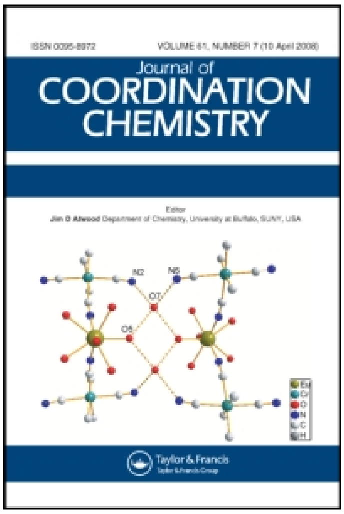

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of Cr(III), Mn(II), Co(II), Ni(II), and Cu(II) complexes with a hexadentate hemi-cage ligand formed with bipyridine

A. L. Williams[a]; A. A. Bhuiyan[b]; M. O. Turner[a]; F. Millett[a]; B. Durham[a]
[a] Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA [b] Department of Physical Science, Arkansas Tech University, Russellville, AR 72801, USA

To cite this Article Williams, A. L. , Bhuiyan, A. A. , Turner, M. O. , Millett, F. and Durham, B.(2011) 'Synthesis and characterization of Cr(III), Mn(II), Co(II), Ni(II), and Cu(II) complexes with a hexadentate hemi-cage ligand formed with bipyridine', Journal of Coordination Chemistry, 64: 1, 48 — 56, First published on: 13 December 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.539213

URL: http://dx.doi.org/10.1080/00958972.2010.539213

Journal of Coordination Chemistry
Vol. 64, No. 1, 10 January 2011, 48–56

Synthesis and characterization of Cr(III), Mn(II), Co(II), Ni(II), and Cu(II) complexes with a hexadentate hemi-cage ligand formed with bipyridine

A.L. WILLIAMS†, A.A. BHUIYAN‡, M.O. TURNER†,
F. MILLETT† and B. DURHAM*†

†Department of Chemistry and Biochemistry, University of Arkansas,
Fayetteville, AR 72701, USA
‡Department of Physical Science, Arkansas Tech University,
Russellville, AR 72801, USA

(*Received 17 August 2010; in final form 5 November 2010*)

A series of transition metal complexes, Cr(III), Mn(II), Co(II), Ni(II), and Cu(II), have been prepared and characterized using the hemi-cage ligand previously reported by Beeston *et al.* [R.F. Beeston, W.S. Aldridge, J.A. Treadway, M.C. Fitzgerald, B.A. Degraff, S.E. Stitzel. *Inorg. Chem.*, **37**, 4368 (1998)]. The ligand is composed of three bipyridyl groups covalently bound to a central benzene ring through ethyl groups. Preliminary DFT calculation with Cr(III) indicates that the ligand will allow the three bipyridyl groups to coordinate to a metal with a pseudooctahedral coordination geometry. Comparison of UV-Vis spectra, magnetic susceptibility, and cyclic voltammetry indicates that the complexes are remarkably similar to the corresponding bipyridine complexes, $M(bpy)_3^{n+}$. No evidence was found to indicate that the ligand restricts the motion of the bipyridyl groups enough to change the chemical properties.

Keywords: Hemi-cage ligand; Bipyridine; Synthesis; Electrochemistry

1. Introduction

The chemistry of most transition metal complexes formed with bipyridine has been thoroughly investigated. A review [1] describes the basic chemistry as well as many of the applications of these complexes. Beeston *et al.* [2] described the synthesis of an interesting variant of the basic ligand that involves attaching three bipyridyl moieties to a central benzene ring. The new hexadentate ligand is described as a hemi-cage, and complexes containing the hemi-cage have been reported with ruthenium(II) [2], iron(II) [2], and zinc(II) [3]. The scarcity of applications of the ligand can be ascribed to the difficulty of its synthesis and lack of commercial availability. Recently both of the starting materials for the ligand have become commercially available and the synthesis of the ligand from these reagents involves only a single step followed by purification.

