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A novel ruthenium(II)-cobaloxime supramolecular complex for photocatalytic H₂ evolution: Synthesis, characterisation, and mechanistic studies

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Abstract

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 RuCl₃·xH₂O to produce [Ru(pbt)₂Cl₂].0.25CH₃COCH₃, **2**, which was then reacted with 1,10-phenanthroline-5,6-dione (phendione), **3** in order to produce [Ru(pbt)₂(phendione)](PF₆)₂·4H₂O, **4**. Compound **4** was then reacted with 4-pyridinecarboxaldehyde in order to produce [Ru(pbt)₂(L-pyr)](PF₆)₂·9.5H₂O, **5** (where L-pyr = (4-pyridine)oxazolo[4,5-*f*]phenanthroline). Compound **5** was then reacted with [Co(dmgbF₂)₂(H₂O)₂] (where dmgbF₂ = difluoroboryldimethylglyoximate) in order to produce the mixed-metal binuclear complex, [Ru(pbt)₂(L-pyr)Co(dmgbF₂)₂(H₂O)](PF₆)₂·11H₂O·1.5CH₃COCH₃, **6**. [Ru(Me₂bpy)₂(L-pyr)Co(dmgbF₂)₂(OH₂)](PF₆)₂, **7** (where Me₂bpy = 1,10-phenanthroline, 4,4'-dimethyl-2,2'-bipyridine) and [Ru(phen)₂(L-pyr)Co(dmgbF₂)₂(OH₂)](PF₆)₂, **8** were also synthesised. All complexes were characterized by elemental analysis, UV-visible absorption, ¹¹B, ¹⁹F, and ⁵⁹Co 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)

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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 H₂ gas in the presence of H⁺ ions. A proposed mechanism for the generation of hydrogen is presented.

Introduction

Due to the fact that fossil fuel reserves are rapidly diminishing, emphasis has been placed on the use of renewable energy to meet the fuel needs of the world. Solar-to-chemical energy conversion is one of the most attractive for sustainable development; thus there is a growing need for the direct generation of molecular hydrogen from water as a result of a convenient and clean energy vector, while utilising renewable resources, for example, water and sun light.^{1–6} However, splitting water into hydrogen and oxygen is a complex multi-electron redox process⁷ involving high energy barriers that requires either an electric potential or a catalyst to lower energy barriers. The splitting of water into oxygen and hydrogen has utilised catalysts that are derived from expensive and rare noble metals, for example Pt, Pd, Rh, *etc.*,^{8, 9} which are not competitive to fossil fuels, and unsuitable to meet global demands.¹⁰ More recently and in the past, efforts in research have shifted from heterogeneous to the use of homogeneous catalytic processes that are based on cheaper and abundant first-row transition metals.^{11–19}

The entire water-to-hydrogen process first requires the oxidation of water to protons and O₂ followed by the reduction of protons to hydrogen. Success has been achieved on water oxidation,^{20–22} but, however, our focus is on the latter reaction designed to produce H₂. While one approach is to mimic the core of natural hydrogenases,^{23–26} there have also been reports of cobaloxime-containing complexes that are efficient electrocatalysts for hydrogen evolution.^{7, 27–39} Cobaloximes are composed of a Co(II) centre, two equatorial glyoxime ligands and two exchangeable axial ligands, which influence the catalytic activity.³⁸ Lehn and co-workers pioneered the first studies on homogeneous photogeneration of hydrogen using [Co(dmgH)₂(OH)₂] (where dmgH = dimethylglyoximate) as a catalyst with [Ru(bpy)₃]²⁺ as photosensitizer and triethanolamine (TEOA) as a sacrificial electron donor in a DMF solution.¹⁵

Connolly *et al.*,²⁸ Razavet *et al.*,³⁸ and more recently, Dempsey *et al.*^{7, 29} carried out thorough investigations of the mechanisms and kinetics of H₂ reduction by cobaloximes. Whereas three different pathways were postulated, all proceed through the same intermediate, a Co(III)-hydride (Co(III)-H) complex that possesses a high hydridic character. Depending on the relative concentrations of protons and Co(I), Co(III)-H is either protonated and releases H₂ in a heterolytic pathway or Co(III)-H is reduced by Co(I) to form Co(II)-H, followed by protonation and H₂ release.²⁹ The former pathway is energetically unfavourable since the formation of Co(III) involves high energy barriers. A third, homolytic and energetically more favourable pathway was suggested in which two Co(III)-H species release H₂ and form Co(II) in a reductive elimination step.^{29, 38} More recently, Muckerman and Fujita⁴⁰ carried out theoretical studies of the reduction potentials of [Co(dmgBF₂)₂(H₂O)₂] in an acetonitrile solution so as to shed light on its electrocatalytic mechanism for hydrogen production. Muckerman and Fujita⁴⁰ proposed three mechanisms, all of which are believed to proceed through the formation of Co(III)-H. Their results indicate that the mechanism involving a Co(II)-H intermediate is the most likely.

In an approach to couple an H₂ evolution catalyst to a photosensitizer for photocatalytic H₂ generation, Fihri *et al.*^{12, 13} synthesized a series of supramolecular catalysts comprising a cobaloxime-based catalytic centre and a Ru(II)-based photosensitizer. The coupling was performed by replacing one of the axial H₂O ligands of the cobaloxime with a pyridine-functionalized ruthenium(II)-polypyridine complex. These complexes were tested for

photochemical hydrogen generation from $[\text{Et}_3\text{NH}]\text{BF}_4$, where it was found that the mixed-metal binuclear ruthenium(II)-cobalt(II) complexes were more efficient in hydrogen production than their corresponding multi-component systems under the same conditions. A complex containing a BF_2 -bridged Co(II) centre was found to be superior when compared to those with an H-bridged Co(III) centre because the Co(II) state in the former is more easily reducible and more resistant towards side reactions, for example, acidic hydrolysis and hydrogenation.^{12, 13}

Li et al.⁴¹ also studied related mixed-metal binuclear ruthenium(II)-cobalt(II) complexes with and without linker conjugation in order 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 was found to exhibit higher activity for hydrogen production.⁴¹

Over the years, our research group has been interested in the synthesis and characterisation of bridging and terminal ligands for the construction of mixed-metal complexes that have at least one ruthenium(II) metal centre. In this work, we followed the approach by Fihri et al.^{12, 13} and synthesized three novel mixed-metal binuclear catalysts containing a Ru(II) photosensitizer and a cobaloxime for photocatalytic H_2 production in acetonitrile. The photocatalysts differ in their terminal ligands around the ruthenium(II) metal centre, and have the formulae $[\text{Ru}(\text{pbt})_2(\text{L-pyr})\text{Co}(\text{dmgBF}_2)]\text{PF}_6$ **6**, $[\text{Ru}(\text{Me}_2\text{bpy})_2(\text{L-pyr})\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)](\text{PF}_6)_2$ **7**, and $[\text{Ru}(\text{phen})_2(\text{L-pyr})\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)](\text{PF}_6)_2$ **8**. We chose those terminal ligands in order to elucidate the effects of ligand structural variations on the activity of photocatalytic behaviour for the production of hydrogen in acidic media. In this paper, we report for the first time, EPR and NMR (^{11}B , ^{19}F , and ^{59}Co) spectroscopic studies, followed by photocatalytic and photochemical studies on compound **6**. The precursor compound (compound **5**) to compound **6** bearing the Ru(II) photosensitizer and L-pyr bridging ligand, but no Co(II) metal centre, was examined in order to study the effect of molecular coupling on an intra-molecular electron transfer and catalytic activity.

