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14. ABSTRACT

Several novel ligands and complexes (including mononuclear,binuclear, and trinuclear) were synthesized and characterized. All ligands and complexes were characterized by elemental analysis, UV-visible, 1H NMR, and EPR spectroscopy, and cyclic voltammetry, where appropriate. Photocatalytic studies were carried out in acidified acetonitrile. Initial studies were also carried out with water oxidation catalysts (WOCs) in order to generate O2 and H+ ions in aqueous media. Hydrogen was not generated on photolysis of a novel mixed-metal ruthenium(II)-cobalt(II) complex, Ru(bpy)2(tbtp)Co(dmgBF2)2(H2O)](PF6)2•5H2O in acidic acetonitrile solution; while oxygen was produced in water on photolysis in the presence of a WOC, Na6[Bi2Co4(H2O)2W16O58]•65H2O, and [Ru(bpy)3]Cl2. Electrosynthetic studies involving Co(II) and Ni(II) complexes proved that H2 was produced on several electrodes in aqueous media.

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Front matter

Abstract: Several novel ligands and complexes (including mononuclear, binuclear, and trinuclear) were synthesized and characterized. All ligands and complexes were characterized by elemental analysis, UV-visible, ^1H NMR, and EPR spectroscopy, and cyclic voltammetry, where appropriate. Photocatalytic studies were carried out in acidified acetonitrile. Initial studies were also carried out with water oxidation catalysts (WOCs) in order to generate O_2 and H^+ ions in aqueous media. Hydrogen was not generated on photolysis of a novel mixed-metal ruthenium(II)-cobalt(II) complex, $Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$ in acidic acetonitrile solution; while oxygen was produced in water on photolysis in the presence of a WOC, $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}] \bullet 65H_2O$, and $[Ru(bpy)_3]Cl_2$. Electrosynthetic studies involving Co(II) and Ni(II) complexes proved that H_2 was produced on several electrodes in aqueous media.

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Tasks for The University of Southern Mississippi's Team

Task 1: To carry out the methodology as depicted in the proposal

Task 2: Joint manuscript based on results from Task 1 will be submitted for publication in peer-reviewed journals.

Task 1: To carry out the methodology as depicted in the proposal.

Production of hydrogen with ruthenium(II)-cobalt(II) photocatalysts

I. Background and Significance

The production of hydrogen on a large scale from renewable solar energy with inexpensive catalysts is an ideal method for sustainable energy production,[2-7] and has attracted extensive attention during recent decades. Although heterogeneous photocatalysis by multiple components has been extensively studied, there have been relatively few reports on homogeneous catalysis of light-driven hydrogen production by transition metal complexes before 2000.[8-12] In most cases, either with hetero- or homogeneous catalyst systems, noble metal-based (Pt, Pd, Rh, *etc.*) compounds were used as catalysts.[13] Hydrogen production through the reduction of water appears to be a convenient solution for long-term storage of renewable energy. However, due to the high cost of these metals, there is a search for viable hydrogen production catalysts based on cheap and abundant first-row transition metals.[14] Homogeneous catalyst systems based on first-row transition metals for photochemical hydrogen production have been scarcely reported in the last century, but recently, increasing attention has been focused on the use of non-precious metal-based homogenous catalysis.[15-25]

Photocatalytic systems with cobaloxime-containing complexes as catalysts.

There have been reports of some cobaloxime-containing complexes that are efficient electrocatalysts for hydrogen evolution.[26-30] Lehn and co-workers pioneered the first studies on homogeneous photogeneration of hydrogen using $[Co(dmgH)_2(OH_2)_2]$ (where $dmgH^-$ = dimethylglyoximato) as a catalyst with $[Ru(bpy)_3]^{2+}$ as photosensitizer and triethanolamine (TEOA) as a sacrificial electron donor in a DMF solution.[10] The turnover number (TON) based on the cobaloxime was reported to be 16 in a one hour irradiation. Addition of 6 to 15 equivalents of the $dmgH_2$ ligand was found to be necessary to inhibit ligand dissociation and to replace any hydrogenated ligand formed by side reactions. It was found that dissolution of CO_2 in the reaction solution resulted in an increase of the hydrogen production efficiency about twice that observed in the absence of CO_2. This increase may be mainly a pH effect since CO_2 dissolution was thought to cause a decrease in the apparent pH of the medium.[10]

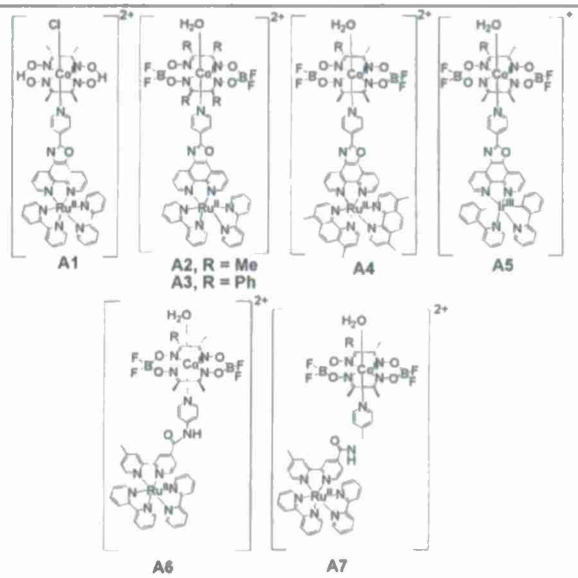


Figure 1. A series of sensitizer-cobaloxime conjugates.

Fontecave, Artero, *et al.*[16,17] have developed a series of mixed-metal binuclear ruthenium(II)-cobalt(II) and iridium(III)-cobalt(II) photocatalysts by replacing one of the axial H_2O ligands of the cobaloxime with pyridine-functionalized ruthenium(II)-polypyridine complexes (A1-A5, Figure 1) for photochemical hydrogen generation from $[Et_3NH]BF_4$. The mixed-metal binuclear ruthenium(II)-cobalt(II) dyads are more efficient in hydrogen production than their corresponding multi-component systems under the same conditions. Complex A2 containing the BF_2-bridged Co(II) center is superior to A1 with the H-bridged Co(III) center because the Co(II) state in A2 is more easily reducible and more resistant towards the side reactions, such as acidic hydrolysis and hydrogenation.[16,17] The supramolecular photocatalyst A2 with the $[Ru(bpy)_2(L\text{-}pyr)]^{2+}$ (L-pyr = (4-pyridine)oxazolo[4,5-f]phenanthroline) unit as photosensitizer performs up to 103 turnovers in the presence of 100 equiv. of both Et_3N and $[Et_3NH]BF_4$ in acetone during a 15 h irradiation ($\lambda > 350$ nm).[17] In comparison, the maximum turnover for the corresponding iridium(III)–cobalt(II) multi-component system was 165 under the same conditions and the quantum yield of hydrogen was

0.12. In common with the ruthenium(II)–cobalt(II) system reported by Lehn and co-workers,[10] the photocatalytic activity of the dyads decreased by a factor of 1/3 on addition of water to the reaction medium. More recently, uses of cobalt-containing systems have been reported as important as hydrogen producing agents.[23,31-37]

Li *et al.*[38] have studied related heterobinuclear ruthenium(II)-cobalt(II) systems with (A6) and without (A7) linker conjugation in an investigation to determine which of the two compounds were better photocatalysts for the generation of hydrogen under homogeneous conditions. While both complexes were more active than the corresponding multi-component systems, the non-conjugated bridge (A7) exhibited higher activity for hydrogen production.[38] There has only been one report involving osmium(II) in the generation of H_2 from water,[39] where Miyake and co-workers designed and prepared novel diphosphine ligands bearing an $[Os(tpy)_2]^{2+}$ (where tpy = 2,2':6',2"-terpyridine) moiety as a light harvesting unit and found that rhodium complexes including diphosphine ligands bearing an $[Os(tpy)_2]^{2+}$ moiety worked as effective photocatalysts for the production of hydrogen.[39] This is the very first report utilizing an osmium(II) metal center as a photocatalyst for the production of hydrogen.

Also interesting was a report of a water soluble ruthenium(II) compound of an oligomer of bpy (oligo-bpy), which was found to catalyze visible light-induced hydrogen evolution from aqueous media in the presence of colloidal platinum and triethylamine as a sacrificial electron source.[40] Recently, Jacques *et al.*[41] reported an investigation of a new family of cobalt(III) and nickel(II) diimine-dioxime complexes as efficient and stable electrocatalysts for hydrogen evolution from acidic non-aqueous solutions with slightly lower overvoltages and much larger stability towards hydrolysis as compared to previously reported cobaloxime catalysts.[16,17] A mechanistic study was also carried out to show that hydrogen evolution likely proceeded through a bimetallic homolytic pathway. The presence of a proton-exchanging site in the ligand is believed to provide a mechanism for tuning the electrocatalytic potential for hydrogen evolution of the cobalt(III) and nickel(II) diimine-dioxime complexes in response to variations of the acidity of the solution.[41]

Objectives:

The research motivation and long term goals: The development of new photosensitizers for hydrogen production is a challenging problem. Although the ultimate goal is to use water as a feedstock, many potential hydrogen-evolving catalysts are tested for catalytic activity in organic solvents, as they often are not soluble or stable in aqueous media. The motivation for this project is based on an investigation of a new family of cobalt(III) and nickel(II) diimine-dioxime complexes[41] as efficient and stable electrocatalysts for hydrogen evolution from acidified non-aqueous solutions with slightly lower overvoltages and much larger stabilities towards hydrolysis as compared to previously reported cobaloxime catalysts.[16,17] The bridging BF_2 groups in such complexes is believed to increase the stability of the catalysts in acidic solutions.[23] Another motivating factor for this research project is the recent findings by Brewer and co-workers[24,42-44] who reported photophysical and photocatalytic studies involving the use of $Ru^{II}_2Rh^{III}$ trinuclear complexes that exhibited the ability to produce hydrogen from aqueous media. Another is based on a recent report of photocatalytic hydrogen production from water in self-assembled supramolecular iridium(III)–cobalt(II) systems as reported by Jasimuddin *et al.,* where supramolecular photosynthetic systems made up of $[Ir(ppy)_2(bpy)]^+$ and $[Co(bpy)_3]^{2+}$ cores (ppy = 2-phenylpyridinate, and bpy = 2,2'-bipyridine) were used as *in situ* self-assemblies in aqueous media to generate H_2 upon visible light irradiation, where one of the complexes recorded a relatively high turnover number of 20.[45]

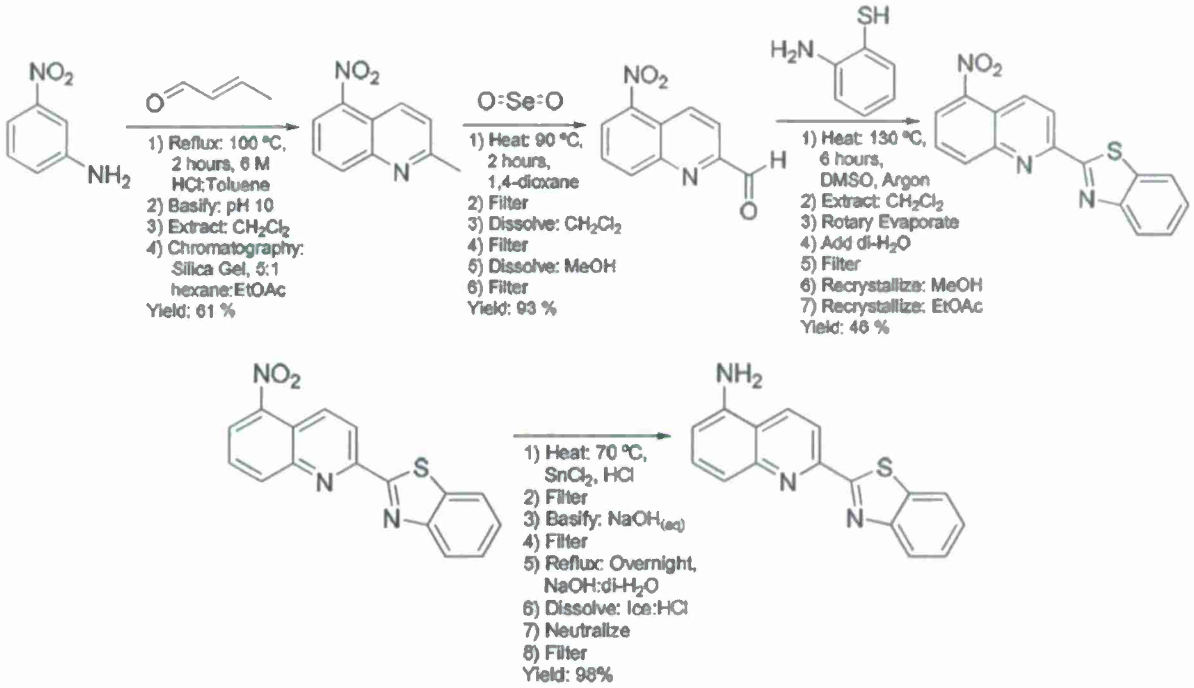
Three important directions are: (a) design of photosensitizers capable of harvesting a broad part of the solar spectrum with high molar extinction coefficients and long lifetime of excited states; (b) improvement of photostability of sensitizers; and (c) development of water and acid stable photocatalysts. The electrocatalytic behavior of proton sources in organic solvents is markedly different from those in aqueous media, and this needs to be addressed to make compounds that have the ability to produce hydrogen via an electrolytic process in acidic aqueous media. Even though some excellent work has been reported by Fihri et al.[16,17] with the use of ruthenium(II)-cobalt(II) compounds as potential photocatalysts, and more recently, a study by Jacques *et al.*,[41] more definitive studies to define the mode of action of new ruthenium(II)-cobalt(II)/cobalt(III)-containing complexes are warranted. In currently published studies,[16,17,41] there is little or no information regarding the performance of the reported compounds for photocatalytic hydrogen production in aqueous media at various pH values or in the presence of a variety of sacrificial reductants. A detailed solution phase X-ray scattering, Raman, EPR and NMR spectroscopic study identifying the key intermediates in this process in aqueous media (before and after electrochemical or irradiation processes) are lacking in all studies as reported by Fontecave and co-workers.[16,17,41] More important, the reported ruthenium(II)-cobalt(II) complexes[16,17] have some limitations, for example, such complexes are not stable in highly acidic aqueous media. Being encouraged by the recent findings of Brewer and co-workers[24,42-44] and Jasimuddin *et al.*,[45] our long term goal is to prepare supramolecular mixed-metal complexes with ruthenium(II) and cobalt(II)/cobalt(III) metal centers (with diimine-dioxime and polypyridines as ligands; along with a novel phosphine-based moiety as a bridging ligand) that possess all of the features that are currently lacking in the reported ruthenium(II)-cobalt(II)complexes,[16,17] are very stable in acidic and weakly aqueous solution, and have the ability to produce hydrogen when photolyzed in aqueous media. Our long term goals are to: (1) synthesize, characterize, and carry out physical studies on mixed-metal complexes with ruthenium(II) and cobalt(II)/cobalt(III) metal centers; (2) carry out an investigative electrocatalytic study in aqueous and non-aqueous media; and (3) carry out investigative mechanistic and photocatalytic studies in aqueous and non-aqueous media. The proposed work for the future will generate water-soluble compounds with mixed-metal complexes with ruthenium(II) and cobalt(II)/cobalt(III) metal centers (as highly charged cations that have bromides, chlorides or nitrates as counter ions) in conjunction with suitable bridging ligands. For photoinduced hydrogen production, photocatalysts with large molar extinction coefficients (to efficiently collect radiant energy) and relatively long excited-state lifetimes (to allow electron-transfer quenching to occur) would be desirable. We will also implement combinatorial synthesis and high-throughput parallel screening techniques for the discovery of novel photocatalysts that can catalyze photoinduced water reduction to yield hydrogen gas. In addition to identifying promising photocatalysts, parallel high-throughput analytical techniques will be utilized in order to give us considerable insight into the mechanisms governing the complex process of photoinduced hydrogen production. Furthermore, it is anticipated that mixed-metal ruthenium(II)-based mixed-metal catalysts should generate hydrogen from an acid source; and our results have confirmed that expectation.

Approach: The results:- Artificial photosynthetic studies with mixed-metal binuclear Ru(II)-Co(II) complexes.

1. Synthesis, characterization, electrosynthetic and photocatalytic studies involving complexes for the production of hydrogen in aqueous media.

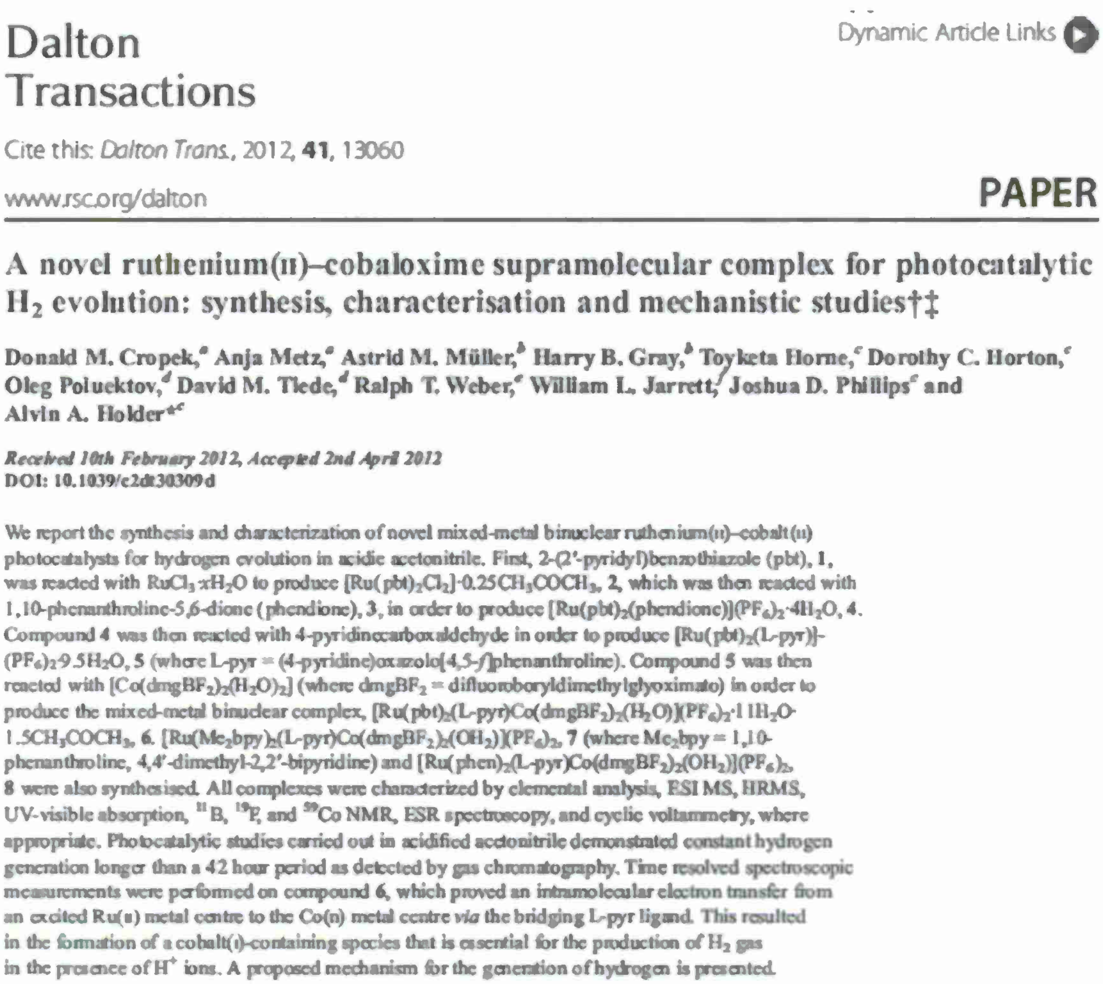
First, I would like to thank my researcher, Mr. Luke Seymour, and the following undergraduate students who helped made this research project and took it to completion: Mr. Stuart Ramsdale, Ms. De'Andra Newton (a summer SURE REU student), Ms. Michelle Gordon (an AGEM summer REU student), Ms. Javelyn Stubbs (an AGEM summer REU student), and Mr. Patrick Taylor.

We are very happy to report the synthesis of the elusive ligand, 2-(5-aminoquinoline)-benzothiazole, which will be utilized by Irene in her future studies with her hydrogenase enzymes. Scheme 1 shows the complete synthesis of 2-(5-aminoquinoline)-benzothiazole as carried out by Mr. Luke Seymour during the funding period. Please see the supplementary files for the full synthetic procedures and characterizations of 2-(5-aminoquinoline)-benzothiazole.



