3** (**Table 2.6**).

In the single crystal of **2**, electrons would prefer the following two hopping pathways with hopping distance in each case of 10.914 Å along the *a* axis.



In compound **3**, electrons can only transfer between C_{60} s and they should prefer to hop from one C_{60} to another C_{60} with one unit charge difference.



In summary, among these three fullerides, compound **1** exhibits the highest electrical conductivity due to its highest degree of mixed-valency and its shortest intersite electron jump distance. Although **2** and **3** have similar relative concentration of electron donors and acceptors, the much higher conductivity observed in **3** can be explained by possible existence of C_{60} - C_{60} close contact in **3**.

Magnetic Properties

EPR spectra of solid samples were recorded on a Bruker X-band EPR spectrometer equipped with a temperature controller. A Quantum Design MPMS-XL SQUID magnetometer was used to measure dc magnetic susceptibilities of finely ground polycrystalline samples **1-3** between 300 and 5 K at 100 mT static magnetic fields. A sample holder contribution and diamagnetic susceptibility (χ_0) of the compound were

subtracted from the experimental values. The value of χ_0 was obtained from literature^{1,18} which is in good agreement with the calculated value using Pascal's constants.¹⁹

According to Hund's rule, C_{60}^{2-} should have a triplet ground state ($S = 1$). However, many previous observations have demonstrated that C_{60}^{2-} prefers a singlet ground state ($S = 0$) with a close-lying triplet excited state ($S = 1$).^{5,7,20-24} Although neutral C_{60} has a triply degenerate LUMO, upon reduction, the excess electrons on the buckyball lower the symmetry which results in the Jahn-Teller splitting of orbitals (**Figure 2.14**). Similarly, for C_{60}^{3-} , instead of having a spin quartet, it prefers a doublet ground state ($S = 1/2$).⁷

The corresponding molecular formulas for compound **1** and **3** are $[Ru(bpy)_3]^{1+}_2(C_{60}^{2-})$ and $[Ru(bpy)_3]^{2+}(C_{60}^{1-})_2$ respectively. By elemental analysis, their purity has been demonstrated. However, compound **2** turned out to be a mixture with minor amount of compound **1**. The derived formula $[Ru(bpy)_3]_{1.07}(C_{60})$ for compound **2** can be rewritten as $0.93 \{[Ru(bpy)_3]^{2+}(C_{60}^{2-})\} \cdot 0.07 \{[Ru(bpy)_3]^{1+}_2(C_{60}^{2-})\}$. The presence of impurity $Ru(bpy)_3^{1+}$ exhibits small but significant contributions to the magnetic properties.

In compound **1**, both $[Ru(bpy)_3]^{1+}$ and C_{60}^{2-} are EPR active. The signal at 285 K is a single line with $g = 1.9999 (\pm 0.0002)$. According to literature, $[Ru(bpy)_3]^{1+}$ should exhibit a broad signal ($\Delta H_{p-p} = 100 \sim 150$ G) at 285 K.²⁵ However, in the presence of a much sharper signal from C_{60}^{2-} near RT, the signal from $[Ru(bpy)_3]^{1+}$ is almost completely obscured (**Figure 2.15**). Since the width of $[Ru(bpy)_3]^{1+}$ peak is strongly temperature dependent, by cooling down, the $[Ru(bpy)_3]^{1+}$ signal became narrower and

stronger.²⁵ At 230 K, a bump at ~3385 G started to show up. It was noticed that the signal of C_{60}^{2-} at near RT is very weak indicating the singlet ground state for most C_{60}^{2-} anions. The signal is mainly contributed from the minor portion of thermally accessible triplet state in C_{60}^{2-} and the possible paramagnetic impurity $C_{120}O^n$.^{7,24} More detailed discussions about C_{60}^{2-} signal will be carried out in the section for compound **2**.

The temperature dependence of the magnetic susceptibility of solid **1** is shown in **Figure 2.16**. From 300 K to 100 K, the product $\chi_M T$ behaves as a linear function of temperature. The data can be fit to the following equation.

$$\chi_M = \frac{C}{T} + \chi_{TIP} \quad (1)$$

From 100 K to 300 K, compound **1** shows paramagnetism with two contributions. One of them obeys the Curie law yielding $C = 0.5014 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$. The other contribution is the so-called Van Vleck temperature-independent paramagnetism (TIP) with $\chi_{TIP} = 15.9 \times 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$.^{1,19,26} Generally, in alkali-metal doped C_{60} , χ_{TIP} was found to be less than $1 \times 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$.¹ Since the HOMO and LUMO of $[\text{Ru}(\text{bpy})_3]^{1+}$ and C_{60}^{2-} are of similar energy and their energy separation is small, the sizable experimental χ_{TIP} can be speculated to mainly arise from the Zeeman mixing of the ground state of $[\text{Ru}(\text{bpy})_3]^{1+}$ and the abundant low-lying excited states in C_{60}^{2-} .^{1,20,25,27,28} By using equation (2), considering the spin multiplicity of $[\text{Ru}(\text{bpy})_3]^{1+}$, the theoretical curie constant C_0 was calculated to be $0.75 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$.

$$C = \frac{Ng^2\beta^2}{3k} S(S+1) = \frac{g^2}{8} S(S+1) \quad (2)$$

In equation (2), N is Avogadro's number and β is electronic Bohr magneton. k represents the Boltzmann constant while g represents g-factor. In the cgsemu unit system, $N\beta^2/3k$ is equal to 0.12505 (very close to 1/8).¹⁹ The smaller experimental curie constant observed ($C = 0.5014 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) might be explained by a possible antiferromagnetic coupling between two $[\text{Ru}(\text{bpy})_3]^{1+}$. This is consistent with the small curvature observed below 100 K in the $\chi_M \cdot T$ vs. T curve. Also, from single-crystal structural analysis, compound **1** has short center-to-center distances between $\text{Ru}(\text{bpy})_3 \cdots \text{Ru}(\text{bpy})_3$ (8.119 Å) and $\text{Ru}(\text{bpy})_3 \cdots \text{C}_{60}$ (8.836 Å). The possible close contact between two $[\text{Ru}(\text{bpy})_3]^{1+}$ makes antiferromagnetic coupling a possibility.

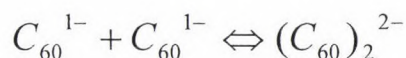
In compound **2**, since $[\text{Ru}(\text{bpy})_3]^{2+}$ has no unpaired electron,²⁵ the C_{60}^{2-} and impurity $[\text{Ru}(\text{bpy})_3]^{1+}$ needs to be considered as the major source for EPR signal. The EPR spectrum of **2** at 292 K exhibits a broad single line with $g = 2.0028 (\pm 0.0002)$. A broad signal **I** is superimposed with a narrow signal **II** (**Fig. 2.17**). The total integral intensity only accounts for a few percent of the total C_{60} , which indicates that the majority of C_{60}^{2-} possesses diamagnetic ground state. As temperature decreased, signal **I** (at RT, $\Delta H_{\text{p-p}} = 30 \text{ G}$) became narrower and weaker while signal **II** increased and became more dominant. The feature of signal **I** allows it to be assigned to the thermally populated triplet ($S=1$) excited state of C_{60}^{2-} .^{24,26} For signal **II**, there are mainly two possible sources. First, the curie impurity $[\text{Ru}(\text{bpy})_3]^{1+}$ ($S = 1/2$) shows a broad signal with a strong temperature-dependent linewidth. As temperature becomes lower, the signal of $[\text{Ru}(\text{bpy})_3]^{1+}$ grows up. Secondly, C_{120}O is a common impurity in solid C_{60} samples (up to 1%) because of the exposure to air and light.⁷ With reduction, $\text{C}_{120}\text{O}^{n-}$ ($n = 1, 3, 5$) can give rise to a sharp signal as well.⁷

Generally, compound **2** represents similar dc magnetic behavior as compound **1** (**Figure 2.18**). However, over the whole temperature range, by fitting data into equation (1), much smaller Curie constant ($C = 0.05898 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) and χ_{TIP} ($4.97 \times 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$) were obtained. This can be explained by the presence of 2 equivalents of paramagnetic $[\text{Ru}(\text{bpy})_3]^{1+}$ ($S = \frac{1}{2}$) in compound **1**.³⁰ The temperature-dependent χ_{TIP} is mainly due to the coupling between the $^1\text{A}_1$ ground state of $[\text{Ru}(\text{bpy})_3]^{2+}$ and the rich close-lying excited states in C_{60}^{2-} .^{20,28,29} By using equation (2), the actual spin is calculated to be 0.107. By eliminating the contributions from curie impurities, the spins originated from C_{60}^{2-} only arises from less than 4 % of the total C_{60} species. This is in accordance with the EPR result that the major C_{60}^{2-} has singlet ground state.

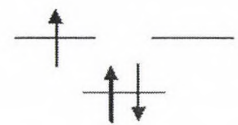
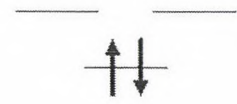
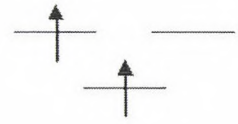
In the EPR spectrum of solid **3** (**Figure 2.19**), a characteristic broad signal of C_{60}^{1-} ($S = \frac{1}{2}$) was observed with $g = 2.0014 (\pm 0.0002)$ at 292 K.²⁴ The peak-to-peak linewidth decreased from 40G to 20 G as temperature decreased from 292 K to 100 K.²⁴ Since the linewidth is proportional to the electron spin-lattice relaxation rate, at higher temperature, faster electron spin-lattice relaxation rate resulted in broader signal.²⁴

SQUID measurement of solid **3** displays slightly different magnetic behavior with comparison to solid **1** and **2** (**Figure 2.20**). The data is reproducible with measurements on different batches of samples. Three segments were found in the χ_M vs T curve. From 300 K to 210 K, χ_M gradually increased as T decreased. The data can be fitted into equation (1) with $C = 0.55045 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ and $\chi_{\text{TIP}} = 3.94 \times 10^{-3} \text{ emu}\cdot\text{mol}^{-1}$. Considering spins from C_{60}^{1-} ($S = \frac{1}{2}$) in solid **3**, curie constant should be $0.75 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$.¹⁹ The smaller experimental value again indicates possible antiferromagnetic coupling this time

between adjacent C_{60}^{1-} anions. This speculation is consistent with the negative Weiss constant θ obtained by fitting data linearly from 210 to 300 K in χ_M^{-1} vs T curve (**Figure 2.21**). As temperature continued to decrease, χ_M almost leveled off. Below 150 K, χ_M resumed to increase with a steeper slope. It seems that there exists a phase transition in the range of 150 to 210 K. A possible phase transition can be speculated to be the partial dimerization of C_{60}^{1-} forming diamagnetic $(C_{60})_2^{2-}$. This reversible phase transformation has been reported before in the similar temperature range.^{7,31} Furthermore, possible close contact between C_{60} s indicated from powder diffraction data also supports the possibility of partial dimerization. Differential scanning calorimetry measurements were done to detect the phase transition (Appendix I). An obvious crystallization transition was observed at ~ 170 K when the solid sample was warmed up from 145 K to 293 K during the first measurement. However, the transition disappeared in the second measurement on the same batch of sample, which is probably due to the decomposition of sample by its exposure to the air.



In summary, EPR data demonstrated that in compound **1** and **2**, C_{60}^{2-} prefers singlet ground state. In compound **3**, C_{60}^{1-} exhibits doublet ground state. Since both C_{60}^{1-} and C_{60}^{2-} are both rich in low-lying excited states, Van Vleck temperature-independent paramagnetism was observed in all three compounds.

T_{1u} (LUMO)  C_{60}	$C_{60}^{1-} \quad S = \frac{1}{2}$ 	$C_{60}^{3-} \quad S = \frac{1}{2}$ 
	 $C_{60}^{2-} \quad S = 0$	 $C_{60}^{2-} \quad S = 1$

$$\Delta_{S-T} = \sim 0.08 \text{ eV}$$

Figure 2.14: Illustration of LUMOs for C_{60} and C_{60}^{n-} ($n=1-3$). Δ_{S-T} represents the calculated energy difference between C_{60}^{2-} (singlet) and C_{60}^{2-} (triplet).²¹

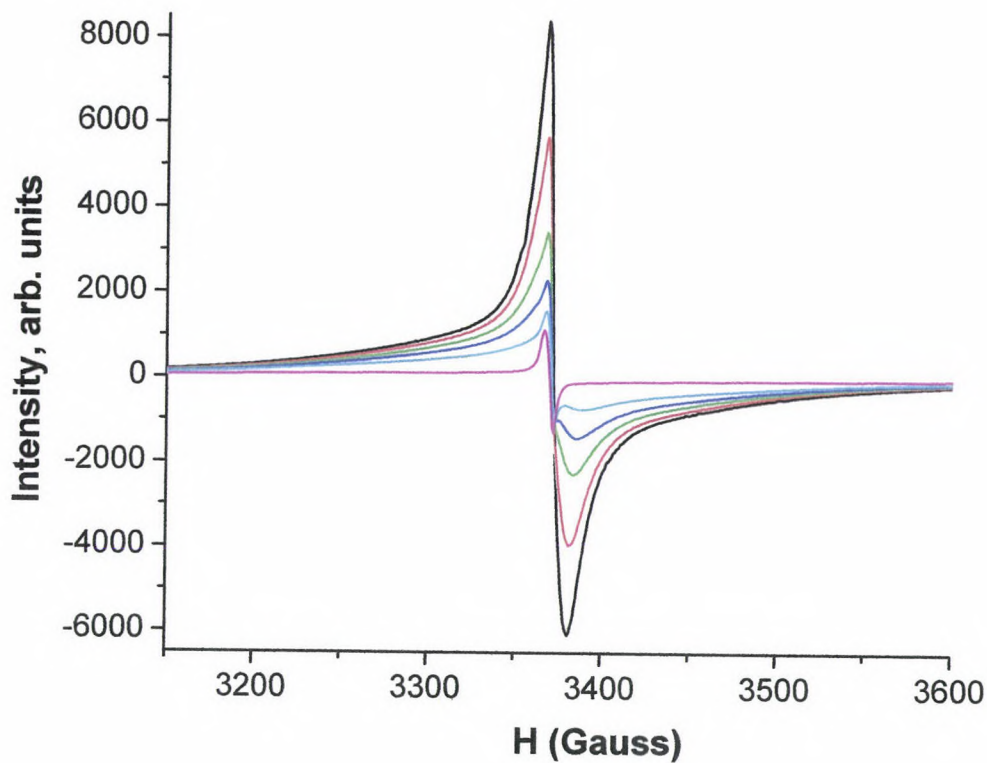


Figure 2.15: EPR spectra of solid sample **1** at 285 K (violet), 230 K (cyan), 205 K (blue), 180 K (green), 150 (red), and 125K (black).

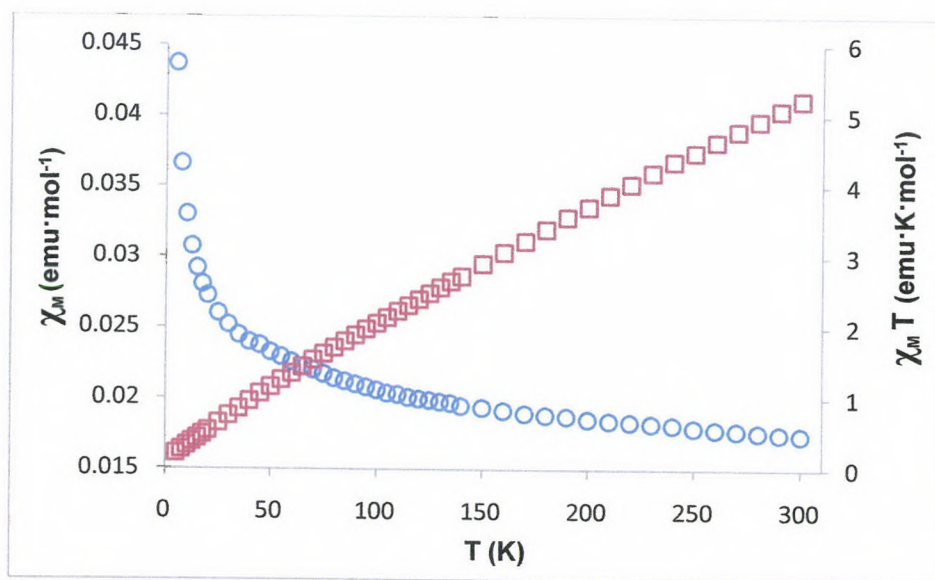


Figure 2.16: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for compound **1** at 100mT magnetic field.

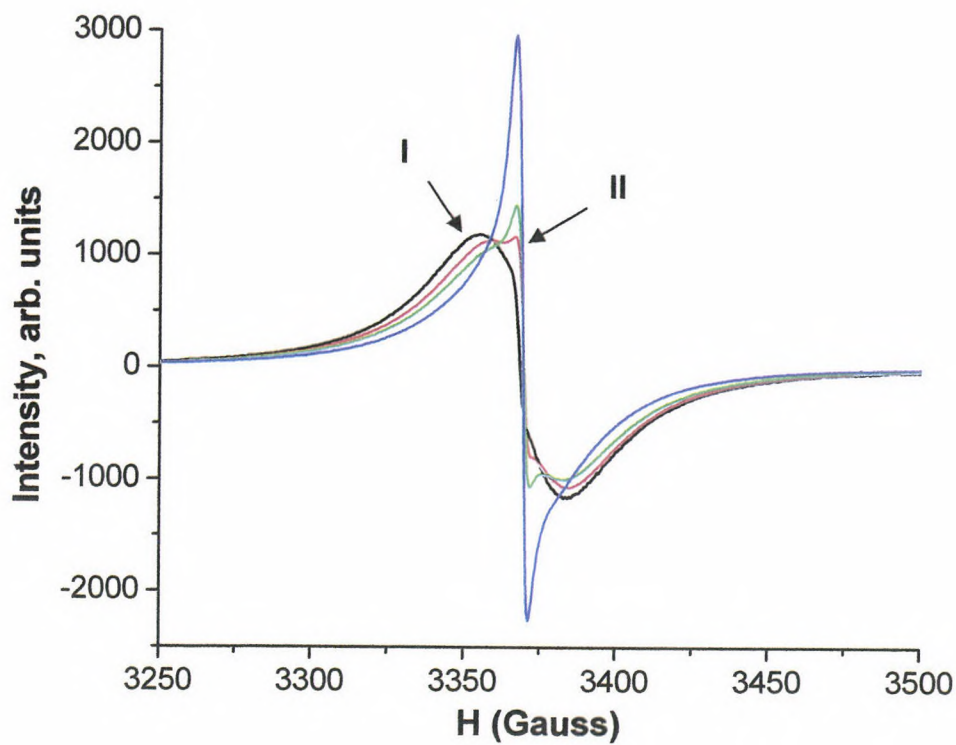


Figure 2.17: EPR spectra of solid sample **2** at 292 K (black), 260 K (red), 235 K (green), and 165 K (blue).

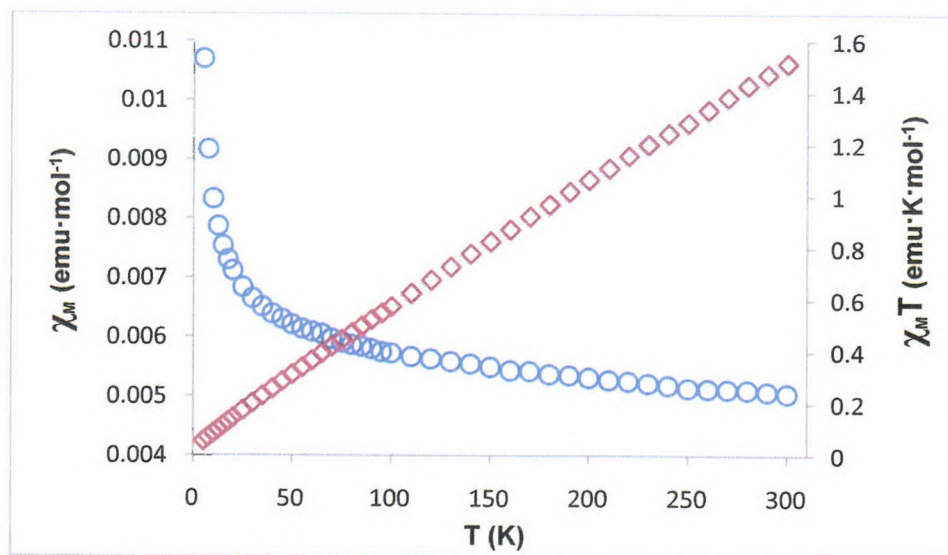


Figure 2.18: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for compound **2** at 100mT magnetic field.