Results and discussion

Compound **6** was synthesized (Scheme 1) in good yields by the substitution of one axial water ligand of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ by the pyridine moiety of compound **5**; while compounds **7** and **8** were prepared as by Horne *et al.*⁴² All complexes were characterized by elemental analysis, UV-visible, ^{11}B , ^{19}F , and ^{59}Co NMR, ESR spectroscopy, and cyclic voltammetry, where appropriate.

ESI MS analysis

Low and high resolution ESI MS data were acquired for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, compounds **4**, **5**, and **6** (see ESI, Fig. S1–S4). In all mass spectral analyses, we have assigned M as the molecular ion minus any solvates. A base peak for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ occurred at $m/z = 418.58$ which is indicative of the presence of the $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2 + \text{H}]^+$ species. Compound **4** gave the following m/z values: 368.0 (100%, $[\text{M} - 2\text{PF}_6]^{2+}$) and 881.0 (100%, $[\text{M} - \text{PF}_6]^+$). High resolution ESI MS gave $m/z = 880.9938$. Compound **5** gave m/z : 412.0 (100%, $[\text{M} - 2\text{PF}_6]^{2+}$) and 969.0 (100%, $[\text{M} - \text{PF}_6]^+$). High resolution ESI MS also gave $m/z = 969.0368$ for compound **5**. Compound **6** was found to be unstable in the chamber of the mass spectrometer, but the mass spectrum showed the presence of the following species: m/z values: 412.0 (100%, $[\text{M} - 2\text{PF}_6 - \text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})]^{2+}$), 969.0 (100%, $[\text{M} - \text{PF}_6 - \text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})]^+$). $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ was also detected in the mass spectrometer at $m/z = 418$, which is the m/z ratio found between m/z values of 412.0 and 431.8. This m/z ratio could be due to $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]^+$ being formed from the reaction between H_2O (in CH_3CN) and the $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})]^+$ species.

FT IR and UV-visible spectral studies

FT IR spectra were acquired for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, compounds **4**, **5**, and **6** (see ESI, Fig. S5–S8). $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ has a (B–O) stretching frequency at 1160.47, while the (B–F) stretching frequency occurs at 954.14 and 826.29 cm^{-1} .^{43, 44} The main stretching frequency for the PF_6^- anion occurs at 827.91 and 827.73 cm^{-1} for compounds **4** and **5**, respectively. The stretching frequency of 823.43 cm^{-1} is a combination of (B–F) and (PF_6^-) stretching frequencies for compound **6**, while the (B–F) stretching frequency occurs at 1161.09 cm^{-1} . The stretching frequency for C=O in compound **4** occurs at 1699.10 cm^{-1} ; while the stretching frequency for C=N occurs at 1620.04, 1603.70, and 1614.14 cm^{-1} for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, compounds **5** and **6**, respectively. The UV-visible spectrum of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ in acetonitrile (Figure 1 and ESI, Fig. S9), show the main spectral bands occur at 260 (sh), 318, 424, and 1163 nm, with the molar extinction coefficients being 6.5×10^3 , 2.5×10^3 , 3.6×10^3 , and $120 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. In DMSO, the main spectral bands occur at 268, 337 and 472 nm, with the molar extinction coefficients being 7.9×10^3 , 1.9×10^3 , and $3.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. These values compare well with the electronic spectrum of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ in water as reported by Wangila and Jordan,⁴⁵ where the main spectral bands for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ occur at 260, 326, and 456 nm with the molar extinction coefficients being 6.38×10^3 , 2.06×10^3 , and $4.04 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The differences in the molar extinction coefficients values are due to solvatochromism as a result of the two different solvent systems.

All of the ruthenium(II) complexes (Figure 1 and ESI, Fig. S9) have extensive light absorbing properties which are characterized by UV-visible spectrophotometry. Compounds **4**, **5**, **6**, **7**, and **8**, all possess intense intra-ligand transitions in the UV region, while the lowest Ru(d) bridging ligand (BL) CT bands occur in the low energy visible spectrum.

The MLCT bands for compounds **4**, **5**, **6**, **7**, and **8**, occur at 458, 466, 466, 439, and 431 nm, respectively. The molar extinction coefficients for all compounds are listed in Table 1. Compound **4** absorbs at 947 nm (= $82 \text{ M}^{-1} \text{ cm}^{-1}$); while compound **5** (Figure 1 and S9, supplementary) absorbs at 723 nm (= $360 \text{ M}^{-1} \text{ cm}^{-1}$); and compound **6** absorbs at 720 nm (= $400 \text{ M}^{-1} \text{ cm}^{-1}$) and 1136 nm (= $100 \text{ M}^{-1} \text{ cm}^{-1}$). Note the artifact at 1286 nm for compound **6** is due to poor subtraction of Woods anomalies in the spectrophotometer.

The main feature with compound **6** is the observance of a very broad absorption band at 1136 nm, which is blue-shifted when compared to 1163 nm of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ in acetonitrile. This blue shift is due to the coordination of the pyridine moiety from the bridging L-pyr ligand in compound **5**. These broad bands at 1136 and 1163 nm indicate the presence of a low-spin Co(II) metal centre in $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6**. This is due to the transition within the octahedral 2E_g ground state, which is split by the Jahn-Teller effect and tetragonal ligand field, ($^2\text{A}_{1g} \rightarrow ^2\text{B}_{1g}$). Such broad bands, along with such an explanation were observed for $[\text{Co}(\text{dmvi})_2(\text{phen})] \cdot 2\text{CHCl}_3$ (where dmvi = the dimethylviolurate anion),⁴⁶ $[\text{Co}(\text{tpy})_2]^{2+}$,⁴⁷ $\text{K}_2\text{Ba}[\text{Co}(\text{NO}_2)_6]$,⁴⁸ $[\text{Co}(\text{1-oxa-4,7-diazacyclononane})_2]\text{I}_2$,⁴⁹ and the $[\text{Co}(\text{CN})_5]^{3-}$ anion.^{50, 51}

¹¹B, ¹⁹F, and ⁵⁹Co NMR spectroscopic studies

In an NMR spectroscopic study, ¹¹B, ¹⁹F, and ⁵⁹Co NMR spectra were acquired for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** in DMSO-*d*₆ at ambient temperature (Figures 2 – 4). These NMR spectroscopic studies were carried out so as to enable us to verify whether there is coordination of the L-pyr bridging ligand (BL) to the Co(II) metal centre, and what environmental effect there is on the BF₂ moiety and the Co(II) metal centre in the absence and presence of the pyridine moiety of the bridging ligand.