Scheme 1. The complete synthesis of 2-(5-aminoquinoline)-benzothiazole.

Since the last report, we have published our research findings in the peer-reviewed journal, *Dalton Transaction.*[1] Such research findings involved mixed-metal binuclear Ru(II)-Co(II) complexes and $[Co(dmgBF_2)_2(OH_2)_2]$ (where $dmgBF_2$ = difluorboryldimethylglyoximato), with terminal ligands 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (4,4'-Me2phen), and 2-(pyridine-2yl)bezo[*d*]thiazole (pbt); and the bridging ligand 2-pyridin-4-yl-1-oxa-3,7,8-triaza-cyclopenta[l]phenanthrene) (L-pyr).[1] Figure 2 shows the abstract of the publication that arose from our research findings.[1]



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PAPER

A novel ruthenium(II)–cobaloxime supramolecular complex for photocatalytic H_2 evolution: synthesis, characterisation and mechanistic studies†‡

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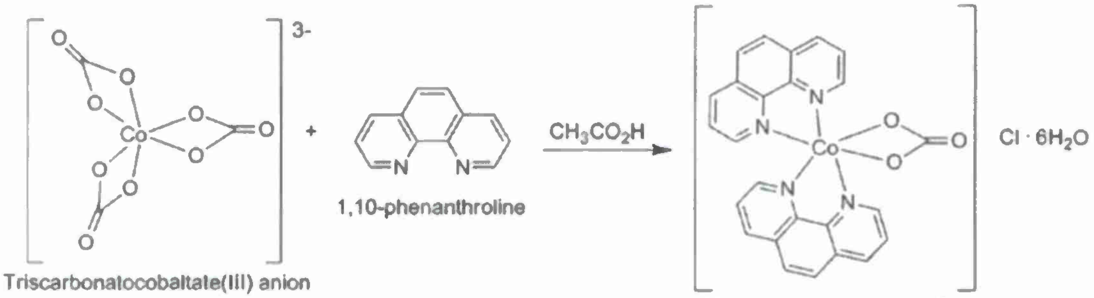
We report the synthesis and characterization of novel mixed-metal binuclear ruthenium(II)–cobalt(II) photocatalysts for hydrogen evolution in acidic acetonitrile. First, 2-(2′-pyridyl)benzothiazole (pbt), 1, was reacted with $RuCl_3 \cdot xH_2O$ to produce $[Ru(pbt)_2Cl_2] \cdot 0.25CH_3COCH_3$, 2, which was then reacted with 1,10-phenanthroline-5,6-dione (phendione), 3, in order to produce $[Ru(pbt)_2(phendione)](PF_6)_2 \cdot 4H_2O$, 4. Compound 4 was then reacted with 4-pyridinecarboxaldehyde in order to produce $[Ru(pbt)_2(L\text{-}pyr)](PF_6)_2 \cdot 9.5H_2O$, 5 (where L-pyr = (4-pyridine)oxazolo[4,5-*f*]phenanthroline). Compound 5 was then reacted with $[Co(dmgBF_2)_2(H_2O)_2]$ (where $dmgBF_2$ = difluoroboryldimethylglyoximato) in order to produce the mixed-metal binuclear complex, $[Ru(pbt)_2(L\text{-}pyr)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 11H_2O \cdot 1.5CH_3COCH_3$, 6. $[Ru(Me_2bpy)_2(L\text{-}pyr)Co(dmgBF_2)_2(OH_2)](PF_6)_2$, 7 (where Me_2bpy = 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine) and $[Ru(phen)_2(L\text{-}pyr)Co(dmgBF_2)_2(OH_2)](PF_6)_2$, 8 were also synthesised. All complexes were characterized by elemental analysis, ESI MS, HRMS, UV-visible absorption, ^{11}B, ^{19}F, and ^{59}Co NMR, ESR spectroscopy, and cyclic voltammetry, where appropriate. Photocatalytic studies carried out in acidified acetonitrile demonstrated constant hydrogen generation longer than a 42 hour period as detected by gas chromatography. Time resolved spectroscopic measurements were performed on compound 6, which proved an intramolecular electron transfer from an excited Ru(II) metal centre to the Co(II) metal centre *via* the bridging L-pyr ligand. This resulted in the formation of a cobalt(I)-containing species that is essential for the production of H_2 gas in the presence of H^+ ions. A proposed mechanism for the generation of hydrogen is presented.

Figure 2. An abstract of the research findings published in Dalton Transactions.[1]

We synthesized several cobalt(III)-containing complexes. The complex $[Co(phen)_2CO_3]Cl \cdot 6H_2O$ 1 was synthesized using the scheme shown below:

Reaction 1: Synthesis of $[Co(phen)_2CO_3]Cl \cdot 6H_2O$

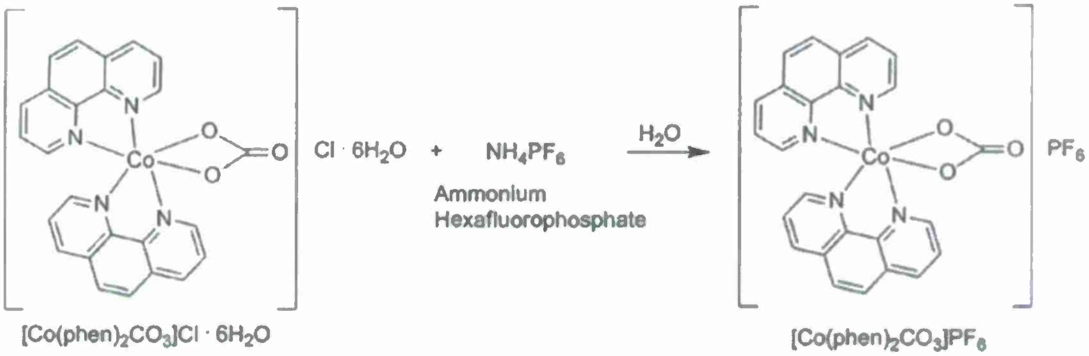
$$KHCO_3 + CoCl_3 \cdot 6H_2O + H_2O_2 \longrightarrow K_3[Co(Co_3)_3]$$



$[Co(phen)_2CO_3]$ Cl · $6H_2O$
1

$[Co(phen)_2CO_3]PF_6$ was synthesized by conversion of the chloride salt into a PF_6^- salt as shown below.

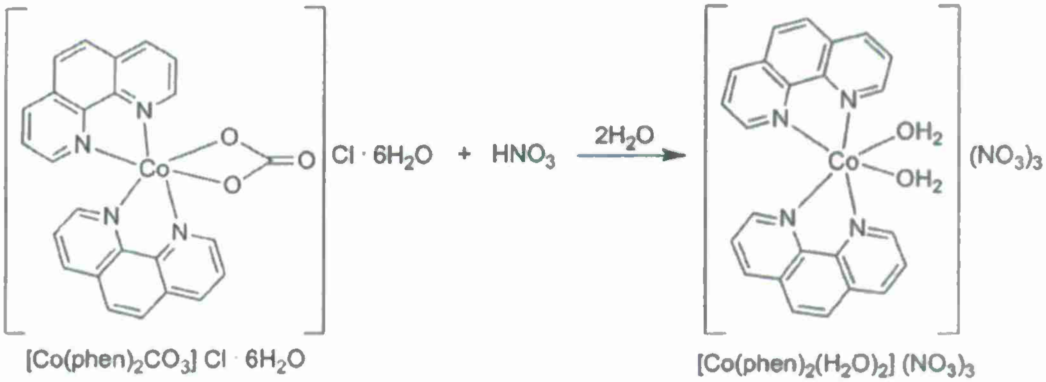
Reaction 2: Synthesis of $[Co(phen)_2CO_3]PF_6$.



A single crystal of $[Co(phen)_2CO_3]Cl \cdot 5H_2O$ was grown by slow evaporation.

$[Co(phen)_2(H_2O)_2](NO_3)_3$ 2 was synthesized by the acid hydrolysis of compound 1 with excess nitric acid as shown in the scheme below:

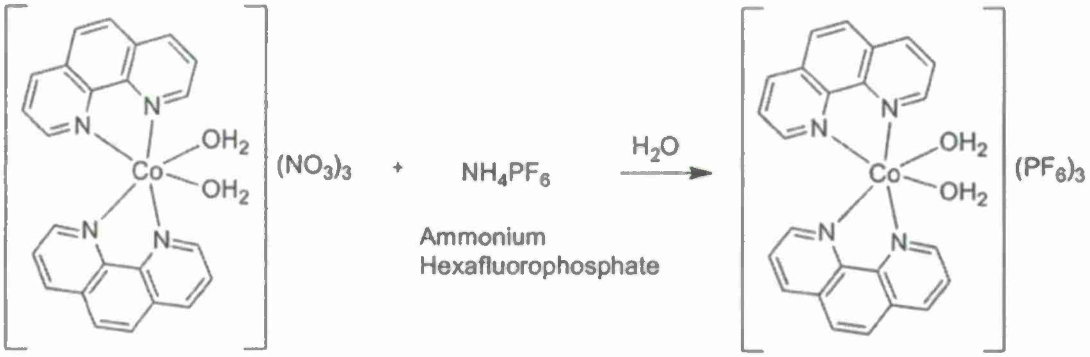
Reaction 3: Synthesis of $Co(phen)_2(H_2O)_2](NO_3)_3$



2

Once more, $[Co(phen)_2(H_2O)_2](PF_6)_3$ was also synthesized as shown in the scheme below:

Reaction 4: Synthesis of $Co(phen)_2(H_2O)_2](PF_6)_3$



$[Co(phen)_2(H_2O)_2]\ (NO_3)_3$ $[Co(phen)_2(H_2O)_2]\ (PF_6)_3$

Syntheses of Complexes

Compounds 1 and 2 were prepared using a procedure as carried out by Holder and his research group. The structural components of the complexes were confirmed by FT IR, ^1H NMR and ^{59}Co NMR, UV-visible, and fluorescence spectroscopies, and X-ray crystallography, where appropriate.

X-ray crystallographic studies

The crystal structure of compound 1 is shown in figure 3, where the carbonate anion and phen ligands are bidentate in nature. The packing diagrams are shown in figures 4 and 5.

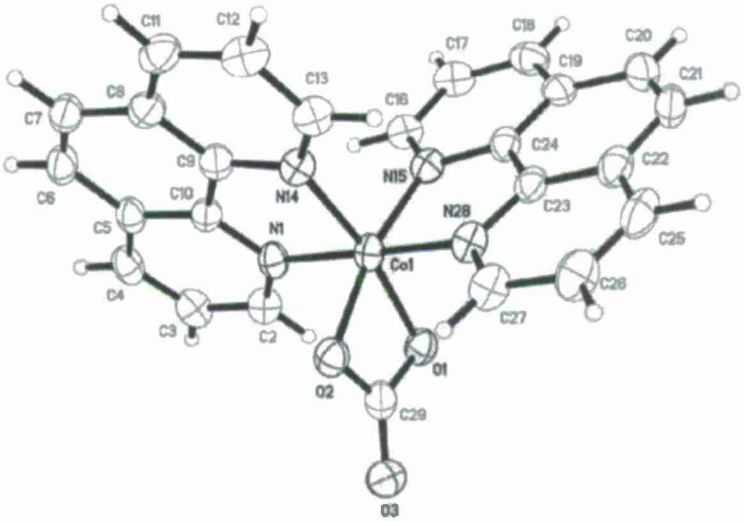


Figure 3. An Ortep diagram of the $[Co(phen)_2CO_3]^+$ cation.

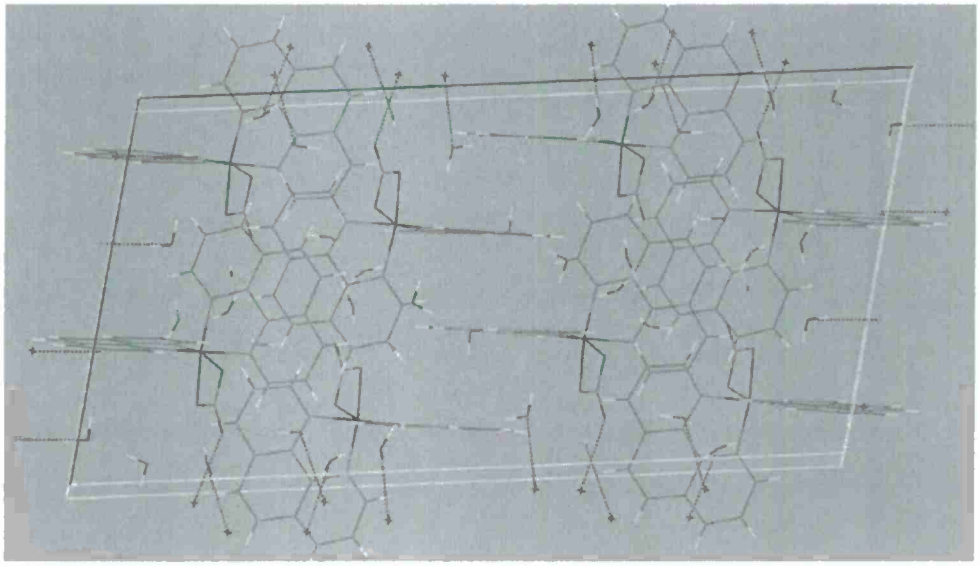


Figure 4. A packing diagram of the $[Co(phen)_2CO_3]^+$ cation.

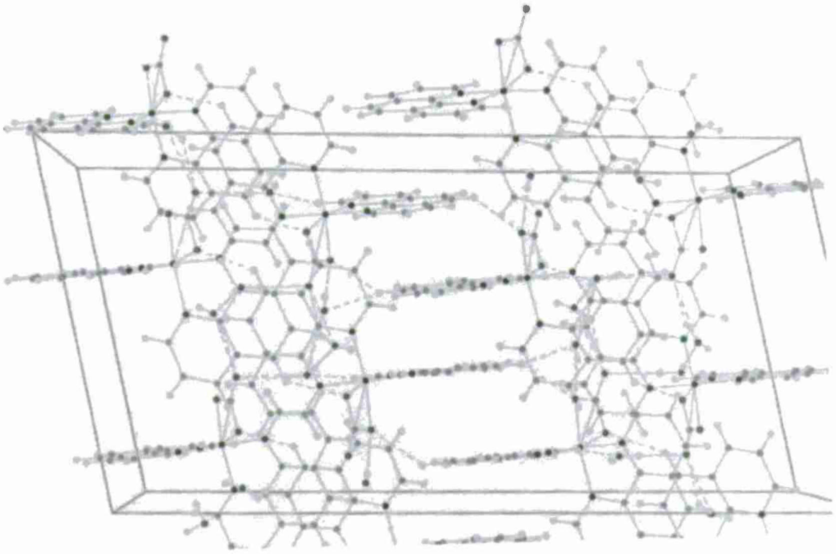


Figure 5. A packing diagram of the $[Co(phen)_2CO_3]^+$ cation.

^1H and ^{59}Co NMR spectral analysis

^1H and ^{59}Co NMR spectra and spectral analysis were acquired on all complexes. Figures 6 and 7 show the ^1H NMR spectra of compounds 1; while Figures 8 and 9 show the ^{59}Co NMR spectra of compounds 1 and 2, while Table 1 shows the respective chemical shifts of the ^{59}Co NMR data for $[Co(phen)_2CO_3]PF_6$ and $Co(phen)_2(H_2O)_2](PF_6)_3$. All the spectra of the compounds showed peaks at δ = 7.0 to 9.5 ppm indicating the presence of aromatic rings from the 1,10-phenanthroline ligand. The shifts of the peaks were based on the different compounds that were attached to the complexes. For all ^{59}Co NMR spectra, all of four complexes showed peaks in the range 7000 - 8000 ppm. These peaks proved the presence of Co(III) as the metal center (Table 1).

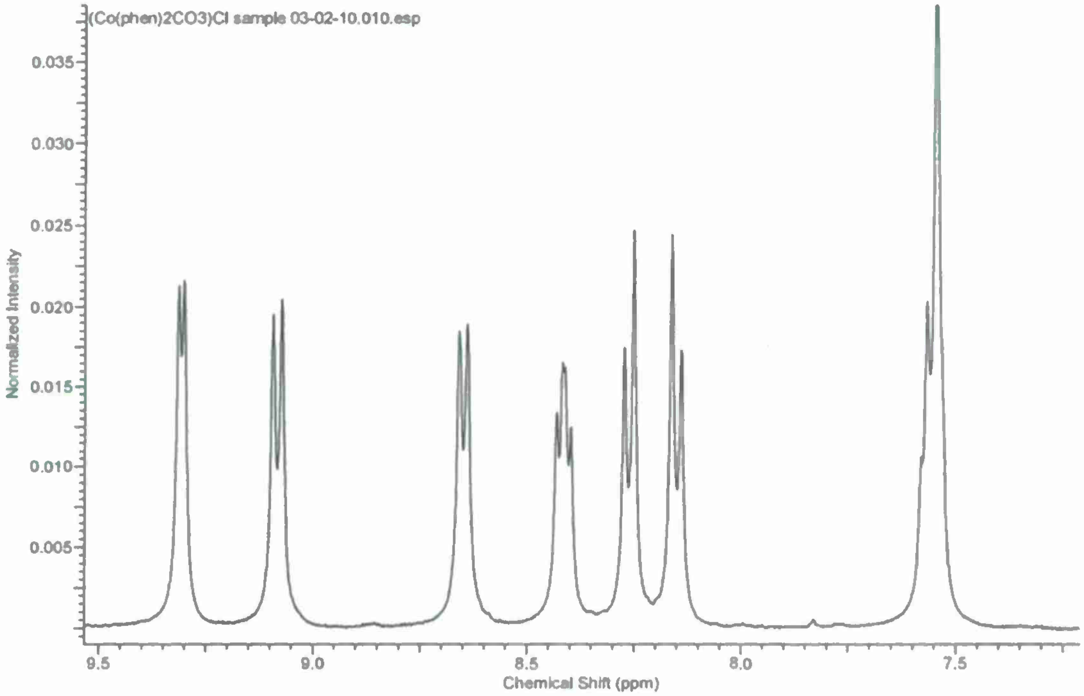


Figure 6. A ${}^{1}H$ NMR spectrum of compound 1 as a powder dissolved in D_2O.

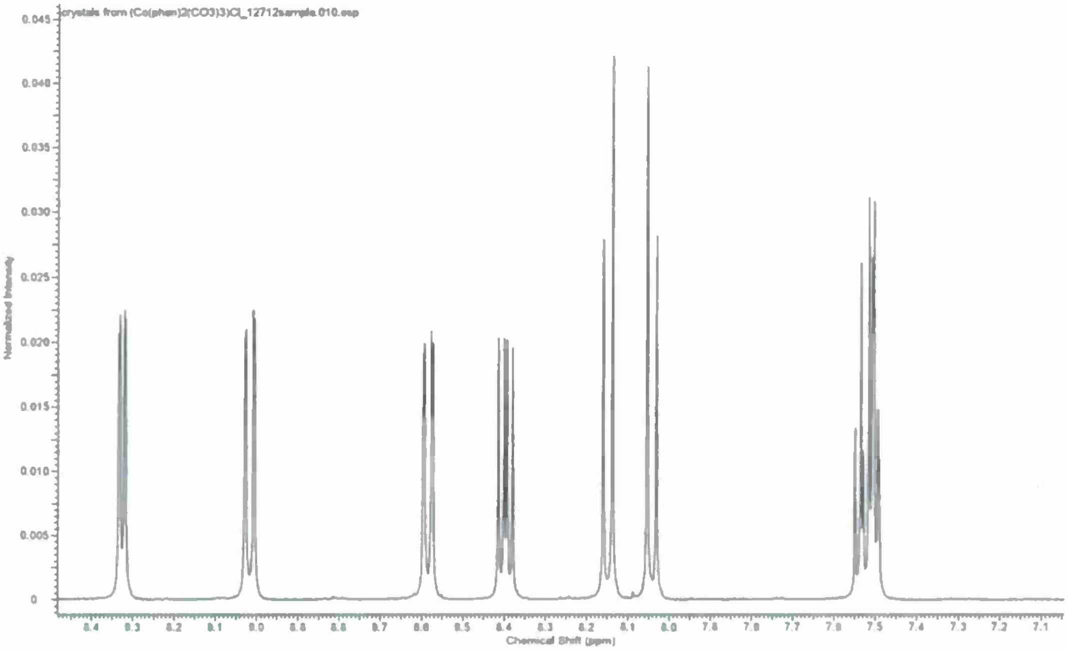


Figure 7. A ${}^{1}H$ NMR spectrum of crystals from compound 1 dissolved in D_2O.

