Cantaurus, Vol. 11, 27-30, May 2003 © McPherson College Division of Science and Technology

Synthesis and Characterization of 4, 11-dimethyl-1, 4, 8, 11, tetraazabicyclo hexadecane Chromium

Trenton Parsell

ABSTRACT

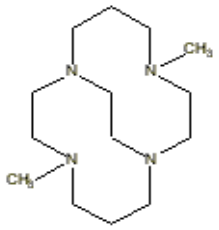
A new complex of Chromium(III) and the cross-bridged macrocyclic ligand 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane has been synthesized. Complexation of Tungsten, Vanadium, and Molybdenum was unsuccessful. The Cr(III)**(L)** complex was characterized using UV-Visible spectroscopy λ_{max} = 583nm , IR Spectroscopy, X-Ray Crystallography, and magnetic susceptibility u_{eff} = 3.95. These tests support a Cr(III) complex not the Cr(II) complex that was expected.

Keywords: *Ligand, Chromium, Macrocycle, spectroscopy*

INTRODUCTION

The effect of ligand rigidity on the overall stability of complexes is becoming more and more common in designing ligands for reactions that take place in chemically unfriendly environments. These complexes decompose less rapidly because of there relative kinetic inertness (Hubin T.J., *et al,* 1998). Ligands are molecules or ions that are bonded or directly attached to a transition metal ion. Ligands that can attach to a metal more than one time are known as chelates, if a ligand can bond to a metal in two different places it is a bidentate chelate, if there are three points of attachment it is a tridentate chelate, ect.

As the number of points of attachment to the metal increases the stability of the complex increases both kinetically and thermodynamically (Meissler and Tarr 1999). These more stable complexes are less likely to break down into the starting materials allowing them to perform reactions in conditions where other complexes would decompose rapidly (Meissler and Tarr 1999).



(1)

Figure 1. 4,11-dimethyl-1,4,8,11-tetraazabicyclo tetradecane **(1)**

Tetradentate ligands that have their points of attachment bridged together to form a ring are known as macrocycles. This study focuses primarily on using the macrocyclic ligand 1,4,8,11-tetraazacyclo tetradecane or more specifically its cross-bridged version 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane **(Figure 1)**. The macrobicycle of this ligand tends to form complexes with a distorted octahedral geometry binding a metal ion in four places, leaving two cis equatorial sites to perform reactions (Hubin, T.J.; et al, 2000). It was anticipated that a second or third row transition metal could be successfully complexed with the ligand, as only one second row complex exists and complexation of a third row had never been accomplished before. First Tungsten (W^{4+}) then Molybdenum (Mo^{3+}) and finally Vanadium (V^{3+}) were used in attempted syntheses but all were unsuccessful. After these failures Chromium was chosen and successfully inserted into the cross-bridged cyclam.

MATERIALS AND METHODS

The following chemicals were purchased from Aldrich: Tetrabutylammonium chloride (TBACl), and Mercury(II) Tetrathiocyanato Cobaltate(III) ($Hg[Co(SCN)_4]$). Chemicals supplied from the McPherson College chemistry lab include Acetonitrile (CH_3CN), Hydrochloric acid (HCl), and Potassium Bromide (KBr). Wes Hoffert provided the Cr(III)[**(1)**ClOH]Cl that was used for the characterization process.

The elemental analysis of the product was performed by Quantitative Technologies, Inc. The FAB^+ Mass spectroscopy was performed by the Analytical Service of the University of Kansas on a VG ZAB HS spectrometer equipped with a xenon gun using NBA, and NBA + H_2O.

The magnetic susceptibility measurements were taken on a Johnson Matthey MSB magnetic susceptibility balance. The balance was standardized using Mercury(II) Tetrathiocyanato Cobaltate(III).

UV-Vis spectra were collected on a Varian Cary 50 Bio spectrometer. IR spectroscopy was performed on a Nicolet 320 Avatar FT IR using a solid KBr pellet sample. Dr. Stephen Archibald at the University of Hull, England collected the crystal data on a Stoe IPDS-II imaging plate diffractometer.

The original synthesis of the cyclam ligand was completed as an Advanced Inorganic Chemistry lab in the fall of 2002. For preparation of the B-cyclam **(1)**, used to complex the metal, the literature procedure was followed (Weisman, G. R.; et al, 1990).