---

*Corresponding author. Email: bdurham@uark.edu

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.539213

The structure of the new ligands suggests some interesting questions regarding the dynamics of the coordinated bipyridyl chelates. These questions also relate to some chemical problems that remain to be addressed with bipyridine complexes. For example, the electrochemistry of the copper [4] and nickel [1] bipyridine complexes are poorly understood because of the uncertainty of the coordination sphere of the electrochemical products. A hemi-cage ligand offers the potential of restricting the changes in the coordination sphere over the time period of the electrochemical experiment. Similarly, the photolability of the complexes may be significantly reduced because loss of the bipyridine is restricted by the structure of the ligand. This was demonstrated by Beeston *et al.* [2] with the ruthenium(II) complex.

With these questions in mind, we have undertaken a systematic study of transition metal complexes of the hemi-cage ligand. In this manuscript we report the preparation, characterization, and comparison of several complexes with first row transition metals. At this stage of the investigation, emphasis is on the comparison of the properties and electrochemistry of the trichelated bipyridine complexes, $M(bpy)_3^{n+}$ with complexes prepared with the hemi-cage ligand $M(\text{hemi-cage})^{n+}$.

2. Experimental methods

2.1. *Materials and equipment*

$[Cr(bpy)_3](PF_6)_3$, $[Mn(bpy)_3](PF_6)_2$, $[Co(bpy)_3](PF_6)_2$, $[Ni(bpy)_3](PF_6)_2$, and $[Cu(bpy)_3](PF_6)_2$ were prepared according to procedures previously reported [5, 6]. 5,5′-Dimethyl-2,2′-bipyridine and 1,3,5-tris(bromomethyl)benzene were obtained from Sigma-Aldrich. CM-52 cation-exchange media was from Whatman. UV-Vis spectra were recorded in acetonitrile with a HP8452A diode array spectrometer. Magnetic susceptibility measurements were performed on the complexes as solids using a Johnson Matthey magnetic susceptibility balance. No diamagnetic corrections for the ligands were made. Electrochemical measurements were performed with a CH Instruments potentiostat. The working electrode was a platinum disk electrode, a platinum wire was used as the auxillary electrode, and a saturated calomel electrode was used as the reference electrode. Cyclic voltammetry was performed with the complexes dissolved in acetonitrile containing $0.1\,\mathrm{mol\,L^{-1}}$ tetrabutylammonium hexafluorophosphate. NMR spectra were obtained using a Bruker 300 MHz spectrometer. Elemental analysis was performed by Columbia Analytical Services, Tuscon, AZ. ESI mass spectra were obtained by direct injection (by-passed LC column) into a Bruker "Esquire LC" ion trap mass spectrometer.

2.2. *Synthesis*

2.2.1. 1,3,5-Tris(5′methyl-2,2′-bipyridin-5-yl)ethylbenzene, (5-bpy-2C)$_3$Bz. The procedure used was similar to that originally reported by Beeston *et al.* [2] with the significant exception that commercially prepared 5,5′-dimethyl-2,2′-bipyridine and 1,3,5-tris(bromomethyl)benzene were used. We have chosen to maintain the ligand abbreviations originally reported by Beeston *et al.* [2].