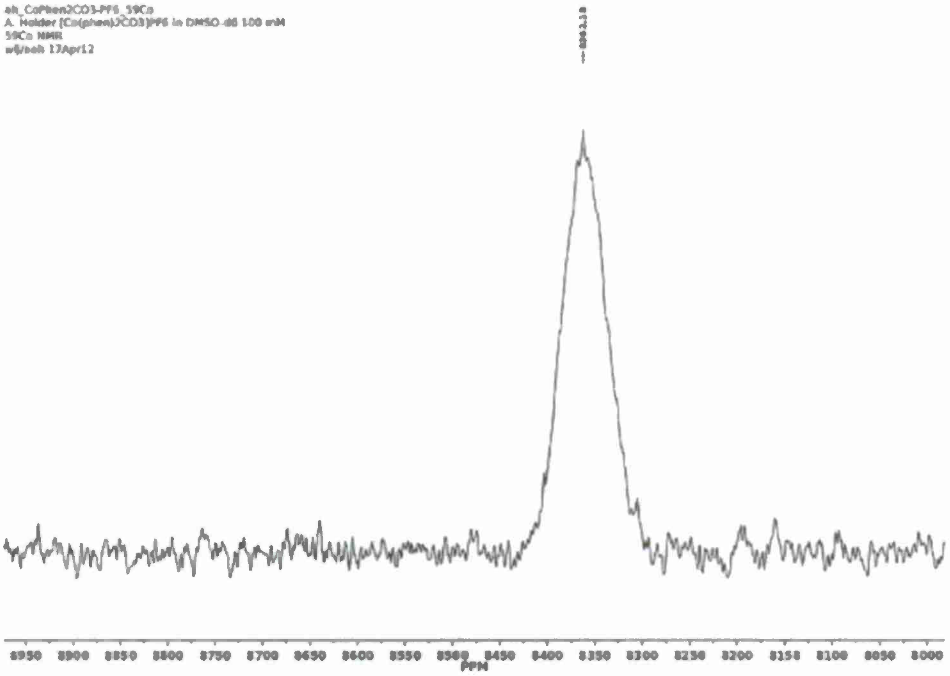


Figure 8. A ^{59}Co NMR spectrum of $[Co(phen)_2CO_3]PF_6$ in DMSO-d$_6$.

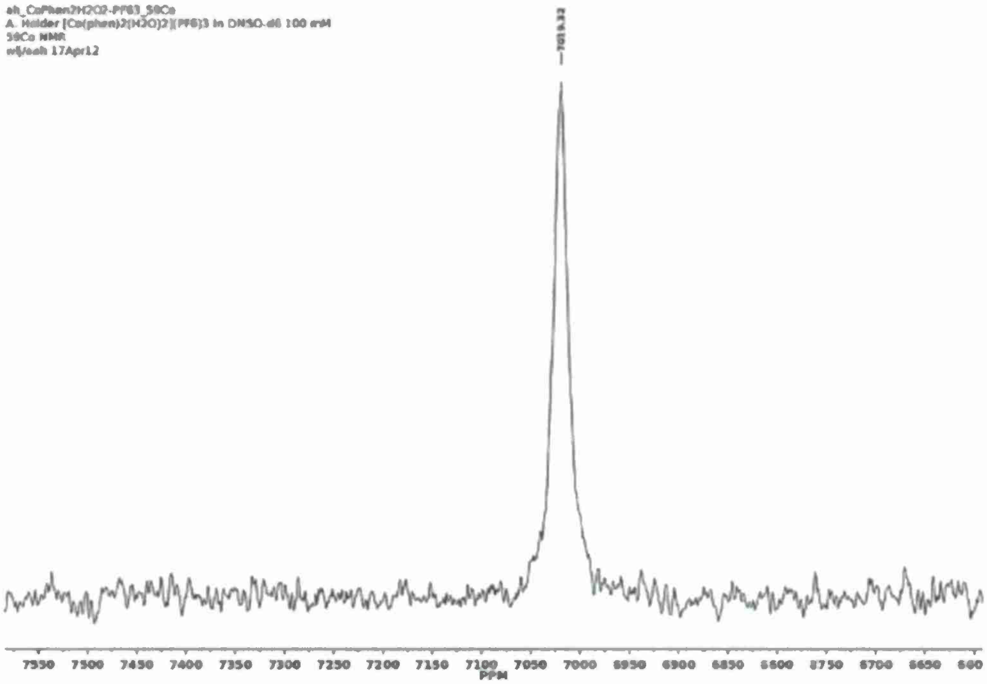
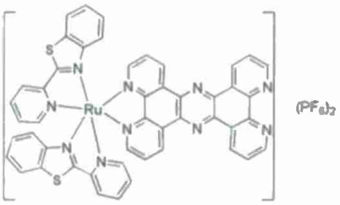


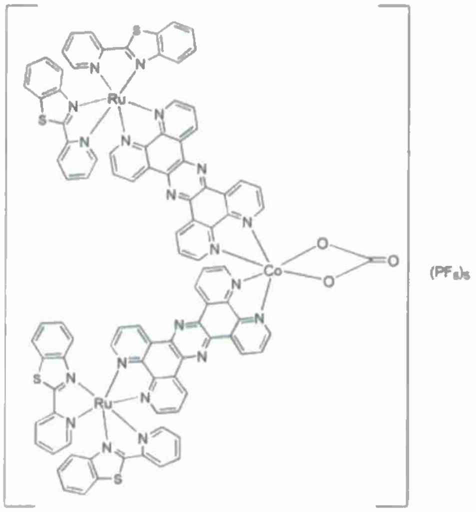
Figure 9. A ^{59}Co NMR spectrum of $[Co(phen)_2(H_2O)_2](PF_6)_3$ in DMSO-d$_6$.

We have synthesized [Ru(pbt)$_2$(tpphz)](PF$_6$)$_2$ 3; then attempted to synthesize compound 4, which is analogous to compound 1, but note, we propose that compound 4 is a mixed-metal trinuclear ruthenium(II)-cobalt(III) complex.



Chemical Formula: $C_{48}H_{28}F_{12}N_{10}P_2RuS_2$
Molecular Weight: 1199.93

3



Chemical Formula: $C_{97}H_{56}CoF_{30}N_{20}O_3P_5Ru_2S_4$
Molecular Weight: 2663.77

4

A ^{59}Co NMR spectrum was acquired for compound 4 in DMSO-d$_6$ (see figure 10). Table 1 shows the ^{59}Co NMR chemical shifts for compounds 1, 2, and 4.

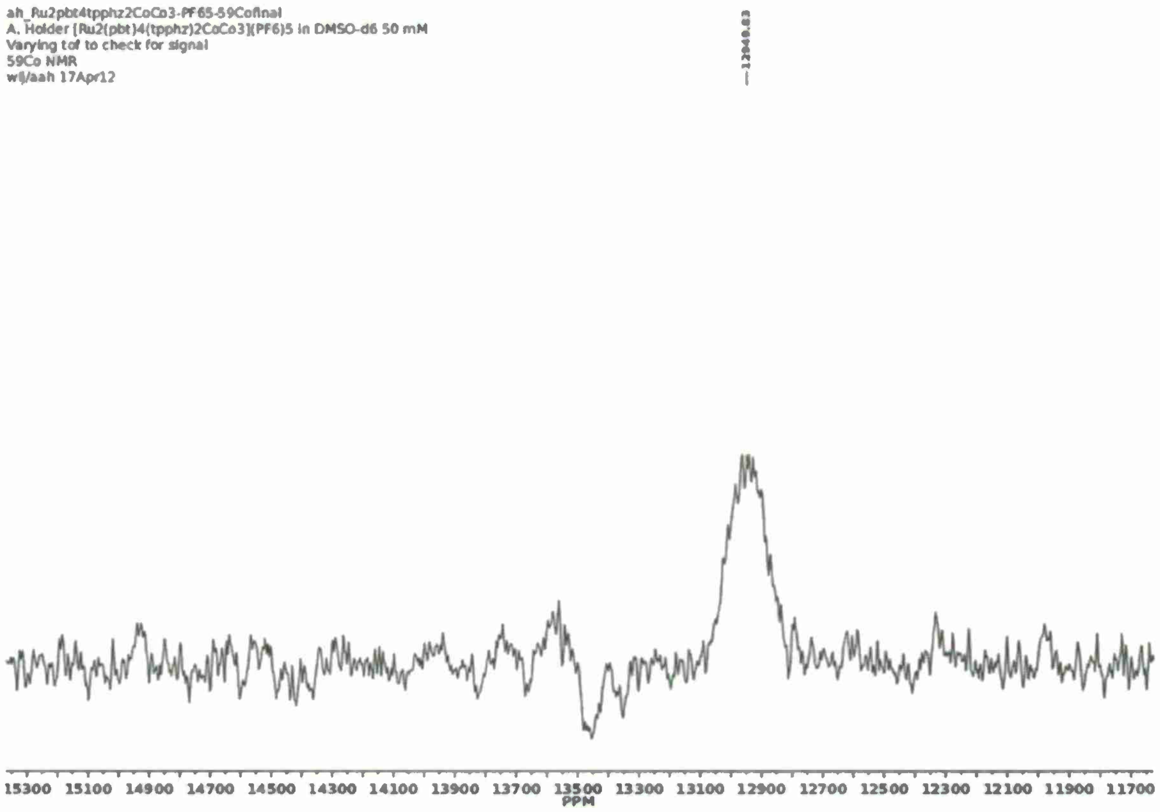


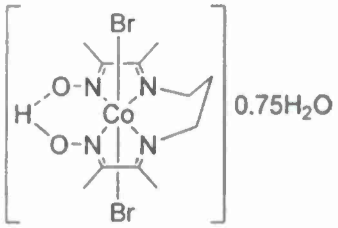
Figure 10. A ^{59}Co NMR spectrum of compound $[Ru_2(pbt)_4(tpphz)_2CoCO_3](PF_6)_5$ 4 in DMSO-d_6.

Table 1: ^{59}Co NMR spectroscopic data of the complexes in DMSO-d_6.

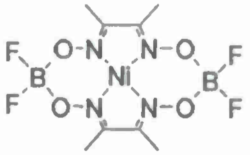
Complexes	δ/ppm
1	8,362.18
2	7,019.32
4	12,949.83

Complexes used for the electrosynthesis of hydrogen in aqueous media

We have synthesized and characterized the following Co(II) and Ni(II complexes, where the Co(II) compound has the ligand, N2N2'-propanediylbis(2,3-butandione 2-imine-3-oxime ((DOH)(DO)pn).



[Co(DOH)(DO)pnBr$_2$]·0.75H$_2$O
Molecular Weight: 471.55



[Ni(dmgBF$_2$)$_2$]
Molecular Weight: 384.51

We were able to synthesize [Co(DOH)(DO)pn(H$_2$O)$_2$](ClO$_4$)$_2$, and were successful in growing a single crystal for X-ray crystallography. Figure 11 shows an Ortep diagram of [Co(DOH)(DO)pn(H$_2$O)$_2$](ClO$_4$)$_2$.

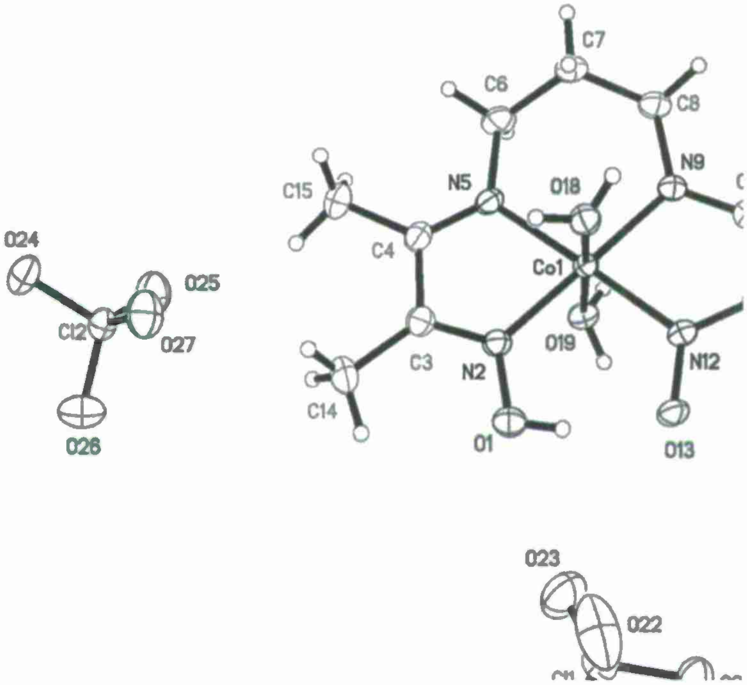
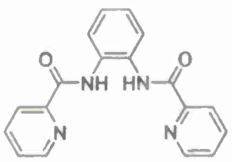


Figure 11. An Ortep diagram of [Co(DOH)(DO)pn(H$_2$O)$_2$](ClO$_4$)$_2$.

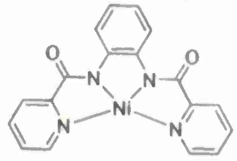
The following ligands and complexes were also synthesized; then the Co(II) and Ni(II) complexes were sent to Anja for electrocatalysis in order to produce H_2 in aqueous media.

bphen



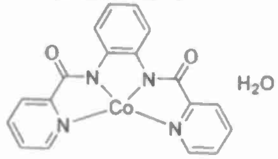
Chemical Formula: $C_{18}H_{14}N_4O_2$
Molecular Weight: 318.33

[Ni(bphen)]

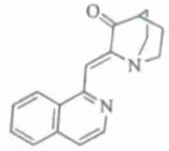


Chemical Formula: $C_{18}H_{12}N_4NiO_2$
Molecular Weight: 375.01

[Co(bphen)].H_2O

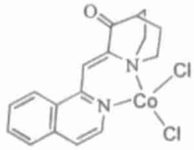


Chemical Formula: $C_{18}H_{14}CoN_4O_3$
Molecular Weight: 393.26



quin

Molecular Weight: 264.32



[Co(quin)Cl_2]

Chemical Formula: $C_{17}H_{18}Cl_2CoN_2O$
Molecular Weight: 394.16

Figure 12 shows a plot of percentage of hydrogen versus time for the production of hydrogen during the electrolysis of each compound on the electrode (see Anja for full experimental details).

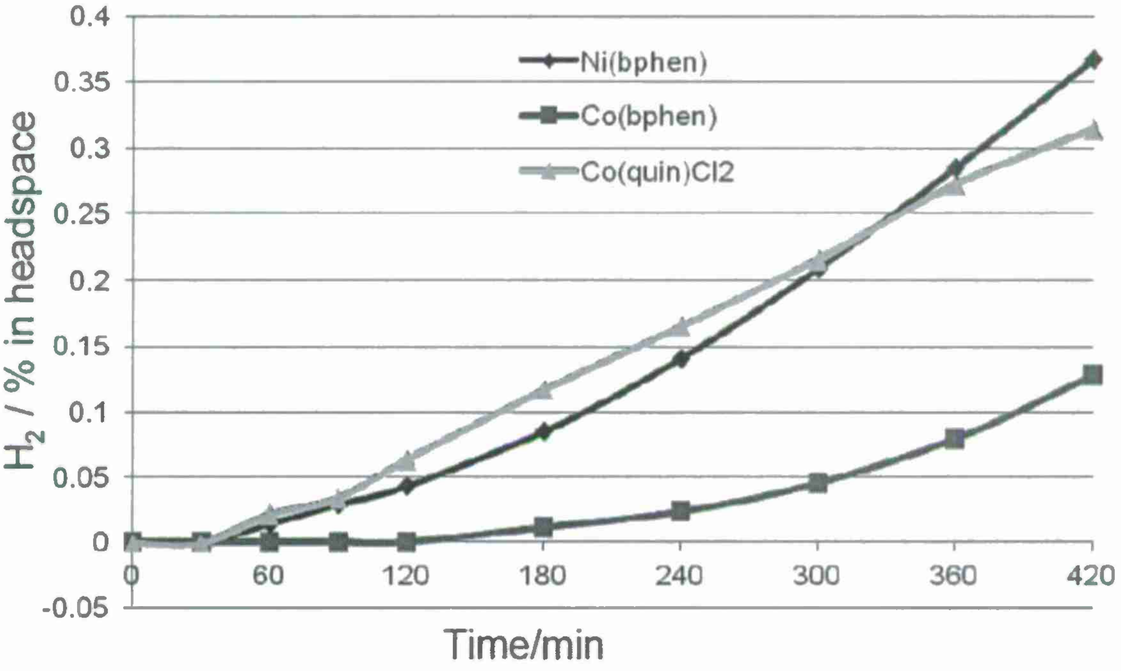
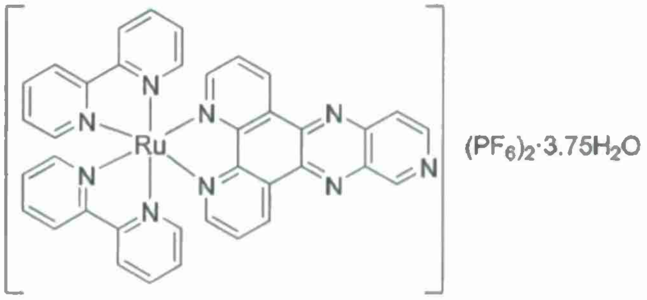
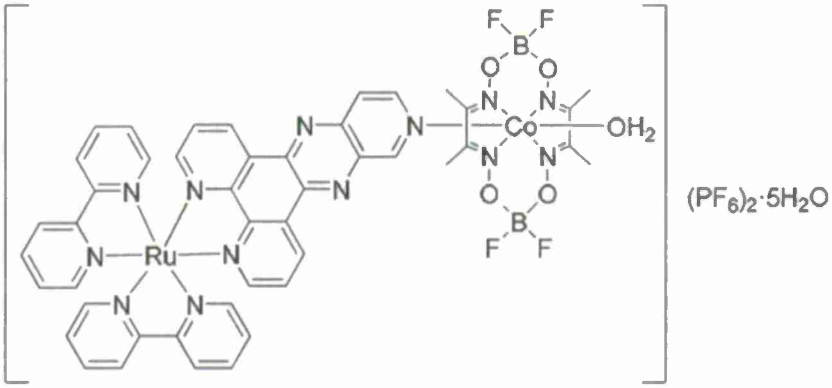


Figure 12. A plot of percentage of hydrogen versus time for the production of hydrogen, A bias of -0.79 versus NHE at pH 6.2. Overpotential = 420 mV.

We were also successful in synthesizing $[Ru(bpy)_2(tbtp)](PF_6)_2 \cdot 3.75H_2O$ (where tbtp = 4,5,9,11,14-pentaaza-benzo[*b*]triphenylene) and $[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$. Please see the supplemental file for full synthetic procedures and characterizations. Studies involving $[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$ as a novel photocatalyst was carried out by Anja, who found out that hardly any hydrogen was produced in acidic acetonitrile solution with *p*-cyanoanilinium cation (as a source of H^+ ions).

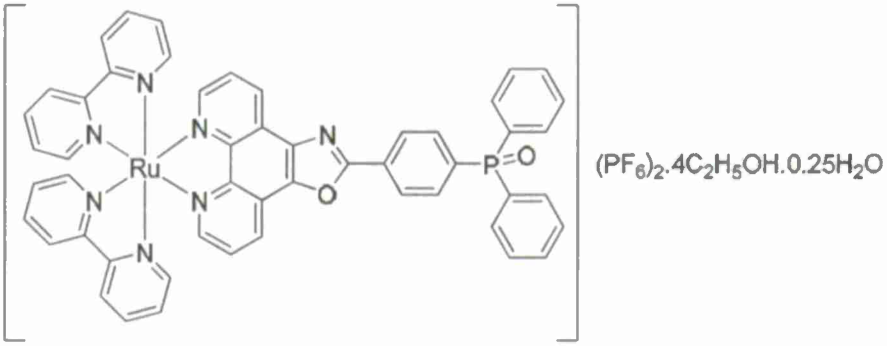


$[Ru(bpy)_2(tbtp)](PF_6)_2 \cdot 3.75H_2O$
Molecular Weight: 1054.21



$[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$
Molecular Weight: 1479.499

It must be noted that a mononuclear ruthenium(II) complex (shown below) with a triphenylphosphine oxide ligand was synthesized and characterized:



$[Ru(bpy)_2(L\text{-}PPh_2)](PF_6)_2.4C_2H_5OH.0.25H_2O$
Chemical Formula: $C_{59}H_{60.5}F_{12}N_7O_{6.25}P_3Ru$
Molecular Weight: 1389.63
Elemental Analysis, calculated: C, 50.99; H, 4.39; N, 7.06; P, 6.69; Ru, 7.27
Found: C, 52.39; H, 3.82; N, 6.78; P, 6.65; Ru, 6.04

This compound will be used by Anja for the electrosynthesis of hydrogen in the presence of $[Co(dmgBF_2)_2(OH_2)_2]$ in aqueous media.