Figure 2 shows the ^{11}B NMR spectra for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6**. Chemical shifts of 0.69, 3.55, and 39.04 ppm were found for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, the chemical shift of 39.04 ppm having the highest intensity. On the other hand, compound **6** produced chemical shifts at 0.66, 1.47, 2.98, and 37.95 ppm. It must be noted that the highest intensity occurs at 37.95 for compound **6**. The chemical shifts for compound **6** are believed to be due to presence of various diastereoisomers and possible conformations (types A–C as shown below) that could be present in DMSO- d_6 . Such conformations have been reported for $[\text{Co}(\text{dmgBF}_2)_2(\text{py})]^-$ and $[\text{Cu}(\text{dmgBF}_2)_2(\text{CO})]^-$ anions.^{52, 53} On the other hand, the three chemical shifts for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ could be due to the presence of the conformations (types A–C shown below).

Figure 3 shows the ^{19}F NMR spectra for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6**, with the predominant species resonating at -148.4 ppm for both compounds. Chemical shifts of -145.6 , -146.6 , and -148.4 ppm are present for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, while chemical shifts at -143.8 , -145.6 , -145.9 , -146.2 , and -148.4 ppm, are present for compound **6**. The numerous chemical shifts for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ could possibly due to the presence of possible conformations (types A–C) existing in the dmgBF_2 ligand; while those present in compound **6** could also be due to a combination of the possible conformations (types A–C) in the dmgBF_2 ligand, and the various diastereomers in the DMSO- d_6 solution. The chemical shifts of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** can be compared to that of $[(\text{Ph-Me}_2\text{diimineO})_2\text{BF}_2]\text{CoBr}_2$ as reported by Berben and Peters,⁵⁴ where -147 ppm was measured for the BF_2 moiety in CD_2Cl_2 .

Transition metal NMR chemical shifts are useful probes of the structure and reactivity of many coordination complexes since those chemical shifts allow for tiny variations at the coordination metal centre under investigation.⁵⁵ It is known that the isotope ^{59}Co exhibits the largest known shielding range.⁵⁶ It is also 100% naturally abundant, possesses a relatively high magnetogyric ratio, and by virtue of the magnetic mixing of its occupied and excited d orbitals, it may experience substantial paramagnetic deshielding ($>15,000$ ppm) that will reveal subtle changes in the chemical environment of a cobalt metal centre.⁵⁶ The ^{59}Co NMR properties have been extensively studied for cobaloximes $[\text{RCo}(\text{dmgH})_2\text{L}]$ (where dmgH = dimethylglyoximate).^{57–59} Based on these facts, we have decided to use ^{59}Co NMR spectroscopy as a tool in order to verify whether we have formed the mixed-metal binuclear compound **6**. Figure 4 shows the ^{59}Co NMR spectra for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6**, where the chemical shift for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ occurs at 5652 ppm; while that for compound **6** occurs at 5401 ppm. There is an upfield shift on substitution of one of the axial water molecules in $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ by the pyridine moiety in compound **5**. Clearly, this is evidence of the formation of our mixed-metal binuclear complex. Our ^{59}Co NMR chemical shifts can be compared to a series of vitamin B_{12} model complexes that were reported by Tavagnacco *et al.*⁵⁹ (Table 2). In Table 2, the ^{59}Co NMR chemical shifts for both $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** are more downfield when compared to the values as reported by Tavagnacco *et al.*⁵⁹. These differences are likely due to a solvent effect since our spectra were measured in DMSO- d_6 instead of acetone- d_6 . It must be noted that there is a solvent influence on the ^{59}Co NMR chemical shifts for some cobalt(III) complexes, for example $[\text{Co}(\text{CN})_6]^{3-}$ as reported by Taura.⁶⁰ Our chemical shifts for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** are more downfield when compared to the solution ^{59}Co NMR chemical shifts of vitamin B_{12} ($= 4650 \pm 20$ ppm), B_{12} coenzyme ($= 4480 \pm 30$ ppm), methyl cobalamin ($= 4215 \pm 10$ ppm), and dicyanocobyrinic acid heptamethyl ester ($= 4095 \pm 5$ ppm) as reported by Medek *et al.*³⁷

ESR spectroscopic studies

In this study, ESR spectroscopy is used to gather relevant information about the compounds that contain a paramagnetic Co(II) metal centre. As such, we now report ESR spectroscopic studies for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compounds **6** – **8**, but with the main focus on $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6**.

Q-band ESR studies

We were also able to acquire Q-band ESR spectra (ESI, Fig. S10) for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** in DMSO at 100 K. The spectra exhibit a larger amount of g- and A-strain as seen in similar systems studied by Harmer *et al.*⁶¹ who carried out X- and Q-band ESR spectroscopic studies on corrin nitrogens and remote dimethylbenzimidazole nitrogen interactions in Cob(II)alamin. Their ESR parameters were as follows: $g_1 = 2.272$, $g_2 = 2.230$, $g_3 = 2.004$, $A_1^{\text{Co}} = 30$ MHz, $A_2^{\text{Co}} = 40$ MHz, and $A_3^{\text{Co}} = 305$ MHz). Their EPR parameters compare favourably with our A_1^{Co} and A_2^{Co} values, but our A_3^{Co} value is nearly seven times greater (our spin Hamiltonian parameters are shown in Table 3). In addition, the DMSO solvent does not form a good glass. Both facts cause difficulties in interpreting the spectra. Whereas no resolved hyperfine is seen in compound **6**, there is an increase in line width from approximately 7 G in $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ compared to approximately 32 G in compound **6**, indicating the coordination of the pyridine moiety from compound **5**.

X-band ESR studies

We were able to acquire X-band ESR spectra for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compounds **6** – **8** in DMSO at 4 K. The ESR spectra in Figure 5 reveal the hyperfine structural features of the Co(II) metal centre of the cobaloxime moiety for compounds **6** – **8**, all of which compare well with those complexes as reported by Rangel *et al.*^{62, 63} ESI Fig. S11 shows the ESR spectrum of compound **8** at a warmer temperature of 101 K, where the hyperfine features were more defined. The spectrum has a larger g tensor anisotropy where three g features are discernable. This is exhibited in the high field region as a result of the hyperfine coupling of the unpaired electron with cobalt (^{59}Co , $I = 7/2$) and nitrogen (^{14}N , $I = 1$) atoms. Each of the eight lines in the ESR spectrum of compound **8** (ESI, Fig. S11) which arise from coupling to the cobalt(II) centre is further split into three relative intensities 1:1:1, all due to the super hyperfine coupling with one axially bound nitrogen from the pyridine moiety of the bridging ligand, L-pyr. This ESR spectrum is assigned to a low spin cobalt(II)-containing compound with one axially bound substituted pyridine moiety of the bridging ligand, L-pyr. This neatly correlates with the evidence as gathered through our UV-visible-NIR and ^{59}Co NMR spectroscopic studies for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6**.

Table 3 also shows the spin Hamiltonian parameters obtained the X-band ESR experiment for the respective compounds in DMSO.

Electrochemical studies

Elemental analysis and NMR spectroscopic data are consistent with the L-pyr ligand of compound **5** coordinating to the cobalt(II) metal centre of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$. This was further supported by ascertaining the redox properties of the ruthenium(II) metal complexes through cyclic voltammetry. Cyclic voltammograms (Figure 6) of compounds **6** – **8** show a reversible $\text{Co}^{\text{II/I}}$ redox couple occurring at -0.45 V (in CH_3CN with Ag/AgCl as a reference electrode). A similar value of -0.45 V was also obtained for $[\text{Ru}(\text{bpy})_2(\text{L-pyr})\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2](\text{PF}_6)_2$ as reported by Fihri *et al.*¹³ Table 4 shows the respective electrochemical data obtained for compounds **6** – **8**.