2.2.2. [Cr((5-bpy-2C)$_3$Bz)](PF$_6$)$_3$·H$_2$O. $CrCl_3 \cdot 6H_2O$ (0.119 g, 0.447 mol), (5-bpy-2C)$_3$Bz (0.356 g, 0.534 mol), and mossy zinc (0.4 g, excess) were refluxed in 30 mL of methanol, under nitrogen, for 1 h. The solution was dark blue. After cooling and exposure to air the solution turned red. The solvent was removed to yield a green solid by rotary evaporation. The solid was dissolved in water and passed through a CM-52 cation-exchange column (45 × 1.9 cm). Two yellow bands were eluted. The second and more intense band was collected and the complex precipitated by the addition of 1 mL of a concentrated aqueous solution of NH_4PF_6. The solid was recovered by vacuum filtration, washed with water, then diethyl ether, and finally dried in an oven. The product at this point contains small amounts of Zn((5-bpy-2C$_3$)Bz)(PF$_6$)$_2$ as indicated by ESI-MS. The zinc complex could be removed by two additional elutions through a CM-52 column. Yield 0.206 g, 39%. ESI (m/z): 718 [M^+]. Anal. Calcd for $CrC_{45}H_{44}N_6OF_{18}P_3$ (%): C, 46.84; H, 3.66; N, 7.28. Found (%): C, 46.14; H, 3.78; N, 7.17.

2.2.3. Mn[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$. $MnSO_4$ (0.0745 g, 0.49 mmol) and (5-bpy-2C)$_3$Bz (0.335 g, 0.50 mmol) were added to 40 mL of 1 : 1 ethanol : water solution, which was stirred for 2 h at room temperature (the solution turned yellow immediately after stirring was started). After 2 h, the solution was filtered and the ethanol was removed by rotary evaporation. Additional water was added to the mixture and saturated aqueous NH_4PF_6 was added to precipitate the complex. The yellow precipitate was vacuum filtered on a membrane filter, washed with ether, and air dried. Yield: 0.288 g (58%). MS(ESI) (m/z): 360.6 [M^{2+}].

2.2.4. Co[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$. $CoCl_2 \cdot 6H_2O$ (0.105 g, 0.44 mmol) and (5-bpy-2C)$_3$Bz (0.305 g, 0.46 mmol) were dissolved in 50 mL methanol, at which time the solution began to turn yellow. The solution was refluxed for 30 min and then allowed to cool. The solvent was removed by rotary evaporation after cooling. This residue was dissolved in water and saturated aqueous NH_4PF_6 was added to precipitate the complex. The yellow precipitate was collected by vacuum filtration on a membrane filter, washed with ether, and then placed into a desiccator to dry. Yield: 0.267 g (60%). MS(ESI) (m/z): 362.5 [M^{2+}]. Elemental analysis calculated for $CoC_{45}H_{42}N_6P_2F_{12}$ (%): C, 53.21; H, 4.17; N, 8.27. Found (%): C, 51.98; H, 4.20; N, 7.15.

2.2.5. Ni[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$. $NiCl_2 \cdot 6H_2O$ (0.025 g, 0.105 mmol) and (5-bpy-2C)$_3$Bz (0.067 g, 0.100 mmol) were added to 30 mL of 1 : 1 ethanol : water and the solution was heated on a hot plate with stirring. The solution turned pink. The ethanol was boiled off before allowing the solution to cool. After the addition of 10 mL water, saturated aqueous NH_4PF_6 was added to precipitate the complex, which was collected by vacuum filtration on a membrane filter. The red precipitate was washed with ether, dried on a hot plate, and then allowed to cool in a desiccator. Yield: 0.089 g (83%). MS(ESI) (m/z): 362.0 [M^{2+}]. Elemental analysis calculated for $NiC_{45}H_{42}N_6P_2F_{12}$ (%): C, 53.23; H, 4.17; N, 8.28. Found (%): C, 52.52; H, 4.16; N, 8.03.

2.2.6. Cu[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$·H$_2$O. $Cu_2(acetate)_4 \cdot H_2O$ (0.0105 g, 0.05 mmol) and (5-bpy-2C)$_3$Bz (0.0666 g, 0.1 mmol) were added to 30 mL of a 1 : 1 ethanol : water solution, and allowed to stir. The stirring was stopped once the solution turned blue, after approximately 5 min. The ethanol was removed by rotary evaporation, and after the addition of 10 mL of water, saturated aqueous NH_4PF_6 was added to precipitate the complex. The blue precipitate was collected by vacuum filtration on a membrane filter, washed with ether, and allowed to dry in a desiccator. Yield: 0.033 g (32%). MS(ESI) (*m*/*z*): 364.4 [M^{2+}]. Elemental analysis calculated for $CuC_{45}H_{44}N_6OP_2F_{12}$ (%): C, 52.98; H, 4.15; N, 8.24. Found (%): C, 52.04; H, 4.28; N, 8.10.

