Assessing the stability of the Co(I) species of two mononuclear dichlorocobalt compounds bearing 2,2'-bipyridine and trans-2-(2'-quiolyl)methylene-3-quinuclidione via ^{59}Co NMR spectroscopy, electrochemical, and catalyzed proton electroreduction studies

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Abstract

The Co(I) species resulting from the reduction of two mononuclear species $[\text{CoL}_n\text{Cl}_2]$ (where L = 2,2'-bipyridine (bpy) and $n = 2$, or L = trans-2-(2'-quiolyl)methylene-3-quinuclidione (quin) and $n = 1$), was studied by ^{59}Co NMR spectroscopy, UV-visible-NIR spectroscopy, and spectroelectrochemical techniques. A quasi-stable Co(I) species produced by the reduction of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ was studied and gave a ^{59}Co NMR spectroscopic chemical shift of 2934 ppm in $\text{CD}_3\text{CN}-\text{D}_2\text{O}$ (4:1, v/v) and a broad peak of $\lambda_{\text{max}} = 600$ nm in the UV-visible region of the spectrum. The Co(I) species generated from $[\text{Co}(\text{quin})\text{Cl}_2]$ (when reduced by electrochemical methods) was found to be unstable and produced a transient of $\lambda_{\text{max}} = 530$ nm. Both $[\text{CoL}_n\text{Cl}_2]$ species were examined as electrocatalysts for the proton reduction in an acetonitrile-water solvent mixture in the presence of *p*-cyanoanilinium tetrafluoroborate. The electrochemical properties of both species showed a dependence on the supporting electrolyte which also affected the electrocatalytic behavior. The simulation of the cyclic voltammograms in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v) allowed for the extraction of kinetic data and suggested a homogenous reaction following the reduction to a Co(I) metal centre with rate constants $k = 0.01 \text{ s}^{-1}$ and 2 M s^{-1} for the Co(I) species with the ligands, bpy and quin, respectively. Analysis of the head space of controlled potential electrolysis experiments for an hour, in the presence of *p*-cyanoanilinium tetrafluoroborate, confirmed the production of hydrogen, and also showed that the supporting electrolyte affected the production of hydrogen at a glassy carbon electrode in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (either 1:1 or 4:1, v/v). A mechanism was postulated which involved a $\text{Co}^{\text{III}}-\text{H}$ species as the most likely candidate and appeared to involve both a homolytic and a heterolytic pathway towards the production of hydrogen.

Keywords: Cobalt(II), ^{59}Co NMR spectroscopy, electrochemistry, electrocatalysis, hydrogen production

1 Introduction

Hydrogen has been suggested as the leading candidate [1-5] for a clean, renewable and high-energy-density source. Hydrogenases catalyze the (reversible) reduction of protons into molecular hydrogen efficiently in nature. Unlike the most efficient synthetic catalysts reported for various transformations, the active sites of most enzymes contain only abundant first-row transition metals. As such, the search for catalysts that can facilitate the reduction of protons to hydrogen, using cheap and Earth abundant metals, is an area of current interest [1, 6-19].

Many molecular hydrogen evolution catalysts operate at substantial over-potentials [10, 17, 20, 21]. Cobaloximes [9, 20, 22] and many other classes of cobalt-containing complexes [23] have been promising compounds for the production of hydrogen in acidic media. With cobaloximes and similar macrocyclic cobalt-containing complexes, hydrogen evolution is initiated upon reduction to a Co(I) metal centre, which then reacts with a proton donor to form a Co(III)-hydride (Co^{III}-H). The Co^{III}-H intermediate can either undergo subsequent protonation to release molecular hydrogen and a Co(III) species that can be further reduced to regenerate the catalyst (heterolytic route) or react with another Co^{III}-H to eliminate molecular hydrogen by a homolytic route. Alternatively, Co^{III}-H can be reduced further to form Co^{II}-H, which can react via similar heterolytic or homolytic pathways (**Scheme 1**) [20, 21].