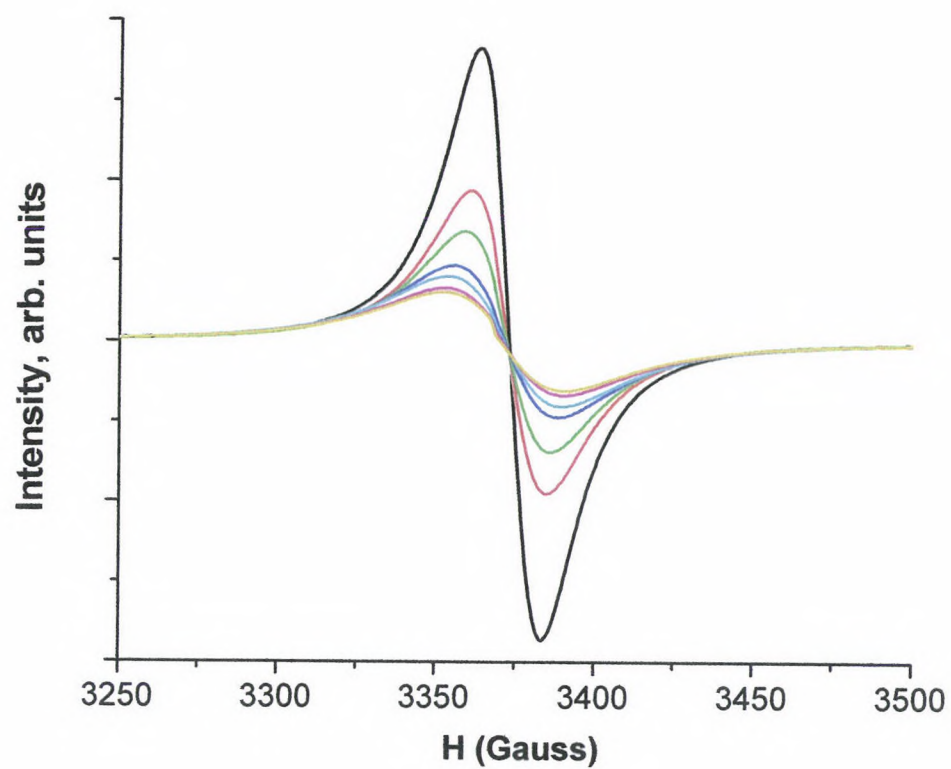


Figure 2.19: EPR spectra of solid sample 3 at 292 K (dark yellow), 225 K (violet), 200 K (cyan), 175 K (blue), 145 K (green), 130 K (red), and 100 K (black).

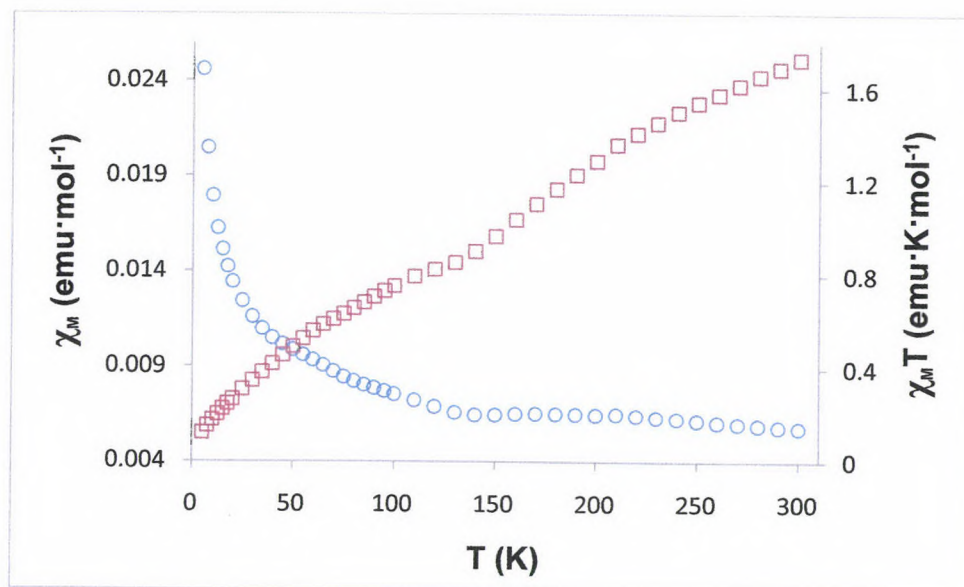


Figure 2.20: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for compound **3** at 100mT magnetic field.

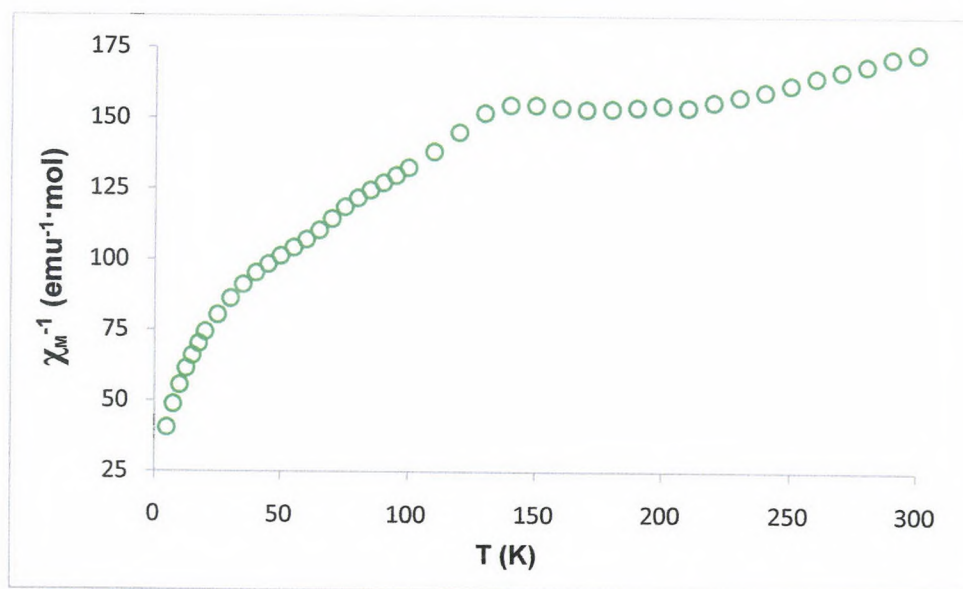


Figure 2.21: Temperature dependence of the reciprocal of molar magnetic susceptibility of compound **3** at 100mT magnetic field.

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CHAPTER III

SYNTHESIS AND CHARACTERIZATION OF RUTHENIUM RING- SUBSTITUTED BIPYRIDINE COMPLEX FULLERENE SALTS

Introduction

One important feature of ruthenium bipyridine complex is its broad tunability of electrochemical properties by ligand substitution.¹ By using 4, 4'-dimethyl-2, 2'-bipyridine (4DMB), 5, 5'-dimethyl-2, 2'-bipyridine (5DMB), 4, 4'-di-tert-butyl-2, 2'-bipyridine (TBB) or 4, 4', 5, 5'-tetramethyl-2, 2'-bipyridine (TMB) as ligands (**Figure 3.1**), the redox potentials of ruthenium complexes can be varied but are still in the similar region.¹ This opens up a new direction for synthesizing many possible ruthenium ring-substituted complex C₆₀ salts. Changing the size of the ligand could change the lattice structure of resulting fulleride salts. Also, changing the chemical structure of the ligand shifts the HOMO and LUMO of ruthenium complexes, thus affecting the barrier of electron transfer in the conduction. The effect of ligand substitution on electronic and magnetic properties has been studied in detail in this chapter.

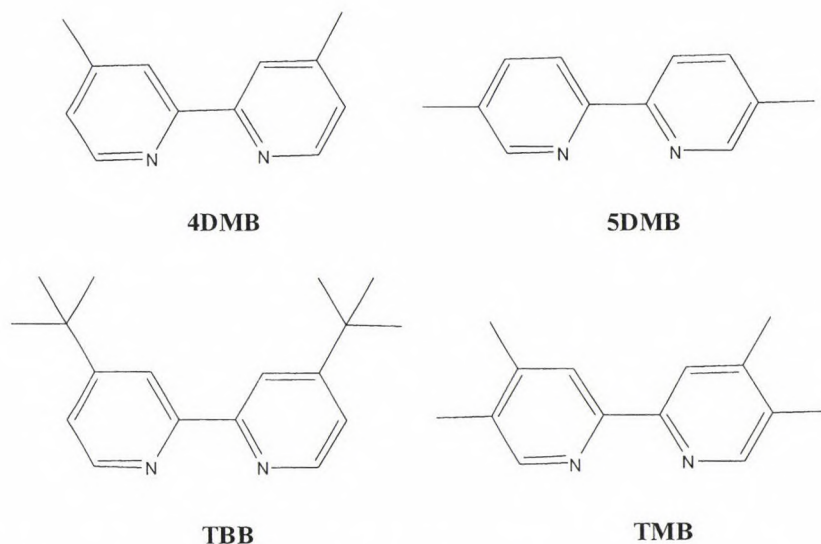


Figure 3.1: Molecular structures of ligand 4DMB, 5DMB, TBB and TMB.

Experimental

Preparation of Metal Complexes

[Ru(4DMB)₃](PF₆)₂ (A)

Synthesis of this complex is similar to that of [Ru(bpy)₃](PF₆)₂ (vide supra, Chapter II) except that the mixture was refluxed for 12 hours at 100 °C producing a dark red solution with a noticeable amount of precipitates at the bottom of the flask. The final product is a brick red polycrystalline solid after multiple recrystallization from EtOH/acetone.

[Ru(5DMB)₃](PF₆)₂ (B)

The complex was prepared by using the same method used for [Ru(bpy)₃](PF₆)₂, except 5, 5'-demethyl-2, 2'-bipyridine was used.

[Ru(TBB)₃](PF₆)₂ (C)

The procedure followed was the same as that for [Ru(bpy)₃](PF₆)₂ with the substituted 4,4'-di-tert-butyl-2, 2'-bipyridine ligand. The compound was recrystallized from ethanol only.

[Ru(TMB)₃](PF₆)₂ (D)

The synthesis of 4, 4', 5, 5'-tetramethyl-2, 2'-bipyridine (TMB) was described elsewhere.² A similar procedure as that for the above two compounds was used except that the purification was slightly different. Since TMB shows limited solubility in most of the organic solvents, washing by EtOH is not sufficient to remove the excess TMB.

However, the solids can dissolve in acetonitrile and then the insoluble TMB ligand can be removed by filtration. The filtrate was collected and the solids were obtained by rotoevaporating off the solvent. Recrystallization from EtOH/acetone yielded a reddish orange crystal.

Electrochemical Properties of Metal Complexes

Cyclic voltammograms of metal complexes **A-D** are shown in **Figure 3.2**. The corresponding half-wave potential of each redox couple are listed in **Table 3.1**.

Preparation of Neural Metal Complexes

Reductive Bulk Electrolysis

Controlled-potential electrolytic reductions were performed to produce the following four neutrally-charged metal complexes.³⁻⁵ A similar procedure as that for $[\text{Ru}(\text{bpy})_3]^0$ was used except that the reductive potential was different for each compound.

$[\text{Ru}(\text{4DMB})_3]^0$ (A-0)

To achieve the maximum equilibrium concentration, the reductive potential E was set to be -2.0 V. At the end of electrolysis, only small amount of solids were obtained and the solution showed an intense reddish violet color. As compared to $[\text{Ru}(\text{bpy})_3]^0$, **A-0** displayed a much higher solubility in acetonitrile as compared to $[\text{Ru}(\text{bpy})_3]^0$. In order to increase the yield, prior to the filtration, the final solution was cooled and the volume

reduced by at least one third under vacuum. Only a small amount of acetonitrile was applied to wash off the supporting electrolyte.

$[\text{Ru}(\text{5DMB})_3]^0$ (B-0)

The reductive potential is -2.075 V. The final solution was no longer violet but light tomato color. A significant amount of black solids was obtained by filtration. The solubility of **B-0** in acetonitrile was much lower than that of **A-0** but was still a little higher than that of $[\text{Ru}(\text{bpy})_3]^0$.

$[\text{Ru}(\text{TBB})_3]^0$ (C-0)

E is -2.005 V close to that of **A-0**. It turned out that $[\text{Ru}(\text{TBB})_3]^{1+}$ only has moderate solubility in acetonitrile as determined by the observation of orangish brown suspension at the end of one-electron reduction. This can be explained by the presence of two bulky tert-butyl groups on the ligand. The final solution was reddish violet with a lot of solids present. The color of **C-0** solid is brownish rather than pure black as was the color for the other zero-valent solids.

$[\text{Ru}(\text{TMB})_3]^0$ (D-0)

The reductive potential was set to be -2.18 V which is more than 100 mV more negative than the above three. **D-0** showed small solubility in acetonitrile and the solution was violet color.

Spectra of Neutral Metal Complexes

UV-visible spectra of **A-0** and **B-0** are shown in **Figure 3.3** while those of **C-0** and **D-0** are shown in **Figure 3.4**. They all have similar peak positions but different shapes.

Synthesis and Characterization of Metal Complex Fullerides

General Method

The neutral metal complex is mixed with C_{60} in the desired stoichiometry to obtain the ionic salts predicted from **Chart 3.1**. The experimental steps are very similar to those for preparing $[Ru(bpy)_3^{m+}]_n(C_{60}^{n-})_m$.

Outcomes

As a whole, 16 ionic salts are predicted from **Chart 3.1**. However, five of them containing C_{60}^{3-} have not been successfully synthesized yet. Those five are $[Ru(4DMB)_3^{1+}]_3(C_{60}^{3-})$, $[Ru(5DMB)_3^{1+}]_3(C_{60}^{3-})$, $[Ru(TBB)_3^{1+}]_3(C_{60}^{3-})$, $[Ru(TMB)_3^{1+}]_3(C_{60}^{3-})$, and $[Ru(TMB)_3^{2+}]_3(C_{60}^{3-})_2$ respectively. Although C_{60}^{3-} anion has been detected by UV-vis-NIR spectroscopy in the solution, it turned out to be difficult in isolating discrete C_{60}^{3-} salts as solids with acceptable purity. As compared to C_{60}^{1-} and C_{60}^{2-} , C_{60}^{3-} is more sensitive to both oxygen and water.⁶ Therefore, more attention must be paid to the solvent purity and also the O_2/H_2O level in the glove box. Besides, a suitable organic solvent with appropriate polarity as well as a large potential window

down to at least -2.2 V vs. Fc / Fc^+ is required for the isolation. The formulas of the other eleven ionic salts synthesized are listed in **Table 3.2**.

Identification of Cations and Anions

The oxidation states of cation/anion in each prepared ionic salt were identified by UV-visible-NIR spectroscopy.^{1,7} Their spectra were shown in **Figure 3.5 ~ Figure 3.8**.

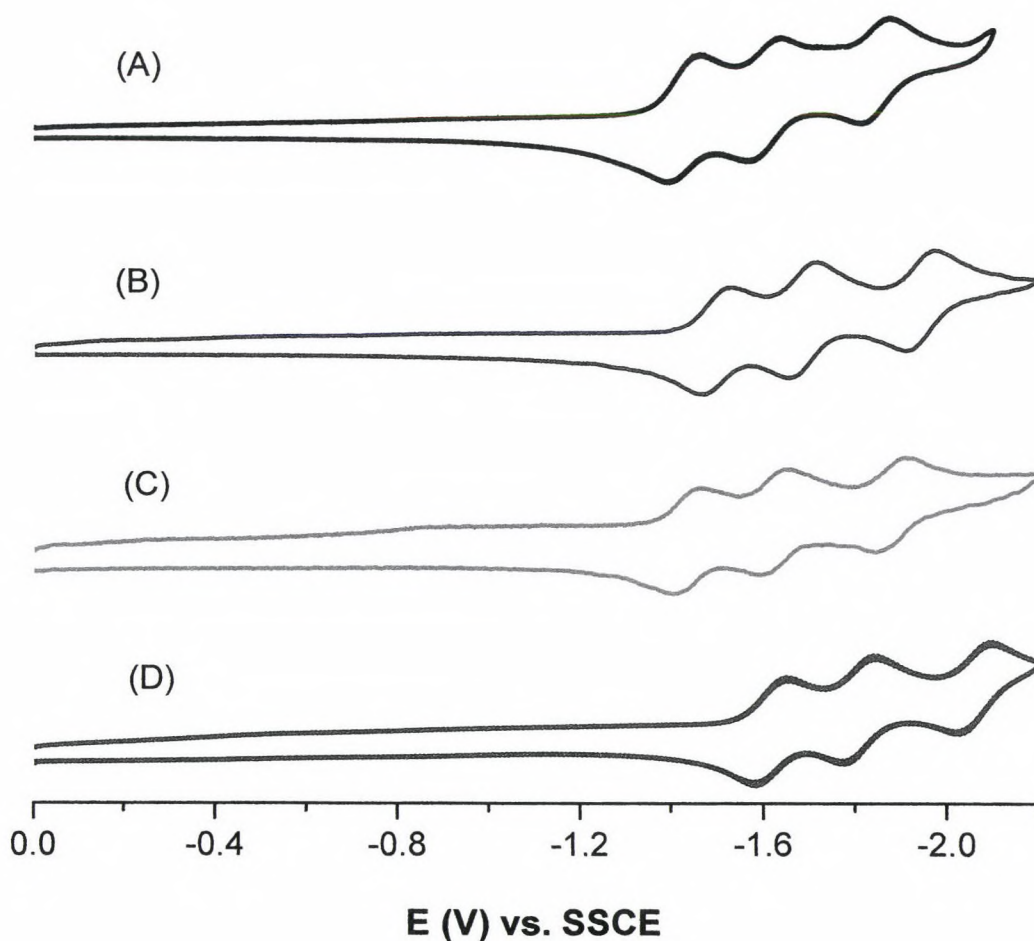


Figure 3.2: Cyclic voltammograms of (A) $[\text{Ru}(\text{4DMB})_3](\text{PF}_6)_2$ (B) $[\text{Ru}(\text{5DMB})_3](\text{PF}_6)_2$ (C) $[\text{Ru}(\text{TBB})_3](\text{PF}_6)_2$ (D) $[\text{Ru}(\text{TMB})_3](\text{PF}_6)_2$ in acetonitrile with TBAPF_6 as supporting electrolyte, Pt as auxiliary electrode, glassy carbon as working electrode and SSCE as reference electrode.

Table 3.1: Half-wave potentials for compound A-D vs. different reference electrodes.

Complex	$E_{1/2}$ (V) vs. SSCE			$E_{1/2}$ (V) vs. Ag/Ag^+			$E_{1/2}$ (V) vs. Fc/Fc^+		
	+2/+1	+1/0	0/-1	+2/+1	+1/0	0/-1	+2/+1	+1/0	0/-1
$\text{Ru}(\text{4DMB})_3^{2+}$	-1.43	-1.60	-1.84	-1.68	-1.76	-2.00	-1.82	-1.99	-2.23
$\text{Ru}(\text{5DMB})_3^{2+}$	-1.49	-1.68	-1.94	-1.74	-1.94	-2.21	-1.88	-2.07	-2.33
$\text{Ru}(\text{TBB})_3^{2+}$	-1.44	-1.62	-1.88	-1.68	-1.88	-2.13	-1.83	-2.01	-2.27
$\text{Ru}(\text{TMB})_3^{2+}$	-1.61	-1.81	-2.06	-1.86	-2.05	-2.31	-2.00	-2.20	-2.45

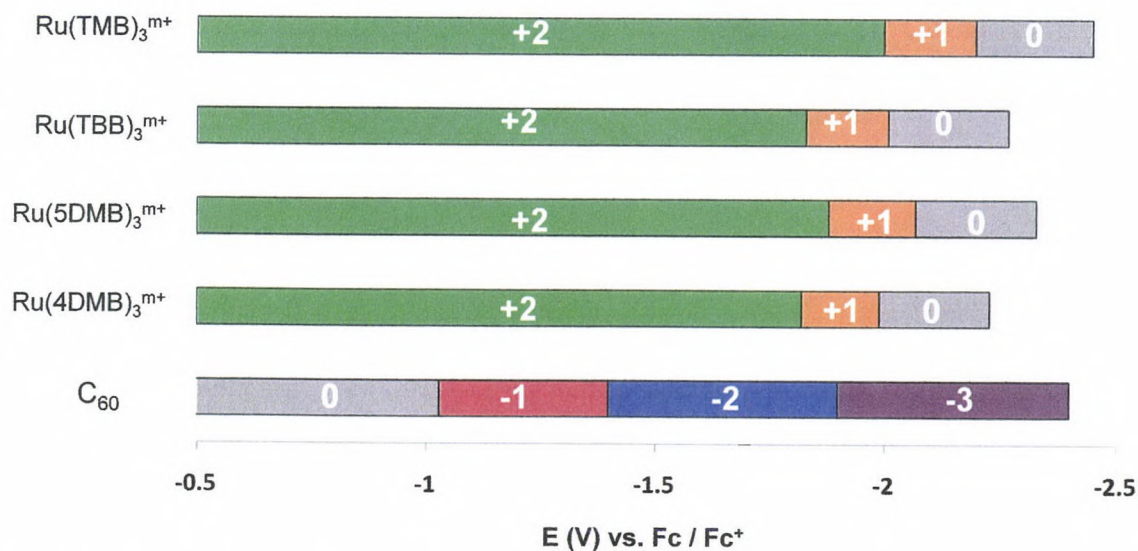


Chart 3.1: Electrochemical data of compound A-D and C_{60} referenced to ferrocene/ferrocenium couple.