2.2.7. Cr(5,5′-dmbpy)$_3$(PF$_6$)$_3$. $CrCl_3 \cdot 6H_2O$ (0.265 g, 1 mmol), 25 mL 0.1 mol L^{-1} $HClO_4$, and three pieces of zinc amalgam were combined in a 50 mL Erlenmeyer flask. N_2 gas was bubbled through this mixture until the solution was a light blue. 5,5′-Dimethyl-2,2′-bipyridine (0.5438 g, 3 mmol) was dissolved in 100 mL of 0.01 mol L^{-1} $HClO_4$ and the solution was purged with N_2 gas. Fifteen milliliter of the Cr(II) solution was added to the 5,5′-dimethyl-2,2′-bipyridine solution *via* syringe, being careful to minimize exposure to air. The resulting black solution was exposed to air and filtered. Saturated aqueous NH_4PF_6 was added to the yellow filtrate, and the yellow precipitate was collected by vacuum filtration on a membrane filter. ESI (*m*/*z*): 718 [m^+]. Yield: 0.157 g (39.25%).

2.3. *DFT calculations*

The theoretical calculations of geometry and energies were performed by using the PQS program (version 3.3) developed by Parallel Quantum Solutions {PQS Version 3.2; Parallel Quantum Solutions, 2013 Green Acres Road, Fayetteville, AR 72703; 2005. See: www.pqschem.com}. We chose to use the B3LYP functional. The all-electron 6-311G(d,p) Pople triple-z basis set was used for all atoms except cobalt, which was represented using the modified Pople 6-31G basis set optimized for first row transition metals. The geometry of the complex was relaxed maintaining *C3* symmetry.

3. Results

The hemi-cage ligand was synthesized in a single step from commercially available starting materials in high yield using the procedure described by Beeston *et al.* [2]. The Cr(III) complexes were prepared using methods analogous to the procedures previously reported for the corresponding tris-bipyridine or phenanthroline complexes. Unfortunately, the initial product obtained with this method was contaminated with the Zn(II) complex and purification (monitored by ESI-MS) proved to be very difficult, although possible with repeated cation-exchange chromatography. Reaction of $CrCl_3(THF)_3$ with (5-bpy-2C$_3$)Bz failed to give the desired complex but provided an excellent route to [Cr((5-bpy-2C$_3$)Bz)Cl$_2$]Cl.

The other complexes were readily prepared by simple combination of a metal salt and an excess of the ligand in ethanol/water followed by precipitation as the hexafluorophosphate salts. Purification sufficient to provide good elemental analysis proved difficult. This problem has been noted previously [2]. Repeated separations by column chromatography improve the elemental analysis. Despite the difficulty with elemental