2. Synthesis, characterization, and photocatalytic studies involving water oxidation complexes (WOC) for the production of oxygen and hydrogen in aqueous media.

We have begun to carry out studies in order to generate both O_2 and H^+ ions from water, where H^+ ions will be utilized by our proposed water soluble and acid stable complexes for the generation of hydrogen.

Hydrogen production through the reduction of water appears to be a convenient solution for long-term storage of renewable energy. However, due to the high cost of these metals, there is a search for viable hydrogen production catalysts based on cheap and abundant first-row transition metals.[14] Homogeneous catalyst systems based on first-row transition metals for photochemical hydrogen production have been scarcely reported in the last century, but recently, increasing attention has been focused on the use of non-precious metal-based homogenous catalysis.[15-25] Despite intense global efforts to develop viable "abiological" (artificial photosynthetic) water splitting systems, breakthroughs are needed in selectivity, speed, and stability of three important operational units, viz., a sensitizer for light absorption and catalysts for water reduction and oxidation. The development of a viable water oxidation catalyst (WOC) has proven to be very challenging.[46] More recently efforts have been utilized in oxidation of water to simultaneously produce O_2 and H^+ ion. Recently Yin *et al.*[47] reported that the complex $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, (Fig. 13) comprising a Co_4O_4 core stabilized by oxidatively resistant polytungstate ligands, is a hydrolytically and oxidatively stable homogeneous water oxidation catalyst that self-assembles in water from salts of earth-abundant elements (Co, W, and P). In this study, $[Ru(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) was used as the oxidant. Yin *et al.*[47] observed catalytic turnover frequencies for O_2 production ≥ 5 s^{-1} at pH = 8. The rate's pH sensitivity reflects the pH dependence of the four-electron O_2-H_2O couple. Extensive spectroscopic, electrochemical, and inhibition studies firmly indicate that $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is stable under catalytic turnover conditions: Neither hydrated cobalt ions nor cobalt hydroxide/oxide particles were produced in situ.

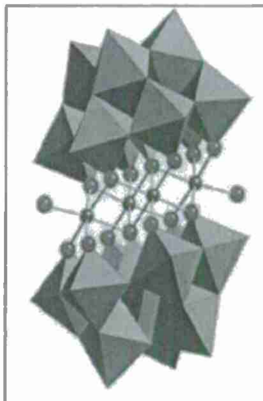


Figure 13. X-ray structure of the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion in combined polyhedral ($[PW_9O_{34}]$ ligands) and ball-and-stick (Co_4O_{16} core) notation. Co atoms are purple; O/OH_2(terminal), red; PO_4, orange tetrahedra; and WO_6, gray octahedra. Hydrogen atoms, water molecules, and sodium cations are omitted for clarity.

Recently, McCool *et al.*[48] reported water oxidation with the molecular Co_4O_4 cubane complex $[Co_4O_4(O_2CMe)_4(py)_4]$ (Fig. 14). $[Co_4O_4(O_2CMe)_4(py)_4]$ was found to catalyze efficient water oxidizing activity when powered by a standard photochemical oxidation source (with $[Ru(bpy)_3]^{3+}$) or electrochemical oxidation.

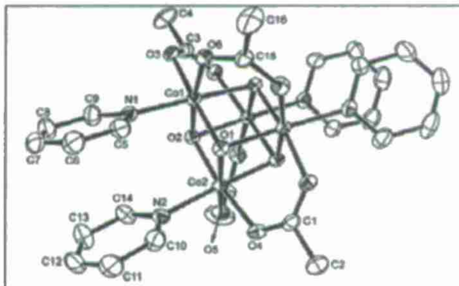


Figure 14. Labeled *ORTEP* (30% probability) representation of the core in $[Co_4O_4(O_2CMe)_4(py)_4]$. Hydrogen atoms are omitted for clarity.

The pH dependence of catalysis, the turnover frequency, and in situ monitoring of catalytic species have revealed the intrinsic capabilities of the Co_4O_4 cubane core. The catalytic activity of $[Co_4O_4(O_2CMe)_4(py)_4]$ and analogous Mn_4O_4 cubane clusters was attributed to the cubical core topology, which is analogous to that of nature's water oxidation catalyst, a cubical $CaMn_4O_5$ cluster.[48]

More recently, La Ganga *et al.*[49] reported the photoinduced water oxidation to molecular oxygen takes place in systems made of $[Ru(bpy)_3]^{2+}$ as the photosensitizer, $[Co_4O_4(O_2CMe)_4(py)_4].0.5NaNO_3.8H_2O$ as the molecular catalyst and $Na_2S_2O_8$ as the sacrificial electron acceptor. It was found that the photochemical quantum yield of the process reached 30%, and depended on pH and catalyst concentration. Transient absorption spectroscopy experiments which were aimed to verify the first events of the photocatalytic process were also reported. In all of these studies, the most common photosensitizer used is $[Ru(bpy)_3]^{2+}$. The choice of $[Ru(bpy)_3]^{2+}$ as the photosensitizer is due to the useful properties of such a species, including absorption in the visible region, relatively long-lived excited-state lifetime, reversible redox processes, and stability in the ground and excited states.[50] More recently, dendritic, tetranuclear Ru(II) polypyridine complexes have been identified and used as efficient photosensitizers for photoinduced water oxidation schemes involving sacrificial acceptors.[51,52] It was reported that the interplay of $[Ru((\mu\text{-}2,3\text{-dpp})Ru(bpy)_2)_3]^{8+}$ (2,3-dpp = 2,3-bis(2'-pyridyl)pyrazine) with the tetraruthenium polyoxometalate species $[(Ru_4O_4(OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, in the presence of persulfate ions, affords water oxidation with an excitation wavelength-independent (excitation between 400 and 700 nm) photochemical quantum yield $\Phi = 0.30$, leading to the continuous evolution of molecular oxygen at pH 7.[52] It was also found that the photodecomposition of the photosensitizer, which was a limiting factor for continuous production of oxygen, was prevented and almost suppressed compared to other reported systems.[52]

It must be stressed that in all of these systems, while their activity is usually quantified by measurement of O_2 produced, little is known about the mechanism under which they produce O_2. In addition to the H_2 evolving catalysts, we (along with Prof. Charles Dismukes of Rutgers University, Anja and Robert Ofoli) started to work on water oxidation catalysts (WOC) in order to complete the water splitting reaction. WOCs oxidize water and produce O_2, protons and electrons.

The mysterious Simmonds' complex: X-ray crystallography was carried out on $K_6[SiW_{11}Co(H_2O)O_{39}]\bullet 12H_2O$, chemical Formula: $K_6SiW_{11}CoH_{26}O_{52}$, and molecular weight: 3202.02. Elemental analysis: calculated (found): Co, 1.84(1.80); K, 7.33 (7.05); Si, 0.88 (0.89); W, 63.16 (51.1). Figure 15 shows an Ortep diagram of $K_6[SiW_{11}Co(H_2O)O_{39}]\bullet 12H_2O$. The crystal structure was solved by Dr. Don VanDerveer of Clemson University, but later sent to Bruker in order to locate the presence of the Co(II) metal center. So far the presence of the Co(II) metal center has not been located in the crystal.

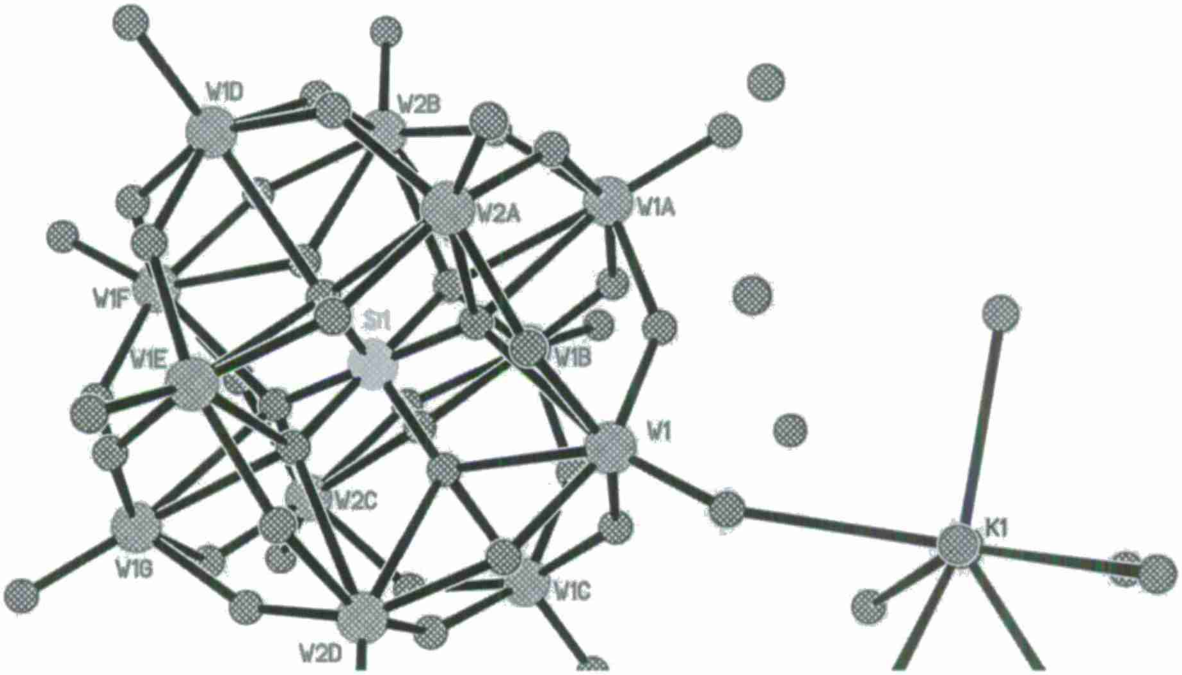


Figure 15. An Ortep diagram of $K_6[SiW_{11}Co(H_2O)O_{39}]\bullet 12H_2O$.

On another note, we have prepared a potential WOC Ni(II) complex which contains Sb(III). We have formulated it as $K_{12}H_2[Ni_5(OH)_6(H_2O)_3Sb_2W_{18}O_{66}]\bullet 34H_2O$. We also prepared a novel WOC, viz., $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}]\bullet 65H_2O$. The complex, $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}]\bullet 65H_2O$.was sent to Rutgers University to be tested as a WOC, with $[Ru(bpy)_3Cl_2$ as a photosensitizer and the persulfate anion as sacrificial electron acceptor. Figure 16 shows a plot of O_2 produced versus time with $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}]\bullet 65H_2O$ as a WOC. Full details of the experimental conditions are yet to be provided by the Rutgers personnel

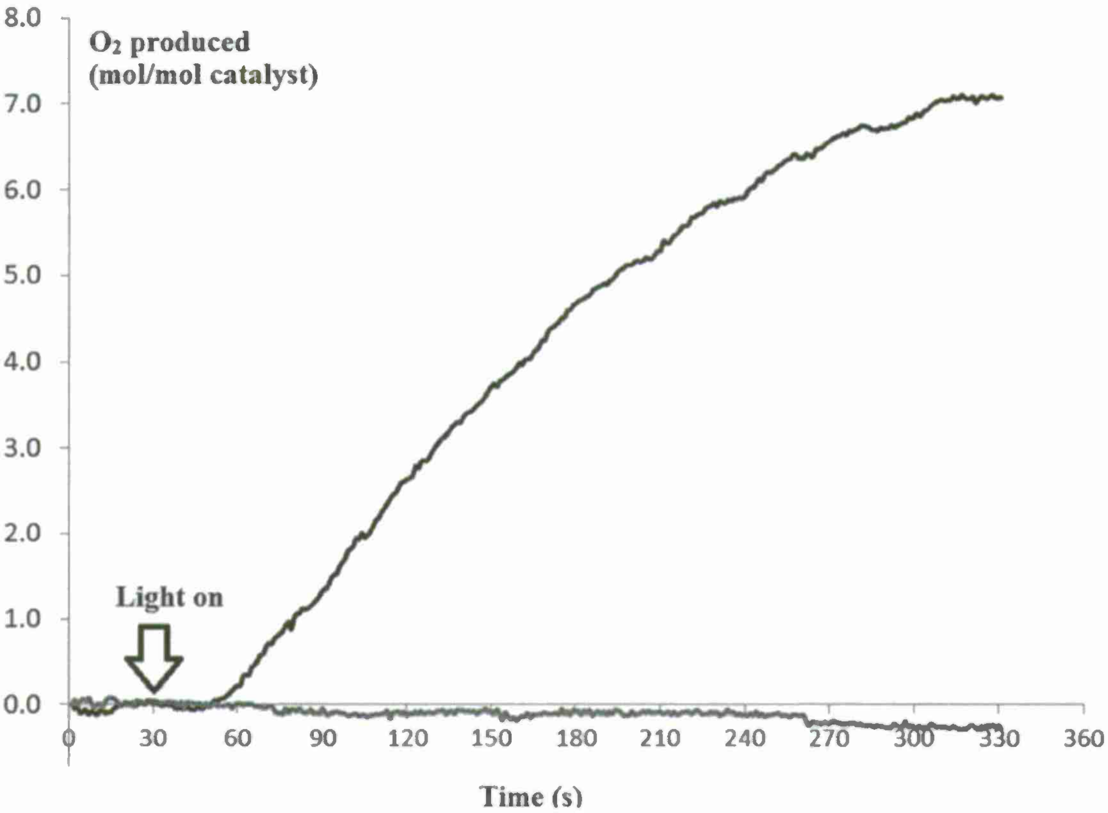
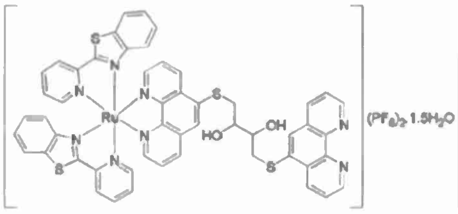
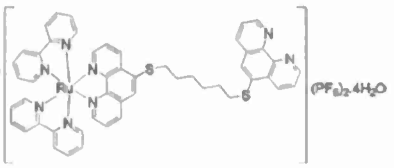


Figure 16. A plot of O_2 produced versus time with $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}]\bullet 65H_2O$ as a WOC.

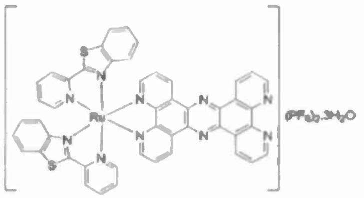
The following ligands where $phen_2C_6S_2$ = 1,6-bis(1,10-phenanthrolin-5-ylsulfanyl)hexane and phen$_2$DTT = 1,4-bis(1,10-phenanthrolin-5-ylsulfanyl)butane-2,3-diol were used to prepare the following mononuclear and binuclear complexes:



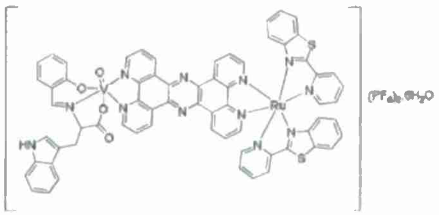
$[Ru(pbt)_2(phen_2DTT)](PF_6)_2.1.5H_2O$



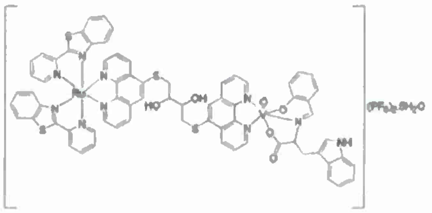
$[Ru(bpy)_2(phen_2C_6S_2)](PF_6)_2.4H_2O$



$[Ru(pbt)_2(tpphz)](PF_6)_2.3H_2O$



[Ru(pbt)$_2$(tpphz)VO(sal-*L*-tryp)](PF$_6$)$_2$.6H$_2$O



[Ru(pbt)$_2$(phen$_2$DTT)VO(sal-*L*-tryp)](PF$_6$)$_2$.5H$_2$O

Table 2 shows the respective formula weights of each complex; while Figures 17 and 18 show the UV-visible spectra of each compound in the respective solvent.

Complex	MW/g mol^{-1}
[Ru(pbt)$_2$(tpphz)](PF$_6$)$_2$•3H$_2$O	1254
[Ru(bpy)$_2$(phen$_2$C$_6$S$_2$)](PF$_6$)$_2$•4H$_2$O	1282
[Ru(bpy)$_2$(phen$_2$DTT)](PF$_6$)$_2$•1.5H$_2$O	1353
[Ru(pbt)$_2$(tpphz)VO(sal-*L*-tryp)](PF$_6$)$_2$•6H$_2$O	1681
[Ru(pbt)$_2$(phen$_2$DTT)VO(sal-*L*-tryp)](PF$_6$)$_2$•5H$_2$O	1790

Table 2. Formula weights of all complexes.

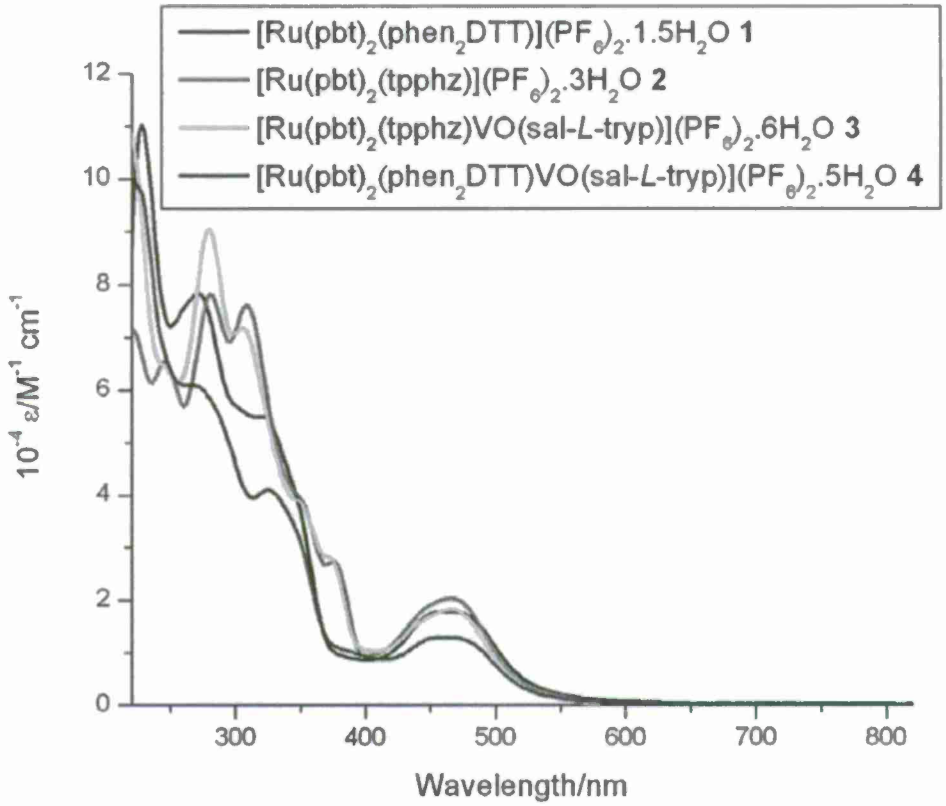


Figure 17. The UV-visible spectra of the synthesized complexes.

Note the labeling here:

1 = $[Ru(pbt)_2(phen_2DTT)](PF_6)_2.1.5H_2O$

2 = $[Ru(pbt)_2(tpphz)](PF_6)_2.3H_2O$

3 = $[Ru(pbt)_2(tpphz)VO(sal\text{-}L\text{-}tryp)](PF_6)_2.6H_2O$

4 = $[Ru(pbt)_2(phen_2DTT)VO(sal\text{-}L\text{-}tryp)](PF_6)_2.5H_2O$

Note: Compounds 1 and 2 were dissolved in 100% acetonitrile, while compounds 3 and 4 were dissolved in 2:1 MeOH/MeCN (v/v).