Electrocatalytical studies

Electrocatalytical studies were carried out on compound **6**. Compound **6** clearly displays electrocatalytic activity (Figure 7) in acetonitrile on the addition of *p*-cyanoanilinium tetrafluoroborate as a proton source (where [complex] = 1.0 mM, and [H⁺] was varied, 1.5, 3.0, 5.0, and 10.0 equivs.). Figure 7 shows a catalytic peak at the Co(II/I) couple for compound **6** where a catalytic wave corresponding to hydrogen evolution was observed at -0.5 V vs. Ag/AgCl, a process that is comparable with that of [Ru(bpy)₂(L-pyr)Co(dmgbF₂)₂(H₂O)](PF₆)₂.¹³ Upon addition of *p*-cyanoanilinium tetrafluoroborate, catalytic currents were observed near the Co^{II/I} redox couple, where increasing acid concentration produced a change from a reversible process to an irreversible process. It is also noticed that a second redox couple appears on addition of three equivalents of the proton source. We are yet to ascertain the species that are formed upon addition of three equivalents of the proton source. As reported in literature,^{29, 33, 34} we can conclude that since Co(II) is regenerated during H₂ production, there is no return oxidation wave.

Photocatalytic studies with compounds **6** and **8**

Photocatalytic studies were carried out on compounds **6** and **8** in acetonitrile as solvent, and in the presence of *p*-cyanoanilinium tetrafluoroborate as a proton source in order to quantify the amount of H₂ being produced on irradiation 300 nm. We used either Et₃N or triethanolamine ((EtOH)₃N) as a sacrificial electron donor in our study. One problem encountered with the use of these sacrificial reducing agents, is that when increasing their concentration for faster quenching while keeping the pH constant by increasing the amount of acid accordingly, the catalysts showed degradation effects. It has been reported in the literature that cobaloximes degrade in acetonitrile in the presence of a strong acid such as *p*-cyanoanilinium.²⁷ While a 1 M concentration of (EtOH)₃N with only 90 mM proton source led to a good H₂ production rate, the same concentrations for Et₃N yielded only very small amounts of H₂ probably due to the higher pH of the solution as the pK_a of Et₃N is higher (10.7) than that of (EtOH)₃N (7.8). Consequently we used different concentrations for the two electron donors and adjusted the donor/acid molar ratios to 1.5 for Et₃N (85 mM) and a ratio of three (3) for (EtOH)₃N (440 mM). The concentration of catalyst was always 300 μM. Compound **6** produces higher H₂ evolution rates when compared to compound **8** (see Figure 8) in each experiment with an average rate of 100 μL h⁻¹ using Et₃N (TOF = ~1 h⁻¹) and over 200 μL h⁻¹ using (EtOH)₃N (TOF = ~2 h⁻¹). The production remained fairly constant for approximately eight hours, but then declined to an average of 20 μL h⁻¹ with either electron donor. H₂ evolution was maintained over a period of at least 42 hours. Compound **8** displayed a production rate of 64 μL h⁻¹ using Et₃N (TOF = ~0.5 h⁻¹) and 100 μL h⁻¹ using (EtOH)₃N (TOF = ~1 h⁻¹) over the first eight hours and then also slowed down. In the absence of any catalyst, no H₂ production was observed under the same conditions. A solution containing compound **5** and [Co(dmgbF₂)₂(H₂O)₂] as separate compounds produced H₂ at a slow rate of approximately 8 μL min⁻¹ which proves that the supramolecular complex (compound **6**) with the sensitizer covalently coupled to the catalytic centre offers a more efficient electron transfer. The graphs in Figure 9 display the absolute amount of H₂ produced in the reactor for compounds **6** and **8** as well as compound **5** plus [Co(dmgbF₂)₂(H₂O)₂] as separate species.

The turnover frequency is lower than those reported for similar cobaloximes. Fihri *et al.*¹³ achieved 32 turnovers during the first hour and then observed a declined rate of 7–8 h⁻¹ in acetone; while Li *et al.* reported a TON of 48 over 8 h of illumination.^{13, 41} However, comparing catalyst performance across laboratories using different experimental set-ups is difficult. In particular, the photon flux of the illumination source has to be taken into consideration.

The low vapour Hg lamp used for photocatalysis emits four discrete wavelengths with a total photon flux of $1 \times 10^{16} \text{ s}^{-1} \text{ cm}^{-2}$ (see material section for lamp and calculation details) and 5 mW cm^{-2} total irradiance. Fihri *et al.*¹³ and Li *et al.*⁴¹ used a 150 W or 500 W illumination source, respectively. The commonly used 1.5 AM standard light source emits a continuum and provides a total irradiance of 100 mW cm^{-2} . Based on the total photon flux in our experiment, an H_2 quantum yield of 2.2% was estimated. The results also indicate that the sacrificial electron donor significantly affects the H_2 evolution rate making an independent evaluation of catalyst performance based solely on catalytic rate difficult.

Photochemical Studies

Photochemical studies were carried out on compounds **5** and **6**. In Figure 9, the steady-state photoluminescence of compound **6** (blue line) is compared to that of compound **5** (black line). The difference in area suggests a quenching factor of approximately 2.4. In order to observe an intra- molecular electron transfer, triethylamine (Et_3N) was added to the reaction solution as a sacrificial electron donor. A Stern-Volmer analysis revealed a linear relationship between the concentration of Et_3N and the lifetime of the excited $^*\text{Ru(II)}$, where we determined a quenching rate for triethylamine of $k_q = 3400 \pm 160 \text{ M}^{-1} \text{ s}^{-1}$.

The strong photoluminescence of the compounds limited the observation wavelengths for transient absorption (TA) measurements to a maximum of 590 nm. After performing preliminary experiments, TA probe wavelengths of 420, 530 and 590 nm were chosen. At each wavelength, a series of three experiments were performed: First, absorption was measured for either compound alone (catalyst or precursor) at a concentration of a $100 \mu\text{M}$. In the next step NEt_3 was added as electron source in a sufficient amount to observe quenching ($>1\text{M}$), and finally p-cyanoanilium tetrafluoroborate was added as proton source at a concentration of 26 mM. The reagents were added without exposure to air using a custom-made cuvette described in the method section. In addition to the transient absorption measurements, steady-state UV-visible absorption spectra were taken before and after each experiment.

Figure 10a displays the TA over $8 \mu\text{s}$ following excitation for compound **6** on the right and compound **5** on the left for the three selected observation wavelengths. Without Et_3N only the fast decay of $^*\text{Ru(II)}$ was observed at 420 nm (top graph, black or blue line, respectively). In the presence of Et_3N , but absence of a proton source, the catalyst shows a long-lived absorption emerging rapidly after excitation (red line). We attributed this to the formation and stabilization of Ru(II)-BL-Co(I) species originating from $^*\text{Ru(II)-BL-Co(II)}$ that becomes Ru(III)-BL-Co(I) . Ru(III)-BL-Co(I) then reacts with Et_3N to form Ru(II)-BL-Co(I) . With no electron donor or without the Co(II) moiety, this species does not exist, and consequently no TA is observed in compound **5** even in the presence of Et_3N . The absorption remains infinitely under anaerobic conditions.