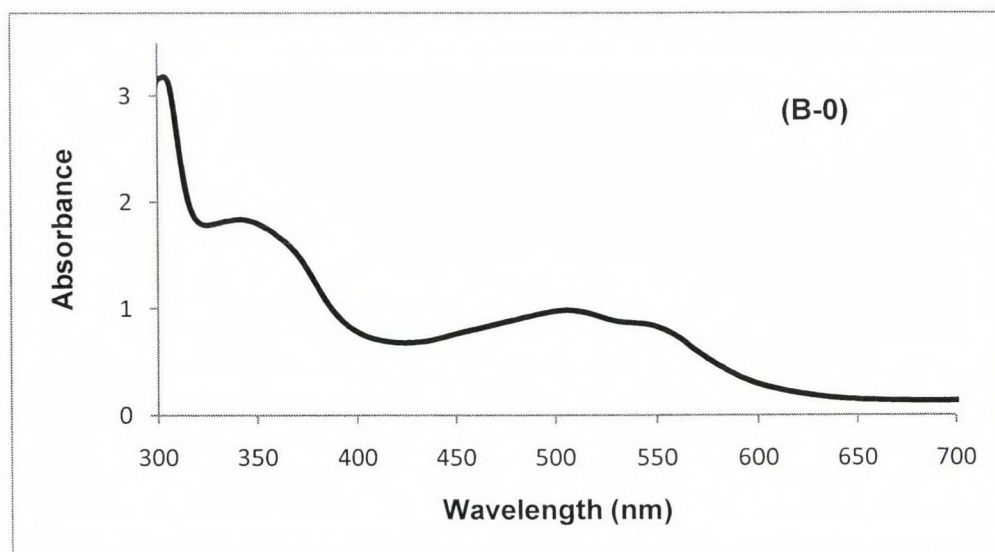
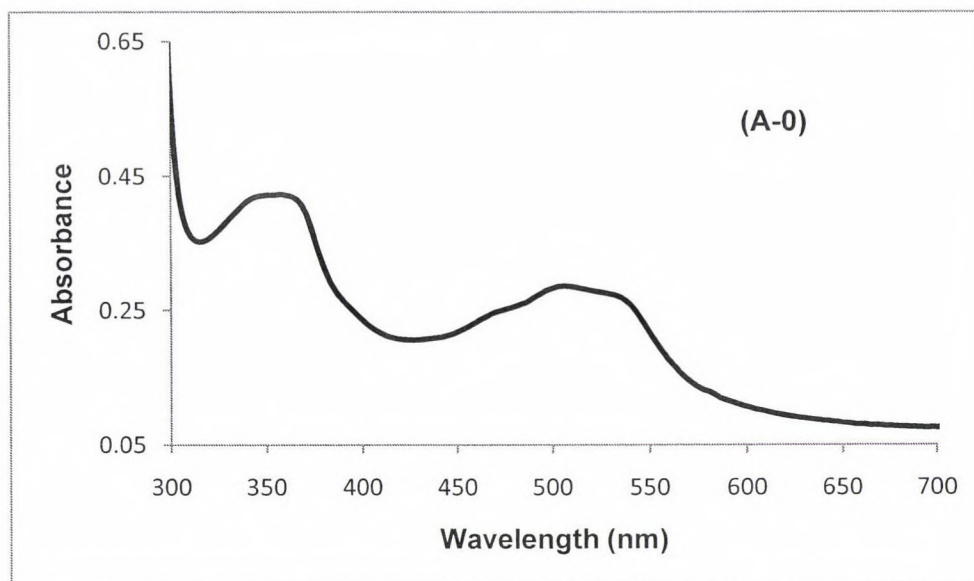


Figure 3.3: UV-visible spectra of (A-0) [Ru(4DMB)₃]⁰ and (B-0) [Ru(5DMB)₃]⁰ in acetonitrile measured in 1mm air-tight quartz cells.

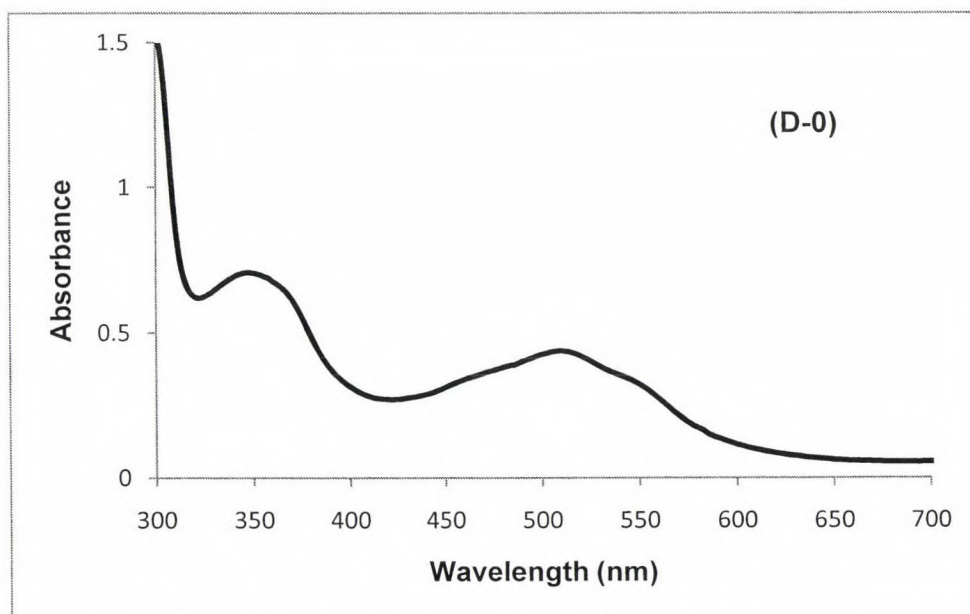
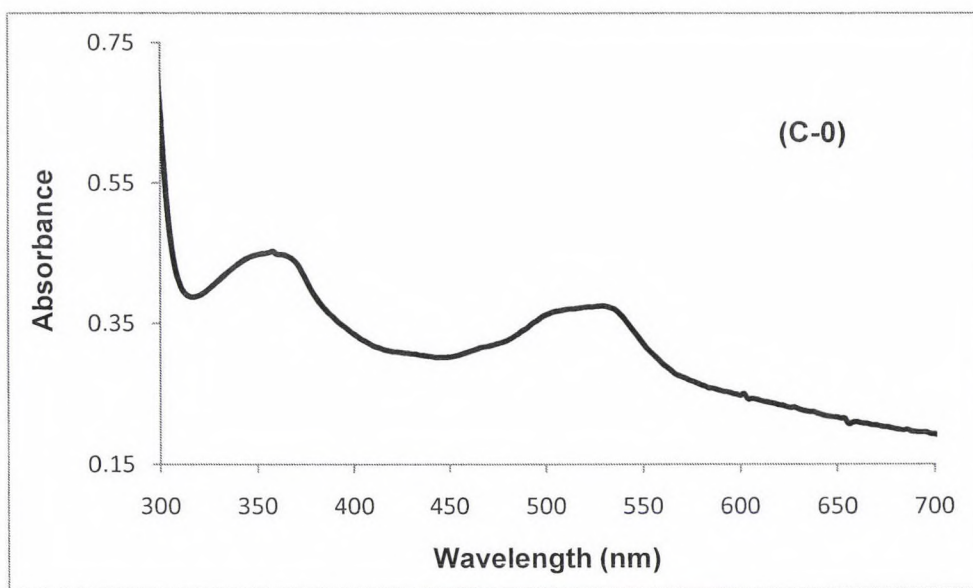


Figure 3.4: UV-visible spectra of (C-0) $[\text{Ru}(\text{TBB})_3]^0$ and (D-0) $[\text{Ru}(\text{TMB})_3]^0$ in DMF measured in 1mm air-tight quartz cells.

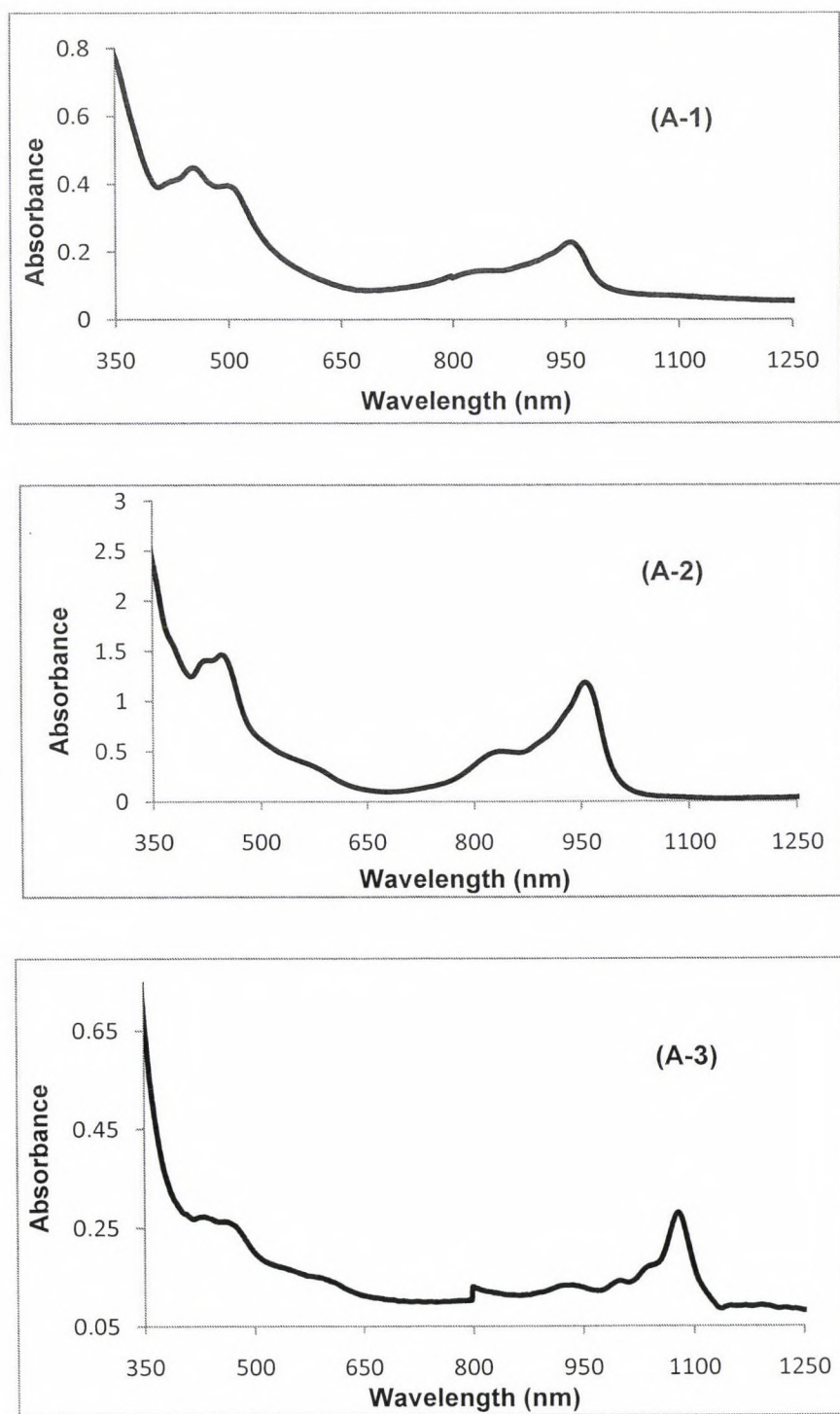


Figure 3.5: UV-vis-NIR spectra of (A-1) $[\text{Ru}(\text{4DMB})_3]_2(\text{C}_{60})$, (A-2) $[\text{Ru}(\text{4DMB})_3](\text{C}_{60})$, (A-3) $[\text{Ru}(\text{4DMB})_3](\text{C}_{60})_2$ in benzonitrile.

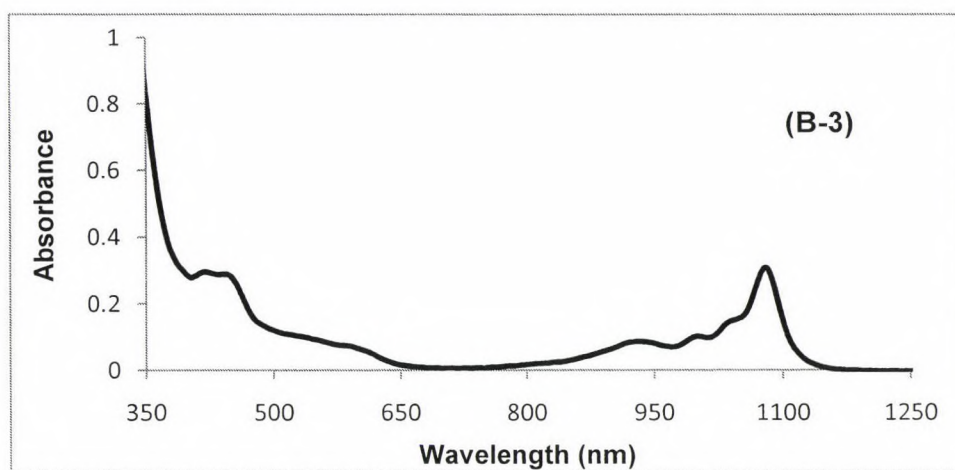
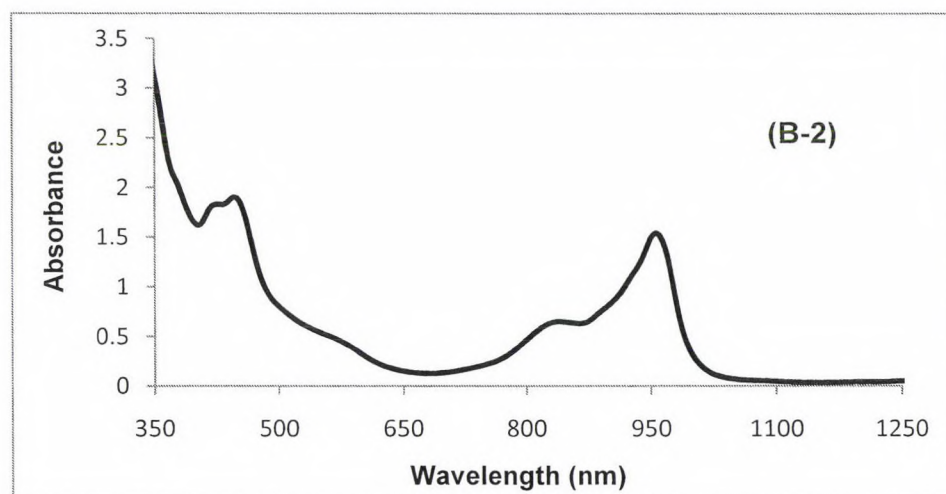
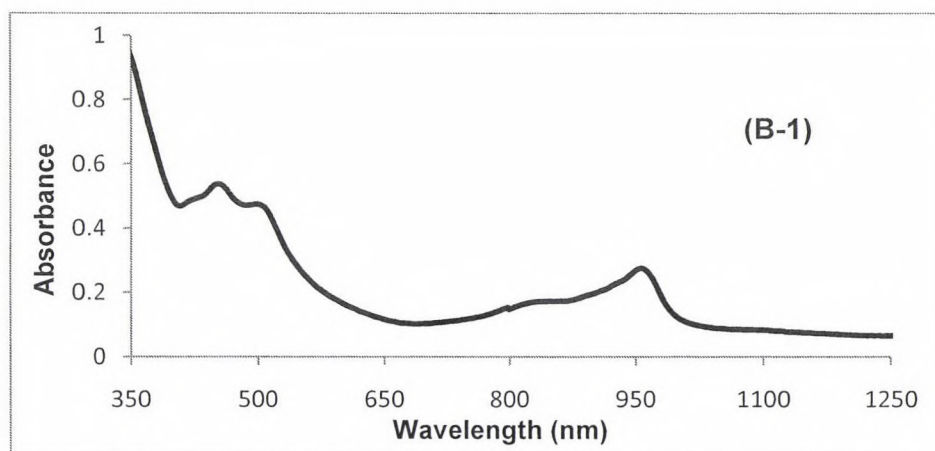


Figure 3.6: UV-vis-NIR spectra of **(B-1)** $[\text{Ru}(\text{5DMB})_3]_2(\text{C}_{60})$, **(B-2)** $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})$, **(B-3)** $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})_2$ in benzonitrile.

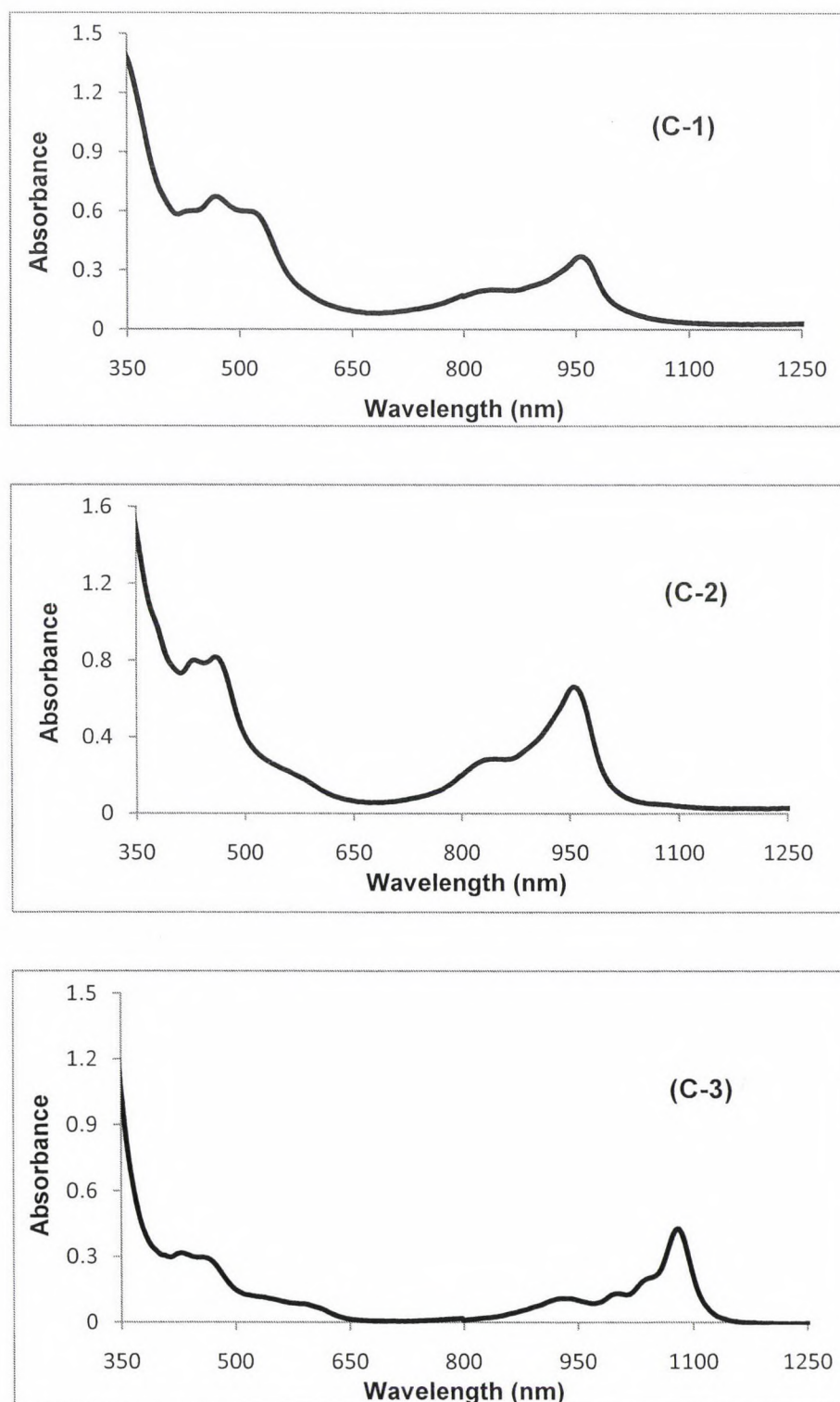


Figure 3.7: UV-vis-NIR spectra of (C-1) $[\text{Ru}(\text{TBB})_3]_2(\text{C}_{60})$, (C-2) $[\text{Ru}(\text{TBB})_3](\text{C}_{60})$, (C-3) $[\text{Ru}(\text{TBB})_3](\text{C}_{60})_2$ in benzonitrile.

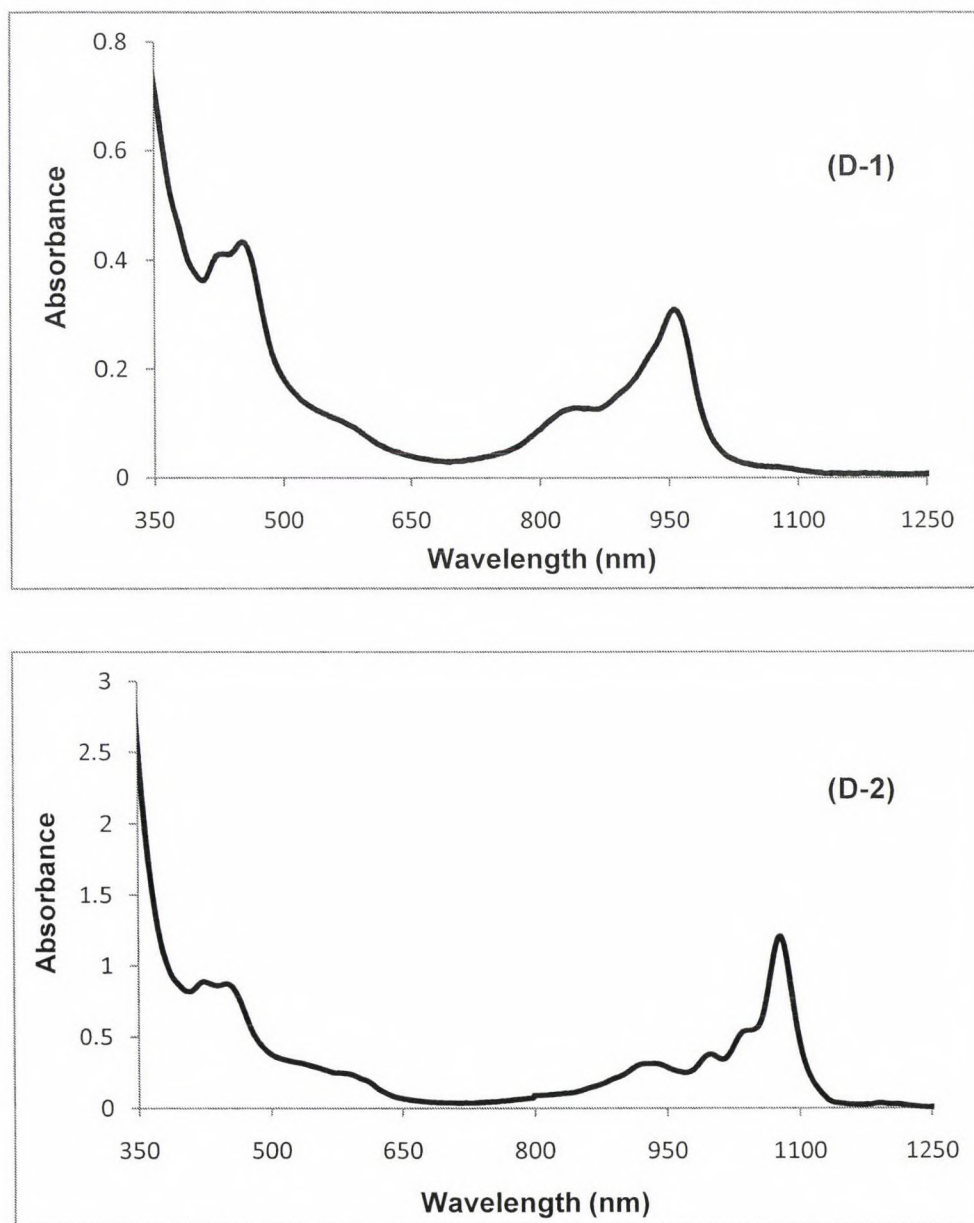


Figure 3.8: UV-vis-NIR spectra of **(D-1)** $[\text{Ru}(\text{TMB})_3](\text{C}_{60})$, **(D-2)** $[\text{Ru}(\text{TMB})_3](\text{C}_{60})_2$ in benzonitrile.

