

Exploration and profiling of mixed-substituent Triazacyclohexane complexes of CrCl₃ through synthesis and characterization

Noor Zulfiqar^{1*} & Urooj Hamid²

^{1,2}Department of Chemistry, University of Agriculture, Faisalabad, Pakistan. Email: noorz12340@gmail.com*

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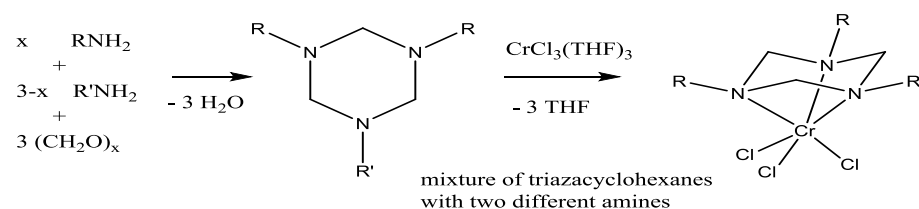
ABSTRACT

A mixture of Triazacyclohexane complexes of CrCl₃ with two different amines has been prepared. The complexes with EtO(CH₂)₃NH₂ and Octyl(NH₂) have been separated by column chromatography and then identified and characterized the isolated complexes with the help of analytical tools, NMR (including Evans method), UV-Vis and ESI-MS. Used average mass of the complexes to get a yield of 98.2% and the amount of prepared complexes reacting with was 298.40 mg. The prepared mixture was then subjected to the column chromatography and the mixture of two complexes was separated with an amount of 0.1338 g with Octyl(NH₂) and 0.1450g with EtO(CH₂)₃NH₂ and a sufficient amount of formaldehyde such that 0.058 g was also obtained. The above solution was then analyzed by NMR, MS and UV-Vis spectroscopy for the confirmation of the product formed.

Keywords: Triazacyclohexane; CrCl₃; Complexes; THF (Tetrahydrofuran).

1. Introduction

Chromite coordination and organometallic compounds have both been produced using a lot of CrCl₃(THF)₃ as a starting material [1]. It was first described sixty years ago how to make anhydrous CrCl₃, which is insoluble in both water and organic solvents. It was originally extracted using THF using the Soxhlet equipment and Zn dust. The preparation of anhydrous CrCl₃, on the other hand, is a risky and time-consuming procedure that involves treating Cr₂O₃·xH₂O with CCl₄ at 630°C, creating the very lethal gas phosgene. As a result, it is costly. Another process was described in which anhydrous- CrCl₃ was created by the reaction of CrCl₃·6H₂O with excess ThionylChloride (SOCl₂) [2]. In this procedure, a distinct type of hygroscopic CrCl₃ was generated, and by simply adding THF, CrCl₃(THF)₃ could be formed [3]. The utmost convenient as well as attractive technique is the reaction of CrCl₃·6H₂O with the excess of Me₃SiCl in THF which results in deposition of the CrCl₃(THF)₃ beside alongside formation of by products like HCl and Me₃SiOSiMe₃ i.e, (CrCl₃·6H₂O + 12 Me₃SiCl → CrCl₃(THF)₃ + 12 HCl + 6 Me₃SiOSiMe₃). The excess Me₃SiCl (~60 equiv/Cr) is necessary to add in order to obtain a completely anhydrous CrCl₃(THF)₃ [4]. On the other hand (for example, when 25 equiv. of the Me₃SiCl/Cr was added in accordance to the literature), the hydrated CrCl₃(THF)₂(H₂O) is formed which was speciously sold as the CrCl₃(THF)₃ in the past [5]. The objective of this work is to prepare Triazacyclohexane complexes of CrCl₃ with two different amines, one with further functionality and one without, and isolation of pure complexes by column separation with full characterisation of one or both of the mixed-substituent complexes. The substituent's to be added are EtO(CH₂)₃NH₂ and Octyl(NH₂). The mixture of the two complexes is obtained by the following reaction;

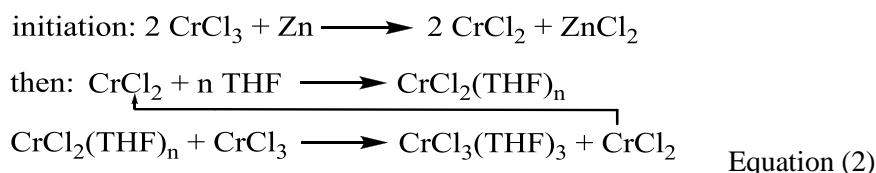


Equation (1)