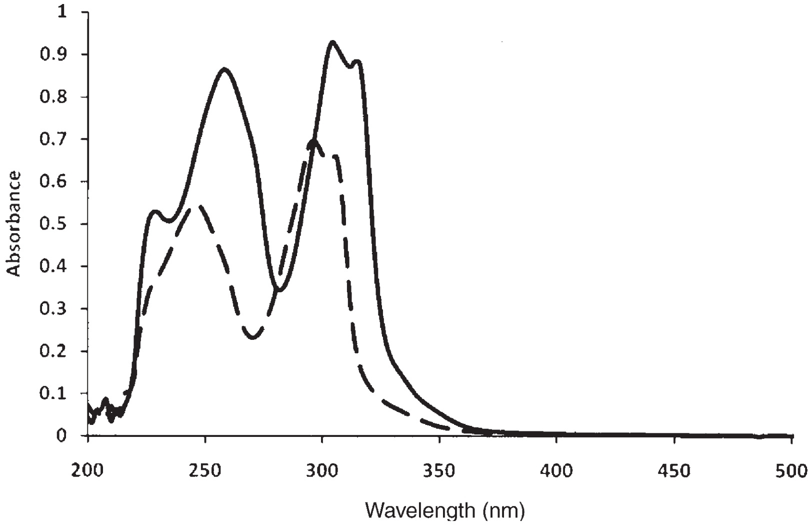

Figure 1. Comparison of the UV-Vis spectra of Co(bpy)$_3^{2+}$ (dashed line) and Co((5-bpy-2C)$_3$Bz)$^{2+}$ dissolved in acetonitrile.

analysis, the ESI mass spectra of the complexes typically show only a single prominent peak corresponding to the parent ions.

All of the complexes except that of Cr(III) exhibited very similar absorption spectra over the range of 200–500 nm. These spectra were also very similar to the corresponding spectra of the tris-bipyridine complexes. The spectra can be described as containing two sets of two absorption bands. One set is centered at 250 nm and the other at approximately 300 nm. In each case, the absorption bands for the complexes formed with the hemi-cage ligand are shifted to longer wavelengths by approximately 10 nm. A representative example is illustrated in figure 1 which shows a comparison of Co(bpy)$_3^{2+}$ and Co((5-bpy-2C)$_3$Bz) in acetonitrile. The UV region of the spectrum of the Cr(III) complexes is complicated and the common absorption features are obscured by other bands.

Cu(bpy)$_3^{2+}$ and Cu((5-bpy-2C)$_3$Bz) also show a weak but very well-defined absorption at 680 nm ($\varepsilon = {\sim}60\,\text{cm}^{-1}(\text{mol L}^{-1})^{-1}$). Ni((5-bpy-2C)$_3$Bz) shows two weak bands at 350 and 520 nm. The UV-Vis spectrum of Cr((5-bpy-2C$_3$)Bz)$^{3+}$, Cr(bpy)$_3^{3+}$, and Cr(5, 5′-dmbpy)$_3^{3+}$ are all very similar except for a shift in energy. Three weak bands appear in the spectrum of each complex between 400 and 500 nm. Cr((5-bpy-2C$_3$)Bz)$^{3+}$ has absorptions at 420, 448, and 478 nm and Cr(5,5′-dmbpy) has bands of similar energy at 424, 448, and 480 nm. The corresponding molar absorptivities are 450, 380, 170 $(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$ for both complexes.

Magnetic susceptibility measurements indicated that the magnetic moments of Co[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$, Ni[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$, and Cu[(5-bpy-2C)$_3$Bz](PF$_6$)$_2$ are 3.8, 2.41, and 1.62 BM, respectively. For comparison, the corresponding tris-bipyridine complexes, M(bpy)$_3^{2+}$, were found to have magnetic moments of 3.25, 2.73, and 1.62 BM.

Cyclic voltammetry of Cr((5-bpy-2C)$_3$Bz)$^{3+}$ in acetonitrile with 0.1 mol L^{-1} TBAH is illustrated in figure 2 and reveals two reversible electrochemical processes very similar