Results and Discussion

Four-probe Electrical Conductivity

The room-temperature electrical conductivities of all eleven ruthenium complex fullerides lie in the range from $10^{-3} \sim 10 \text{ S}\cdot\text{m}^{-1}$ (**Table 3.2.**). They are all semiconductors.

There are four groups of ionic salts with four different ligands. Among each group, the most insulating salt turned out to be the one with the general formula $[\text{RuL}_3](\text{C}_{60})$. In $[\text{RuL}_3](\text{C}_{60})$, the molar ratio of cation to anion is 1:1 and both ions bear two unit electric charges with opposite sign. Its poor conduction ability can be explained by its least mixed-valency indicated from the calculated disproportionated distributions of redox species in solution.^{8,9}

As we can see in **Table 3.1** and **Chart 3.1**, $[\text{Ru}(\text{4DMB})_3]^{m+}$ shows very similar redox potentials to $[\text{Ru}(\text{TBB})_3]^{m+}$. Therefore, it is reasonable that their corresponding ionic C_{60} salts exhibited similar mixed-valency in the solution. The most conducting solids in these two groups turned out to be $[\text{RuL}_3]_2(\text{C}_{60})$. These salts have the highest amount of mixed-valency (thus the highest relative number of electron donors/acceptors) as well as multiple possible electron hopping pathways. Also, by comparing groups of 4DMB, TBB, and TMB, lowest conductivity was observed as the ligand becomes more bulky. With larger ligand, the structure of ionic salts should tend to be more expanded which might result in longer intersite electron-hopping distances.

Generally, in each group, as the degree of mixed-valency increases, the conductivity increases. However, in the 5DMB group, $[(\text{RuL}_3)]_2(\text{C}_{60})$ shows smaller

conductivity than $[\text{RuL}_3](\text{C}_{60})_2$ although it exhibits higher mixed-valency based on the calculated distribution of redox species in solution. One explanation is that $[\text{RuL}_3](\text{C}_{60})_2$ might possess a crystal packing structure which includes much shorter intersite distances than $[\text{RuL}_3]_2(\text{C}_{60})$ and thus lower potential barrier for electrons to hop. Another interesting thing is that, as shown in **Table 3.2**, more than half C_{60}^{2-} should be disproportionated to C_{60}^{3-} . Also, significant amount of RuL_3^{2+} should be present as well. However, the UV-vis-NIR spectrum of $[(\text{RuL}_3)]_2\text{C}_{60}$ (L = 5DMB) does not show obvious peaks assignable specifically to C_{60}^{3-} and $[\text{RuL}_3]^{2+}$. For $[\text{RuL}_3]^{2+}$, since its absorption peaks are very similar to $[\text{RuL}_3]^{1+}$, it would not be easy to distinguish it from RuL_3^{1+} .¹ For C_{60}^{3-} , considering its predicted concentration and the values of its extinction coefficients ($\epsilon = 14,000$ at 788 nm; $\epsilon = 6,000$ at 1367 nm), it should be able to be identified in the spectra if assuming that C_{60}^{3-} in solution is stable. However, the discrepancy of disproportionations between solid state and solution phase should be also taken account.

Overall, $[\text{Ru}(5\text{DMB})_3]_2\text{C}_{60}$ and $[\text{Ru}(5\text{DMB})_3](\text{C}_{60})_2$ show the highest conductivity among the eleven compounds. They both show electrical conductivity similar to $[\text{Ru}(\text{bpy})_3]_2\text{C}_{60}$ and $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$.

To fully understand the electrical properties and the magnetism described in next section, single-crystal structures are necessary. Much effort has been devoted to crystal growth but so far no diffraction quality crystals have been obtained.

Ligand	Compound	σ (S • m ⁻¹)	RuL ₃ ²⁺	RuL ₃ ¹⁺	RuL ₃ ⁰	C ₆₀	C ₆₀ ¹⁻	C ₆₀ ²⁻	C ₆₀ ³⁻
4DMB	[RuL ₃] ₂ (C ₆₀)	0.60 (±35%)	0.250	1.734	0.016	0	0	0.766	0.234
	[RuL ₃](C ₆₀)	0.012 (±30%)	0.9997	0.0003	0	0	0.0003	0.9997	0
	[RuL ₃](C ₆₀) ₂	0.45 (±35%)	1	0	0	0.0015	1.9970	0.0015	0
5DMB	[RuL ₃] ₂ (C ₆₀)	3.1 (±23%)	0.5494	1.4483	0.0023	0	0	0.453	0.547
	[RuL ₃](C ₆₀)	0.0039 (±20%)	0.9999	0.0001	0	0	0.0001	0.9999	0
	[RuL ₃](C ₆₀) ₂	7.4 (±22%)	1	0	0	0.0015	1.9970	0.0015	0
TBB	(RuL ₃) ₂ (C ₆₀)	0.31 (±20%)	0.287	1.707	0.009	0	0	0.722	0.278
	[RuL ₃](C ₆₀)	0.0091 (±15%)	0.9998	0.0002	0	0	0.0002	0.9998	0
	[RuL ₃](C ₆₀) ₂	0.20 (±35%)	1	0	0	0.0015	1.9970	0.0015	0
TMB	[RuL ₃](C ₆₀)	0.0028 (±10%)	1	0	0	0	0.0001	0.9998	0.0001
	[RuL ₃](C ₆₀) ₂	0.055 (±11%)	1	0	0	0.0015	1.9970	0.0015	0

Table 3.2: Electrical conductivities of eleven ruthenium complex fullerenes and their calculated disproportionated distributions of redox species in solution at room temperature.

Magnetism

SQUID measurements were done to investigate the magnetic properties of all eleven ruthenium complex fullerenes. Neither superconductivity nor ferromagnetism was found. All complexes exhibited paramagnetism including a temperature-independent portion and a Curie paramagnetism portion. Since their magnetic properties appear similar, only $[\text{Ru}(\text{5DMB})_3]_a(\text{C}_{60})_b$ (**B-1~B-3**) were given detailed interpretation. In addition, some comparison was made between $[\text{Ru}(\text{5DMB})_3]_a(\text{C}_{60})_b$ and $[\text{Ru}(\text{bpy})_3]_a(\text{C}_{60})_b$. The magnetic data for all other eight compounds are included in Appendix II.

In compound $[\text{Ru}(\text{5DMB})_3]_2(\text{C}_{60})$ (**B-1**), unpaired electrons on $[\text{Ru}(\text{5DMB})_3]^{1+}$ are the major source of magnetic spins. The $\chi_M \cdot T$ vs. T curve (from 300 to 50 K) can be fitted linearly generating the following equation. (**Figure 3.9**)

$$\chi_M = \frac{C}{T} + \chi_{\text{TIP}} \quad (1)$$

Curie constant was calculated to be $0.5029 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ while χ_{TIP} equals $6.63 \times 10^{-3} \text{ emu} \cdot \text{mol}^{-1}$. By comparing **B-1** with $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60})$ ($C = 0.5014 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, $\chi_{\text{TIP}} = 15.9 \times 10^{-3} \text{ emu} \cdot \text{mol}^{-1}$), similar spin concentrations were found. In addition, a possible antiferromagnetic coupling was indicated by the obvious curvature in the temperature range of 5~50 K in the $\chi_M \cdot T$ vs. T curve (**Figure 3.9**). This is in accordance with the negative θ value obtained from linearly fitting χ_M^{-1} vs. T curve from 100 to 300 K (**Figure**

3.10). The smaller χ_{TIP} value indicates that the coupling between the ground state of cation $[\text{Ru}(\text{5DMB})_3]^{1+}$ and low-lying excited states of anion C_{60}^{2-} is relatively weaker than that between the cations and anions in $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60})$.

The magnetism of compound (**B-2**) $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})$ can be also expressed by equation (1). By fitting $\chi_{\text{M}} \cdot T$ vs. T curve (**Figure 3.11**) linearly over the entire temperature range, $C = 0.01596 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ and $\chi_{\text{TIP}} = 4.7 \times 10^{-3} \text{ emu} \cdot \text{mol}^{-1}$. By using equation (2)¹⁰, the total spin was calculated to be 0.031.

$$C = \frac{Ng^2\beta^2}{3k} S(S+1) = \frac{g^2}{8} S(S+1) \quad (2)$$

Since $[\text{Ru}(\text{5DMB})_3]^{2+}$ is diamagnetic¹¹, the spins are mainly from C_{60}^{2-} assuming compound **B-2** is pure. This result is consistent with the statement that the majority of C_{60}^{2-} possesses a singlet ground state ($S = 0$).¹² The small bump at around 50 K might be assigned to the antiferromagnetic transition of contaminant oxygen in the sample chamber of MPMS-XL instrument (**Figure 3.12**). This bump became less obvious when the amount of sample used was increased.

The dc magnetic susceptibility measurement of compound (**B-3**) $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})_2$ generated very similar temperature dependence of molar susceptibility as compared to $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$. (**Figure 3.13, 3.14**) By fitting $\chi_{\text{M}} \cdot T$ vs. T curve linearly from 300 to 200 K, Curie constant was found to be $0.475 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ and χ_{TIP} is $6.06 \times 10^{-3} \text{ emu} \cdot \text{mol}^{-1}$. Fitting χ_{M}^{-1} vs. T in this temperature range produced a negative θ value which indicated a possible antiferromagnetic transition. From 150 to

200K, the molar susceptibility almost leveled off, which might be explained by the presence of a possible phase transition. Similarly to $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$, this transition can be speculated to be the dimerization of C_{60} forming diamagnetic $(\text{C}_{60})^{2-}$.

Summary

In this chapter, the synthesis of eleven ruthenium polypyridine complex C_{60} salts has been fully described. The ligand substitution has a potential effect on the room temperature conductivity. All eleven compounds exhibit conductivity in the semiconductor range. However, their magnetic properties are qualitatively similar to those $[\text{Ru}(\text{bpy})_3]_n(\text{C}_{60})_m$ analogs. For ionic salts with the same stoichiometries between ions, their molar susceptibilities show similar temperature dependence.

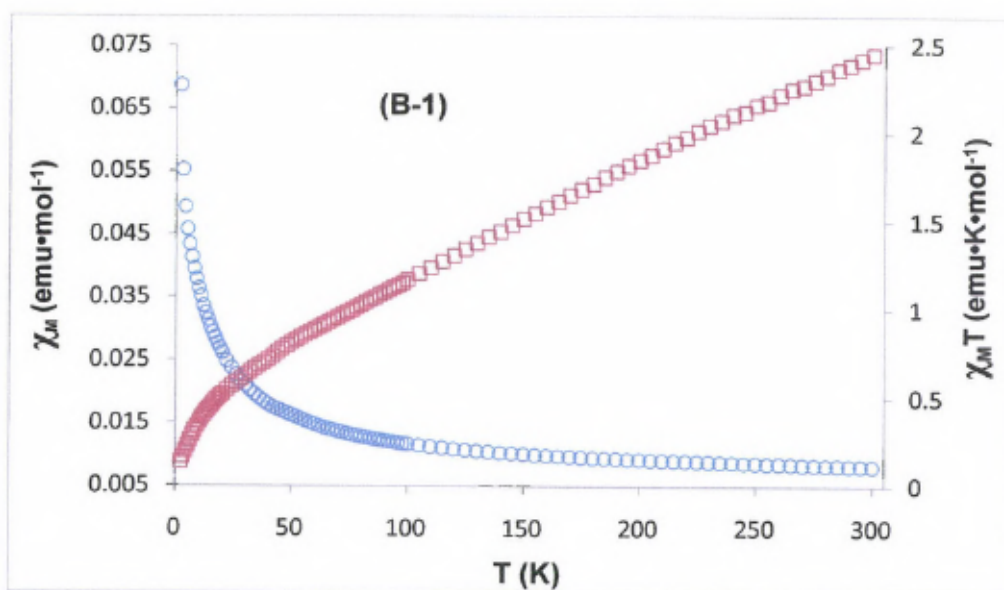


Figure 3.9: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for (B-1) $[\text{Ru}(\text{5DMB})_3]_2(\text{C}_{60})$ at 100mT magnetic field.

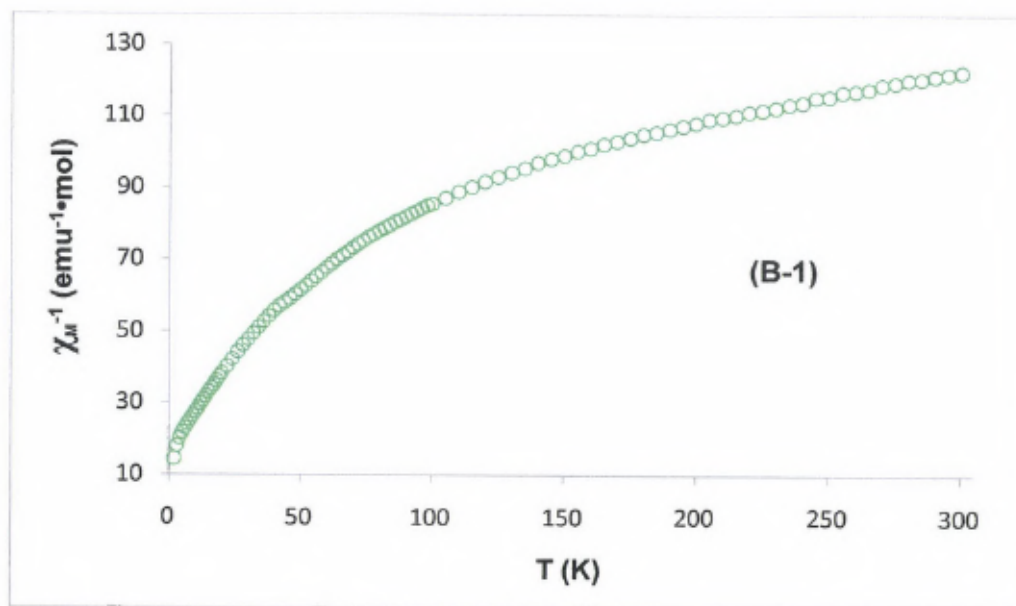


Figure 3.10: Temperature dependence of the reciprocal of molar magnetic susceptibility of (B-1) $[\text{Ru}(\text{5DMB})_3]_2(\text{C}_{60})$ at 100mT magnetic field.

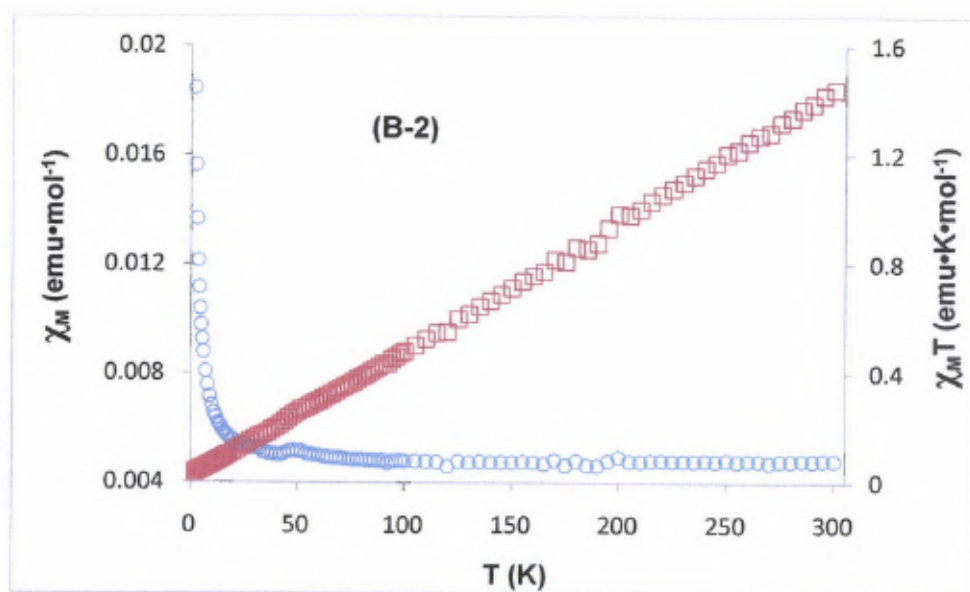


Figure 3.11: Temperature dependence of molar magnetic susceptibility (○) and the product of molar susceptibility and temperature (□) for **(B-2)** $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})$ at 100mT magnetic field.

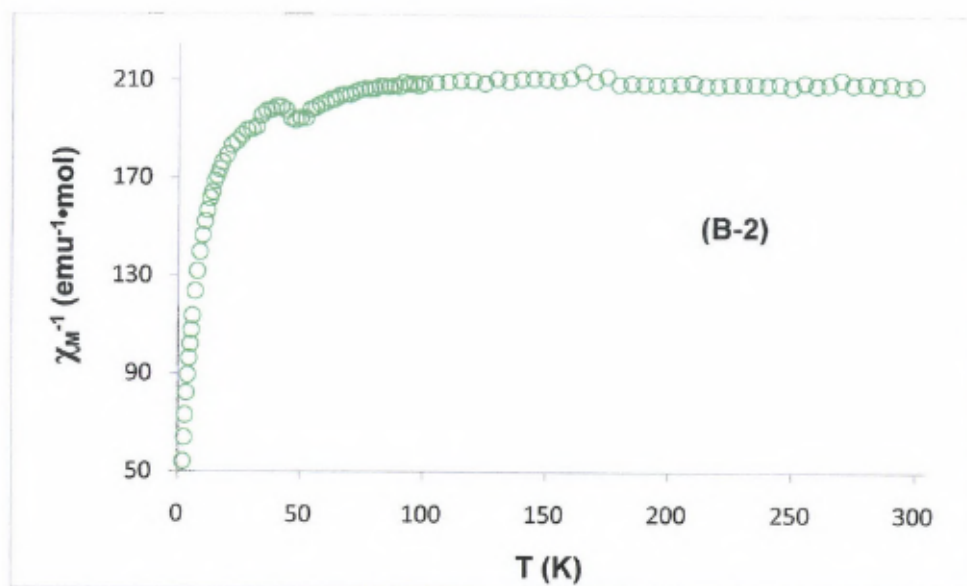


Figure 3.12: Temperature dependence of the reciprocal of molar magnetic susceptibility of **(B-2)** $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})$ at 100mT magnetic field.

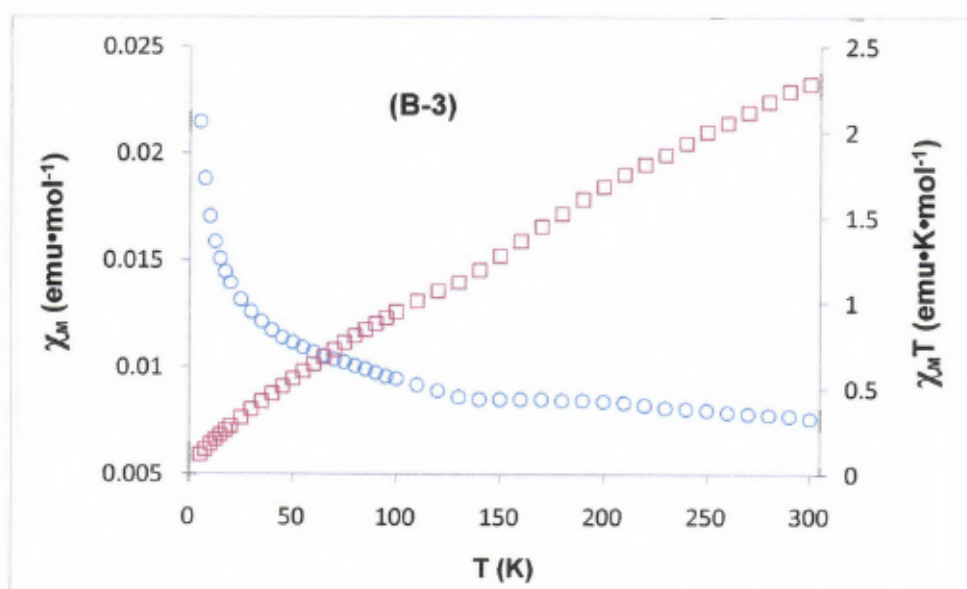


Figure 3.13: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for (B-3) $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})_2$ at 100mT magnetic field.