Scheme 1. Hydrogen evolution pathways of cobalt containing complexes [21].

Our research group and collaborators have been interested in the development of transition metal complexes that contain cobalt metal centres [24-31], as well as inorganic reaction mechanisms that involve electron transfer processes [25, 26, 32-36]. In a recent report, we outlined the preparation and application of a novel mixed-metal binuclear ruthenium(II)–cobalt(II) photocatalysts ([Ru(pbt)₂(L-pyr)Co(dmgBF₂)₂(H₂O)](PF₆)₂ (where pbt = 2-(2'-pyridyl)benzothiazole, L-pyr = (4-pyridine)oxazolo[4,5-f]phenanthroline, and dmgBF₂ = difluoroboryldimethylglyoximate) for photocatalytic production of hydrogen [24]. Others [16] have shown the effect of a non-innocent ligand in the production of hydrogen. Important insight into the structure-function relationships and catalytic properties such as the over-potential and turnover frequency for H₂ evolution have been determined over the years and is summarized in a review by Artero *et al.* [23].

In another study [37], it was shown that changing the ligands from 2,2'-bipyridine to a quinolone-type system resulted in an improved behaviour of a mononuclear catalyst towards hydrogen evolution. It has also been shown that ligand modification in cobalt containing catalysts to lower the over-potential leads to a decrease in the turn over frequency (TOF) of the hydrogen producing catalyst [10, 37].

Polypyridyl-containing cobalt complexes, e.g., [Co(bpy)₃]²⁺ (where bpy = 2,2'-bipyridine), has long been shown to act as a pre-catalyst for light driven hydrogen evolution [38, 39]. Studies also revealed that the [Co(bpy)₃]²⁺ species dissociates in aqueous media to generate [Co(bpy)₂]²⁺ and/or [Co(bpy)₂(H₂O)₂]²⁺, which may also be active pre-catalysts [40]. Polypyridyl-containing cobalt complexes have been employed as the catalytic site in various photocatalytic systems [38, 39, 41] and electrocatalyst [6, 37, 42, 43] reported for hydrogen generation. As a part of our synthetic design and thrust to improve the catalytic centre of our photocatalytic systems, we have investigated and compared the electrocatalytic activity of 2,2'-bipyridine and quinoline derivatives as ligands coordinated to cobalt(II) metal centre, e.g., *cis*-

[Co(bpy)₂Cl₂] (referred from here on in as [Co(bpy)₂Cl₂]) and [Co(quin)Cl₂], respectively, as catalysts for proton reduction (Figure 1).

Figure 1. Comparison of *cis*-[Co(bpy)₂Cl₂], [Co(quin)Cl₂] and a BF₂ capped cobaloxime [Co(dmgBF₂)₂(H₂O)₂].

Recently [44], a 2,2'-bipyridine-containing species, [Co(bpy)Cl₂], was reported as an electrocatalyst for aromatic perfluoroalkylation and cross-coupling reactions and the reaction of its bromide analogue in the reduced state with aryl halides.[45]

The preparation of [Co(quin)Cl₂] [46] has been reported in the literature for a number of years, however, this cobalt(II) species has been overlooked in the catalytic reduction of protons to produce molecular hydrogen. In this report we investigated the stability of the Co(I) species formed by [Co(bpy)₂Cl₂] and [Co(quin)Cl₂] in an acetonitrile/water solvent system, and compared their potential application in the electrocatalytic reduction of protons.

2 Experimental

2.1 Materials and physical measurements

All reagents were purchased from commercial sources and used without further purification. ⁵⁹Co NMR spectra were acquired on a Bruker 400 MHz NMR spectrometer using the Bruker “cpmg1d” pulse sequence for up to 120,000 transients, and referenced to K₃[Co(CN)₆][†] in acetonitrile-d₃ (δ = 293 ppm) [47]. The FIDs were processed using left shift function (-32) in ACD/NMR Processor Academic Edition[‡] to remove acoustic ringing of the probe.