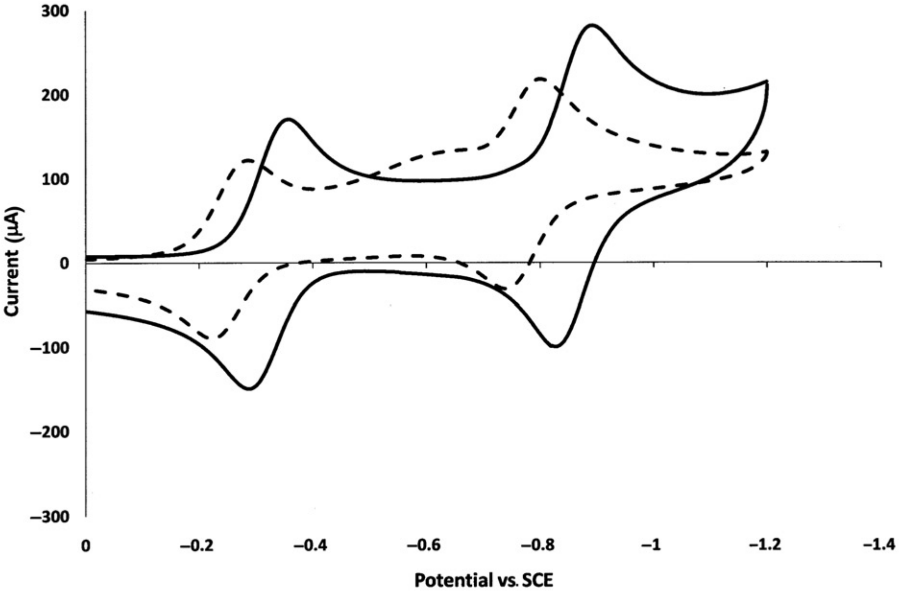

Figure 2. Comparison of the cyclic voltammograms of $Cr(bpy)_3^{3+}$ (dashed line) and $Cr((5\text{-}bpy\text{-}2C)_3Bz)^{3+}$ dissolved in $0.1\,mol\,L^{-1}$ TBAH in acetonitrile.

to those observed with $Cr(bpy)_3^{3+}$. The $E_{1/2}$'s of the redox reactions of the hemi-cage complex were observed at −0.32 and −0.86 V *versus* SCE and those of $Cr(bpy)_3^{3+}$ were observed at −0.25 and −0.77 V *versus* SCE. Peak-to-peak separation was 0.06 V in each case. For additional comparison, the corresponding potentials of $Cr(5,5'\text{-dmbpy})_3^{3+}$ are −0.35 and −0.78 V. Cyclic voltammetry of the Co(II) analogs also showed reversible behavior with $E_{1/2}$'s of 0.19 V with $Co[(5\text{-}bpy\text{-}2C)_3Bz]^{2+}$ and 0.33 V with $Co(bpy)_3^{2+}$ over the range +1.5 to −1.0 V. The Ni^{2+} complex was electrochemically inactive from +1.5 to −1.0 V under the conditions employed. The Cu(II) complexes showed complex electrochemical behavior with a single quasi-reversible reduction at −0.41 V and the corresponding oxidation at −0.21 V. The current was scan rate dependent and no electrochemical behavior is evident at scan rates above $500\,mV\,s^{-1}$.

4. Discussion

The metal complexes described are readily prepared by mixing the ligand and an appropriate metal salt in an alcohol solvent with the exception of the Cr(III) complex. The chromium complex requires reduction of the Cr(III) salt to Cr(II) which is easily accomplished with zinc metal. Ambient oxygen is sufficient to oxidize the Cr(II) complex to Cr(III). Hexafluorophosphate anion was used as the counterion in all syntheses.

Despite a very large number of attempts no crystals suitable for X-ray diffraction studies have been grown. However, a preliminary DFT study was undertaken. The DFT calculations support a structure with the three bipyridyl groups coordinated to the metal in a pseudooctahedral arrangement as shown in figure 3. The bite angle of