Cyclam (0.049mol, 9.8g) was used for the synthesis of 4,11-dimethyl-1,4,8,11-tetraazabicyclo tetradecane. The first step produced a quantitative yield of cis-Decahydro-1H, 6H-3a,5a,8a, 10a-tetraazapyrene **(2)**. 7.0148 grams of **(2)** were placed in a 1000mL round bottom flask with 610ml of a 95% ethanol solution and (14.078g, 0.37mol) $NaBH_4$ in a nitrogen gas environment to stir for five days. This reaction yielded a crude form of the ligand that was purified by using vacuum distillation yielding 4.01g (33.8%) pure **(1)**.

Attempted Syntheses

In the glove box anhydrous WCl_4 (0.326 g, 0.001 mole) and **(1)** (0.254 grams, 0.001 mole), were added to a 50mL round bottom flask along with approximately 20mL of DMF as solvent. This flask was placed on a hot plate where it was heated to approximately 50 ^oC and stirred for two days. After two days the mixture was filtered through a filter paper and the liquid was collected in a 25ml vial. The mass spec for this complex had no corresponding peaks for a product so this process was deemed unsuccessful in yielding any metal complex. The above reaction was attempted twice more substituting anhydrous VCl_2 and $MoCl_3$ these reactions also proved unsuccessful.

Synthesis of Cr(III)(1)Cl_2OH

0.254g (0.001 mole) **(1)** was dissolved in 20ml of Dimethylformamide in a 50mL round bottom flask. 0.123g (0.001M) of anhydrous $CrCl_2$ was added and the solution was left stirring for 48 hours at 50 ^oC. The solution started as a green suspension, which changed to a blue color as the reaction proceeded. This solution was then filtered into a 250ml Erlenmeyer flask. The product was precipitated from the solution with several ether diffusion chambers were set up by filling 25ml vials one third full of the metal ligand solution and placing them into larger containers which were also filled one third full with ether and then covered. Blue crystals were grown and collected in a 25ml vial. This process yielded at least 22.73% (0.0958g). A second synthesis of this complex was attempted in an acetonitrile (CH_3CN) solution but the metal was not soluble enough for the reaction to take place even when refluxed at 50 ^oC for 24 hours. Addition of DMF to this second reaction allowed the reaction to proceed and the same color change was noted.

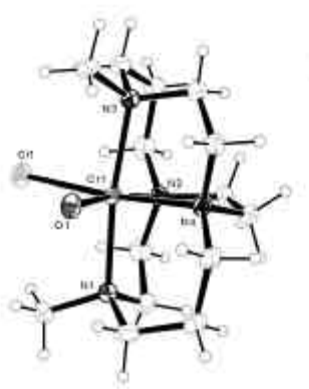


Figure 2. Crystal Structure of Cr(III)[**(1)**ClOH]

RESULTS and DISCUSSION

The expected result of the above reaction was Cr(II)[**(1)**Cl_2] (1=4,11–dimethyl–1,4,8,11–tetraazabicyclo hexadecane) but as the results will show this was not the product isolated (Hubin. T.J.; *et al* 2000). The product was found to be Cr(III)[**(1)**ClOH]Cl •1.5H_2O (421.25g/mol) (**Figure 2**). It is currently unknown how the oxygen found its way into the reaction but it is suspected that the glove box is not completely free of oxygen or that the complex took water from the DMF solvent (an attempt at eliminating the DMF in favor of acetonitrile was unsuccessful because of solubility problems).

Mass Spectroscopy

The FAB^+ Mass spectrum was the first data obtained that indicated a newly formed ligand metal complex. It was first thought that no predominate peaks existed for the ligand metal complex. After discovery of the complex's true formula it is apparent that the peak at m/z = 358.1 corresponded to the weight of Cr(III)[**(1)**$ClOH^+$] also m/z = 341 corresponded to the weight of Cr(III)[**(1)**CL]$^+$. While not as strong as the uncomplexed ligand peak (m/z = 255.2) the complex peak is quite visible (**Figure 3**).