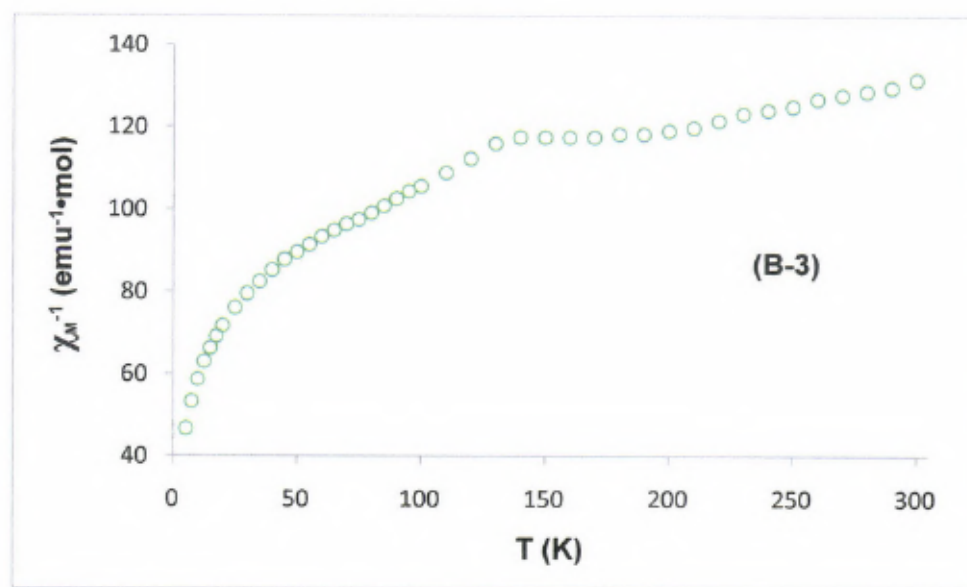


Figure 3.14: Temperature dependence of the reciprocal of molar magnetic susceptibility of (B-3) $[\text{Ru}(\text{5DMB})_3](\text{C}_{60})_2$ at 100mT magnetic field.

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CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF TRIS (2, 2'-BIPYRIDINE)

CHROMIUM COMPLEX FULLERENE SALTS

Introduction

Tris (2, 2'-bipyridine) chromium is well known for its rich photochemistry and electrochemistry.¹⁻⁴ By doping C₆₀ with [Cr(bpy)₃]⁰, interesting properties might be found. From **Chart 4.1**, the significant overlap of potentials between [Cr(bpy)₃]^{m+} and C₆₀ indicates that [Cr(bpy)₃]_n(C₆₀)_m with three different stoichiometries are possible. Also, [Cr(bpy)₃]^{m+} exhibits very similar size to [Ru(bpy)₃]^{m+} while their redox potentials are widely different.⁵⁻⁷ This allows us to study the independent effect of redox potentials on the electric properties of ionic salts, which is also the major goal of this chapter.

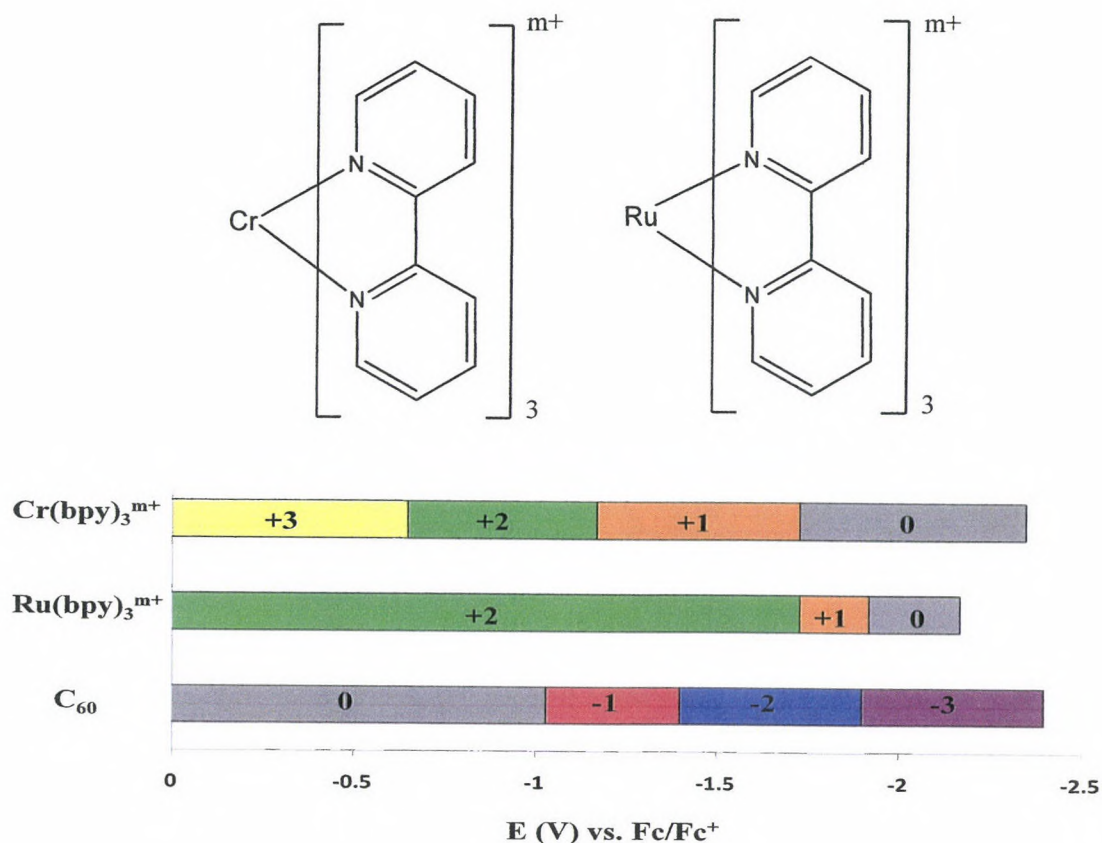


Chart 4.1: Electrochemical data of [Ru(bpy)₃]^{m+}, [Cr(bpy)₃]^{m+} and C₆₀ referring to Fc / Fc⁺.

Experimental Section

$[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_3$

A modified literature procedure was used.^{8,9} $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (1.29 g, 0.005 mol) was refluxed under N_2 over granulated zinc metal (~1 g) in acidic aqueous solution (3 mL 70% perchloric acid diluted in ~20 mL distilled water). The sky blue solution produced after one hour reflux was then cannulated into a N_2 purged suspension of bpy (3.9 g, 0.025 mol) in 10 mL aqueous HClO_4 of pH = 2. Some methanol (~10 mL) was added to increase the solubility of bpy. A red wine solution with significant amount of black precipitates was immediately formed. Under constant stirring, Br_2 (diluted in H_2O /methanol) was added to oxidize the solids from black to yellow. The yellow solids were then collected by filtration, washed well with ethanol, dichloromethane and only small amount of water. Finally, the solids were recrystallized from water. Four characteristic reduction peaks of $[\text{Cr}(\text{bpy})_3](\text{ClO}_4)_3$ were observed in its cyclic voltammograms (**Figure 4.1**).¹

$[\text{Cr}(\text{bpy})_3]^0$

A similar controlled-potential electrolytic reduction as that for $[\text{Ru}(\text{bpy})_3]^0$ was performed to produce the zero valent complex. The reduction potential was set to be -1.913 V. Obvious color changes were observed indicating the formation of different oxidation states. Starting from yellow solution of $[\text{Cr}(\text{bpy})_3]^{3+}$, after one-electron reduction, $[\text{Cr}(\text{bpy})_3]^{2+}$ was generated showing a wine red color. Further reduction turned solution to blue purple which indicated the formation of $[\text{Cr}(\text{bpy})_3]^{1+}$. When the electrolysis approached the end, the solution displayed a light brownish color with a lot of black solids $[\text{Cr}(\text{bpy})_3]^0$ at the bottom. Moderate solubility of $[\text{Cr}(\text{bpy})_3]^0$ in

tetrahydrofuran (THF) and benzonitrile was found. The UV-visible spectrum of $[\text{Cr}(\text{bpy})_3]^0$ in THF showed three characteristic peaks at 446, 484 and 554 nm (**Figure 4.2**).^{4,10,11}

$[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$

A similar stoichiometric chemical synthesis as for $[\text{Ru}(\text{bpy})_3]_n(\text{C}_{60})_m$ was applied to prepare $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$. Three ionic salts were successfully prepared as predicted (**Table 4.1**). Both $[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$ and $[\text{Cr}(\text{bpy})_3](\text{C}_{60})$ show similar violet color with good solubility in benzonitrile while $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ exhibits a totally different grayish brown and is only barely soluble in benzonitrile. The oxidation states of cations/anions were identified by UV-vis-NIR spectroscopy (**Figure 4.3**).^{4,10,12} It is worthwhile pointing out that in the 1:1 molar ratio compound $[\text{Cr}(\text{bpy})_3](\text{C}_{60})$, both $\text{Cr}(\text{bpy})_3$ and C_{60} bear one unit charge with opposite sign. This is different from all the other $[\text{RuL}_3](\text{C}_{60})$ compounds obtained previously. In $[\text{RuL}_3](\text{C}_{60})$ (L= bpy, 4DMB, 5DMB, TBB, TMB), RuL_3 has +2 charge while C_{60} has -2 charge.

Table 4.1: The oxidation states of all three Cr complex fullerenes and their corresponding absorption peaks for cations and anions in benzonitrile.

Formula	Cation	Peaks (cation, nm)	Anion	Peaks (anion, nm)
$[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$	$\text{Cr}(\text{bpy})_3^{1+}$	568	C_{60}^{2-}	844, 966
$[\text{Cr}(\text{bpy})_3](\text{C}_{60})$	$\text{Cr}(\text{bpy})_3^{1+}$	565	C_{60}^{1-}	1086
$[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$	$\text{Cr}(\text{bpy})_3^{2+}$	597 (shoulder)	C_{60}^{1-}	1086

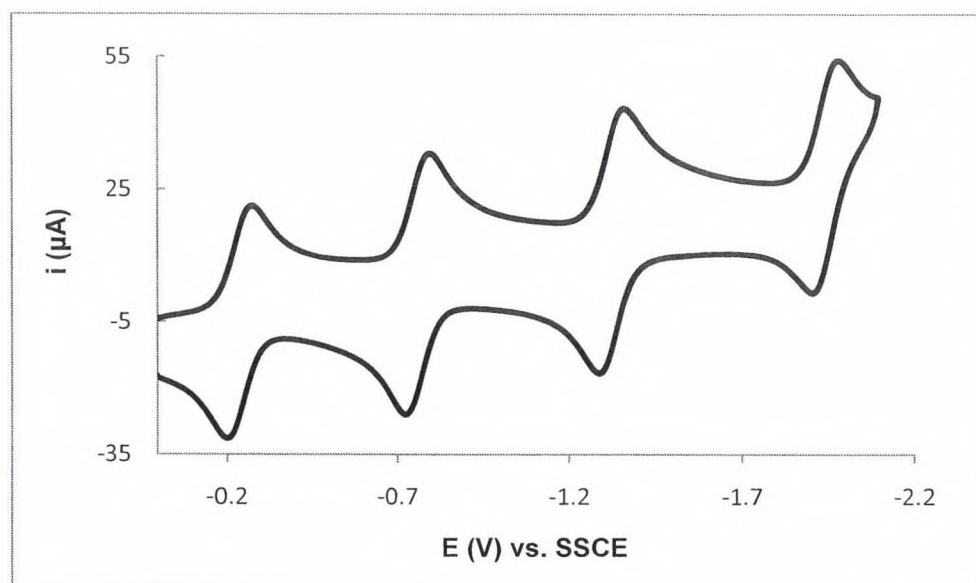


Figure 4.1: Cyclic voltammogram of $\text{Cr}(\text{bpy})_3(\text{ClO}_4)_3$ in 0.1 M $\text{TBAPF}_6/\text{CH}_3\text{CN}$ with Pt as A.E., glassy carbon as W.E. and SSCE as R.E.

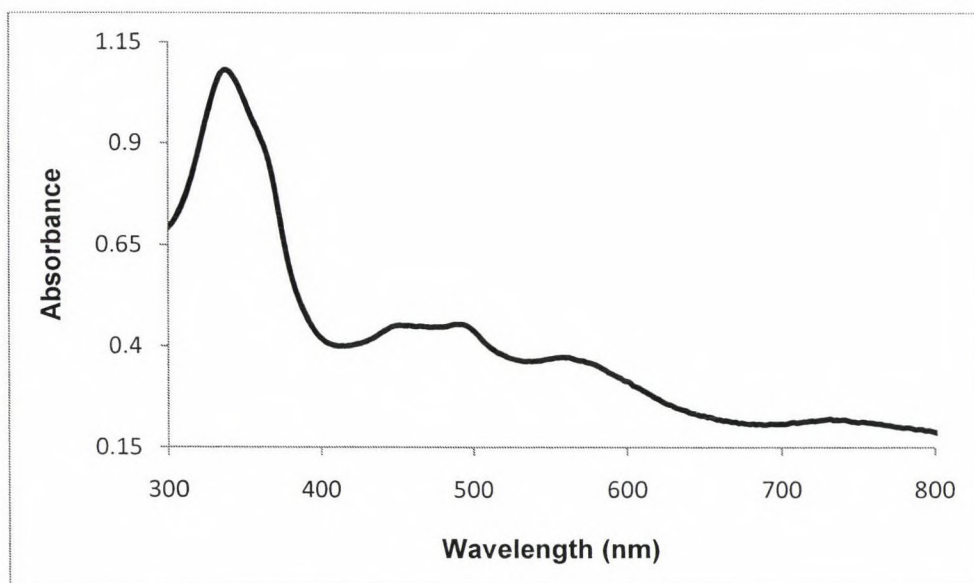


Figure 4.2: UV-visible spectrum of $\text{Cr}(\text{bpy})_3^0$ in THF.

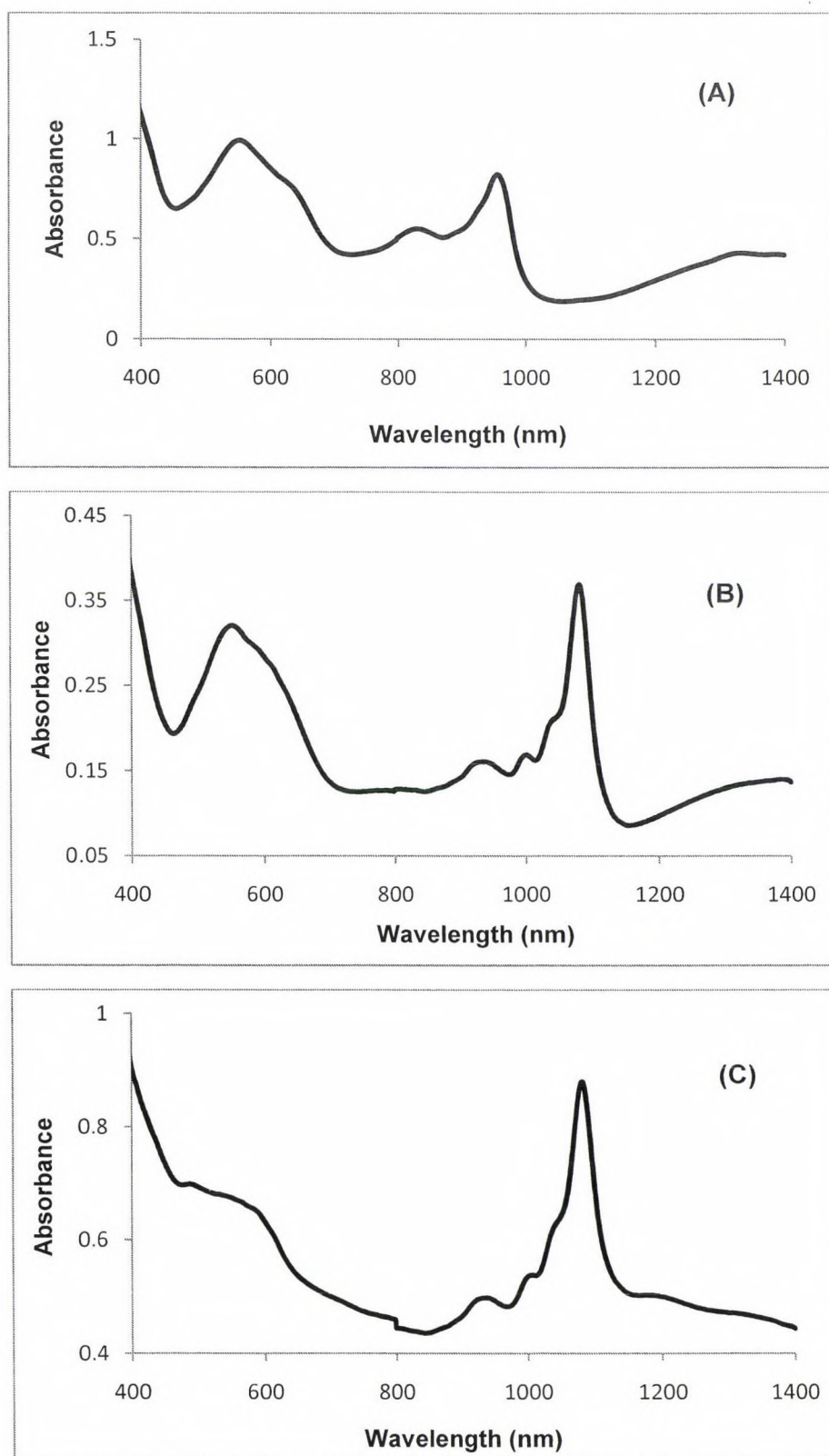


Figure 4.3: UV-vis-NIR spectra of (A) $[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$ (B) $[\text{Cr}(\text{bpy})_3](\text{C}_{60})$ (C) $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ in benzonitrile.

Results and Discussion

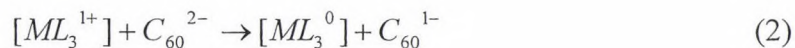
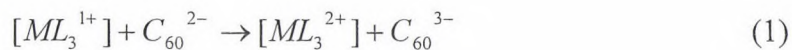
Four-probe Electrical Conductivity

The room-temperature conductivity of $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$ ranges from $10^{-2} \sim 10^1 \text{ S}\cdot\text{m}^{-1}$ in the semiconductor range. The order of descending conductivity is $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2 > [\text{Cr}(\text{bpy})_3](\text{C}_{60}) > [\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$. The information on disproportionation is included in **Table 4.2**. A similar way as for $[\text{Ru}(\text{bpy})_3]_n(\text{C}_{60})_m$ was used to calculate the relative concentration of variable redox species. An example for $[\text{Cr}(\text{bpy})_3]^{1+}(\text{C}_{60})^{1-}$ is shown in **Table 4.3**.

All of the three ionic salts have four possible electron transfer pathways. (**Scheme 4.1**) From the probability and thermodynamic standpoint, only two of them for each compound are favorable. As seen in **Table 4.4**, in each favorable electron transfer reaction, one reactant is at relatively high concentration while the other is of low concentration. As the amount of minor species increases, the probability of electron transfer increases as well. Obviously, among the three, $[\text{Cr}(\text{bpy})_3]^{1+}(\text{C}_{60})^{1-}_2$ has relatively the largest amount of disproportionated electron donor/acceptors. Therefore, as expected, it showed the highest conductivity. The experimental data is in good agreement with the statement that high mixed-valency results in high conductivity.

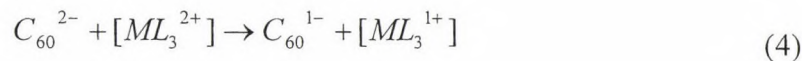
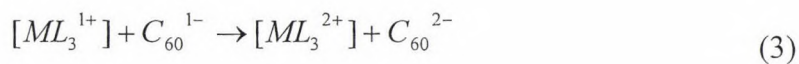
It is interesting to note that the trend of conductivity for $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$ is totally different from what was observed in $[\text{Ru}(\text{bpy})_3]_n(\text{C}_{60})_m$: $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60}) > [\text{Ru}(\text{bpy})_3](\text{C}_{60})_2 > [\text{Ru}(\text{bpy})_3](\text{C}_{60})$. By comparing $[\text{Cr}(\text{bpy})_3]^{1+}_2(\text{C}_{60})$ with $[\text{Ru}(\text{bpy})_3]^{1+}_2(\text{C}_{60})$ specifically, both cations have the same shape, same charge and very similar size. Theoretically, they can be isostructural. However, $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60})$ is about

150 times more conducting. This can be explained by the wide differences of redox potentials for the +2/+1 and +1/0 processes between $[\text{Ru}(\text{bpy})_3]^{m+}$ and $[\text{Cr}(\text{bpy})_3]^{m+}$. As such, the relative extent of the solid state reactions (1) and (2) will be also very different.



Based on **Chart 4.1**, $[\text{Ru}(\text{bpy})_3]^{1+}$ prefers to exchange electrons via reaction (1) while reaction (2) is the dominant electron exchange pathway for $[\text{Cr}(\text{bpy})_3]^{1+}$. The consequences of redox differences are the formation of different disproportionated species which actually participate in the electron conduction. Apparently, $[\text{Ru}(\text{bpy})_3]_2(\text{C}_{60})$ exhibits much higher mixed-valency as compared to $[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$. Therefore, it is much more conducting.