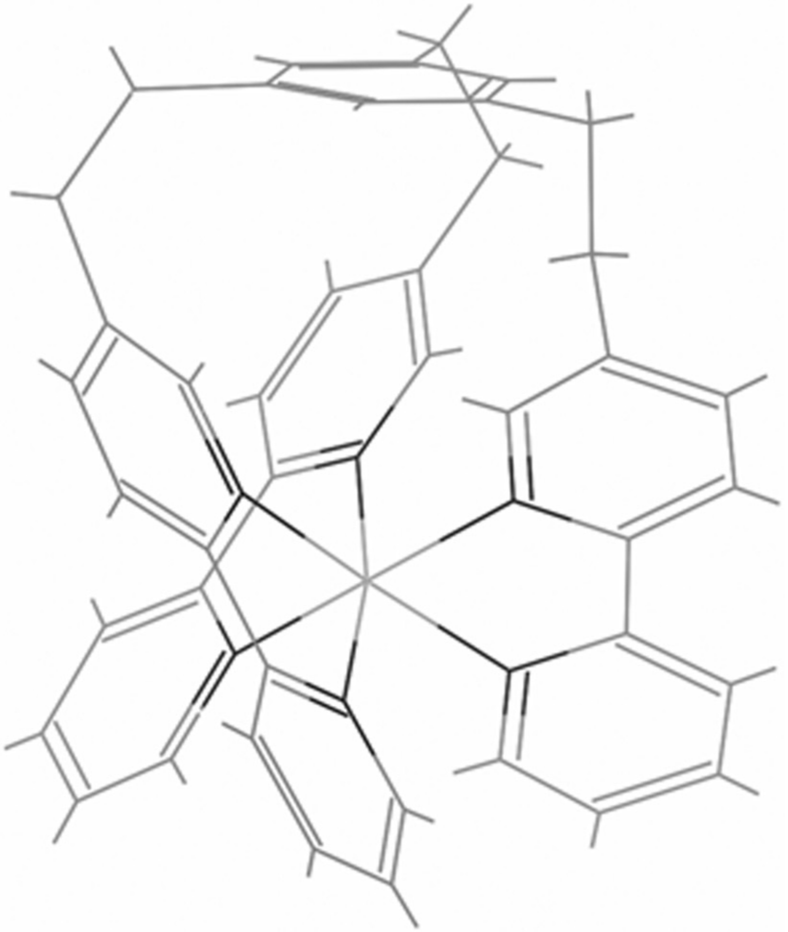

Figure 3. Structure of $Cr((5\text{-bpy-}2C)_3Bz)^{3+}$ obtained from DFT calculations.

the bipyridyl group is too small to form a true octahedral complex. A comparison of the bond distances and angles obtained from the crystal structure of $Cr(bpy)_3^{3+}$ to the calculated structure of $Cr((5\text{-bpy-}2C)_3Bz)^{3+}$ indicates that no unusual bonds or angles are observed in the energy-minimized structure suggesting that the capping ring does not hinder coordination of the bipyridyl groups. Specifically, the chromium–nitrogen bond distances in the crystal structure of $Cr(bpy)_3^{3+}$ reported by Hauser *et al.* [7] are 2.041 and 2.057 A. The DFT calculations yielded bond distances of 2.052 and 2.050. The bond angles around the chromium in the crystal structure are 173.4, 84.7, and 95.5 whereas the DFT calculations yielded 171.5, 79.9, and 93.5.

The magnetic moments are consistent with an octahedral geometry in the cases of Co(II), Ni(II), and Cu(II). In the case of Co(II), the magnetic moment indicates that the hemi-cage ligand does not provide an adequate ligand field to cause the complex to be low spin. Magnetic moments of tetrahedral Ni(II) complexes are typically higher (~4) than those observed with Ni(II) complexes with octahedral geometries (2.8–3.3). A magnetic moment in the range of 1.7–2.2 is expected for d^9 copper complexes [8].

Comparison of the complexes with the corresponding bipyridine complexes indicates very little differences in physical properties. For example, the UV-Vis spectrum of each complex is nearly identical with regard to the number of bands. In every complex, except that of chromium(II), the spectrum can be described as containing two sets of two bands with some additional structure present in some cases. These bands are probably best described as ligand-centered bands involving the bipyridyl groups. No coupling beyond that seen in the tris-bipyridine complexes is observed with the hemi-cage complexes. The maxima of the transitions, however, are all reduced by about 10 nm in the hemi-cage complexes. This shift is even more pronounced with the Cr(III) complexes because of the larger number of bands. In this case, all of the transitions, including the bands that have been assigned as d–d transitions [9] between 400 and 500 are shifted to lower energies. In order to investigate the cause of the shift to lower energy a Cr(III) complex was prepared with 5,5′-dimethyl-2,2′-bipyridine. The physical properties of this complex were nearly identical to those of the hemi-cage complex. These results suggest that the shift in energy is primarily due to the electron-donating effects of the methyl groups and the locations of the methyl groups on the bipyridyl rings. The shift is not consistent with steric effects caused by the covalent bonds between the bipyridyl groups and the central benzene ring.