As shown in the second graph from the top, a long-lived TA is observed occurring at 530 nm in both compounds in the presence of Et_3N . Since compound **5** lacks a Co(II) metal centre, this absorption is likely caused by electron transfer to the organic ligands, in particular when no proton source is available to accept the electrons. This absorption band can offer insight into the stability and efficiency of the catalyst. As will be discussed later, the transient absorption disappears upon the addition of a proton source.

An important electron transfer can be observed at 590 nm in Figure 10b. A long-lived absorption occurs only in compound **6** in the presence of Et_3N (red line) but not in compound **5** (green line). The absorption increases slowly and becomes clearly visible after approximately $10 \mu\text{s}$ and is therefore not detectable in the $10 \mu\text{s}$ time window shown in Fig 10a bottom. This observation in this spectral range clearly points to the build-up of Ru(II)-

BL-Co(I) since it only occurs in the catalyst and in the presence of Et₃N. The absorption persists under anaerobic conditions, and is detectable to the naked eye by a red-shift in colour of the solution. Upon addition of *p*-cyanoanilinium tetrafluoroborate under anaerobic conditions the colour quickly returns to its original hue (data not shown). We believe that the Ru(II)-BL-Co(I) species remains intact as a binuclear supramolecular species, and that this is the very first evidence of its existence.

The steady-state absorption spectra shown in Figure 11 confirm the results obtained with the transient measurements. In the absence of Et₃N no persistent changes to either compound **5** or compound **6** occurred under laser irradiation, indicating stability of either compound under the experimental conditions. In the presence of Et₃N the spectra for either compound show significant differences after laser irradiation. Compound **5** (Figure 11a, green line) shows local absorption maxima at 420 and 530 nm after laser irradiation, the same wavelengths a transient absorption was observed. Compound **6** (Figure 11b, red line) displays the same new local maximum plus an additional band centred around 650 nm which we attribute to the maximum absorption of the Co(I) species and which was captured as TA at 590 nm. Upon addition of *p*-cyanoanilinium tetrafluoroborate as proton source both compounds return to their original spectra (identical to black and blue line, respectively). This indicates the reversal of the electron transfers and the recovery of Co(II) through hydrogen production.

Based on the cumulative data, we suggest a mechanism for the hydrogen evolution process which is based on an intra-molecular electron transfer from an excited *Ru(II) to the Co(II) catalytic metal centre leading to the formation of a reactive Co(I) species (Scheme 2).

Conclusions

We have successfully synthesized a novel mixed-metal ruthenium(II)-cobalt(II) binuclear photocatalyst, which was used for H₂ evolution in acidic acetonitrile solutions. Results from UV-visible, ⁵⁹Co NMR and ESR spectroscopic characterization provided strong evidence of the coupling of the Co(II) metal centre to the Ru(II) metal centre of the photosensitizer through the nitrogen atom of the pyridine moiety in the bridging ligand. Photochemical and spectroscopic measurements proved that the complex remains intact upon illumination in acidic acetonitrile. The intra-molecular electron transfers observed in spectroscopic lifetime measurements are consistent with the H₂ evolution mechanism reported in the literature.^{28, 29, 38} Our results also show how the terminal ligands in compounds **6** and **8** affect the properties of the catalyst and consequently its performance. The redox couple of Co^{II/I} remains constant, while the Ru^{III/II} redox couple varies for compound **6**, compound **7**, and compound **8**. An absorbance band at 1136 nm in the NIR indicates the low spin nature of the Co(II) metal centre within the cobaloxime moiety of compound **6**. Our photocatalytic studies demonstrate the advantage of a binuclear complex facilitating an intra-molecular electron transfer from a Ru(II) photosensitizer to a catalytic Co(II) metal centre in homogeneous catalysis. Future work will focus on the bridging ligand with the goal of synthesizing a mixed-metal binuclear complex which is very stable in aqueous acidic media, but possesses a redox couple of ~ -0.4 V for the Co^{II/I} redox reversible process and exhibits extensive quenching on excitation.

Experimental

Materials and methods

Analytical or reagent grade chemicals were used throughout this study. K₃[Co(CN)₆] was synthesised as described by Bigelow.⁶⁴ All the chemicals including solvents were obtained from Sigma-Aldrich (St. Louis, MO, USA) or other commercial vendors and used as

received. Microanalyses (C, H, N) were performed by CHN and ICP-OES and halide analysis by the Microanalysis Laboratory at the University of Illinois Urbana/Champaign, as well as Desert Analytics, Tucson, AZ and Columbia Analytical Services in Tucson, AZ, U.S.A.

^{11}B , ^{19}F , and ^{59}Co NMR spectra were acquired on a Varian 500 MHz spectrometer with DMSO- d_6 as solvent, and $\text{BF}_3\cdot\text{Et}_2\text{O}$ ($\delta = 0$ ppm), $\text{CF}_3\text{CO}_2\text{H}$ ($\delta = -76.55$ ppm⁶⁵), and $\text{K}_3[\text{Co}(\text{CN})_6]$ ($\delta = 289$ ppm⁶⁰) as external references, respectively, all at room temperature.

ESR spectra were acquired on a BrukerBiospin EMX^{micro} X-band ESR spectrometer and a BrukerBiospin Eleksys E500 ESR spectrometer. FT IR spectra were acquired in the range 4000-400 cm^{-1} using the ATR accessory (with a diamond crystal) on a Nicolet 6700 FTIR spectrophotometer.

Cyclic voltammetric (CV) data were acquired on a Bioanalytical Systems Inc. Epsilon workstation on a C3 cell stand at RT. Acetonitrile solutions which contained 1.0 mM of each analyte and 0.10 M tetra-*n*-butylammonium hexafluorophosphate (TBAP) as supporting electrolyte, were saturated with argon for 15 minutes prior to each acquisition. A blanket of argon gas was maintained throughout the measurements. The measurements were carried out with a three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode. The working electrode was polished before each experiment with alumina slurry.

Electronic spectra were recorded using quartz cuvettes on Olis-modernized Cary 14 UV/Vis/NIR, Spectramax M5 (Molecular Devices) and HP8452 diode array spectrophotometers using acetonitrile as the solvent. Fluorescence spectra were recorded on a Varian Cary Eclipse spectrophotometer using a slit width of 10 nm. ESI MS was acquired on an HP Agilent 1956b single-quadrupole mass spectrometer. Samples were dissolved in acidified methanol and introduced by direct injection using a syringe pump and a flow rate of 100 $\mu\text{L s}^{-1}$, while sweeping the cone voltage from 0 to 200 V at a rate of 10 V min^{-1} . ESI MS were also acquired on a Waters Q-tof Ultima mass spectrometer. Cone voltage was 25 V. The samples were dissolved in the CH_3CN at 1 mg mL^{-1} ; then the resulting solution was diluted with methanol to about 5 $\text{ng }\mu\text{L}^{-1}$. The mobile phase was acetonitrile with a flow rate of 50 $\mu\text{L min}^{-1}$.