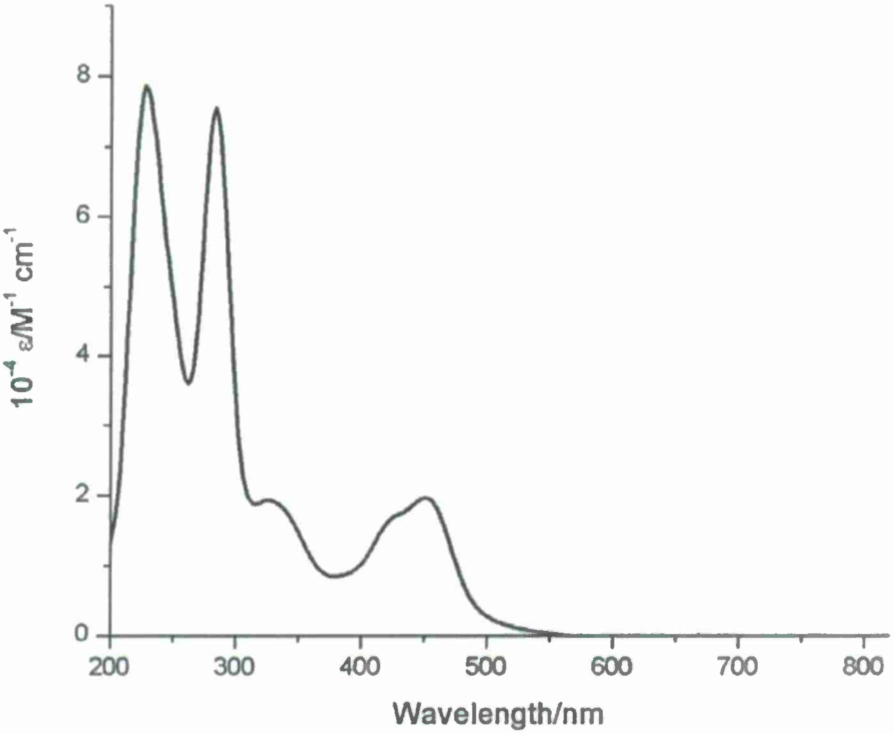


Figure 18. The UV-visible spectrum of the [Ru(bpy)$_2$(phen$_2$S$_2$C$_6$)](PF$_6$)$_2$.4H$_2$O in acetonitrile.

Compounds 3 and 4 (as chloride salts) were sent to Rutgers University to be tested molecules that contain a photosensitiser and an electron acceptor, all in one compound. They were tested with the WOC, [Co$_4$O$_4$(O$_2$CMe)$_4$(py)$_4$], but not O$_2$ was generated on illumination with light as told by the Rutgers University personnel.

Task 2: Joint manuscript based on results from Task 1 will be submitted for publication in peer-reviewed journals.

Broad impacts of the project.

1. It enabled one team member, Alvin Holder, to be awarded an NSF Career Award effective September 01, 2012. This grant will expire on August 31, 2017.

2. Underrepresented individuals were trained and participated in the execution of the project.

3. Undergraduate and graduate students were trained and participated in the execution of the project.

4. Students presented their research findings at local and national meetings.

Publications:

1. Cropek, Donald M.; Metz, Anja; Müller, Astrid M.; Gray, Harry B.; Horne, Toyketa; Horton, Dorothy C.; Poluektov, Oleg; Tiede, David M.; Weber, Ralph T.; Jarrett, William L.; Phillips, Joshua D.; Holder, Alvin A. "A novel ruthenium(II)-cobaloxime supramolecular complex for photocatalytic H_2 evolution: Synthesis, characterisation, and mechanistic studies." *Dalton Trans.* 2012, 41(42), 13060-13073.

Published Textbooks:

1. "Molybdenum: Its Biological and Coordination Chemistry and Industrial Applications. Editor: Alvin A. Holder.

   Chapter 01: Dedications and memories of two icons of Moly, Holder, Alvin A.

   Chapter 02: Molybdenum (*Molybdaenum*): Its history, occurrence, brief inorganic and bioinorganic chemistry, Broome, J. Hugh; Ramsdale, Stuart E.; Holder, Alvin A.; Dasgupta, Tara P.; Hinton, Daniel; Davis, Aaron; Gresham, Amber W.; Shattles, Michael; Wusimanjiang, Yiliyasi; Evans, Bradley; Spangler, Joseph; Holcomb, Mark; Dobbs, Tiffany; Burrell, Jo T.; Arca, Jessa Faye; Rogers, Mallory; Satcher; Nathaniel.

   Publishers: Nova Science Publishers, Inc., 2013, accepted. On the market by March 15, 2013.

Note, although no Army funding was used in the production of the textbook, Alvin Holder acknowledged the Army in the acknowledgement section of the textbook.

Conference Presentations:

Graduate and undergraduate students are highlighted in yellow.

1. The Mississippi INBRE Annual Research Symposium, March 31, 2012, The Thad Cochran Center, The University of Southern Mississippi, Hattiesburg, MS 39406. Title: Development of mononuclear cobalt(III)-containing complexes as potential chemotherapeutic agents." Authors: Jessa Faye Arca, Antonio González-Sarrías, Floyd A. Beckford, Navindra P. Seeram, and Alvin A. Holder.

2. NIH, NIGMS Fourth Biennial National IDeA Symposium of Biomedical Research Excellence (NISBRE), The Omni Shoreham Hotel Washington, DC June 25–27, 2012. Title: “Biomedical applications of cobalt(III)-containing complexes: structural and *in vitro* studies.” Authors: Jessa Faye Arca, Antonio González-Sarrias, Floyd A.Beckford, Navindra P. Seeram, and Alvin A. Holder.

3. The 8th International Symposium on the Chemistry, Biochemistry and Toxicology of Vanadium, August 15-18, 2012, Washington, DC, U.S.A. Title: “Development of binuclear mixed-metal ruthenium(II)-vanadium(IV) complexes as potential photodynamic therapeutic agents.”. Authors: Patrick Taylor, Anthony Magnusen, Fange Liu, Kyle Meyer, Aimin Liu, Yiling Hong, and Alvin A. Holder.

4. Inorganic Photophysics and Photochemistry- Fundamentals and Applications: Dalton Discussion 13, September 10-12, 2012, University of Sheffield, U.K. Title: “A novel ruthenium(II)-cobaloxime supramolecular complex for photocatalytic H_2 evolution: Synthesis, characterisation, and mechanistic studies.” Authors: Donald M. Cropek, Anja Metz, Astrid M. Müller, Harry B. Gray, Toyketa Horne, Dorothy C. Horton, Oleg Poluektov, David M. Tiede, Ralph T. Weber, William L. Jarrett, Joshua D. Phillips, Alvin A. Holder.

5. The following abstract was submitted to the ACS for the spring 2013 National ACS Meeting which will be held in New Orleans:

Photocatalytic hydrogen production with mixed-metal binuclear ruthenium(II)-cobalt(II) complexes: What a difference bridging and terminal ligands can make.

Alvin A. Holder,[a*] Apparao Draksharapu,[b] Jason Olaivar,[a] Erick Moffett,[a] De’Andra Newton,[a] Luke Seymour,[a] Stuart Ramsdale,[a] Donald Cropek,[c] Anja Metz,[c] Ralph Weber,[d] Wesley R. Browne,[b] and William Jarrett[e]

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[b] Stratingh Institute for Chemistry, Faculty of Mathematics and Natural Sciences,
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Champaign, IL 61822, U.S.A.
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Final submitted abstract (150 words allowed):

In this study, $[Ru(bpy)_2(tbtp)](PF_6)_2 \cdot 3.75H_2O$, 1 (where bpy = 2,2'-bipyridine and tbtp = 4,5,9,11,14-pentaaza-benzo[*b*]triphenylene) was reacted with $[Co(dmgBF_2)_2(H_2O)_2]$ (where $dmgBF_2$ = difluorboryldimethylglyoximato) to yield the mixed-metal binuclear complex, $[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$ 2. Complex 2 was characterized; then photocatalytic studies were carried out in acidified acetonitrile. Surprisingly H_2 could not be detected over a three hour period when complex 2 was utilized. This finding is in contrast to $[Ru(pbt)_2(L\text{-}pyr)Co(dmgBF_2)_2(H_2O)](PF_6)_2.11H_2O.1.5CH_3COCH_3$ (where L-pyr = (4-pyridine)oxazolo[4,5-*f*]phenanthroline) which produced H_2 at a rate of 80 uL h^{-1}, or when the unreported complex, $[Ru(pbt)_2(L\text{-}CN)Co(dmgBF_2)_2(H_2O)](PF_6)_2$ (where L-CN = 4-(oxazolo[4,5-f][1,10]phenanthrolin-2-yl)benzonitrile) produced H_2 at a rate of 50 uL h^{-1}. Raman spectroscopic studies were carried out on $[Co(dmgBF_2)_2(H_2O)_2]$, and complexes 1 and 2, as well as time resolved spectroscopic measurements on complexes 1 and 2 in an effort to understand these differences in hydrogen production. It is interesting to note that bridging and terminal ligands can affect the production of hydrogen.

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This information is confidential and will not be disclosed to any other source.

We will acknowledge Professor Harry B. Gray and Dr. Astrid M. Müller, California Institute of Technology, Beckman Institute, Pasadena, CA 91125, for assisting us in carrying out photochemical studies for this research project.

Manuscripts in preparation:

1. An X-ray crystallographic study of the mysterious compound, $K_6[SiW_{11}Co(H_2O)O_{39}]\bullet 12H_2O$

Luke Seymour, Don VanDerveer, Anja Metz, Donald M. Cropek, and Alvin A. Holder

Bruker!! Awaiting the final structure from Bruker, and it should go out in two months time. This manuscript will be submitted to CrystEngComm.

2. A Comparison of the Self Assembled 3-Dimensional Frameworks of Three Cobalt Centred Dipicolinic Acid Complexes.

Varma H. Rambaran, Travis R. Erves, Kristy Grover, Shawna Balof, LaMaryet V. Moody, Stuart Ramsdale, Luke Seymour, Don VanDerveer, Ralph T. Weber, Donald M. Cropek, and Alvin A. Holder

Awaiting the final version from Varma, and it should go out in one month time. This manuscript will be submitted to The Journal of Chemical Crystallography

3. Effect of O_2 production with water oxidation catalysts by several buffers of oxoanions

Robert Ofoli, Luke Seymour, Anja Metz, Donald M. Cropek, and Alvin A. Holder

Robert and Crew are working on this manuscript.

4. Electrosynthesis of hydrogen with nickel(II) and cobalt(II) metal centres with non-traditional ligands

Luke Seymour, Anja Metz, Donald M. Cropek, and Alvin A. Holder

5. Preliminary *in vitro* studies involving binuclear mixed-metal ruthenium(II)-vanadium(IV) complexes as potential photodynamic therapeutic agents

Patrick Taylor, Anthony Magnusen, Fange Liu, Kyle Meyer, Yiling Hong, Stuart Ramsdale, Michelle Gordon, Javelyn Stubbs, Angleica McIntyre, Luke Seymour, Brandon Dreschler, Paul Smith, C. Charles Dismukes, Bradley Arnold, Fengwei

Bai, Jennie Williams, Anja Metz, Donald M. Cropek, William L. Jarrett, and Alvin A. Holder

This manuscript is due for submission to *Dalton Trans.* by mid-February 2013. I am awaiting some data from Dismukes and Jennie Williams, who is repeating our *in vitro* work so that we can have quality phase contrast photos.

Concluding Chapter:

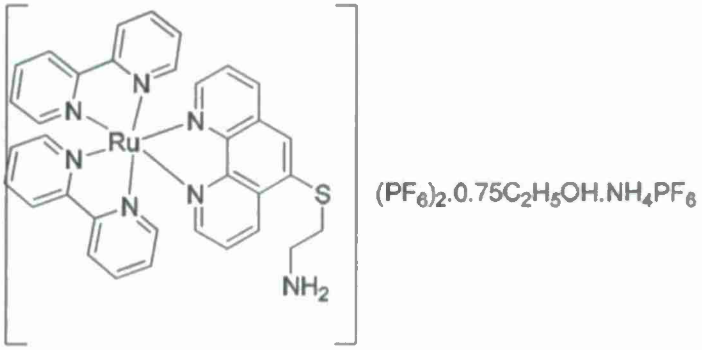
Summary. It is a known fact that fossil fuel reserves are rapidly diminishing. It is know being realized that solar-to-chemical energy conversion is one of the greatest challenges for sustainable development. Thus there is a growing need for the direct generation of molecular hydrogen, a convenient and clean energy vector, from renewable resources. A number of homogeneous light driven catalytic systems for hydrogen production have appeared in the literature, especially those with a $[Ru(bpy)_3]^{2+}$ (where bpy = 2,2'-bipyridine) moiety, which is capable for harvesting photons and driving electrons to a hydrogen-evolving catalyst. The main theme in this project was to develop and test the hydrogen-producing capacity of some novel complexes that bear a photosensitizer (a ruthenium(II) metal center) and a catalytic cobalt(II) metal center, all in one molecule. Several novel ligands and complexes (including mononuclear, binuclear, and trinuclear) were synthesized and characterized. All ligands and complexes were characterized by elemental analysis, UV-visible, ^1H NMR, and EPR spectroscopy, and cyclic voltammetry, where appropriate. Photocatalytic studies were carried out in acidified acetonitrile. Initial studies were also carried out with water oxidation catalysts (WOCs) in order to generate O_2 and H^+ ions in aqueous media. Hydrogen was not generated on photolysis of a novel mixed-metal ruthenium(II)-cobalt(II) complex, $Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$ in acidic acetonitrile solution; while oxygen was produced in water on photolysis in the presence of a WOC, $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}] \bullet 65H_2O$, and $[Ru(bpy)_3]Cl_2$. Electrosynthetic studies involving Co(II) and Ni(II) complexes proved that H_2 was produced on several electrodes in aqueous media.

Conclusions. Hydrogen was not generated on photolysis of a novel mixed-metal ruthenium(II)-cobalt(II) complex, $Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 5H_2O$ in acidic acetonitrile solution; while oxygen was produced in water on photolysis in the presence of a WOC, $Na_6[Bi_2Co_4(H_2O)_2W_{16}O_{58}] \bullet 65H_2O$, and $[Ru(bpy)_3]Cl_2$. Electrosynthetic studies involving Co(II) and Ni(II) complexes proved that H_2 was produced on several electrodes in aqueous media.

Recommendations. The PI recommends that the project should be moved forward to the next step of synthesizing complexes that are stable in aqueous acidic media so that we can utilize such complexes in the generation of hydrogen from H^+ ions that are generated as by-product when water is photolyzed in the presence of a WOC and $[Ru(bpy)_3]Cl_2$. A microfluidic device must be developed at the next stage of another project that will enable the separation of H^+ ions from O_2; then the H^+ ions will and be utilized in another chamber in the presence of *Ralstonia eutropha* strain for generation of hydrogen in aqueous media (see future work below).

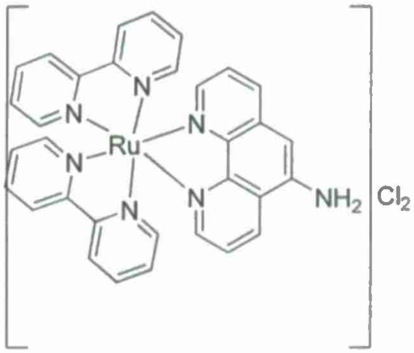
Future work:

We have synthesized and characterized the novel complex $[Ru(bpy)_2(phenSCH_2CH_2NH_2)](PF_6)_2\bullet 0.75C_2H_5OH\bullet NH_4PF_6$



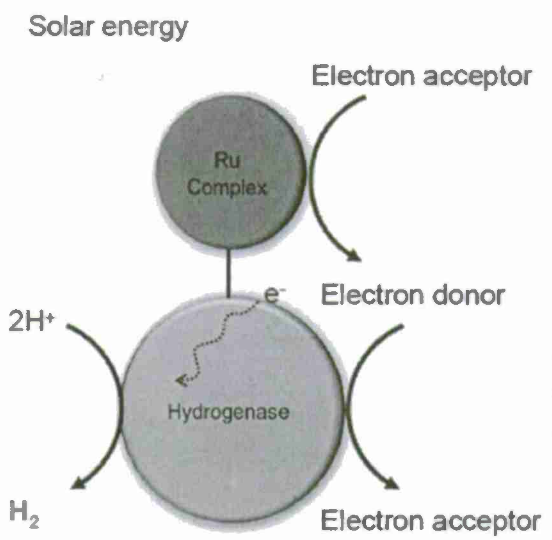
Chemical Formula: $C_{35.5}H_{37.5}F_{18}N_8O_{0.75}P_3RuS$
Molecular Weight: 1156.26
Elemental Analysis: C, 36.88; H, 3.27; F, 29.58; N, 9.69; O, 1.04; P, 8.04; Ru, 8.74; S, 2.77

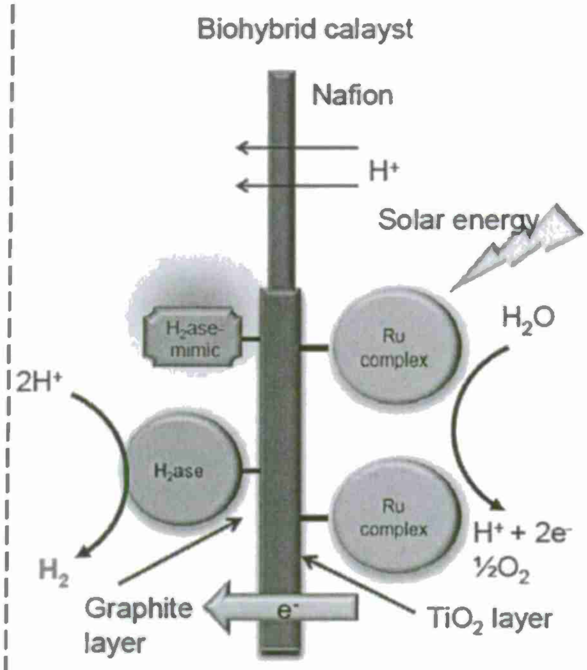
and



$[Ru(bpy)_2(phen\text{-}NH_2)]Cl_2$

These complexes, as chloride salts, will be sent to Irene who will couple such complexes to the *Ralstonia eutropha* strain for generation of hydrogen in aqueous media. In summary, our goal is to produce the following systems for the generation of hydrogen in aqueous media:





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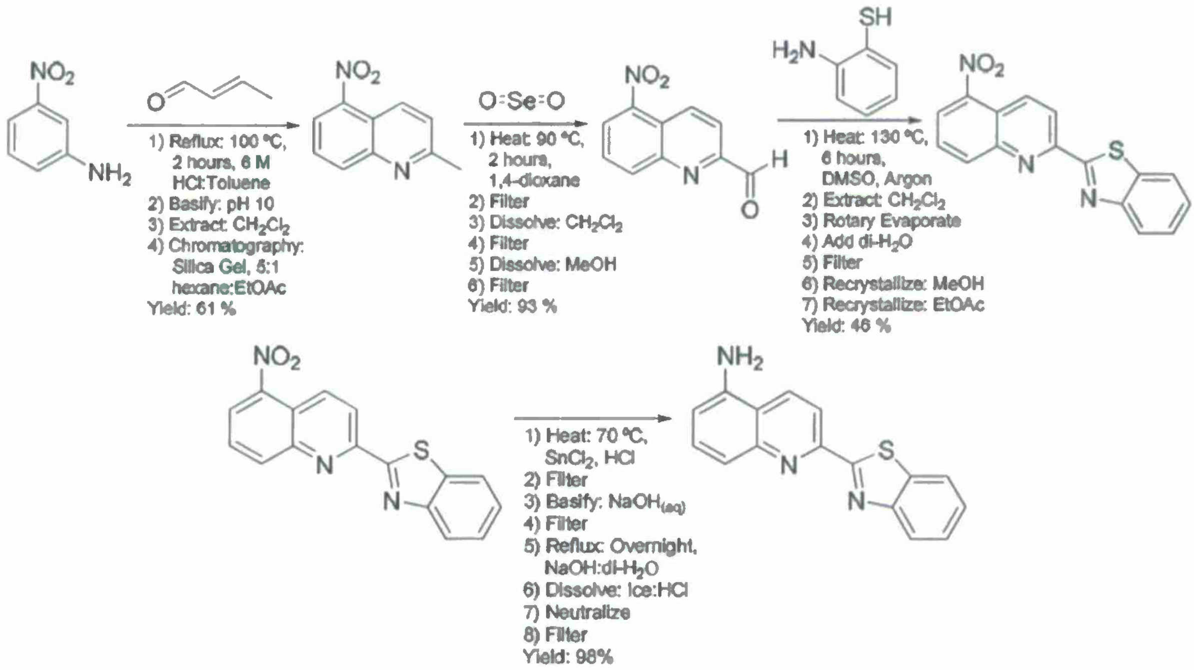
Synthesis of a Novel PBT-like Ligand

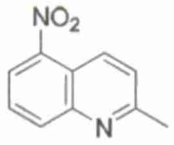
2-(5-aminoquinoline)benzothiazole
Molecular Weight: 277.344

One of our goals was to synthesize a novel pbt-like ligand with an additional ring with an amino group for the purpose of attaching a binuclear mixed metal complex to hydrogenase, a proton producing enzyme.