2. Materials and Methods

2.1. Experimental (or Theoretical)

Due to its labile THF ligands and high solubility in comparison to insoluble anhydrous CrCl_3 , the THF adduct of CrCl_3 is a fantastic starting material for coordination chemistry of chromium. In contrast to the inert CrCl_3 , the product's higher reactivity renders it air-sensitive. Dissolution of CrCl_3 in THF is achieved by catalytic reduction to the much more soluble CrCl_2 and re-oxidation by more CrCl_3 as shown in the following equations:



Approximately 0.1g of Zn dust and 10g of anhydrous CrCl_3 (60mmol) were weighed into a 250ml Schlenk flask, which was then evacuated, dried using a heat source, and replaced with N_2 . 50ml of dry THF was added, degassed several times, and then refilled with N_2 . The mixture was mixed for at least a day, until a thick paste arose, and it was then set aside for the next week. Under vacuum, the solvent was drawn out of the container and into a solvent trap. In order to get a deep purple solution with some solid still present, dried CH_2Cl_2 was introduced. After weighing the empty Schlenk flask with stopper and noting the weight, the solution was filtered into a subsequent 250ml Schlenk flask. The solvent was taken out into a liquid nitrogen trapping while under vacuum, and the purple solid leftover was sterilized with dry Et_2O before being dried in vacuum. The yield was then calculated by recording the weight of the product that was produced.

2.2. Preparation of Mixture of Triazacyclohexanes

Weighed out a mixture of about 1 mmol of the two amines exactly, diluted with 10 ml of toluene and added one equivalent of paraformaldehyde per total amine. The mixture was stirred and then left until the following week. Any water droplets formed were removed by pipette and the toluene solution was distilled first as azeotrope, then pure toluene and checked the temperature of distilling liquids. When no more toluene distills the remaining solvent was pumped off at the high vacuum line. The residue was dissolved in little petroleum ether (40-60C) and any solids filtered off through a plug of MgSO_4 into another small round-bottom flask after weighing empty flask before use and concentrated in portions with solvent removal on the rotary evaporator as necessary followed by high vacuum and warming to 50 °C for 30 min. Weighed the flask again to obtain the yield. Characterised the product by NMR by transferring and dissolving all the product in CDCl_3 and ESI-MS (drop of NMR solution in MS vial filled with MeCN). Calculated the required amount of 1eq of $\text{CrCl}_3(\text{THF})_3$ per triazacyclohexane.

2.3. Preparation of Complexes

A demonstrator weighed out a sufficient amount of $\text{CrCl}_3(\text{THF})_3$ in a glovebox in 1S. Added dry DCM to dissolve the $\text{CrCl}_3(\text{THF})_3$ to give a deep purple solution, added the contents in NMR tube and left for 1hr with occasional swirling. Filtered the mixture, if not fully dissolved, and continue with the solution. DCM was used to pass the solution through a silica column. Collecting the purple fractions of the separated complexes, letting the solvent evaporate in an open vial within the fume hood, and then washing the residue with a little amount of Et_2O (after

crystals have been submitted) and dried in vacuole. When no more purple fractions elute with DCM, added increasing amounts of MeCN (e.g. 2:1, then 1:2 of DCM:MeCN, then pure MeCN). Purpled complex remained on the column, then try to adding an amine, e.g. $i\text{BuNH}_2$ to the MeCN [6]. The different fractions were checked by ESI-MS. Recorded the isolated yield of all fractions.