Photochemical Measurements—Time-resolved and steady-state photochemical measurements were performed at the Beckman Institute Laser Resource Centre (California Institute of Technology). Samples for all experiments were prepared in dry, anaerobic acetonitrile (EMD DriSolv[®]) and placed into a high-vacuum cell consisting of a 1 cm path length fused quartz cuvette (Starna Cells) that was connected to a 10 mL bulb and isolated from atmosphere and the bulb by a high-vacuum Teflon Kontes valve. Anaerobic conditions were achieved by carrying out three freeze-pump-thaw cycles with argon.

Time-resolved data were acquired using 490 nm laser excitation that was provided by 8 ns pulses from a 10 Hz Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series), whose third harmonic was used to pump an optical parametric oscillator (OPO, Spectra Physics Quanta-Ray MOPO-700, tunable in the visible region). Probe light for transient absorption kinetics measurements was delivered by a pulsed 75 W arc lamp (PTI Model A 1010). A digital delay generator controlled the timing between laser excitation and probe light pulses. Sample excitation ($E_{\text{exc}} = 3.2$ mJ/pulse) was collinear with the probe light. After passing through the sample scattered excitation light was rejected by suitable long pass and short pass filters, and probe wavelengths were selected by a double monochromator (Instruments SA DH-10) with 1 mm slits. Transmitted light was detected with a

photomultiplier tube (PMT, Hamamatsu R928), and the PMT current was amplified and recorded with a GageScope transient digitizer. Transient absorption data were recorded in units of OD ($OD = -\log_{10}(I/I_0)$ where I is the time-resolved probe light intensity with laser excitation, and I_0 is the probe light intensity without laser excitation). Samples were continuously stirred. Data were averaged over approximately 1000 shots.

Time-resolved photoluminescence was recorded on the same home-built instrument using the same laser excitation but no probe light. The monochromator was used to select 700 nm emitted light that was detected with the same detection setup described above and recorded as emission intensity.

Photoluminescence lifetimes of the excited $^*Ru(II)$ state were obtained as a function of Et_3N concentration in order to determine the quenching rate by Et_3N by Stern-Volmer analysis.

The quenching rate k_q was calculated using the Stern-Volmer equation ($\tau_0/\tau = 1 + k_q[Q]$, where τ_0 is the intrinsic lifetime, τ is the lifetime with quencher present, and $[Q]$ is the quencher concentration). All instruments and electronics for time-resolved measurements were controlled by software written in LabVIEW (National Instruments). MATLAB R2007a (Mathworks, Inc.) was used for data conversion, while data analysis and graphing was performed using Igor Pro 5.05A (Wavemetrics).

Steady-state UV-visible absorption spectra were recorded in 1 cm path length quartz cuvettes using a Hewlett Packard 8452 spectrophotometer. Steady-state photoluminescence data were acquired in 1 cm path length quartz cuvettes using a Jobin Yvon Spec Fluorolog-3-11 fluorimeter. A xenon arc lamp with wavelength selection provided by a monochromator was used for sample excitation at 490 nm. Right angle emission was selected with a monochromator and detected with a Hamamatsu R928P photomultiplier tube with photon counting.

Photocatalysis—Hydrogen evolution was quantified in a borosilicate immersion well containing two sample ports that were sealed with septa. The illumination was performed from the centre of the well using a Hg immersion lamp (pen-ray model 11SC-1, UVP). The UV portion of the Hg emission spectrum was filtered by the borosilicate reactor so that only the Hg emission lines at 312, 365, 404.7 and 435.8 nm were used for illumination. The reactor was filled with 18 mL acetonitrile containing 85 mM triethylamine as sacrificial electron donor and 55 mM *p*-cyanoanilinium tetrafluoroborate as a proton source. The complex concentration was 300 μM . The solution was flushed with nitrogen before illumination began. Gas samples of 50 μL were taken periodically through the septum using a gas tight syringe and analyzed on a GC equipped with a thermal conductivity detector (Agilent 6890). Hydrogen was identified by its retention time and quantified on an RT-Molsieve column 15 m $\times$ 0.32 mm $\times$ 30 μm (Restek) using argon as carrier gas. A calibration of hydrogen was performed by injecting known amounts of hydrogen gas into an airtight vial of the same volume as the reaction vessel and filled with acetonitrile (18 mL) to account for the fraction that dissolves in the solvent. That way the absolute amount of hydrogen evolved in the reaction vessel could be determined. The detection limit for H_2 in the headspace of the reactor was 5 μL . The oxygen concentration was also monitored in order to detect leakage of the reactor. Control experiments were performed under the same conditions but omitting the photocatalyst.

Estimation of catalyst performance—In order to estimate catalyst performance, the total photon flux [Photons s^{-1}] of the illumination source was calculated using the following formula:

$$\varphi = [P(\lambda_1) \frac{\lambda_1}{hc} + P(\lambda_2) \frac{\lambda_2}{hc}] a$$

where P = the measured power density of the lamp in W/cm^2 , λ = the wavelength in metres, h = the Planck's constant, c = the speed of light, and a = the illuminated area of the lamp (11 cm^2).

The intensity over 312 and 365 nm was measured using an OAI 308 power meter (OAI San Jose, Ca, USA) and for the intensity over 405 and 436 nm an Orion PD (Ophir Optonics) was used. The measured values were 2 and 3 mW cm^{-2} , respectively. However, only 50% of the photons at 405 and 436 nm were absorbed by the catalyst whereas the absorption at 312 and 365 nm was ~90% as determined by power attenuation through the catalyst solution.

Taking this into account, the resulting total photon flux the reaction solution received was $7 \times 10^{16} \text{ s}^{-1}$. Since two photons are required for one H_2 molecule, the theoretical maximum H_2 yield based on the photon flux would be

$$n_{\text{H}_2} = \frac{\varphi}{2N_A} = \frac{7 \times 10^{16}}{2 \times 6.022 \times 10^{23}} = 60 \text{ nmol s}^{-1}$$

or 89 $\mu\text{L}/\text{min}$ at standard conditions. The average H_2 evolution measured for compound **6** using NEt_3 was 2 $\mu\text{L min}^{-1}$, giving a yield of 2.2%.

Synthesis of ligands and complexes

Synthesis of 2-(2-Pyridyl)benzthiazole (pbt), **1** and $[\text{Co}(\text{dmgBF}_2)(\text{H}_2\text{O})_2]$:

Pyridine-2yl)benzo[d]thiazole (pbt) was synthesised as reported by Gangopadhyay *et al.*,⁶⁶ while $[\text{Co}(\text{dmgBF}_2)(\text{H}_2\text{O})_2]$ was synthesized as by Bakac and Espenson.⁶⁷

Synthesis of the complexes—Compounds **7** and **8** were prepared following the procedure of Horne *et al.*⁴²

Synthesis of $[\text{Ru}(\text{pbt})_2\text{Cl}_2] \cdot 0.25\text{CH}_3\text{COCH}_3$, **2:** $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (1.55 g, 7.46 mmol), pbt (3.17 g, 14.9 mmol) and LiCl (4 g, 94.4 mmol) were added to a 100 ml round bottom flask, followed by DMF (40 ml). The mixture was refluxed under argon for nine hours; then cooled. The reaction mixture was rotary evaporated to a minimum volume; then acetone/water 1:1 v/v (400 ml) was added to the mixture. The resulting mixture was cooled in an ice bath; then filtered. The residue was washed thoroughly with water and air dried. Yield = 4.45 g (98%). Calc. for $\text{C}_{24.75}\text{H}_{17.5}\text{Cl}_2\text{N}_4\text{O}_{0.25}\text{RuS}_2$, C, 48.65; H, 2.89; N, 9.17. Found: C, 49.22; H, 2.97; N, 9.68.