It was also found that $[\text{Cr}(\text{bpy})_3]^{1+}(\text{C}_{60}^{1-})$ is almost 20 times more conducting than $[\text{Ru}(\text{bpy})_3]^{2+}(\text{C}_{60}^{2-})$. Although they have same stoichiometry, the cation/anion charge is different. Also, due to the difference in redox potentials, they prefer different electron exchange reactions.



$[\text{Cr}(\text{bpy})_3]^{1+}(\text{C}_{60}^{1-})$ prefers reaction (3) while (4) is the dominant reaction for $[\text{Ru}(\text{bpy})_3]^{2+}(\text{C}_{60}^{2-})$. Interestingly, reaction (3) happens to be the reverse of reaction (4). From **Table 4.2**, it is obvious that $[\text{Cr}(\text{bpy})_3]^{1+}(\text{C}_{60}^{1-})$ has relatively larger amount of

disproportionate species. Therefore, it is more conducting due to its higher mixed-valency.

For $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ and $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$, both cations bear +2 charge and their conductivities are similar too. While the electron transfer mainly resides in the C_{60} manifold for $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$, $[\text{Cr}(\text{bpy})_3]^{m+}$ species also contribute to the electron conduction in $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$.

In summary, the redox potential of cation does have a substantial effect on the conductivity of ionic C_{60} salts. Among the three, $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ seems to be the most promising because of its relatively high conductivity.

Table 4.2: Electrical conductivity data of $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$ and $[\text{Ru}(\text{bpy})_3]_n(\text{C}_{60})_m$ at 25°C and the calculated disproportionation of redox species in solution at room temp. L represents bpy ligand.

Compound	$\sigma \text{ (S}\cdot\text{m}^{-1}\text{)}$	ML_3^{3+}	ML_3^{2+}	ML_3^{1+}	ML_3^0	C_{60}	C_{60}^{1-}	C_{60}^{2-}	C_{60}^{3-}
$[\text{CrL}_3]_2(\text{C}_{60})$	0.06 ($\pm 13 \%$)	0	0	1.9977	0.0023	0	0.0023	0.9977	0
$[\text{RuL}_3]_2(\text{C}_{60})$	9.5 ($\pm 26 \%$)	0	0.068	1.900	0.032	0	0	0.964	0.036
$[\text{CrL}_3^{1+}](\text{C}_{60}^{1-})$	0.36 ($\pm 30 \%$)	0	0.0111	0.9889	0	0	0.9889	0.0111	0
$[\text{RuL}_3^{2+}](\text{C}_{60}^{2-})$	0.018 ($\pm 13 \%$)	0	0.998	0.002	0	0	0.002	0.998	0
$[\text{CrL}_3](\text{C}_{60})_2$	2.27 ($\pm 25 \%$)	0	0.914	0.086	0	0.086	1.914	0	0
$[\text{RuL}_3](\text{C}_{60})_2$	2.0 ($\pm 31 \%$)	0	1.000	0	0	0.0015	1.997	0.0015	0

Table 4.3: Equations for calculating disproportionated redox species for $[\text{CrL}_3](\text{C}_{60})$ in solution with the assumption that $\text{Cr}(\text{bpy})_3^0$ and C_{60} are mixed in exact 1:1 molar ratio. L represents bpy ligand.

$$[\text{CrL}_3^{2+}] + [\text{CrL}_3^{1+}] + [\text{CrL}_3^0] = 1$$

$$[\text{C}_{60}^0] + [\text{C}_{60}^{1-}] + [\text{C}_{60}^{2-}] = 1$$

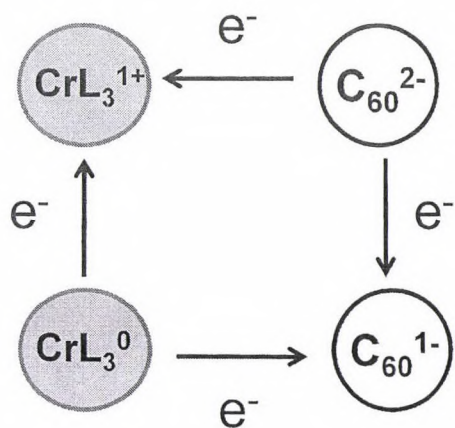
$$2[\text{CrL}_3^{2+}] + [\text{CrL}_3^{1+}] = [\text{C}_{60}^{1-}] + 2[\text{C}_{60}^{2-}]$$

$$E_{eq.} = E_{+1/+2}^0 - \frac{RT}{F} \ln \frac{[\text{CrL}_3^{1+}]}{[\text{CrL}_3^{2+}]}$$

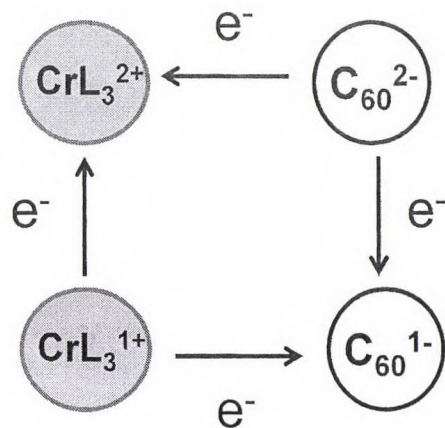
$$E_{eq.} = E_{0/+1}^0 - \frac{RT}{F} \ln \frac{[\text{CrL}_3^0]}{[\text{CrL}_3^{1+}]}$$

$$E_{eq.} = E_{2-/1-}^0 - \frac{RT}{F} \ln \frac{[\text{C}_{60}^{2-}]}{[\text{C}_{60}^{1-}]}$$

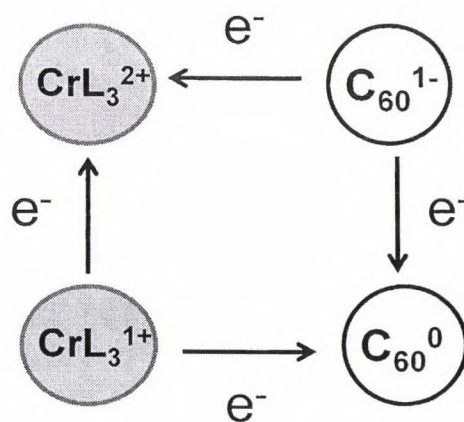
$$E_{eq.} = E_{1-/0}^0 - \frac{RT}{F} \ln \frac{[\text{C}_{60}^{1-}]}{[\text{C}_{60}^0]}$$



(A)



(B)



(C)

Scheme 4.1: Possible electron transfer pathways in compound (A) $[\text{CrL}_3]_2(\text{C}_{60})$ (B) $[\text{CrL}_3](\text{C}_{60})$ (C) $[\text{CrL}_3](\text{C}_{60})_2$. L represents 2, 2'-bipyridine ligand.

Table 4.4: Favorable electron transfer reactions in $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$.

Compound	Favorable Electron Transfer Reactions
$[\text{CrL}_3]_2(\text{C}_{60})$	$\text{CrL}_3^0 + \text{CrL}_3^{1+} \rightarrow \text{CrL}_3^{1+} + \text{CrL}_3^0$ $\text{C}_{60}^{1-} + \text{C}_{60}^0 \rightarrow \text{C}_{60}^0 + \text{C}_{60}^{1-}$
$[\text{CrL}_3](\text{C}_{60})$	$\text{CrL}_3^{1+} + \text{CrL}_3^{2+} \rightarrow \text{CrL}_3^{2+} + \text{CrL}_3^{1+}$ $\text{C}_{60}^{2-} + \text{C}_{60}^{1-} \rightarrow \text{C}_{60}^{1-} + \text{C}_{60}^{2-}$
$[\text{CrL}_3](\text{C}_{60})_2$	$\text{CrL}_3^{1+} + \text{CrL}_3^{2+} \rightarrow \text{CrL}_3^{2+} + \text{CrL}_3^{1+}$ $\text{C}_{60}^{1-} + \text{C}_{60}^0 \rightarrow \text{C}_{60}^0 + \text{C}_{60}^{1-}$

Magnetism

EPR and SQUID measurements were done to investigate the magnetic properties of all three chromium complex ionic C_{60} salts. The experimental data are included in Appendix III & IV. As compared to $[Ru(bpy)_3]_n(C_{60})_m$, $[Cr(bpy)_3]_n(C_{60})_m$ shows much higher magnetization and very different temperature dependence of magnetic susceptibility under the applied field. This is mainly attributed to the multiple unpaired electrons on molecular orbitals of $[Cr(bpy)_3]^{2+}$ and $[Cr(bpy)_3]^{1+}$. The magnetism cannot be simply illustrated by Curie-Weiss law or fitted into the linear equations used for $[Ru(bpy)_3]_n(C_{60})_m$ compound. The complicity of magnetic behavior is a result of combining all the contributions of the magnetically active species in the compound. Not serious effort has been devoted to explain the data.

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APPENDIX I

Differential Scanning Calorimetry (DSC) Curves of $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$

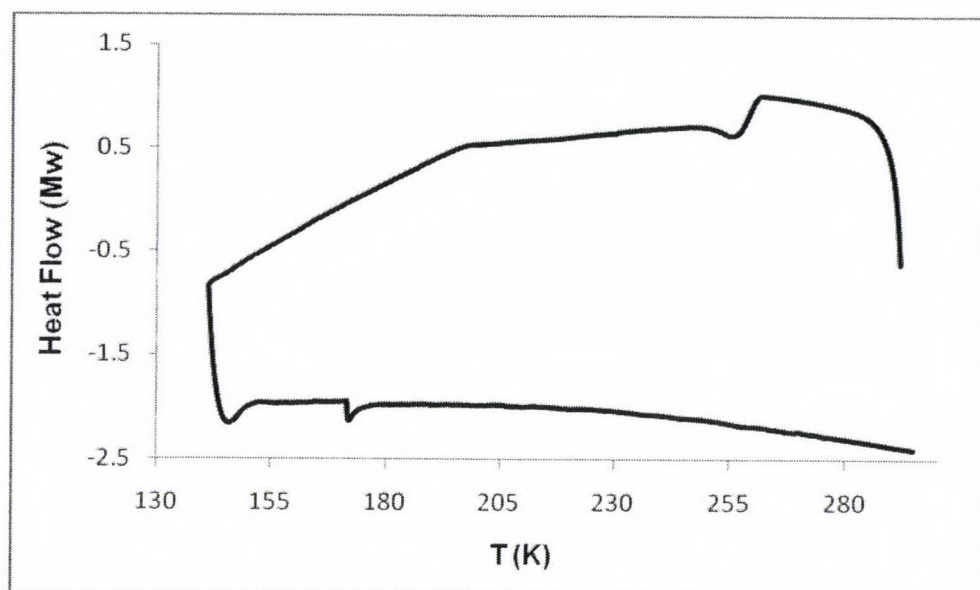


Figure A.1: DSC curve of 8.2 mg $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$ by first cooling down to -145 K and then warm up to near room temperature.

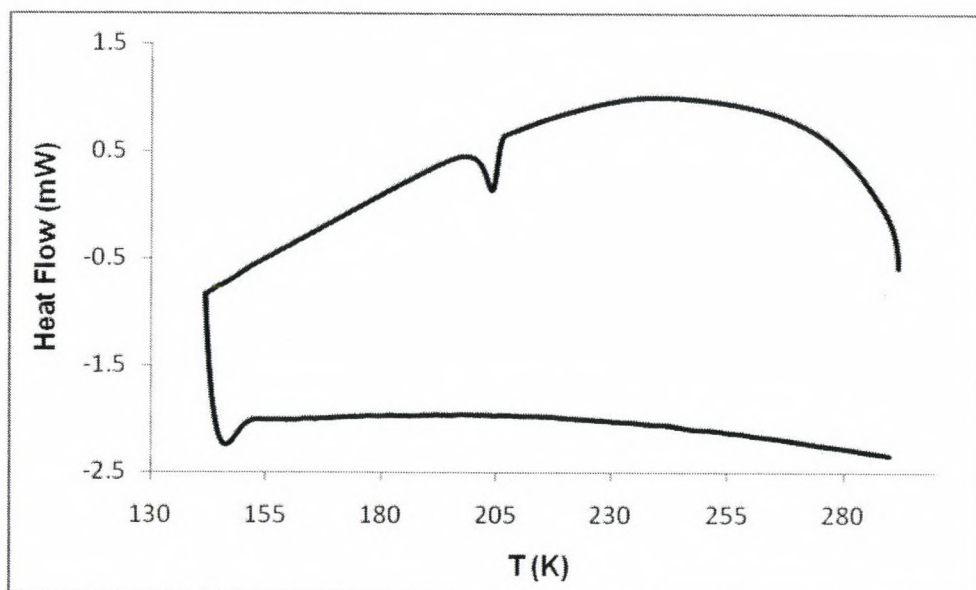


Figure A.2: DSC curve of 8.2 mg $[\text{Ru}(\text{bpy})_3](\text{C}_{60})_2$ for the second time measurement.

APPENDIX II

Magnetic Susceptibility of $[\text{RuL}_3]_n(\text{C}_{60})_m$

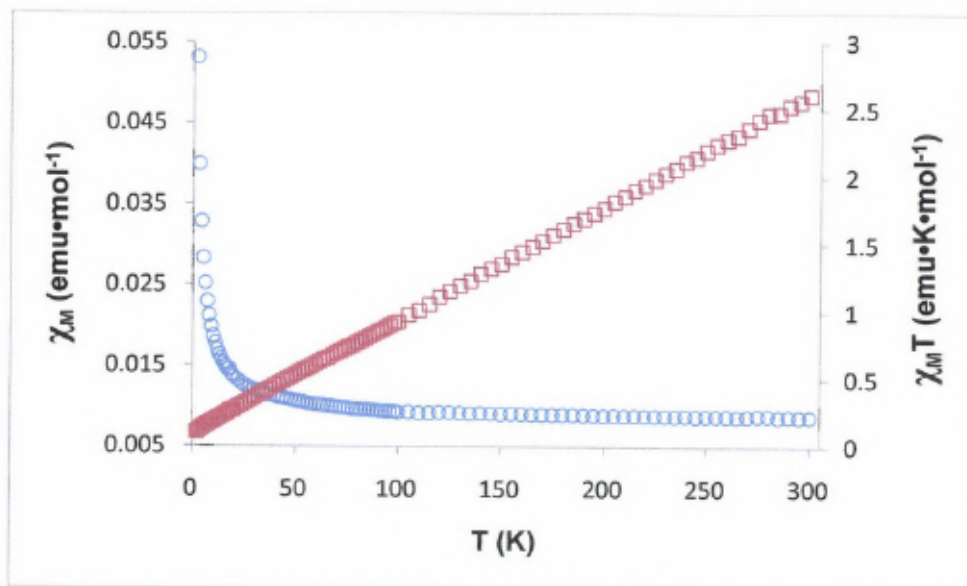


Figure B.1: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for $[\text{Ru}(\text{4DMB})_3]_2(\text{C}_{60})$ at 100 mT magnetic field.

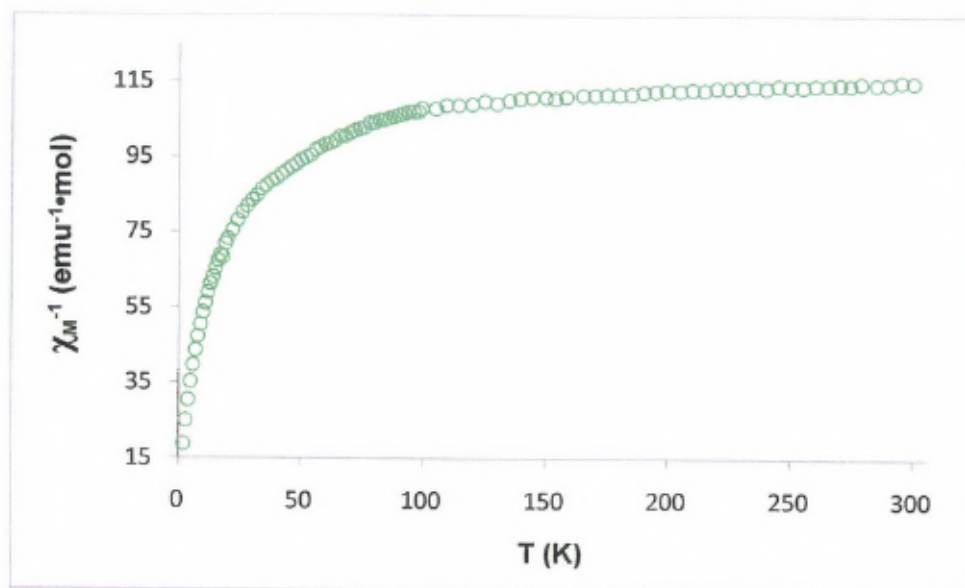


Figure B.2: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{4DMB})_3]_2(\text{C}_{60})$ at 100 mT magnetic field.

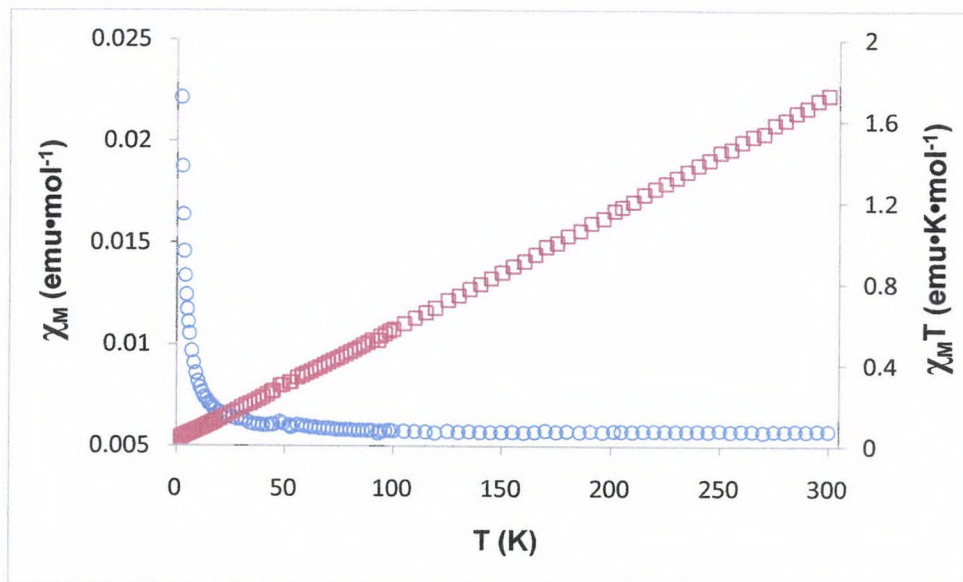


Figure B.3: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for $[\text{Ru}(\text{4DMB})_3](\text{C}_{60})$ at 100 mT magnetic field.

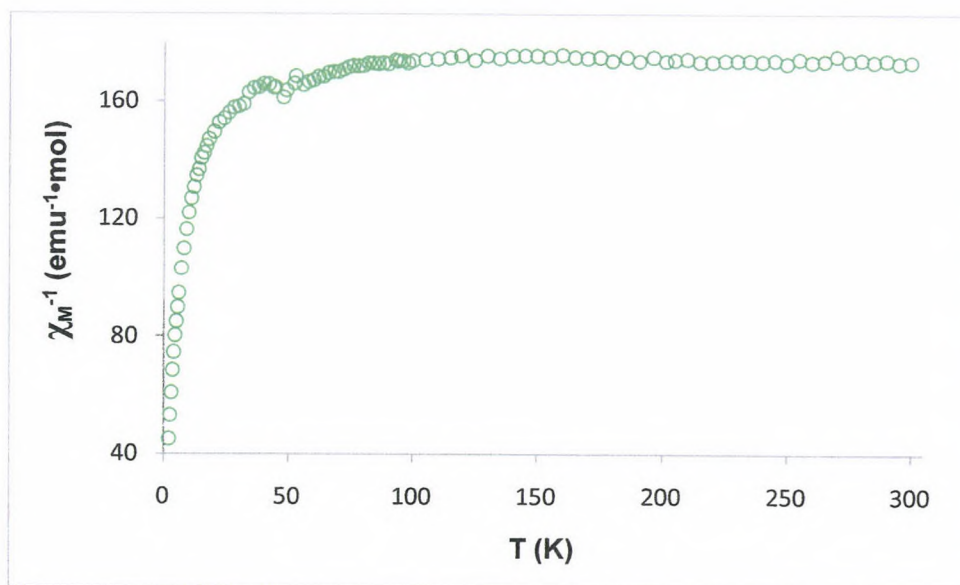


Figure B.4: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{4DMB})_3](\text{C}_{60})$ at 100 mT magnetic field.

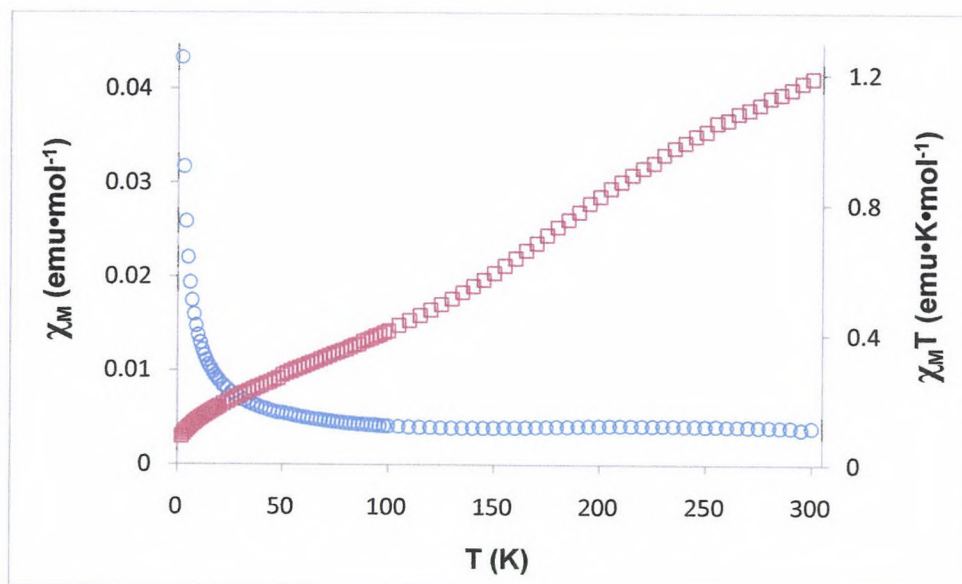


Figure B.5: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for $[\text{Ru}(\text{4DMB})_3](\text{C}_{60})_2$ at 100 mT magnetic field.