The synthesis of 2-methyl-5-nitroquinoline, the first step in the synthesis of our pbt analogue, was repeated five times, which produced a total of over 10 grams of product. Next, the methyl group was oxidized with SeO_2 in 1,4-dioxane to produce the aldehyde, which was then reacted with 2-aminothiophenol to produce the 5-nitro analogue of the target ligand. Finally, the NO_2 group was reduced to NH_2 with tin(II) chloride in HCl giving the novel ligand 2-(5-aminoquinoline)-benzothiazole (5-amino-QBT).

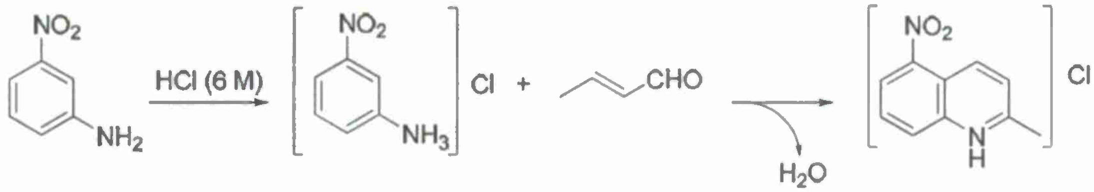


Synthesis of 2-methyl-5-nitroquinoline



2-methyl-5-nitroquinoline
Molecular Weight: 188.18
Structure 1

As adapted from Masato Matsugi, et al. tetrahedron Letters, 2000, 41, 8523. Dorbner-Miller synthesis in a two-phase system: practical preparation of quinolines.



3-nitroaniline (3.080 g, 22.3 mmol) was dissolved in HCl (~6 M, 115 mL), and the mixture was heated in a 100 mL round bottom flask at 100 °C with stirring for 21.5 hours overnight.

Crotonaldehyde (3.7 mL, 44.6 mmol) in toluene (30 mL) was added drop wise down the condenser. Upon addition of the crotonaldehyde solution, the reaction mixture became orange in color, and stirring was increased to 1700 rpm to vigorously mix the toluene layer with the aqueous layer. The reaction mixture was allowed to reflux for 2 hours and then cooled to room temperature. A separatory funnel was used to collect the aqueous layer after the addition of HCl (200 mL, ~6 M), which was then basified to pH 10-11 (10.01) with a saturated NaOH solution.

The product was extracted with CH_2Cl_2 (5 x 100 mL) and the organic layer was washed with brine (5 x 100 mL) and dried over $NaSO_4$ anhydrous. Next, the mixture was vacuum filtered and the filtrate was rotary evaporated to a minimal volume.

Column chromatography was performed using silica gel (70-200 mesh, 60 Å), and 5:1 hexane:EtOAc as eluent. The height was 13 cm and diameter was 5.5 cm. TLC was performed in CH_2Cl_2 with faction 1 representing the mixture before the column, while factions 2-8 from the column were combined, as well as factions 9-15, and factions 16+, which contained the target complex. The collected factions 16 and up were rotary evaporated to a minimal volume and left to crystallize. Yield: 2.5708 g, 13.7 mmol, 61 %. This was repeated 5 times yielding 11.8786 g.

Elemental analysis was performed.

Element	Predicted	Measured	Difference	Measured	Difference	Average
C	63.82	62.72	-1.1	63.28	-0.54	63.00
H	4.28	4.45	0.17	4.67	0.39	4.56
N	14.89	13.55	-1.34	13.45	-1.44	13.50

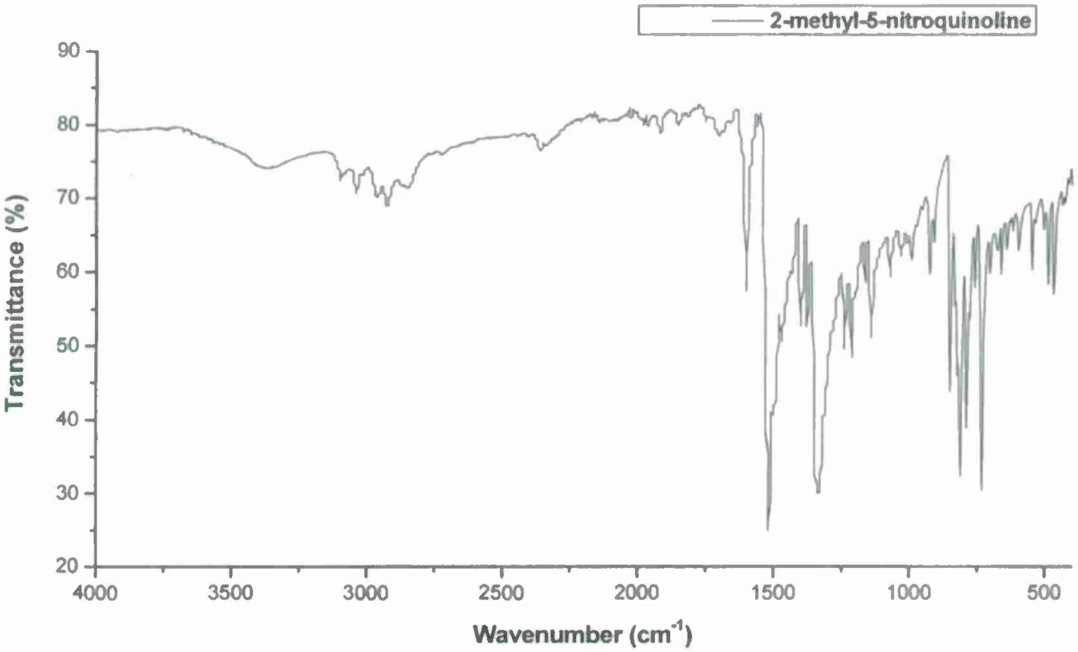


Figure 1. **An FTIR spectrum of 2-methyl-5-nitroquinoline. 1517.73, 1336.45 (NO_2).**

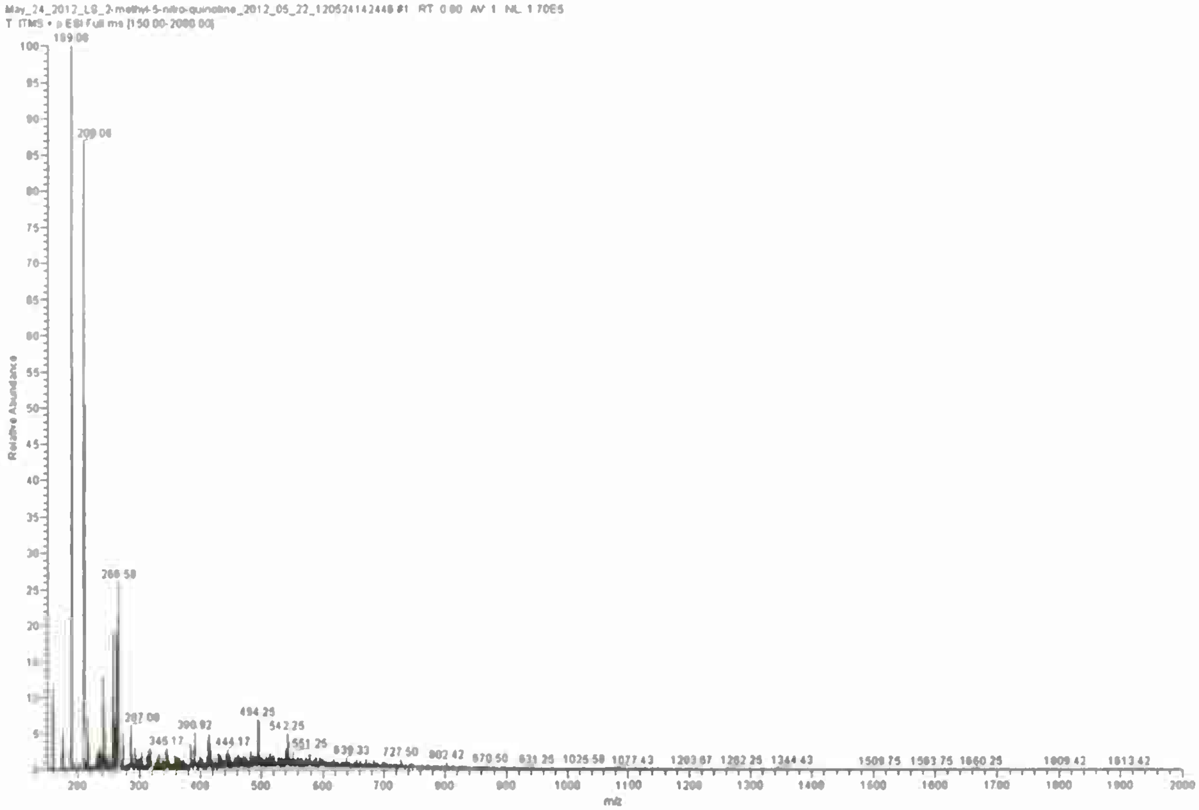


Figure 2. An ESI MS of 2-methyl-5-nitroquinoline in anhydrous methanol with trifluoroacetic acid. $[M + H]^+ = 189.08$.

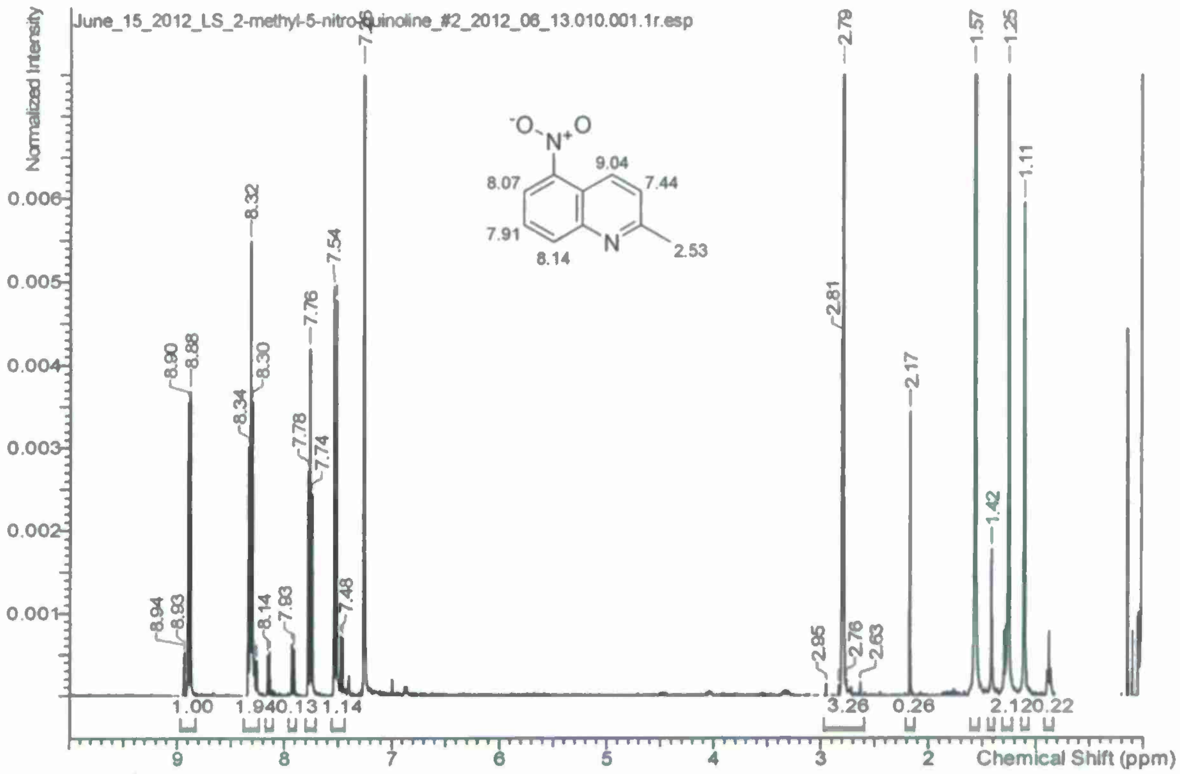
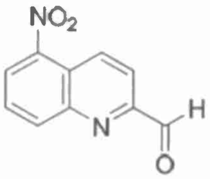


Figure 3. **A ^{1}H NMR spectrum of 2-methyl-5-nitroquinoline in $CDCl_3$ along with the Chemdraw predicted shifts. [CH_3] = 2.79.**

Synthesis of 5-nitroquinoline-2-carbaldehyde

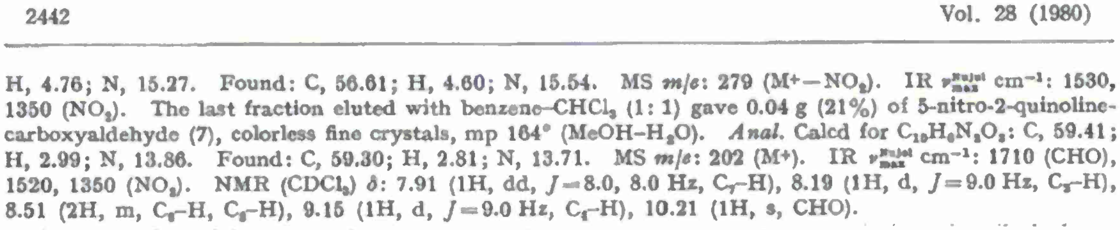


5-nitroquinoline-2-carbaldehyde
Molecular Weight: 202.166
Structure 2

A mixture of 2-methyl-5-nitroquinoline (5.9070 g, 31 mmol) and SeO_2 (6.14 g, 55 mmol) in dioxane (175 mL) was heated at 90 °C for 2 hours in a 250 mL round bottom flask. The reaction mixture was filtered through a frit (30 mL, 30F) to remove solids and the filtrate was rotary evaporated to dryness. The residue was dissolved in CH_2Cl_2 (150 mL) and filtered through a frit (30 mL, 30F). The filtrate was rotary evaporated to dryness.

The residue was redissolved in hot MeOH (5 x 100 mL), filtered through a fine frit, and the filtrate was rotary evaporated to dryness. Next, diethyl ether was added and the flask was sonicated and rotary evaporated to dryness. Yield: 5.8161 g, 93 %. This was repeated 3 times to yield 11.3199 g.

Nishikawa, M.; Saeki, S.; Hamana, M.; Noda, H. *Chem. Pharm. Bull.* **1980**, *28*, 2442.



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H, 4.76; N, 15.27. Found: C, 56.61; H, 4.60; N, 15.54. MS *m/e*: 279 (M^+-NO_2). IR ν_{max}^{Nujol} cm^{-1}: 1530, 1350 (NO_2). The last fraction eluted with benzene–$CHCl_3$ (1: 1) gave 0.04 g (21%) of 5-nitro-2-quinolinecarboxyaldehyde (7), colorless fine crystals, mp 164° (MeOH–H_2O). *Anal.* Calcd for $C_{10}H_6N_2O_3$: C, 59.41; H, 2.99; N, 13.86. Found: C, 59.30; H, 2.81; N, 13.71. MS *m/e*: 202 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1710 (CHO), 1520, 1350 (NO_2). NMR ($CDCl_3$) δ: 7.91 (1H, dd, *J*=8.0, 8.0 Hz, C_7–H), 8.19 (1H, d, *J*=9.0 Hz, C_3–H), 8.51 (2H, m, C_6–H, C_8–H), 9.15 (1H, d, *J*=9.0 Hz, C_4–H), 10.21 (1H, s, CHO).

Figure 4. A snapshot of the expected analytical results for structure 2 as they appear in literature.

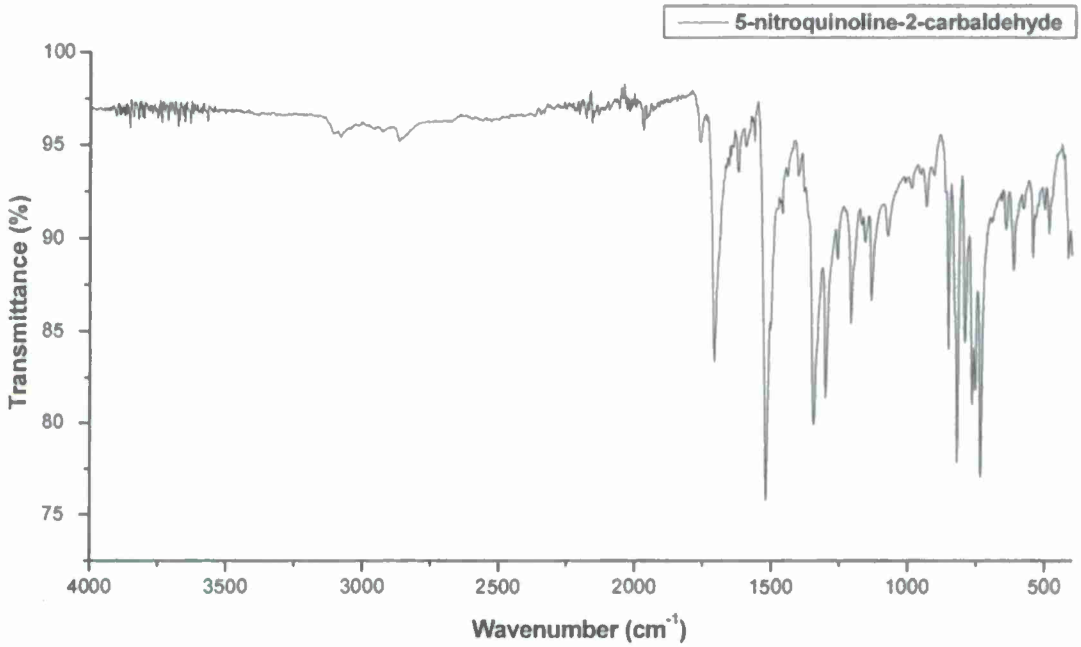


Figure 5. An FTIR spectrum of 5-nitroquinoline-2-carbaldehyde. 2865.75, 1706.72 (HC=O), 1517.73, 1344.16 (NO).