All electrochemical experiments were performed on a BAS Epsilon C3 under an argon atmosphere in the respective solvents at room temperature (ca 20 °C) and are uncorrected for junction potentials. A standard three electrode configuration was employed consisting of a glassy carbon working electrode (3 mm diameter) and a Pt wire as auxiliary electrode. For the reference electrode, AgCl/Ag (BASi, 3.0 M NaCl)

[†] 0.1 M K₃[Co(CN)₆] with 3.5 equivalents of 18-crown-6 ether to aid with dissolution.

[‡] Advanced Chemistry Development, Inc. (ACD/Labs) Release 12.00. Visit <http://www.acdlabs.com>.

was employed, which was separated from the analytical solution by a Vicor® frit and was used in the CH₃CN-H₂O (4:1 and 1:1, v/v). The ionic strength was maintained at 0.1 M using [ⁿBu₄N]Cl, [ⁿBu₄N]Br, NaCl, [ⁿBu₄N]BF₄, or [ⁿBu₄N]ClO₄. When a Ag wire[§] was used as a quasi-reference electrode the Fc⁺/Fc couple showed a reversible wave at +0.34, +0.74, and +0.77 V in acetonitrile/H₂O (4:1, v/v, DMF, and DMSO, respectively in 0.1 M [ⁿBu₄N]BF₄.

Note: The [Co(quin)Cl₂] species adsorbs strongly to electrode and the working electrode must be cleaned between measurements. The adsorptive behaviour almost completely disappears in the presence of an acid source.

All UV-visible spectra were acquired on an Agilent 8453A diode array spectrophotometer. Spectroelectrochemical measurements were regulated at 20 °C with a thermostatted water bath/circulator. A Pt gauze and Pt wire were employed as working and auxiliary electrodes, respectively and a AgCl/Ag or Ag wire was used as a quasi-reference electrode. The ionic strength was maintained at 0.1 M using [ⁿBu₄N]BF₄ or [ⁿBu₄N]ClO₄. Each solution was degassed for at least two minutes in a spectroelectrochemical cuvette (BASi, 1 mm path length) prior to the measurement and the spectra were acquired over 500 s at a constant potential.

Controlled-potential electrolysis measurements for the production of hydrogen were conducted for an hour in a sealed two-chambered H-cell separated by a fine frit, where one chamber held the working and reference electrodes in 10 mL of 4.0 mM of complex in 0.1 M supporting electrolyte, and the second chamber held the auxiliary electrode in 5 mL of the solvent with the supporting electrolyte. A glassy carbon plate (contact area ~2 cm × 1 cm × 3 mm) and Pt wire were used as the working and auxiliary electrodes, respectively, with Ag wire as the reference electrode. The solution was purged with Ar for 20 minutes and then sealed under an Ar atmosphere before the start of each electrolysis experiment. The amount of H₂ evolved was quantified from an analysis of the headspace of the chamber containing the working electrode with a Shimadzu Tracer gas chromatograph 2010 Plus (SH-Rt-Molsieve 30 m × 0.53 mm × 50 µm column; 40 °C isothermal; 1.0 mL min⁻¹ flow rate; He carrier gas, 50 µL injection volume) using a barrier-discharge ionization detector (BID). 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 solvent (10 mL) to account for the fraction which dissolved in the solvent [24].

2.2 Preparation of trans-2-(2'-quioly)methylene-3-quinuclidione (quin) and [Co(quin)Cl₂]
Trans-2-(2'-quioly)methylene-3-quinuclidione (quin) and [Co(quin)Cl₂] were prepared by the method outlined by Coffen and McEntee [46], and the crystal structure of [Co(quin)Cl₂] was reported by Long and Schlemper [48].

2.3 Preparation of [Co(bpy)₂Cl₂]

Dichlorobis(2,2'-bipyridine)cobalt(II) was prepared according to literature methods [49].