Synthesis of $[\text{Ru}(\text{pbt})_2(\text{phendione})](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ **4:** A mixture of $[\text{Ru}(\text{pbt})_2\text{Cl}_2] \cdot 0.25\text{CH}_3\text{COCH}_3$, **2** (2.80 g, 4.58 mmol), 1,10-phenanthroline-5,6-phendione (phendione), **3** (1.184 g, 5.64 mmol), and 1:1 $\text{EtOH}/\text{H}_2\text{O}$ (400 ml) were degassed with argon for twenty minutes; then refluxed under argon for 25 hours. The reaction mixture was cooled to room temperature; then filtered saturated aqueous KPF_6 (400 ml) and NH_4PF_6 (8.0 g) were added to precipitate the product. The mixture was filtered; and the residue was washed with plenty of water and air-dried. The product was dissolved in the minimum volume of acetonitrile; then the solution was filtered. The filtrate was collected and the product was

precipitated with diethyl ether, leaving a solid. Yield = 4.58 g (91%). Calc for $C_{36}H_{30}F_{12}N_6O_6P_2RuS_2$: C, 39.39; H, 2.75; N, 7.66; S, 5.84; Ru, 9.21. Found: C, 39.59; H, 1.95; N, 7.34; S, 6.05; Ru, 9.14. m/z (ESI, positive mode): 368.0 (100%, $[M - 2PF_6]^{2+}$) and 881.0 (100%, $[M - PF_6]^+$). High resolution ESI MS: $m/z = 880.9938$. FT IR (cm^{-1}): 1699.10 (S) (C=O) and 827.91 (VS) (PF_6^-). UV-visible spectrum (CH_3CN), λ_{max}/nm ($10^{-3} M^{-1} cm^{-1}$): 248 (36), 306 (39), 334 sh (31), 458 (12), and 947 (0.082).

Synthesis of $[Ru(pbt)_2(L-pyr)](PF_6)_2 \cdot 9.5H_2O$, **5:** A mixture of $[Ru(pbt)_2(phen)](PF_6)_2 \cdot 4H_2O$, **4** (1.65 g, 1.50 mmol), ammonium acetate (2.38 g, 32.20 mmol) and 4-pyridinecarboxaldehyde (460 μ l, 4.80 mmol) in glacial acetic acid (250 ml) was refluxed at 120 °C for 18 hours. The following day the solution was cooled to room temperature and diluted with water (500 ml). It is then neutralized to pH 7 with concentrated aqueous ammonia changing reddish-orange in appearance. There was an addition of aqueous KPF_6 solution (400 ml) and NH_4PF_6 (7.0 g) was added and a red precipitate is obtained. It was then filtered and the residue washed with water and air dried. After drying, the crude was dissolved with MeCN; then the resulting solution was purified on an alumina column by using MeCN as an eluent. Yield of product = 1.69 g (88%). Calc. for $C_{42}H_{45}F_{12}N_8O_{10.5}P_2RuS_2$: C, 39.26; H, 3.53; N, 8.72; Ru, 7.87; S, 4.99. Found: C, 39.26; H, 2.33; N, 8.65; Ru, 7.26; S, 4.81. m/z (ESI, positive mode): 412.0 (100%, $[M - 2PF_6]^{2+}$) and 969.0 (100%, $[M - PF_6]^+$). High resolution ESI MS: $m/z = 969.0368$. FT IR (cm^{-1}): 1603.70 (m) (C=N) and 827.73 (VS) (PF_6^-). UV-visible spectrum (CH_3CN), λ_{max}/nm ($10^{-3} M^{-1} cm^{-1}$): 280 (67), 312 (58), 466 (19), and 723 (0.36).

Synthesis of $[Ru(pbt)_2(L-pyr)Co(dmgBF_2)_2(H_2O)](PF_6)_2 \cdot 11H_2O \cdot 1.5CH_3COCH_3$, **6:** $[Co(dmgBF_2)_2(H_2O)_2]$ (0.118 g, 0.28 mmol) and $[Ru(pbt)_2(L-pyr)](PF_6)_2 \cdot 9.5H_2O$, **5** (0.3598 g, 0.28 mmol), along with acetone (100 ml) were mixed in a 250 ml round bottom flask. The mixture was stirred at room temperature for three hours; then rotary evaporated to dryness. The resulting solid was washed thoroughly with diethyl ether; then air-dried. Yield = 0.4554 g (90%). Calc. For $C_{54.5}H_{71}B_2CoF_{16}N_{12}O_{18.5}P_2RuS_2$: C, 36.33; H, 3.97; Co, 3.27; N, 9.33; Ru, 5.61; S, 3.56. Found: C, 36.46; H, 2.8; Co, 2.92; N, 9.36; Ru, 5.34; S, 3.72. An ESI mass spectrum was acquired for compound 6, which was found to be very unstable in the chamber of the mass spectrometer. The mass spectrum showed the presence of the following species: m/z (ESI): 412.0 (100%, $[M - 2PF_6 - Co(dmgBF_2)_2(H_2O)]^{2+}$), 969.0 (100%, $[M - PF_6 - Co(dmgBF_2)_2(H_2O)]^+$). $[Co(dmgBF_2)_2(H_2O)_2]$ was also detected in the mass spectrometer. FT IR (cm^{-1}): 1614.14 (m) (C=N), 1161.09 (S) (B-F), and 823.43 (VS) (B-F and PF_6^-). UV-visible spectrum (CH_3CN), λ_{max}/nm ($10^{-3} M^{-1} cm^{-1}$): 280 (52), 312 (44), 464 (15), 720 (0.399), and 1136 (0.101). δ_B (500 MHz; DMSO- d_6): 0.66, 1.47, 2.98, and 37.95 ppm; δ_F (500 MHz; DMSO- d_6): -148.4, -146.3, -145.9, -145.6, and -143.8 ppm; and δ_{Co} (500 MHz; DMSO- d_6): 5401 ppm.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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(A) $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, compounds **4** and **5**.

(B) Compound 6.

Figure 1.

The UV-visible spectra of concentrated solutions of $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, compounds **4**, **5**, and **6** in CH_3CN .

(A) $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$, compounds **4** and **5**.

(B) Compound **6**.

Figure 2. ^{11}B NMR spectra for $[\text{Co}(\text{dmgbF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** in DMSO-d_6 .

Figure 3.
 ^{19}F NMR spectra for $\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2$ and compound **6** in DMSO-d_6 .

(B) Compound 6

Conformations

Figure 4.

^{59}Co NMR spectra for $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ and compound **6** in DMSO-d_6 .

(A) $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$

(B) Compound **6**

Figure 5.
EPR spectra for compounds **6–8** at in DMSO at 4 K.

Figure 6.

Cyclic voltammograms of compounds **6–8** in CH₃CN.

[complex] = 1.0 mM, supporting electrolyte = 0.1 mM tetra-*n*-butylammonium hexafluorophosphate (TBAP). All cyclic voltammometric measurements were carried out with a three-electrode system consisting of a working electrode = glassy carbon, a platinum wire auxiliary electrode, and reference electrode = Ag/AgCl. Scan rate = 100 mV s⁻¹.