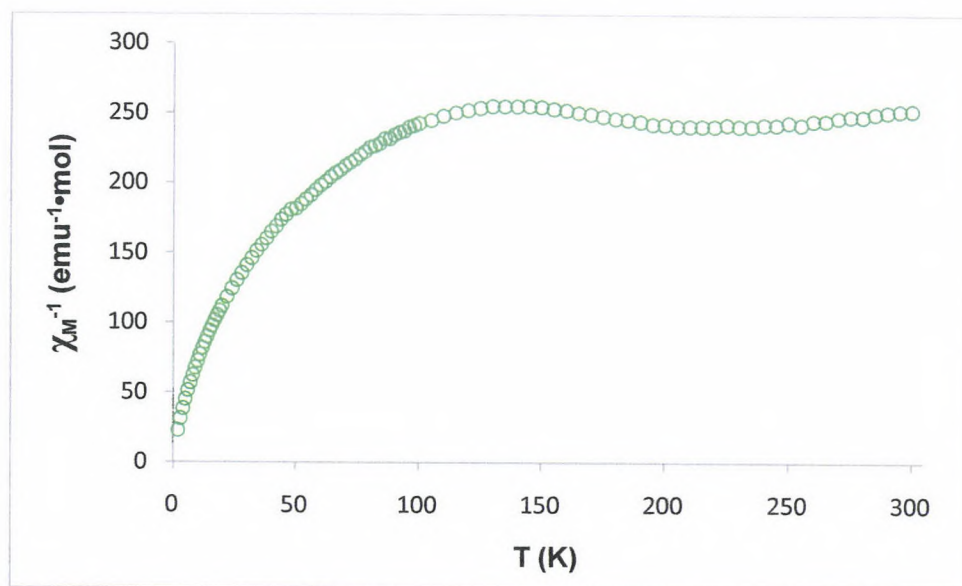


Figure B.6: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{4DMB})_3](\text{C}_{60})_2$ at 100 mT magnetic field.

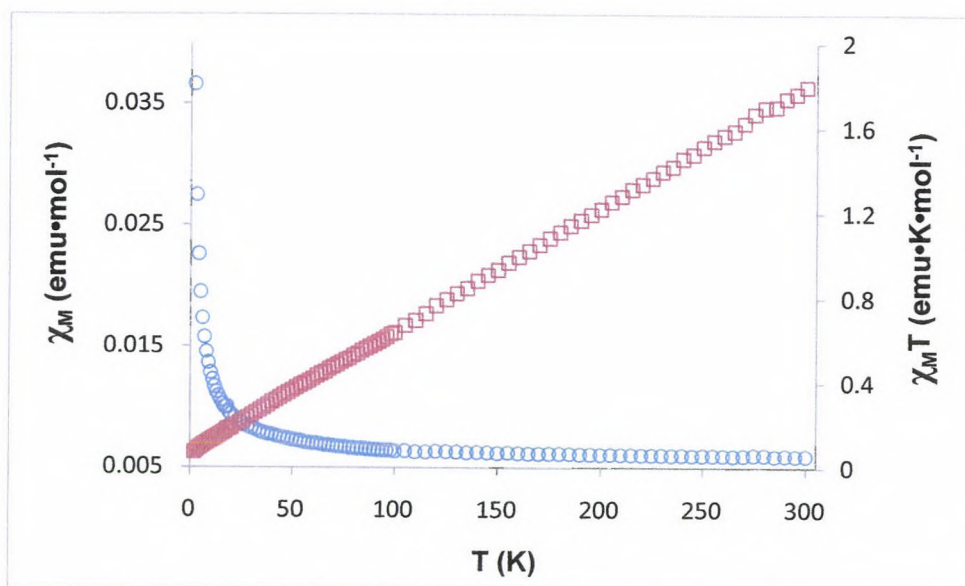


Figure B.7: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for $[\text{Ru}(\text{TBB})_3]_2(\text{C}_{60})$ at 100 mT magnetic field.

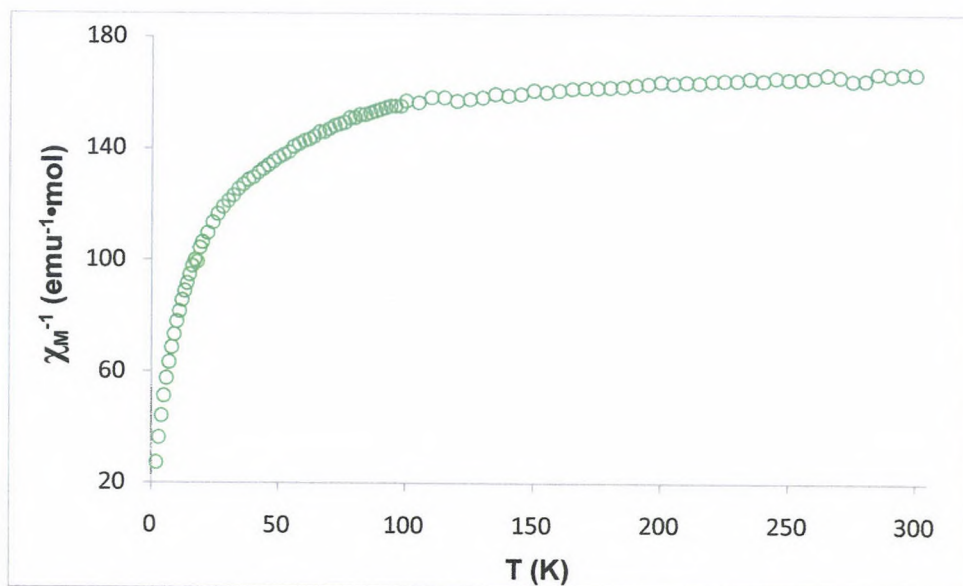


Figure B.8: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{TBB})_3]_2(\text{C}_{60})$ at 100 mT magnetic field.

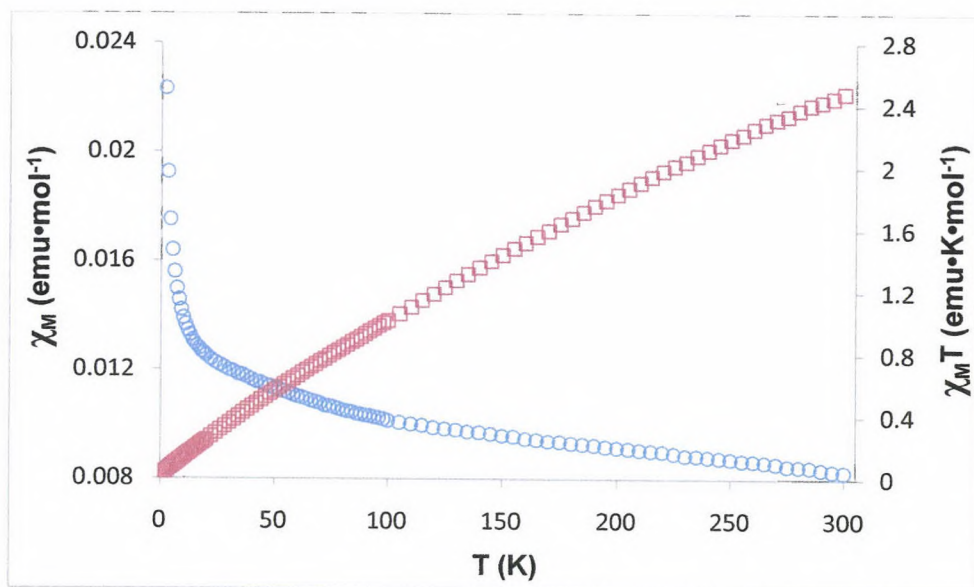


Figure B.9: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for $[\text{Ru}(\text{TBB})_3](\text{C}_{60})$ at 100 mT magnetic field.

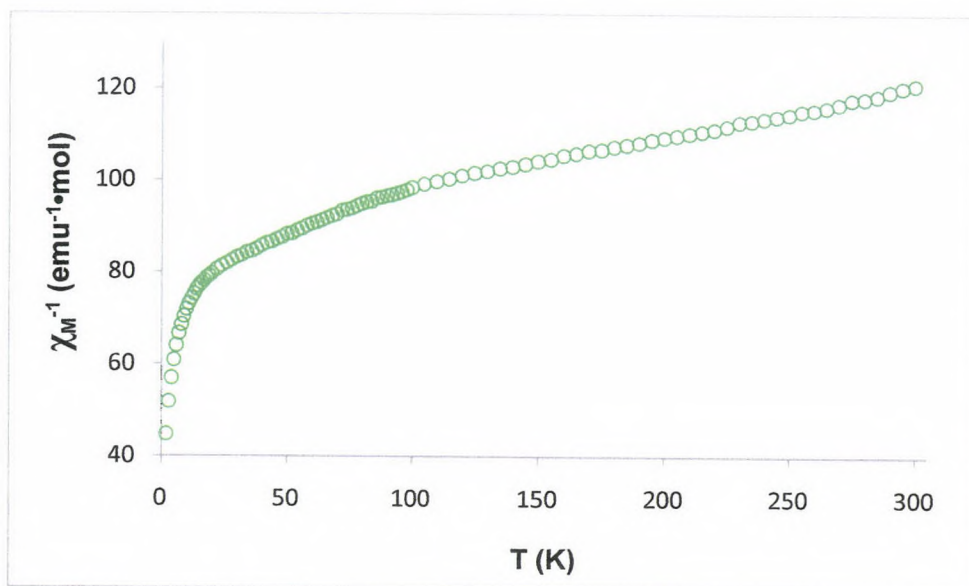


Figure B.10: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{TBB})_3](\text{C}_{60})$ at 100 mT magnetic field.

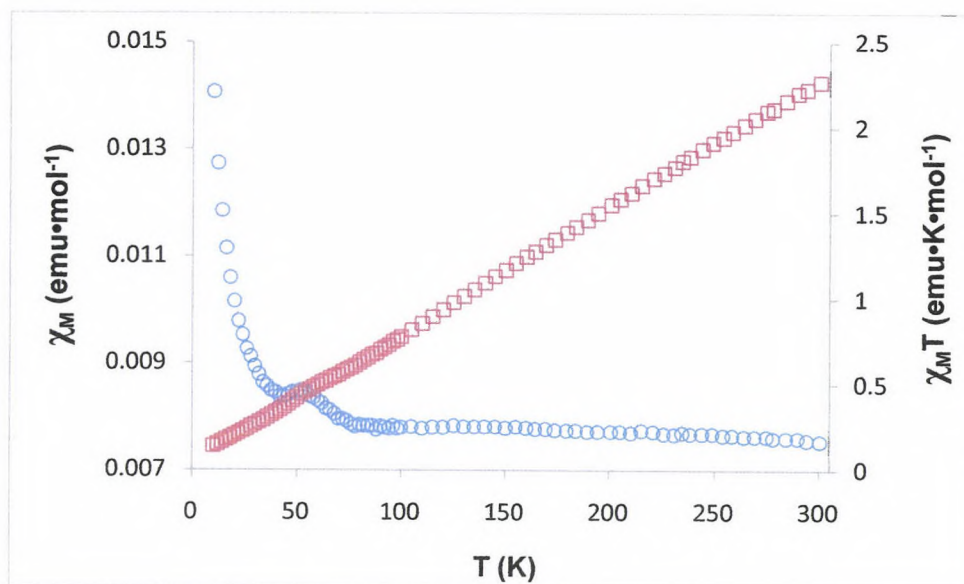


Figure B.11: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility and temperature ($\square$) for $[\text{Ru}(\text{TBB})_3](\text{C}_{60})_2$ at 100 mT magnetic field.

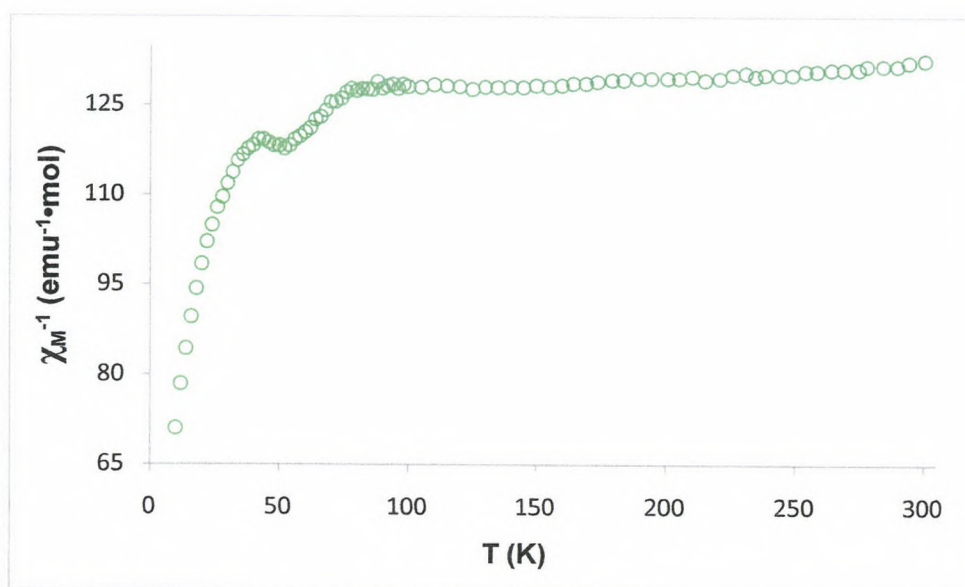


Figure B.12: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{TBB})_3](\text{C}_{60})_2$ at 100 mT magnetic field.

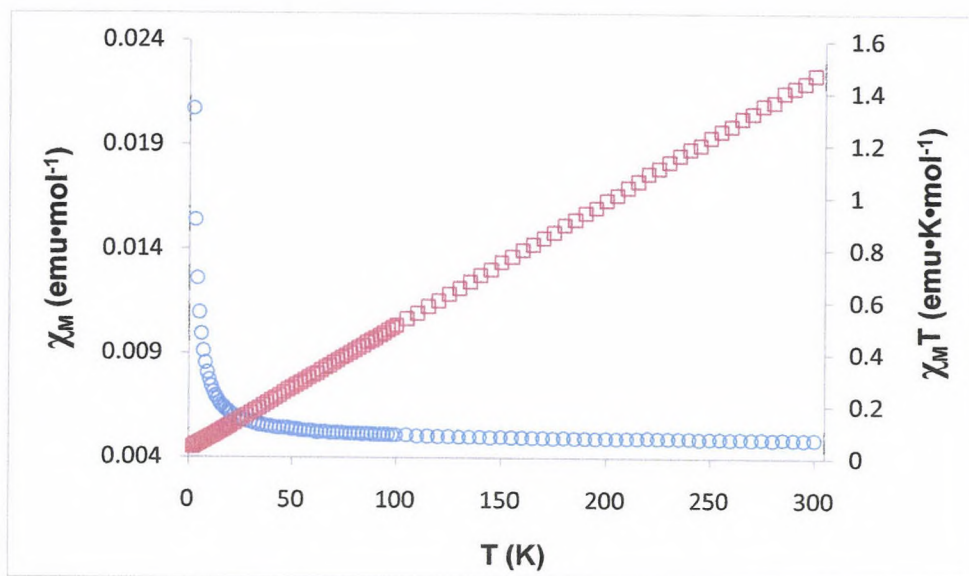


Figure B.13: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility by temperature ($\square$) for $[\text{Ru}(\text{TMB})_3](\text{C}_{60})$ at 100 mT magnetic field.

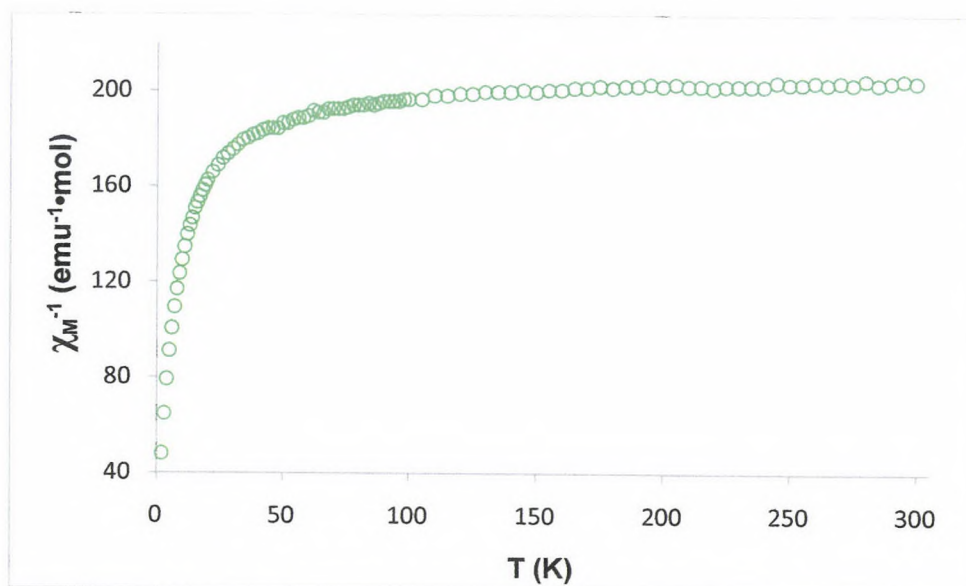


Figure B.14: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{TMB})_3](\text{C}_{60})$ at 100 mT magnetic field.

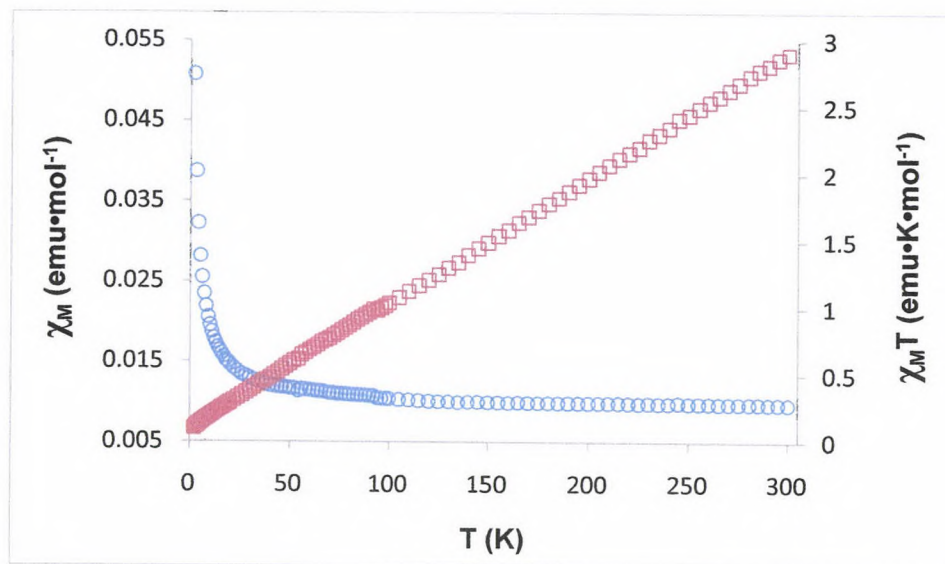


Figure B.15: Temperature dependence of molar magnetic susceptibility ($\circ$) and the product of molar susceptibility by temperature ($\square$) for $[\text{Ru}(\text{TMB})_3](\text{C}_{60})_2$ at 100 mT magnetic field.

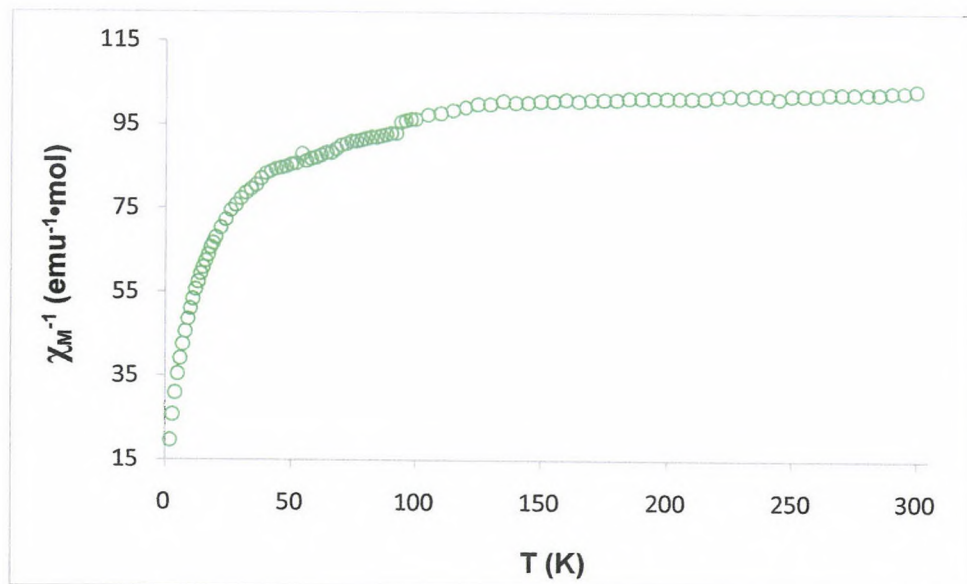


Figure B.16: Temperature dependence of the reciprocal of molar magnetic susceptibility of $[\text{Ru}(\text{TMB})_3](\text{C}_{60})_2$ at 100 mT magnetic field.