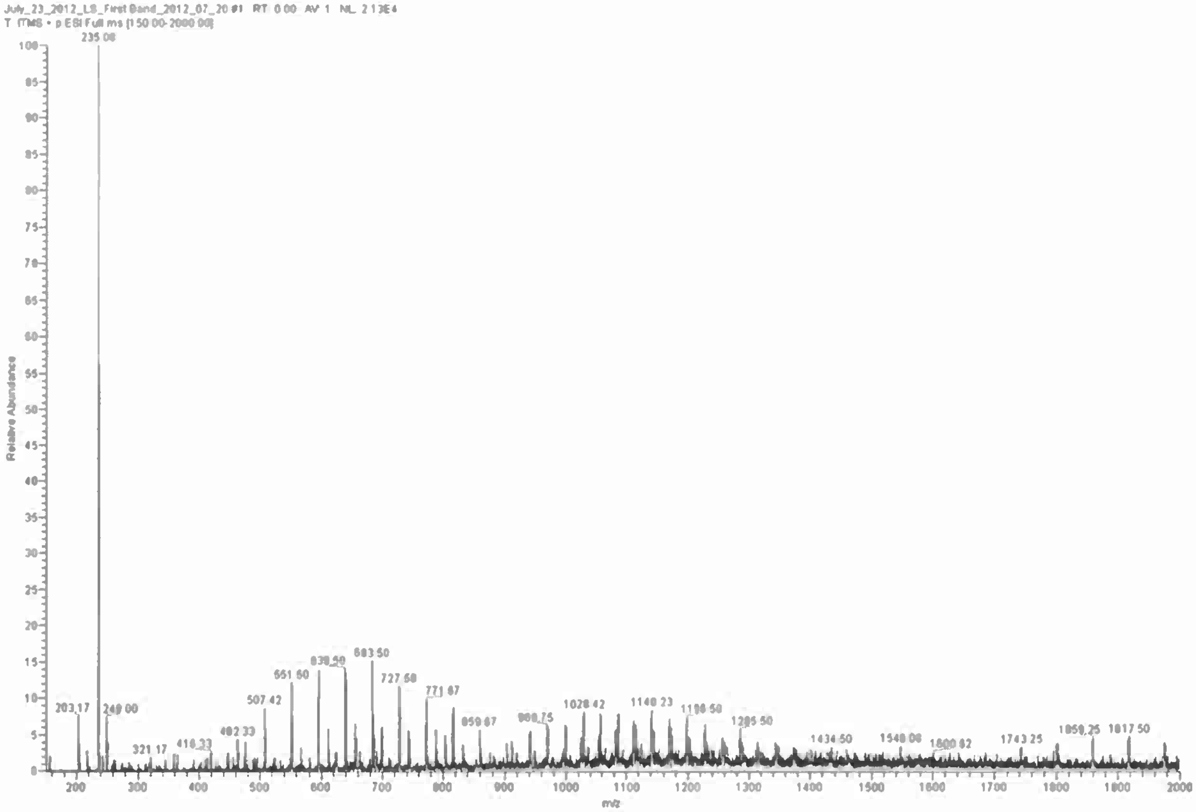


Figure 6. **An ESI MS of 5-nitroquinoline-2-carbaldehyde in anhydrous methanol with trifluoroacetic acid. $[M + H]^+ = 203.17$.**

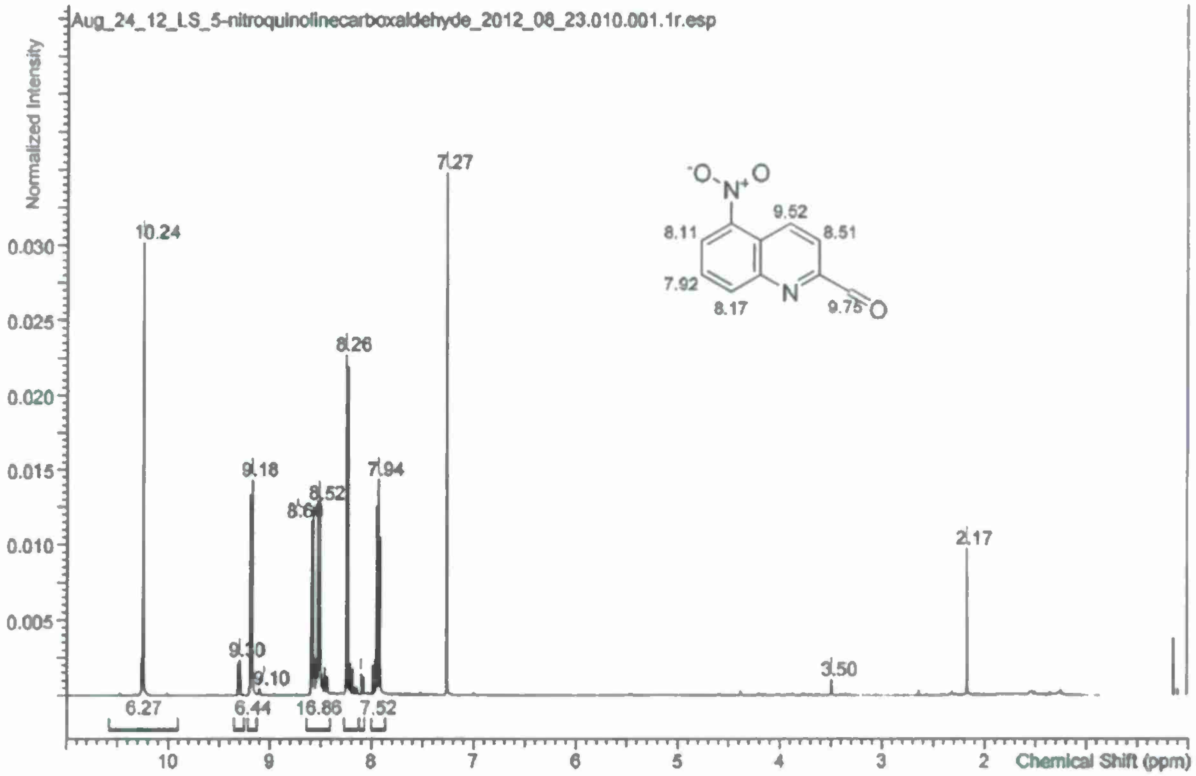
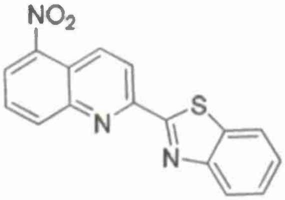


Figure 7. A ^1H NMR spectrum of 5-nitroquinoline-2-carbaldehyde in $CDCl_3$ along with the Chemdraw predicted shifts. [CHO] = 10.24.

Synthesis of 2-(5-nitroquinoline)-benzothiazole



2-(5-nitroquinoline)-benzothiazole
Molecular Weight: 307.327
Structure 3

Structure 3 was synthesized using a modified prep utilizing parts of the synthesis for the reduction of the nitro to the amino group from: Chen, H.; Nilsen, C. N.; Choudhury, A.; Siorgi, K. L. A Safe and Convenient Synthesis of 4-benzyloxy-3-chloroaniline. *Arkivoc* **2008**, (14) 1.

5-nitroquinoline-2-carboxaldehyde (9.9941 g, 49 mmol), 2-aminothiophenol (5.290 mL, 6.1888 g, 49 mmol), and anhydrous DMSO (114 mL) were added to a 250 mL round bottom flask with a stir bar and the orange solution was degassed under argon with stirring at 1000 rpm at room temperature for 15 minutes. Next, the temperature was increased to 130 °C and the orange solution was refluxed with stirring under argon for 6 hours. The solution was cooled to room temperature overnight.

The mixture was transferred to a separatory funnel with di-H_2O (500 mL) and extracted with CH_2Cl_2 (10 x 100 mL) and the organic layer was rotary evaporated to near dryness. Some DMSO may have remained and the slush was redissolved in CH_2Cl_2 (500 mL) and transferred to a separatory funnel with di-H_2O (200 mL) and after vigorous shaking, the organic faction was collected and a second extraction was performed on the aqueous layer with CH_2Cl_2 (3 x 100 mL).

The aqueous layers were rotary evaporated until only DMSO remained. Then the solution was cooled in an ice bath while di-H_2O (200 mL) were added. After cooling, the mixture was filtered through a frit (150 mL, 60F). The dry residue was collected. Yield: 3.3733 g, 11 mmol, 22 %.

The organic layer was rotary evaporated until only DMSO remained. Then, the solution was cooled in an ice bath while di-H_2O (200 mL) was added. After cooling, the mixture was filtered through a frit (30 mL, 30F). The filtrates from both filtrations were discarded.

The two batches were recrystallized separately in methanol, but not all would dissolve.
Yield 1: 0.0282 g, 0.09 mmol, 0.2 %. Residue: 2.3015 g
Yield 2: 1.5318 g, 5 mmol, 10 %. Residue: 4.7143 g
Recrystallization with EtOAc was also attempted but not all would dissolve.

This reaction was repeated to yield 7.0507 g.

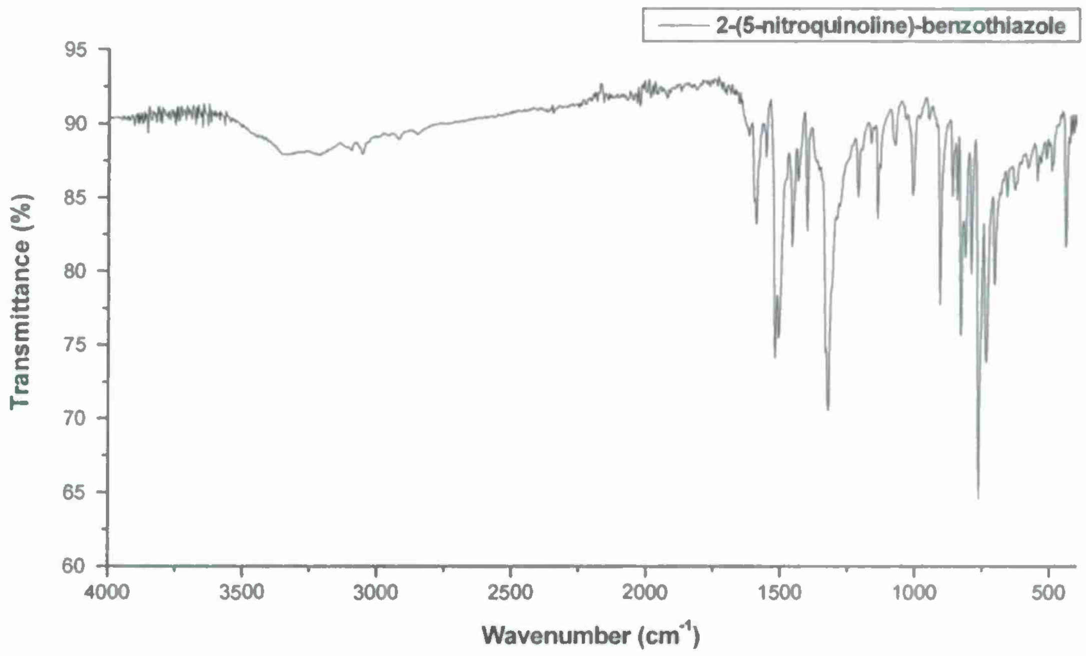


Figure 8. An FTIR spectrum of 2-(5-nitroquinoline)-benzothiazole. 1519.66, 1321.02 (NO).

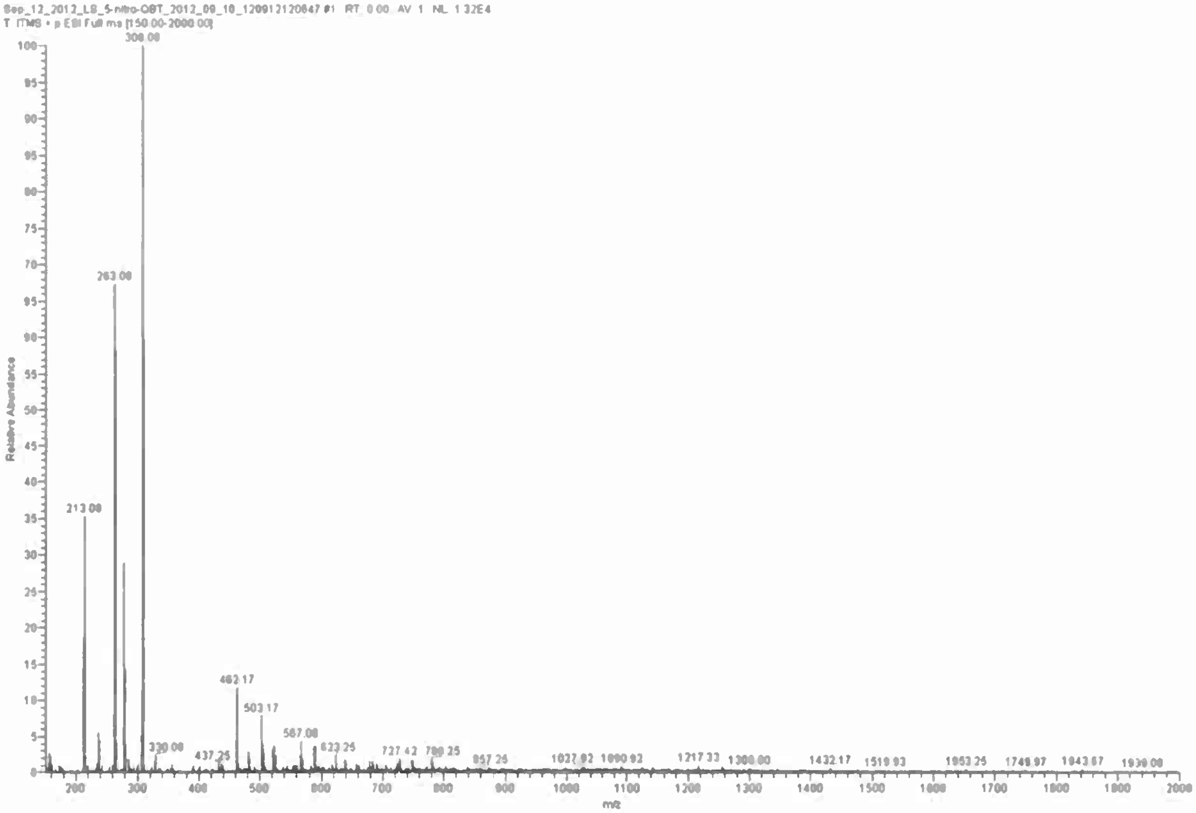


Figure 9. An ESI MS of 2-(5-nitroquinoline)-benzothiazole in anhydrous methanol with trifluoroacetic acid. $[M + H]^+ = 308.08$.

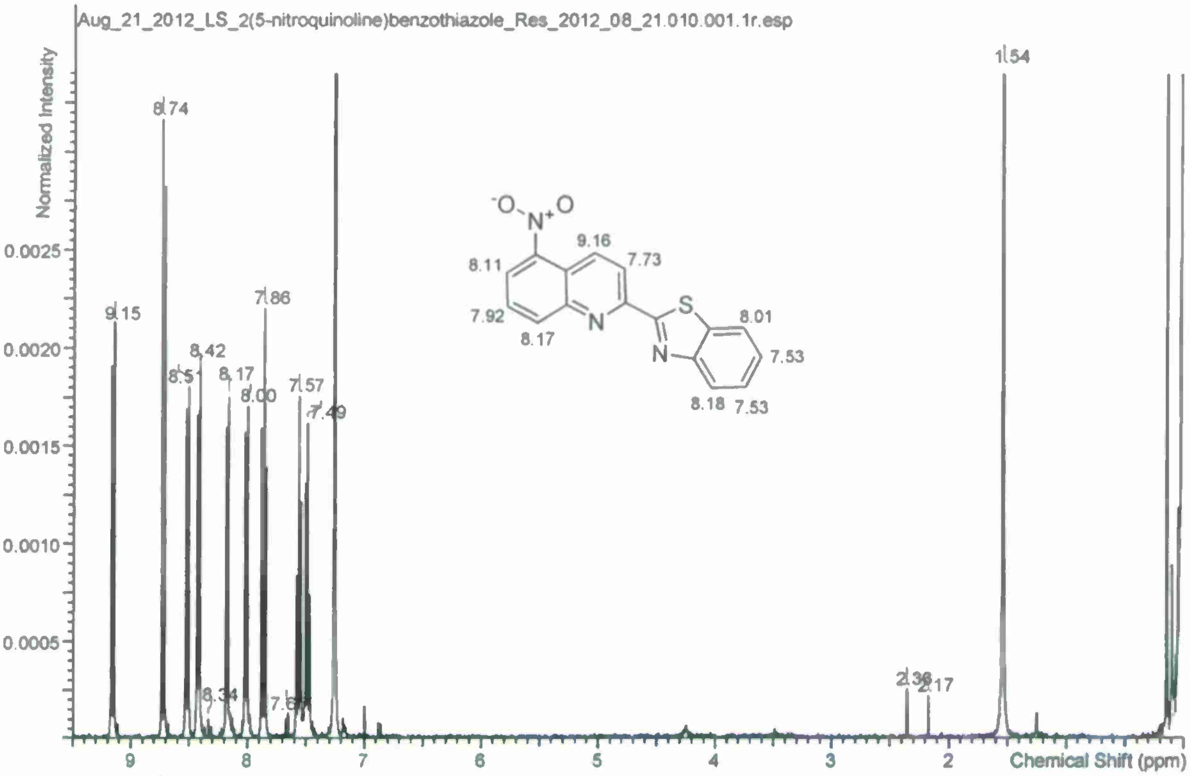
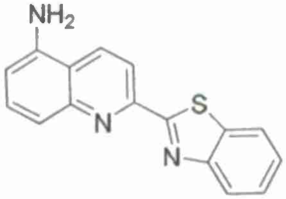


Figure 10. A ^{1}H NMR of 2-(5-nitroquinoline)-benzothiazole in $CDCl_3$ along with the Chemdraw predicted shifts.

Synthesis of 2-(5-aminoquinoline)-benzothiazole



2-(5-aminoquinoline)-benzothiazole
Molecular Weight: 277.344

In a 250 mL round bottom flask with a stir bar was added anhydrous tin(II) chloride (11.59 g, 62 mmol), ethanol (40 mL), and fuming HCl (8 mL). The mixture was heated with stirring (600 rpm) at 70 °C until the solution became clear. Then over the course of 30 minutes, 5-nitro-QBT (4.7737 g, 15.5 mmol) was added in 5 portions. Next, the mixture was heated with stirring for 1.5 hours. TLC was performed in acetone. Di-H_2O (40 mL) was added and the solution was cooled in an ice bath.

Next, the mixture was vacuum filtered through a frit (150 mL, 60F), washed with water, and the residue was air dried. The filtrate was basified with NaOH (10 M). NaOH (10 M) was added to the residue in the frit, which appeared brown. Then it was vacuum filtered, washed with water and air dried. Then, it was recrystallized in methanol, but all residues were recombined and rotary evaporated to dryness. NaOH (12 g) and di-H_2O (~200 mL) were added and the mixture refluxed with stirring overnight. The mixture was filtered, along with the precipitate from the basified filtrate above. The combined residue was washed with plenty water and air dried. The dry solid was transferred to a 1 L beaker, then a minimal volume of concentrated HCl was added to dissolve the solids. Crushed ice was added up to the 670 mL mark. The resulting slush was adjusted to pH 6.99 with aqueous NaOH (saturated) and vacuum filtered, then washed with di-H_2O. The solid was air dried under vacuum. Yield: 4.2029 g, 15.1 mmol, 98 %

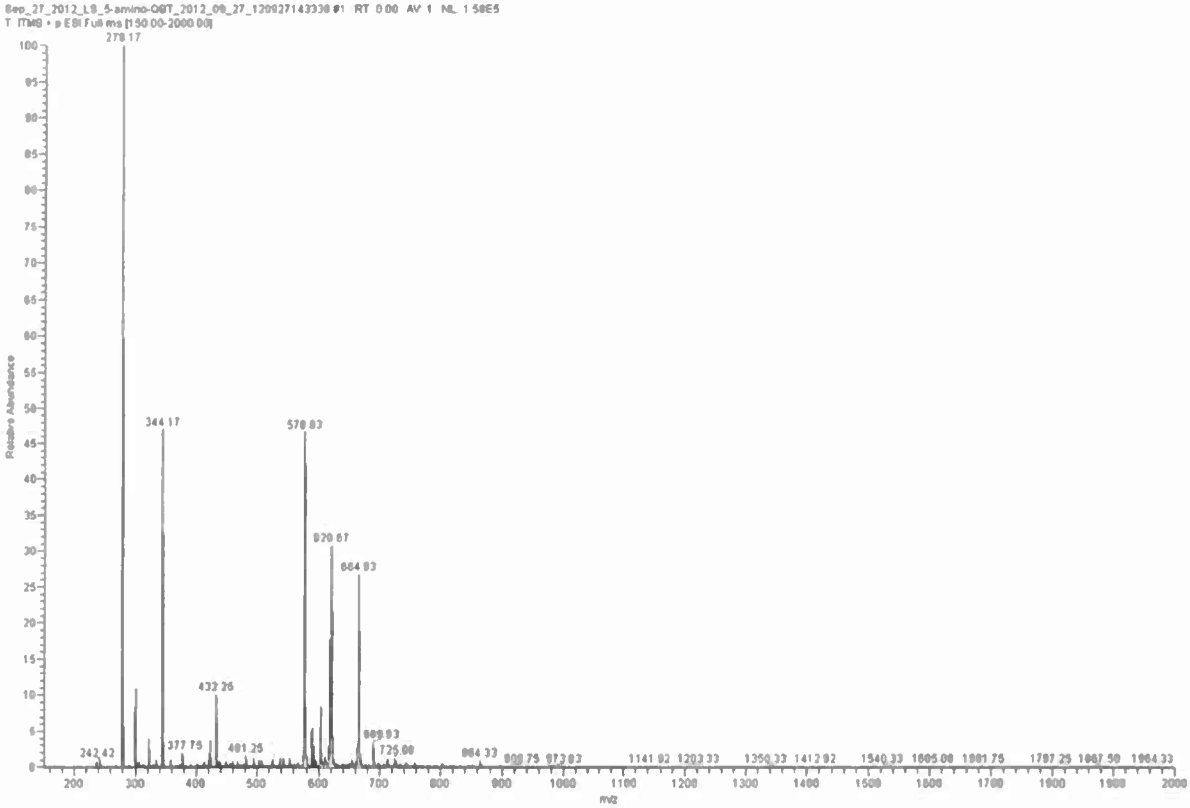


Figure 11. An ESI MS of 2-(5-aminoquinoline)-benzothiazole in anhydrous methanol with trifluoroacetic acid. $[M + H]^+ = 278.17$.