Figure 7.

Cyclic voltammograms involving electrocatalysis with compound **6** in CH₃CN. [complex] = 1.0 mM, supporting electrolyte = 0.1 mM tetra-*n*-butylammonium hexafluorophosphate (TBAP). All cyclic voltammetric measurements were carried out with a three-electrode system consisting of a working electrode = glassy carbon, a platinum wire auxiliary electrode, and reference electrode = Ag/AgCl. Scan rate = 100 mV s⁻¹. [*p*-cyanoanilinium tetrafluoroborate] = 0, 1.5, 3.0, 5.0, and 10.0 mM for each acquired CV.

Figure 8.

Photocatalytic H₂ production in acidic acetonitrile containing 300 μM of each complex (compounds **5**, **6**, and **8**), 85 mM Et₃N plus 41–55 mM *p*-cyanoanilinium tetrafluoroborate, or 440 mM (EtOH)₃N plus 136 mM *p*-cyanoanilinium tetrafluoroborate, respectively.

Figure 9. Steady-state photoluminescence (PL) spectra of 117 μM of compound **5** (black) and 102 μM of compound **6** (blue), normalized to their respective sample concentrations.

Figure 10.

Transient absorption kinetics curves of 117 μM compound **5** (black), 92 μM compound **5** + 1.25 M Et_3N (green), 102 μM compound **6** (blue), and 66 μM compound **6** + 2.5 M Et_3N (red), probed at 420 nm, 530 nm, and 590 nm. Data were acquired in a 10 μs time window (a) and a 100 μs time window (b). The white lines indicate $\Delta A = 0$.

Figure 11. Steady-state absorption spectra of (a) 117 μM compound **5** (black), 92 μM compound **5** + 1.25 M Et_3N after laser irradiation (green), and (b) 102 μM compound **6** (blue), 66 μM compound **6** + 2.5 M Et_3N after laser irradiation (red).

Scheme 1.

Scheme 2.

The proposed mechanism for the generation of hydrogen in acidified acetonitrile.

UV-visible spectroscopic data of the respective complexes in CH_3CN .

Complex	ν/nm	$10^{-3} \nu/\text{M}^{-1} \text{cm}^{-1}$	$2/\text{nm}$	$10^{-3} 2/\text{M}^{-1}$	$\text{cm}^{-1} 3/\text{nm}$	$10^{-3} 3/\text{M}^{-1} \text{cm}^{-1}$	$4/\text{nm}$	$10^{-3} 4/\text{M}^{-1} \text{cm}^{-1}$	$5/\text{nm}$	$5/\text{M}^{-1} \text{cm}^{-1}$
[Co(dmgBF ₂) ₂ (OH ₂) ₂]	228	11	260 sh	6.5	318	2.5	424	3.6	1163	120
[Co(dmgBF ₂) ₂ (OH ₂) ₂]a	—	—	268	7.9	337	1.9	472	3.0	—	—
4	248	36	306	39	334 sh	31	458	12	947	82
5	280	67	312	58	466	19	723	0.36	—	—
6	280	52	312	44	464	15	720	0.399	1136	101
7	—	—	—	—	439	8.4	—	—	1100	66
8	—	—	—	—	431	8.4	—	—	1100	92

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Table 2

⁵⁹Co NMR spectroscopic data for [Co(dmgBF₂)₂(H₂O)₂], compound **6**, and related cobalt-containing complexes.⁵⁹

Compound	/ppm
[Me-Co(dmg) ₂ (H ₂ O)]	4156
[Et-Co(dmg) ₂ (H ₂ O)]	4180
[Pr-Co(dmg) ₂ (H ₂ O)]	4185
[Bu-Co(dmg) ₂ (H ₂ O)]	4195
[i-Pr-Co(dmg) ₂ (H ₂ O)]	4410
[PhCH ₂ -Co(dmg) ₂ (H ₂ O)]	4565
[Me-Co(DOH) ₂ (H ₂ O)]	4630
[Et-Co(DOH) ₂ (H ₂ O)]	4660
[Pr-Co(DOH) ₂ (H ₂ O)]	4670
[i-Pr-Co(DOH) ₂ (H ₂ O)]	4905
[PhCH ₂ -Co(DOH) ₂ (H ₂ O)]	5090
[Me-Co(dmgBF ₂) ₂ (H ₂ O)]	3888
[Et-Co(dmgBF ₂) ₂ (H ₂ O)]	3898
[Pr-Co(dmgBF ₂) ₂ (H ₂ O)]	3912
[Bu-Co(dmgBF ₂) ₂ (H ₂ O)]	3915
[i-Pr-Co(dmgBF ₂) ₂ (H ₂ O)]	4094
[PhCH ₂ -Co(dmgBF ₂) ₂ (H ₂ O)]	4264
[Me-Co(DOBF ₂) ₂ (H ₂ O)]ClO ₄	4588
[Et-Co(DOBF ₂) ₂ (H ₂ O)]ClO ₄	4612
[Pr-Co(dmgBF ₂) ₂ (H ₂ O)]ClO ₄	4678
[PhCH ₂ -Co(DOBF ₂) ₂ (H ₂ O)]ClO ₄	5021
[Et-Co(DOH) ₂ (H ₂ O)]	4660
[Et-Co(DOH) ₂ (benzimid)]	4270
[Et-Co(DOH) ₂ (5,6-Me ₂ -benzimid)]	4250
[Et-Co(DOH) ₂ (im)]	4140

Compound	/ppm
[Et-Co(DOH) ₂ (Me-im)]	4130
[Et-Co(DOH) ₂ (py)]	4140
[Co(dmgBF ₂) ₂ (H ₂ O) ₂] ^d	5652
Compound 6 ^d	5401

^d this work

dmg = dimethylglyoximate

DOH = 2,3,9,10-tetramethyl-1,4,8,11-tetrazaundeca-1,3,8,10-tetraen-11-ol-1-olato dmgBF₂ = difluoroborondimethylglyoximate

DOBF₂ = BF₂-capped version of DOH

Table 3

Spin Hamiltonian parameters obtained from Q- and X-band ESR experiments in DMSO.

Complex	Band	g_x	g_y	g_z	A_1^{Co}/MHz	A_2^{Co}/MHz	A_3^{Co}/MHz	A_N/MHz
[Co(dmgBF ₂) ₂ (H ₂ O) ₂]	Q	2.26	2.16	2.01	30	30	300	
6	Q	2.25	2.165	2.01	30	30	310	
6	X	2.22	2.17	2.015	30	30	280	
7	X	2.22	2.17	2.012	30	30	280	44
8	X	2.23	2.10	2.01	30	30	280	48

Table 4

Electrochemical data for compounds **6–8**.

Complex	$E_{1/2}/V$	Assignment
6	+1.32	Ru^{III}/II
	-0.45	Co^{III}/I
	-0.98	$L\text{-}pyr^{0/-}$
	-1.16	$L\text{-}pyr^{+/ -}$
	-1.27	$Co^{I/0}$
	-1.44	$pbt^{0/-}$
7	+1.29	Ru^{III}/II
	-0.45	Co^{III}/I
8	+1.40	Ru^{III}/II
	-0.45	Co^{III}/I