APPENDIX III

EPR Spectra of $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$

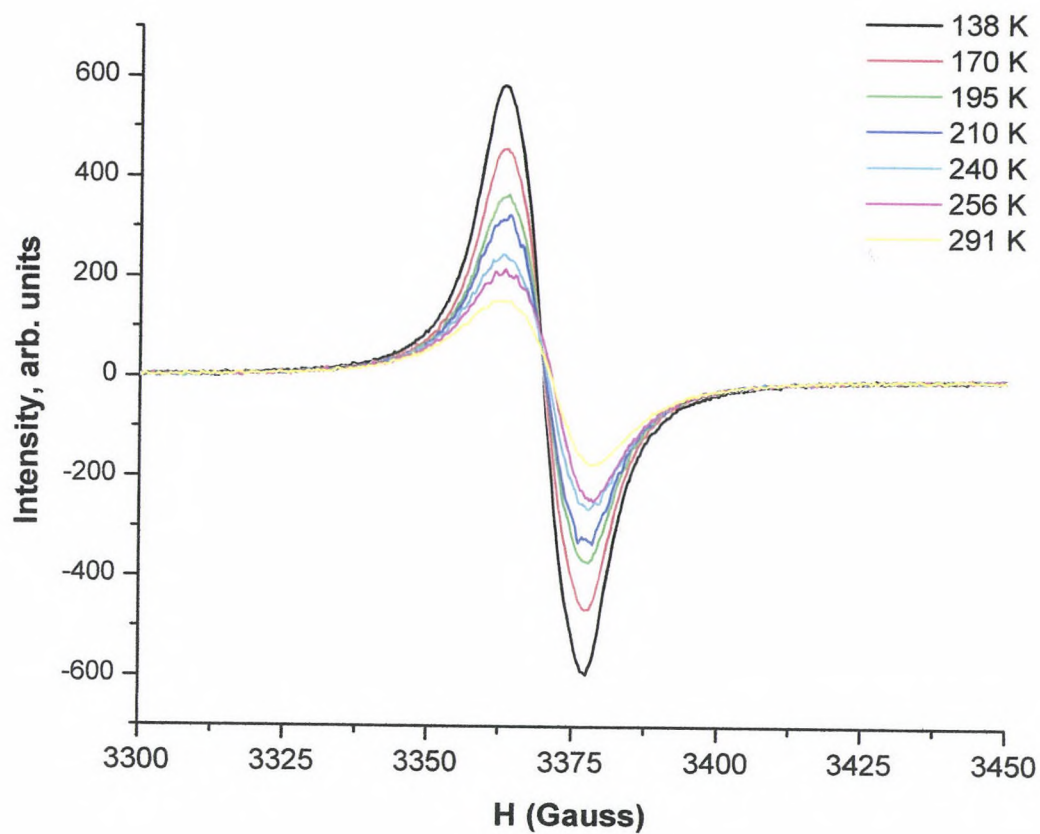


Figure C.1: EPR spectra of $[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$ (2.16×10^{-6} mol) at different temperatures.

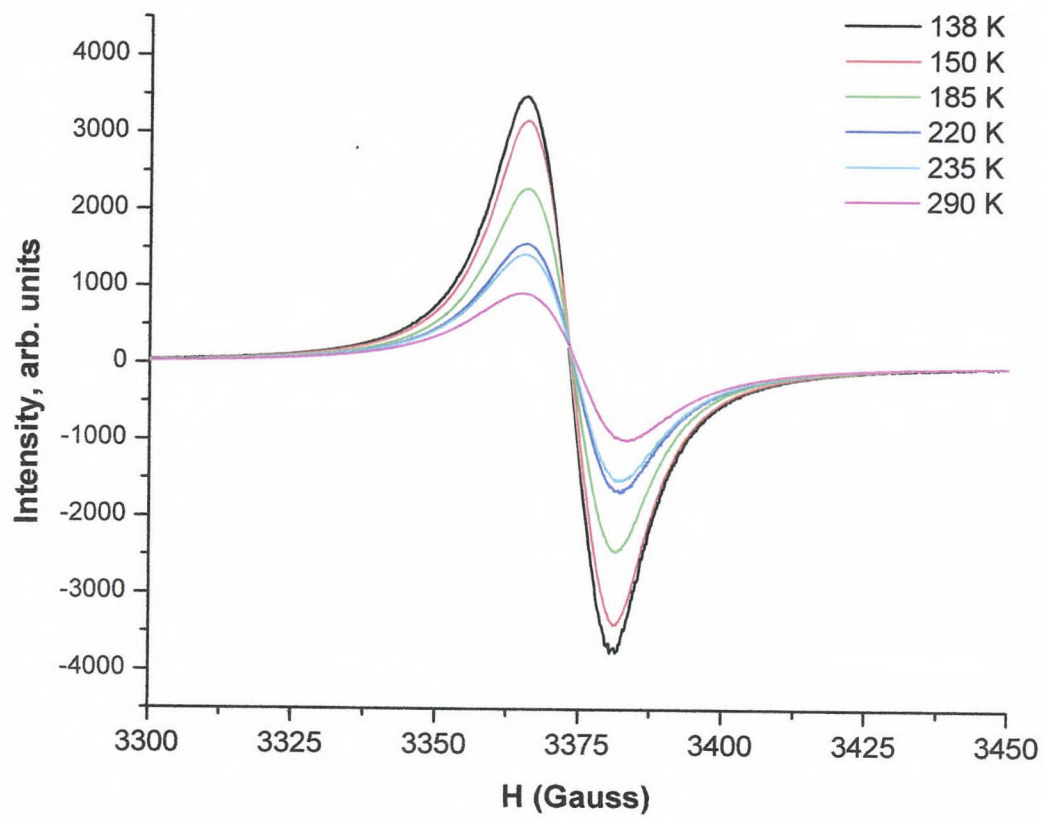


Figure C.2: EPR spectra of $[\text{Cr}(\text{bpy})_3](\text{C}_{60})$ (2.42×10^{-6} mol) at different temperatures

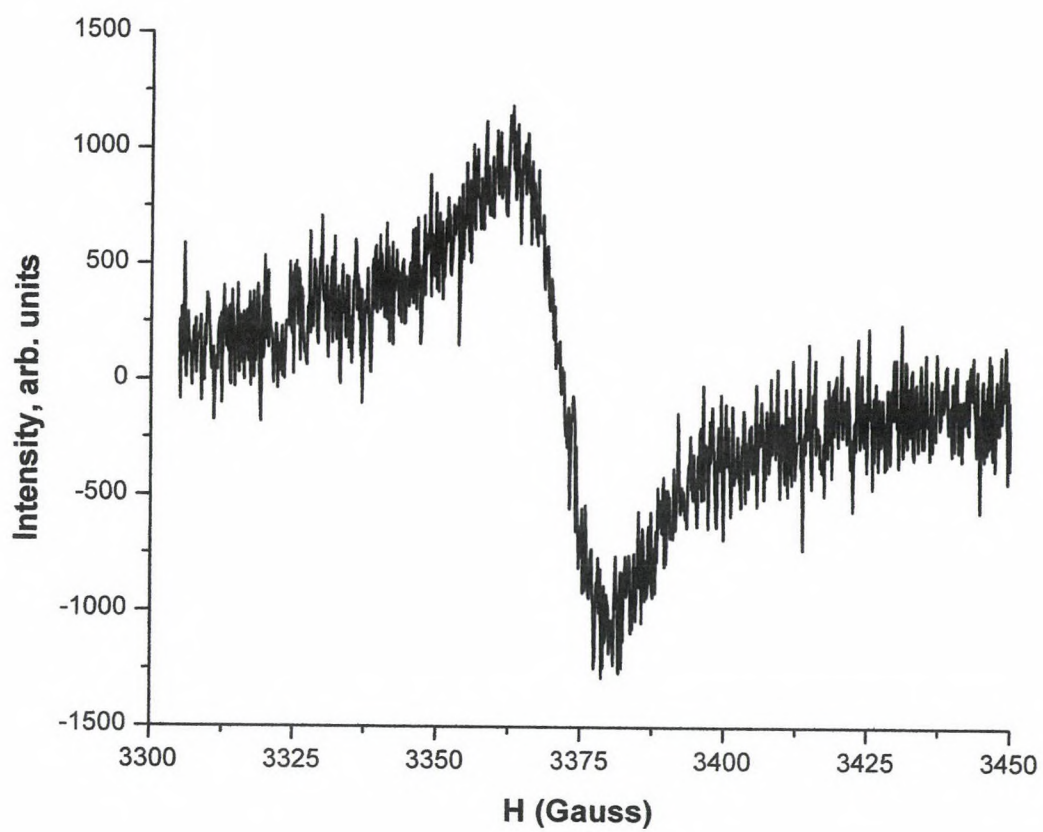


Figure C.3: EPR spectra of $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ (2.5×10^{-6} mol) at 292 K. As temperature cooled down, the signal was more noisy and obscure.

APPENDIX IV

Magnetic Susceptibility of $[\text{Cr}(\text{bpy})_3]_n(\text{C}_{60})_m$

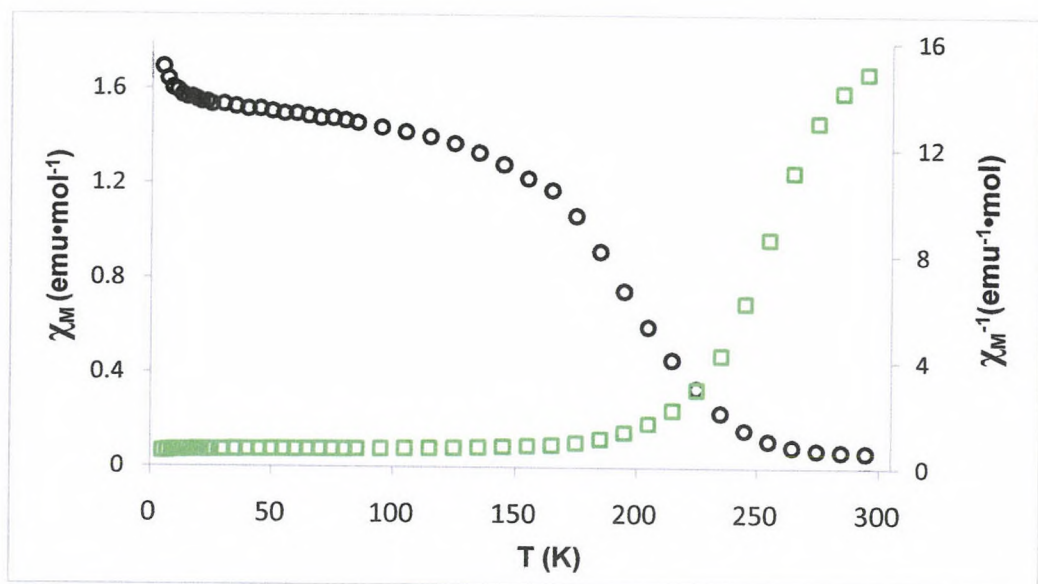


Figure D.1: Temperature dependence of molar magnetic susceptibility (○) reciprocal of molar magnetic susceptibility (□) for $[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$ at 100mT magnetic field.

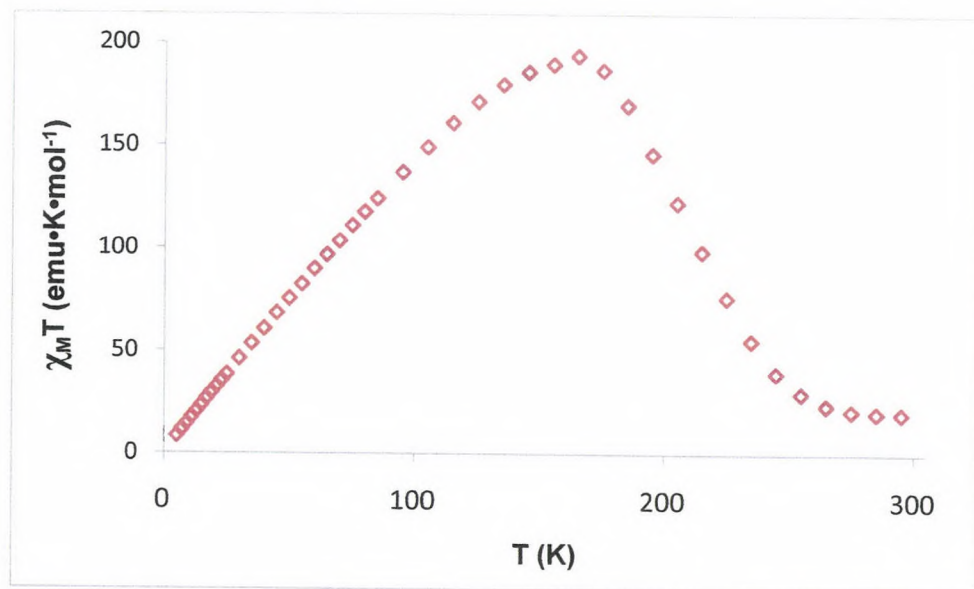


Figure D.2: Temperature dependence of the product of molar susceptibility and temperature of $[\text{Cr}(\text{bpy})_3]_2(\text{C}_{60})$ at 100mT magnetic field.

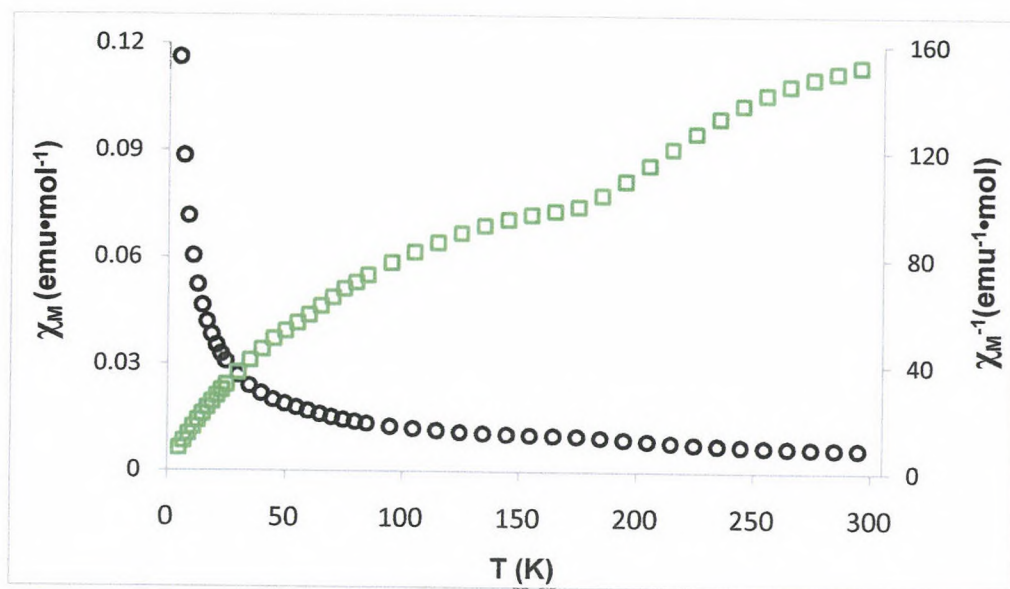


Figure D.3: Temperature dependence of molar magnetic susceptibility ($\circ$) reciprocal of molar magnetic susceptibility ($\square$) for $[\text{Cr}(\text{bpy})_3](\text{C}_{60})$ at 100mT magnetic field.

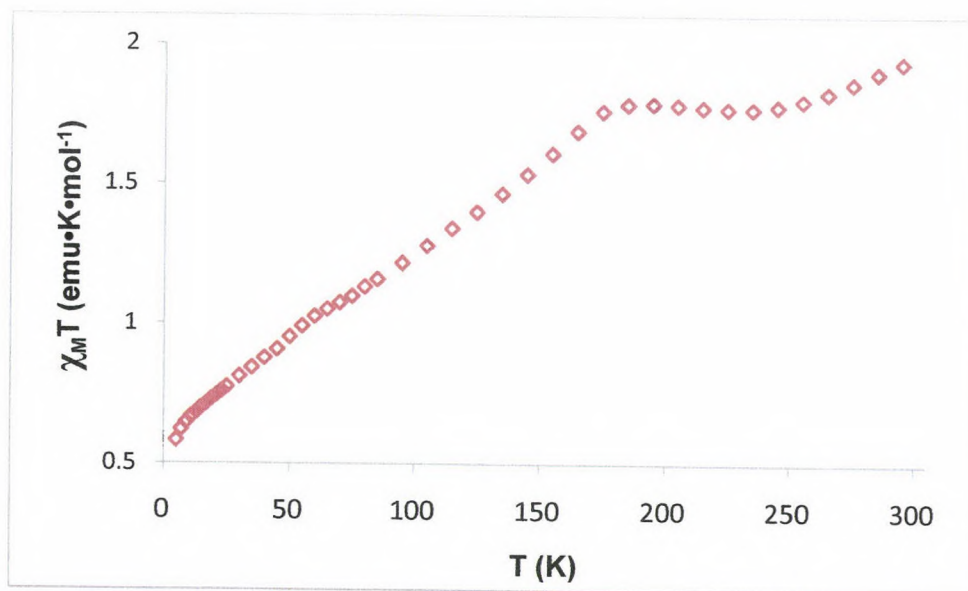


Figure D.4: Temperature dependence of the product of molar susceptibility and temperature of $[\text{Cr}(\text{bpy})_3](\text{C}_{60})$ at 100mT magnetic field.

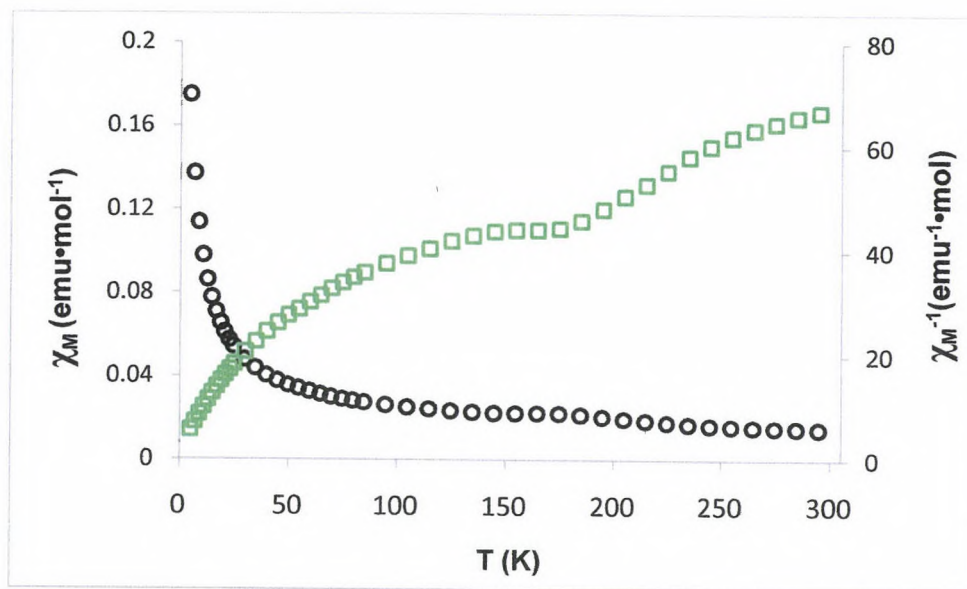


Figure D.5: Temperature dependence of molar magnetic susceptibility ($\circ$) reciprocal of molar magnetic susceptibility ($\square$) for $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ at 100mT magnetic field.

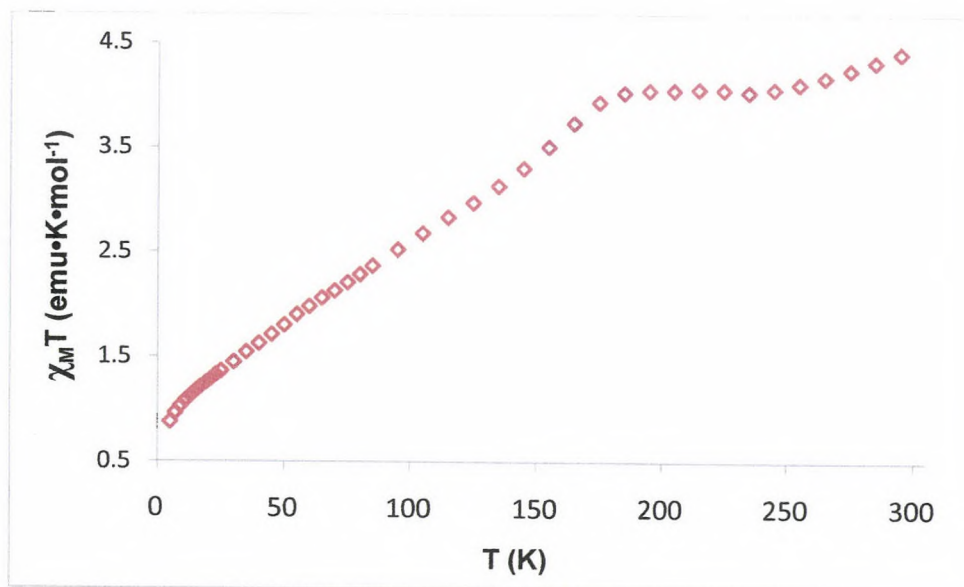


Figure D.6: Temperature dependence of the product of molar susceptibility and temperature of $[\text{Cr}(\text{bpy})_3](\text{C}_{60})_2$ at 100mT magnetic field.