The chemical properties of the hemi-cage complexes are also remarkably similar to the bipyridine complexes as reflected in the electrochemistry. The Cr(III) and Co(II) complexes both exhibit reversible redox properties involving the M(II) and M(III) forms of the complexes similar to that observed with corresponding tris-bipyridine complexes. In both cases, the redox (2+/3+) potentials are shifted to more negative potentials by approximately 100 mV. This shift is consistent with electron donation from the substituents in the 5 and 5′ position. The Cr(III) complex prepared with 5,5′-dimethyl-2,2′-bipyridine has a 2+/3+ potential almost identical to the corresponding hemi-cage complex.

The similarity in electrochemical behavior is more than expected. The bipyridine and hemi-cage complexes of Cu(II) show almost identical electrochemical behavior. Cyclic voltammetry reveals only a single reduction event between 0 and -1 V *versus* SCE. This electrochemical process involves the Cu(II)/Cu(I) couple, is quasi-reversible and scan rate dependent. The scan rate dependence and the quasi-reversible nature of the process suggest that the electron transfer is slow, possibly as a result of a large reorganization barrier. It was hoped that the cage-like structure of the new ligand would restrict this possibility and provide for a reversible process. The case of Ni(II) may be similar although no electrochemical process is observed in the cyclic voltammogram over this range. Apparently, motion of the bipyridyl groups sufficient to remove them from the first coordination sphere is fast with respect to the electrochemical processes. A detailed study of the photochemistry of the Cr(III) complex has been initiated and will be the subject of a future publication.

Acknowledgments

Supported by National Institutes of Health Grant GM 20488 (to F.M. and B.D.). We thank the Arkansas State Wide Mass Spectrometry Facility for reported data. Core facilities were funded by the Arkansas Biosciences Institute. This publication was made possible by Grant Number P20 RR15569 from the National Center for Research Resources (NCRR), a component of the National Institutes of Health (NIH). Its contents are solely the responsibility of the authors and do not necessarily represent the official view of NCRR or NIH.

References

[1] A.G. Sykes. *Advances in Inorganic Chemistry*, Vol. 34, pp. 4–46, Academic Press, New York (1989).
[2] R.F. Beeston, W.S. Aldridge, J.A. Treadway, M.C. Fitzgerald, B.A. Degraff, S.E. Stitzel. *Inorg. Chem.*, **37**, 4368 (1998).
[3] K.D. Oyler, F.J. Coughlin, S. Bernhard. *J. Am. Chem. Soc.*, **129**, 210 (2007).
[4] E. Garribba, G. Micera, D. Sanna, L. Strinna-Erre. *Inorg. Chim. Acta*, **299**, 253 (2000).
[5] B.R. Baker, B.D. Mehta. *Inorg. Chem.*, **4**, 848 (1965).
[6] C. Cornioley-Deuschel, A. von Zelewsky. *Inorg. Chem.*, **26**, 962 (1987).
[7] A. Hauser, M. Mader, W.T. Robinson, R. Murugesan, J. Ferguson. *Inorg. Chem.*, **26**, 1331 (1987).
[8] R.S. Drago. *Physical Methods for Chemists*, 2nd Edn, pp. 484–486, Surfside Scientific Publishers, Gainesville, FL (1992).
[9] E. Konig, S. Herzog. *J. Inorg. Nucl. Chem.*, **32**, 585 (1970).