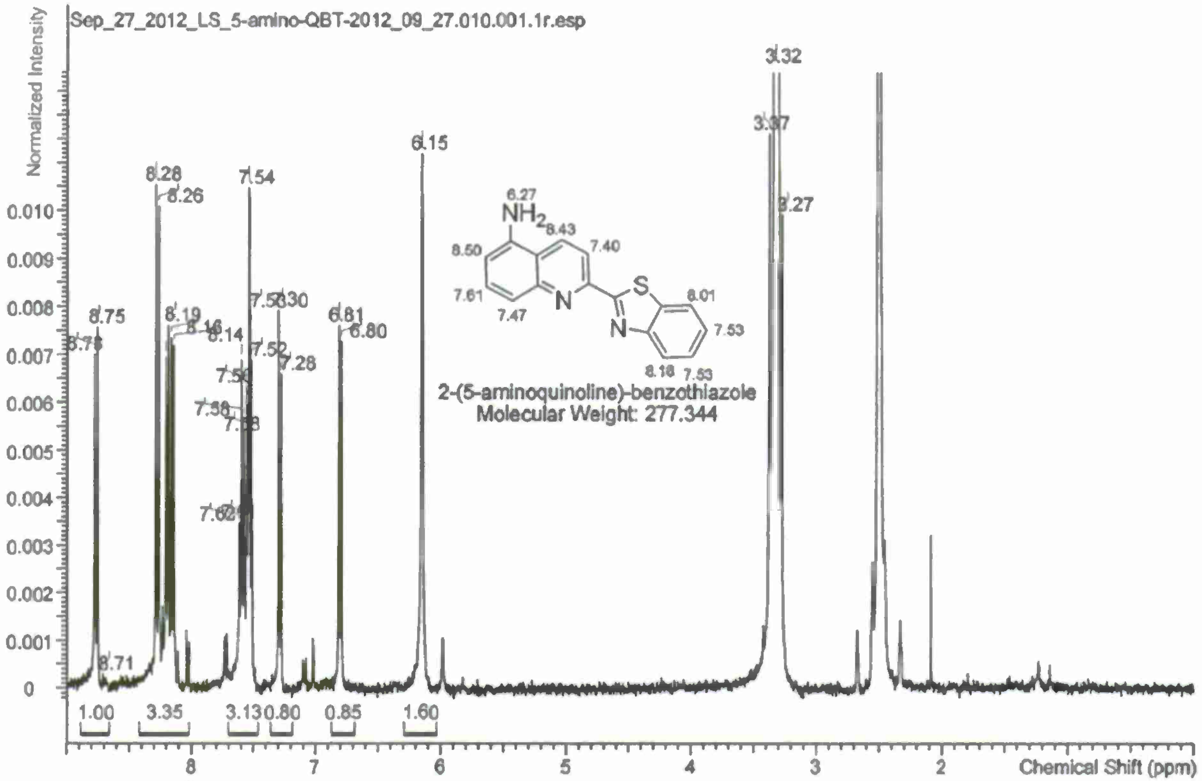
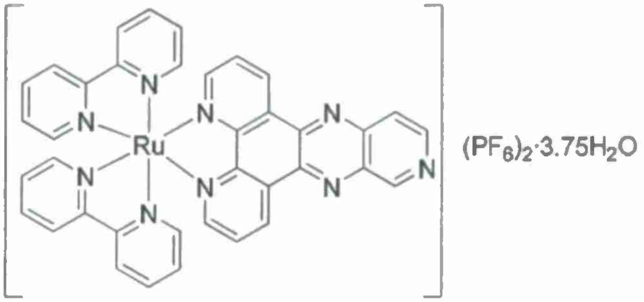


Figure 12. A ^{1}H NMR spectrum of 2-(5-aminoquinoline)-benzothiazole in DMSO-d_6 along with the Chemdraw predicted shifts. [NH_2] = 6.15.

Synthesis of [Ru(bpy)$_2$(tbtp)](PF$_6$)$_2$·3.75H$_2$O



[Ru(bpy)$_2$(tbtp)](PF$_6$)$_2$·3.75H$_2$O
Molecular Weight: 1054.21
Structure 1

[Ru(bpy)$_2$(phendione)](PF$_6$)$_2$ (1.08 g, 0.495 mmol) in CH$_3$CN (60 mL) was added to a 500 mL round bottom flask, which began stirring in an oil bath, and appeared dark orange in color. Next, 3,4-diaminopyridine (0.2475 g, 2.3 mmol) in methanol (270 mL) was added down the condenser and the solution became red. Next, the temperature was increased to 80 °C. The reaction mixture was refluxed at 80.0 °C in a mineral oil bath (hot plate temperature = ~145 °C, IKA C-MAG H57 hot plate) for 24 hours.

Next, the reaction mixture was cooled to room temperature, then rotary evaporated to dryness and NH$_4$PF$_6$ (3 g) was added along with filtered saturated aqueous KPF$_6$ (160 mL). The precipitate was filtered off and air dried.

Column chromatography was performed using Sephadex lipophilic LH-20 at a height of 42 cm and a diameter of 5.5 cm and with 2:1 EtOH:CH$_3$CN as eluent. Faction 1 was discarded. Faction 2-4 were combined. Faction 5-8 were also combined and expected to contain pure product. Yield: 0.4848 g, 0.46 mmol, 93 %

Elemental analysis was performed.

Element	Predicted	Measured	Difference	Measured	Difference	Measured	Difference	Average
C	44.95	43.05	-1.9	41.59	-3.36	40.51	-4.44	41.72
H	2.75	3.04	0.29	3.1	0.35	2.74	-0.01	2.96
N	12.75	10.11	-2.64	10.13	-2.62	10.04	-2.71	10.09
P	6.27	5.31	-0.96					5.31
Ru	10.22	8.28	-1.94					8.28

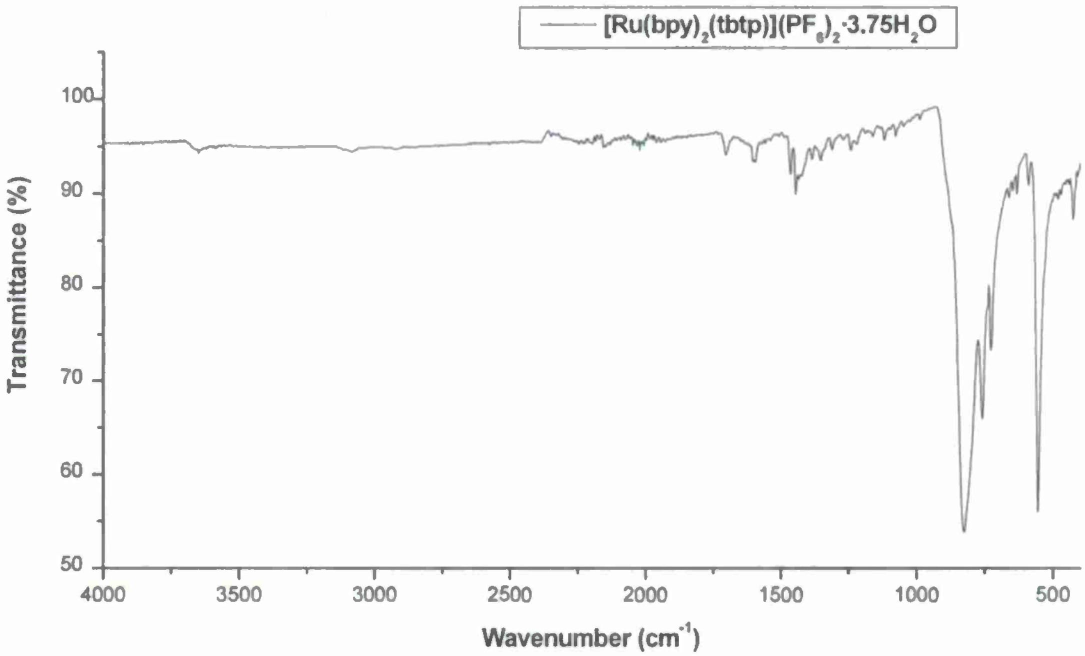


Figure 1. An FTIR spectrum of crude [Ru(bpy)$_2$(tbtp)](PF$_6$)$_2$·5H$_2$O.

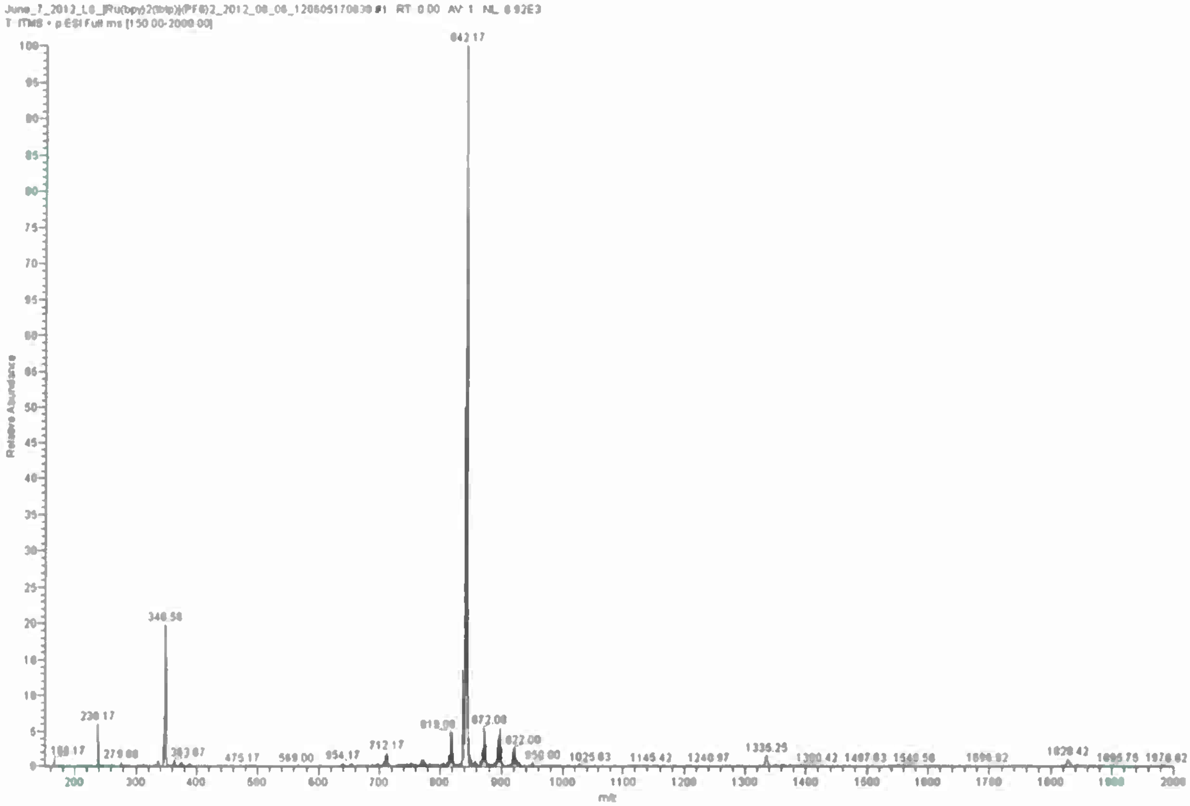


Figure 2. An ESI MS of $[Ru(bpy)_2(tbtp)](PF_6)_2 \cdot 3.75H_2O$ in anhydrous CH_3CN. $[M - PF_6]^+ = 842.17$ and $[M - 2PF_6]^{2+} = 348.58$.

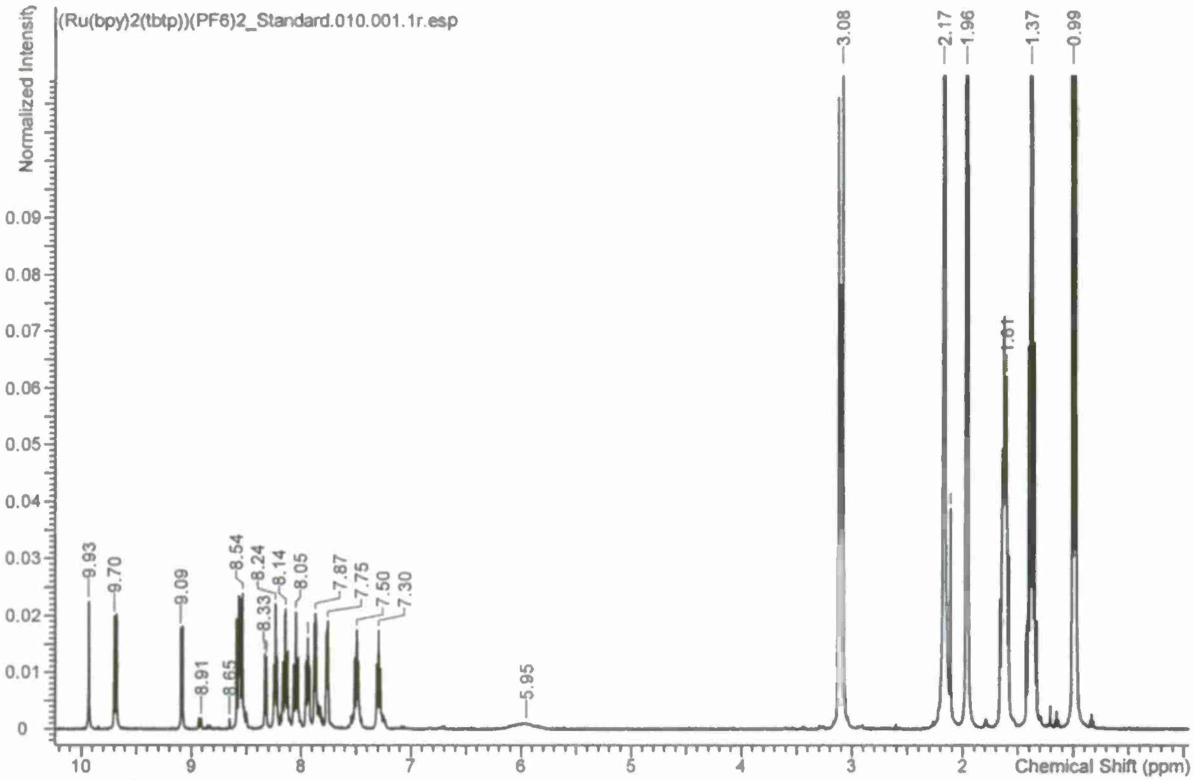
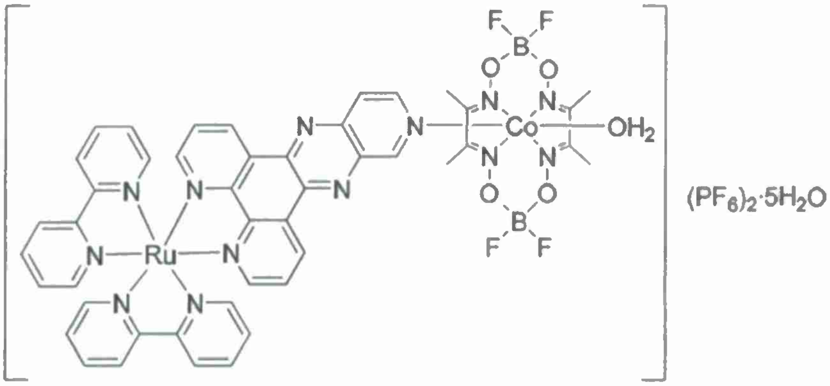


Figure 3. A ^1H NMR of $[Ru(bpy)_2(tbtp)](PF_6)_2 \cdot 3.75H_2O$ in CD_3CN.

Synthesis of $[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2{\cdot}5H_2O$



$[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2{\cdot}5H_2O$
Molecular Weight: 1479.499

To a 250 mL round bottom flask with a stir bar was added $[Ru(bpy)_2(tbtp)](PF_6)_2{\cdot}3.75H_2O$ (0.2 g, 0.1897 mmol) and $[Co(dmgBF_2)_2(H_2O)_2]$ (0.0798 g, 0.1897 mmol) with acetone (100 mL) and was stirred for three hours. Next, the reddish brown reaction mixture was rotary evaporated to dryness. Next, ether was added and the product was sonicated to help free it from the glass. The mixture was vacuum filtered until dry and collected. Yield: 0.2551 g, 0.17 mmol, 91%

Elemental analysis was performed.

Element	Predicted	Measured	Difference	Measured	Difference	Average
C	36.53	37.22	0.69	38.07	1.54	37.645
H	3.34	3.18	-0.16	2.97	-0.37	3.075
N	12.31	10.95	-1.36	11	-1.31	10.975
F	20.55	16.29	-4.26			16.290
Co	3.98	3.43	-0.55			3.430
P	4.19	2.92	-1.27			2.920
Ru	6.83	5.61	-1.22			5.610

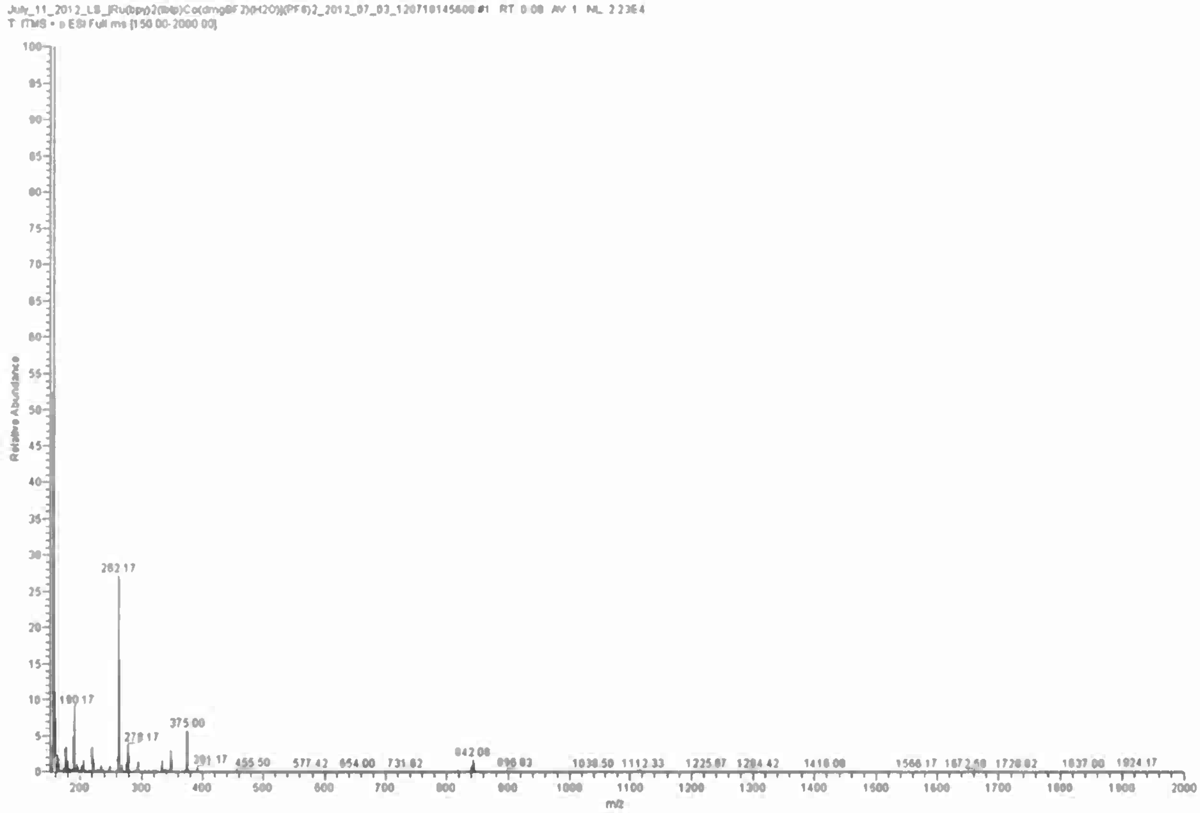


Figure 4. An ESI MS of $[Ru(bpy)_2(tbtp)Co(dmgBF_2)_2(H_2O)](PF_6)_2\cdot5H_2O$. $[M - PF_6]^+ = 1244$.