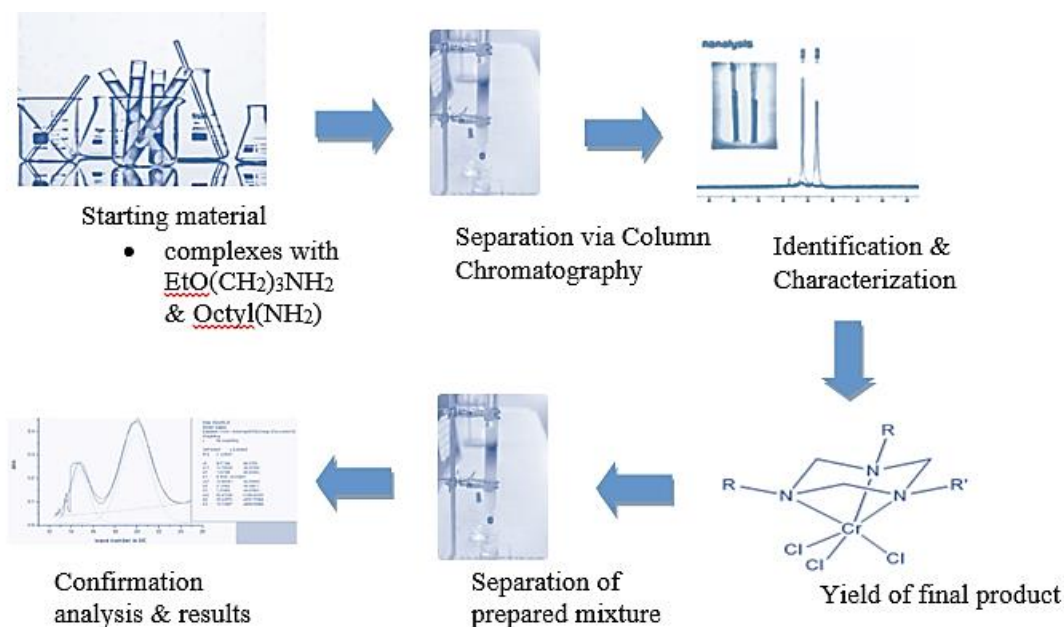


Figure 1. Synthesis of mixed-substituent Triazacyclohexane complexes of CrCl_3

3. Results and Discussion

3.1. UV-Visible Analysis

The product was further introduced for the UV-vis spectroscopy;

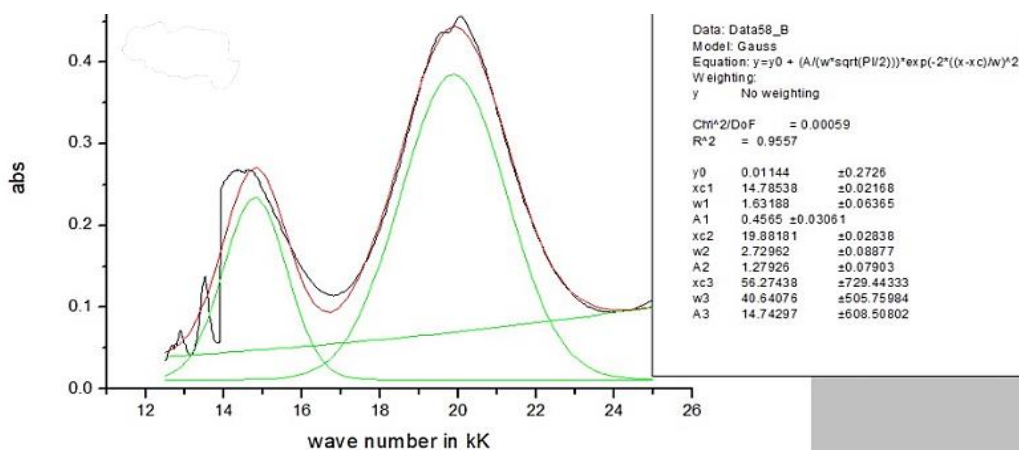


Figure 2. UV-vis spectra for the product obtained

The UV-Visible spectrum of deuterated triazacyclohexane complexes revealed the typical absorbance peak of ligands as shown in Figure 2. The peak around 505 cm^{-1} clearly indicate the benzyl ligand, while this peak shows the co-ordination of chromium ligands in triazacyclohexane complex. The peak at 505 shifted towards high wave length due to the equivalent bands of chromium. The complex demonstrates the characteristic signals at 608 and 729 cm^{-1} that exhibited the confirmation for the formation of triazacyclohexane product [7].

3.2. NMR Analysis

The product formed was sent for the $H^1 + C^{13}$ NMR and the following results were obtained

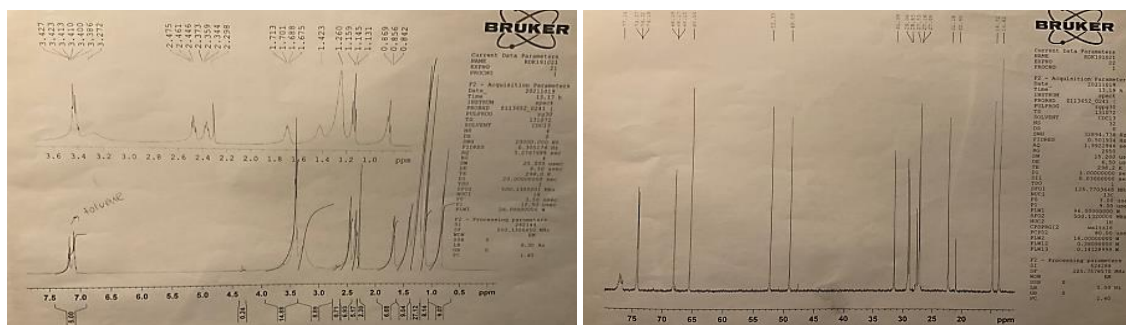


Figure 3. NMR spectra for the product obtained

Table 1. The peaks in the spectra are characterised as follows below table. Using the average masses of the complexes, the product yield was 98.2%