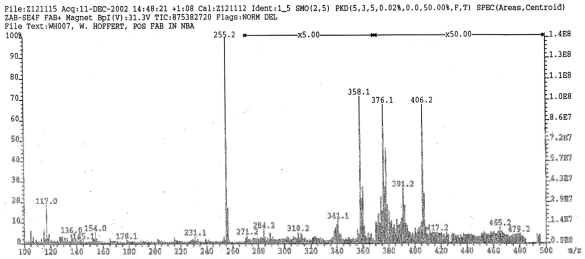


Figure 3. FAB+ Mass Spectroscopy

Elemental Analysis

The first analysis that actually confirmed the existence of a new compound was the elemental analysis obtained from Quantitative Technologies Inc. The percentage of the elements Carbon, Hydrogen, and Nitrogen were analyzed by this method and they were compared to the expected percentages of Carbon, Hydrogen, and Nitrogen the molecule should contain. The calculated percentages based on a Cr(II) complex were 44.57% Carbon, 8.01% Hydrogen, and 18.79% Nitrogen. The actual percentages were found to be 39.98% Carbon, 8.39% Hydrogen, and 12.87% Nitrogen. These percentages did not match the theoretical percentages but with 1.5 H_2O molecules and an OH^- added to the structure ($CrC_{14}H_{34}N_4Cl_2O_{2.5}$ = 421.35g/mol) the results were 39.9% Carbon, 8.13% Hydrogen, and 13.3% nitrogen which matched to 0.4%. This showed that the complex had acquired some impurities (namely O_2) in the structure that should not have been present in the Nitrogen environment of the glove box. While unexpected and unverified this was the first indication that oxygen had somehow contaminated the reaction and oxidized the Cr(II).

Infrared Spectroscopy

The infrared spectroscopy data that was gathered in the McPherson College facilities using a KBr pellet also pointed to the contamination of the product with oxygen. Scanning from 400 to 4000 Wavenumbers showed peaks at 3449 cm^{-1} indicating H_2O/OH^-, 2917 cm^{-1} indicating C-H stretches, and at 1663 cm^{-1} which can be assigned to a C-N stretch. The coordinated nitrogen on Cr(III) have been reported as having absorption bands in the 1000-1040 cm^{-1} range. The spectrum exhibits several peaks between 1016-1072 cm^{-1}, which may be attributed to the Cr(III)-N stretch (Prasad, *et at,* 2002).

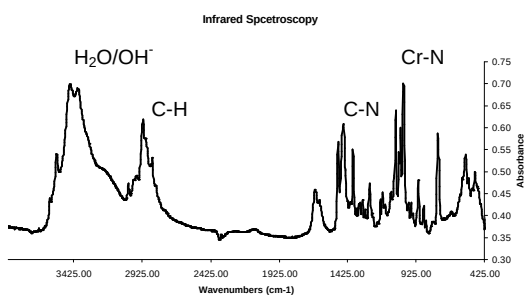


Figure 5. IR Spectrum of [Cr**(1)**ClOH]Cl • 1.5H_2O

UV-Visible Spectroscopy

UV-Vis Spectroscopy was performed with a quartz crystal cuvett from a range of 900nm to 250nm. The complex was a blue color in an acetonitrile solution. Three absorption bands were present with the greatest band occurring at λ_{max} =583nm (ε = 65.8 L/cm•mol), a secondary peak at 431nm (ε = 34.8 L/cm•mol) and a very small peak at approximately 369nm (ε = 17 L/cm•mol). A drop of HCl was added to the solution of complex and an immediate color change (from blue to pink) was observed. Cr(III)[**(1)**ClOH]Cl + HCl ? Cr(III)[**(1)**Cl_2]Cl. This solution only expressed two noticeable absorption bands with the strongest occurring at λ_{max} = 546nm (ε = 59 L/cm•mol) and the weaker band occurring at 416nm (ε = 35 L/cm•mol). It has been reported that Cr(III) tetraazamacrocyclic compounds exhibit bands from 598-583, 389-382, and 344-340 nm these bands are consistent with a distorted octahedral geometry. This closely resembles my results and may be assigned to the following transitions $^4B_{1g}$? $^4E_{g(a)}$, $^4B_{1g}$? $^4E_{g(B)}$, and $^4B_{1g}$? $^4A_{2g}$ respectively (Prasad, *et al*, 2002).

It is theorized that upon the addition of acid the hydroxide group bound to the complex is protenated by the acid transforming it from OH^- to H_2O (a better leaving group). The leaving group has significant influence on the rate of a reaction, with good leaving groups (H_2O for example) increasing reaction speeds by as much as 10^5 (Miessler and Tarr 1999). The complex was also stable when left exposed to oxygen overnight, and using $TBACl_6$ to add Cl to the complex yielded a pink color only after the solution had set for an hour in contrast to the addition of HCl, which changed instantly.