| Node | Shift | Comment (ppm rel. to TMS) |
|------|-------|---|
| CH2 | 3.43 | methylene 2 alpha -N(C)C |
| CH2 | 3.43 | methylene 2 alpha -N(C)C |
| CH2 | 3.43 | methylene 2 alpha -N(C)C |
| CH2 | 2.36 | methylene 1 alpha -N(C)C |
| CH2 | 1.39 | methylene 1 beta -C 1 beta -N(C)C |
| CH2 | 1.29 | methylene 1 beta -C |
| CH2 | 1.29 | methylene 1 beta -C |
| CH2 | 1.29 | methylene 1 beta -C |
| CH2 | 1.29 | methylene 1 beta -C |
| CH2 | 1.29 | methylene 1 beta -C |
| CH2 | 1.29 | methylene 1 beta -C |
| CH2 | 1.55 | methylene 1 beta -C |
| CH2 | 2.65 | methylene 1 alpha -N 1 beta -C |
| NH2 | 2.0 | amine |
| CH2 | 2.53 | methylene 1 alpha -N(C)C 1 beta -O-C |
| CH2 | 3.47 | methylene 1 alpha -O-C 1 beta -N(C)C |
| CH2 | 3.37 | methylene 1 alpha -O-C 1 beta -C |
| CH2 | 1.72 | methylene 1 beta -O-C |
| CH2 | 2.65 | methylene 1 beta -N 1 alpha -N 1 beta -C |
| NH2 | 2.0 | amine |
| CH2 | 2.53 | methylene 1 alpha -N(C)C 1 beta -O-C |
| CH2 | 3.47 | methylene 1 alpha -O-C 1 beta -N(C)C |
| CH2 | 3.37 | methylene 1 alpha -O-C 1 beta -C |
| CH2 | 1.72 | methylene 1 beta -O-C 1 beta -N |
| CH2 | 2.65 | methylene 1 alpha -N 1 beta -C |
| NH2 | 2.0 | amine |

3.3. Column chromatography and the mass spectroscopy analysis

The mixture was then subjected to the column chromatography for isolation and to the mass spectroscopy for the analysis. The following results were obtained;

Table 2. Column chromatography and MS results and discussion

| Column 1 | Column 2 (band 3 from column 1 further isolation) | Column 3 (band 1 from column 1 further isolation) |
|---|--|--|
| Band 1 (DCM-eluent) Strong purple color product | Band 1 (DCM) Dark purple color product Mass spectroscopy suggests that it's a mixture of compounds | Band 1 (DCM) Dark purple color product Almost no product |
| Band 2 (DCM) Light purple color product possible run off | Band 2 (DCM) Very clear purple color runoff and showed no mass spectra | Band 2 (DCM) Separated very slowly, very narrow band and large amount of product |
| Band 3 (2:1, DCM:MeCN) Dark purple color product possibly mixture of non-symmetrical compounds | Band 3 (2:1, DCM:MeCN) Dark color very close in spacing to band 4 | Band 3 DCM:MeCN) Dark purple color indicating a good amount of product 2 octyl groups and 1 ether is present means unsymmetrical product |
| Band 4 (2:1, DCM:MeCN) Light purple color product run off | Band 4 (2:1, DCM:MeCN) Dark purple color and close spacing to band 3 indicating symmetrical (EtOpr) ₃ THFCr ₃ complex | Band 4 No band |

4. Conclusions

This technique for the preparation of mixture of triazacyclohexane complexes of CrCl₃ with two different amines was found to be effective as it contributed in the development of a wide range of unsymmetrical amines. This mixture was then separated by the column chromatography and further analysed by NMR, MS and UV-Visible techniques which confirmed the formation of the product. The yield of this reaction was 98.2%.

5. Limitations of the Study

The exploration and profiling of mixed-substituent triazacyclohexane complexes of CrCl₃ through synthesis and characterization faced challenges in terms of synthetic difficulties, sensitivity to air and moisture, potential structural isomerism, limited characterization techniques, diverse reactivity, lack of comparative data, applicability, and practicality.

Declarations

Source of Funding

This study did not receive any grant from funding agencies in the public or not-for-profit sectors.

Conflict of Interest

The authors declare that they have no conflict of interest.

Consent for Publication

The authors declare that they consented to the publication of this study.

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