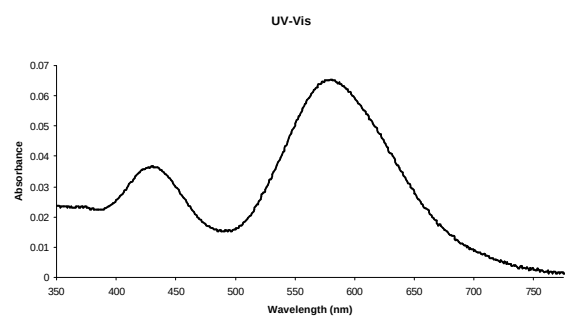


Figure 4. UV-Visible of Cr(III)[**(1)**ClOH]Cl • 1.5H_2O

Magnetic Susceptibility

The magnetic susceptibility of a substance is the measure of magnetism caused by a compound's unpaired electrons (Miessler and Tarr 1999). The magnetic susceptibility readings for the compound were collected in a magnetic susceptibility tube with between 1.72cm and 2.1cm of sample. Three separate tubes were prepared and each tube was measured five times and averaged. Using the data collected and the calculated C_{bal}, a X_g of 1.575×10^{-5} was calculated.

Multiplying this number by the molecular weight yields the magnetic susceptibility per mole of the complex, subtracting the interactions of the metal core electrons, ligands, and ions present in the molecule set X'_M (molar susceptibility) to (0.006569). In compounds where ligands insulate the metal ions the susceptibility

should be dependent on temperature following the Curie Law ($X'=C/T$) (Angelici 1986). A more complex law (Curie-Weiss) exists but in the case of first-row transition metals it is safe to assume that the Curie Law is sufficient. This allows calculation of the effective magnetic moment (u_{eff}) using $u_{eff}=2.83[X'_M(T + \vartheta)]^{1/2}$.

This number was calculated as 3.95 at a temperature of 273K close to the expect value of a Cr(III) complex which usually range between 3.82 to 3.87 at room temperature (Carlin 1986). By applying $u_{eff}=[n(n+2)]^{1/2}$ the number of unpaired electrons was found to be three, the expected results for a Cr(III) complex (Angelici 1986).

The synthesis of a new complex was a success but the reproducibility of our process may be questionable because of the impurity of oxygen from a source not yet fully determined. Several sources of the oxygen may exist including water in the DMF solvent used or O_2 present in the inert gas environment of the glove box. The complexation reaction was run again using an acetonitrile solvent but it was determined that the metal was quite insoluble and the reaction would not take place, however DMF was added to the reaction and more blue crystals were obtained. These crystals have not yet been characterized but they are most likely the same complex. In conclusion, while the insertion of a second or third row transition metal into the ligand was unsuccessful a new Cr(III) complex was created. A future step for this research would be to find an alternate reaction method to create a Mo, V, or W complex or synthesize the Cr(II) complex that was initially expected to result.

ACKNOWLEDGEMENTS

I would like to thank Dr. Hubin for his suggestions, assistance with the attempted synthesis, and lending of materials. I would also like to thank Dr. van Asselt for his help with the writing process and data collection. Finally I would like to thank Wes Hoffert for supplying the Cr(III)[**(1)**ClOH]Cl •1.5H_2O.

LITERATURE CITED

Angelici, Robert J.: Synthesis and Technique In Inorganic Chemistry. University Science Books, Mill Valley, CA. 2nd ed. 48-50.

Carlin, Richard L.; Magnetochemistry. Springer-Verlag Berlin Hidelberg, Germany 1986. pg 63-64.

Hubin, T. J.; McCormick, J. M.; Collinson, S. R.; Buchalova, M.; Perkins, C.M.; Alcock, N. W.; Kahol, P. K.; Raghunathan, A.; Busch, D. H. 2000. New Iron(II) and Manganese(II) Complexes of Two Ultra-Ridgid, Cross-Bridged Tetraazamacrocycles for Catalysis and Biomimicry. Journal of the American Chemical Society. 2512-2522.

Hubin, T. J.; J.M. McCormick; S.R. Collinson; N.W Alcock; N.J. Clase, and D.H. Busch. 1998. Ultra-rigid Cross-Bridged Tetraazamacrocycles and Ligands- The challenge and the solution. Journal of the Chemical Society, Chemical Communication 16: 1675

Miessler, G. L.; Tarr, D. A. 1999. Inorganic Chemistry. 2nd ed. 396-397.

Prasad, R.N.; Mathur, M.; 2002 Synthesis and characterization of Cr(III), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) complexes of 2,12-dimethyl-3-13-di-n-propyl-1,4,11,14-tetraazacycloeicosa-1,2,11,13-tetraene. Journal of the Serbian Chemical Society, 67: 825-832.

Weisman, G. R.; Rogers, M. E.; Wong, E. H.; Jasinsk, J. P.; Paight, E. S. 1990. Cross-Bridged Cyclam. Protenation and Li^+ Complexation in a Diamond-Lattice Cleft. Journal of the American Chemical Society. 8604-8605.