[§] Ag wire serves as a convenient reference across the multiple solvents and simultaneously eliminates the junction potential that will develop across the frit of the AgCl/Ag aqueous reference electrode. The behaviour of the Ag quasi-reference electrode was reproducible across several days of experiments.

3 Results and Discussion

3.1 UV-visible Spectral properties

Cobalt(II)-containing complexes with chlorides as ligands are generally labile in the presence of water [50, 51], and one possibility is that the chloride ligand of the complexes can rapidly undergo solvolysis. In solution, the coordination number of the tetragonal species $[\text{Co}(\text{quin})\text{Cl}_2]$ can increase with the solvent completing the coordination sphere and/or replacing the chloride ligands [50, 52]. The relative magnitude of the molar absorptivities for the d-d transitions is well known to be related to the geometry [50]. In terms of solubility, the quin ligand dissolves readily in common solvents. The $[\text{Co}(\text{quin})\text{Cl}_2]$, a green solid, is sparingly soluble in acetonitrile, acetone, acetone/1,2-difluorobenzene or water, but soluble in DMF, DMSO and $\text{CH}_3\text{CN}/\text{water}$ (4:1, v/v) and consequently, these three solvent mixtures were chosen for a comparative study. The $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species interestingly dissolved in water with sonication, but proved difficult to dissolve in the presence of the supporting electrolyte. It is sparingly soluble in CH_3CN , but dissolves in DMF, DMSO, and mixtures of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$. The metal complexes gave bright green DMF solutions, but yielded yellow brown solutions in the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture. Cobalt(II)-containing species are also known to have a small difference in the crystal field stabilization between tetragonal and octahedral geometries [50]. It was therefore necessary to determine if the mixed solvent system was causing dissociation/solvolysis of the metal complexes, if the structural integrity of the complexes were retained, or if there was a change in the crystal field upon solvation.

The spectral comparison of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Co}(\text{quin})\text{Cl}_2]$ in the three solvent systems is given in Table 1 and Figure S1. The presence of the cobalt(II) metal centre with tetragonal (or possibly trigonal bipyramidal [53]) geometry is confirmed by the appearance of peaks above 600 nm (with ϵ of the order $\leq 10^2$) [50]. In the case of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture, the peaks in this region have a much lower ϵ value relative the other systems. These lower ϵ values ($<10 \text{ M}^{-1} \text{ cm}^{-1}$) are consistent with an octahedral geometry. It can thus be inferred that in this solvent, the cobalt(II) species has adopted an octahedral geometry which has a coordination sphere completed by solvent molecules.

Table 1. Absorption maxima (nm) and molar extinction coefficients ($\text{M}^{-1} \text{ cm}^{-1}$) of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Co}(\text{quin})\text{Cl}_2]$.

Solvent	species	λ_1 (ϵ)	λ_2 (ϵ)	λ_3 (ϵ)	λ_4 (ϵ)
DMF	$[\text{Co}(\text{bpy})_2\text{Cl}_2]$	413 (186)	489 (63)	609 (84)	676 (126)
DMSO	$[\text{Co}(\text{bpy})_2\text{Cl}_2]$	414 (97)	489 (52)	654 sh (4)	--
$\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v)	$[\text{Co}(\text{bpy})_2\text{Cl}_2]$	245 (23300)	455 sh (54)	654 sh (4)	--
DMF	$[\text{Co}(\text{quin})\text{Cl}_2]$	317 (13230)	408 (264)	609 (136)	671 (206)
DMSO	$[\text{Co}(\text{quin})\text{Cl}_2]$	341 (11822)	608 (22)	675 (35)	--
$\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v)	$[\text{Co}(\text{quin})\text{Cl}_2]$	321 (8339)	407 (179)	535 sh (7.7)	626 (2.3)

3.2 Electrochemical studies

3.2.1 Electrochemical behaviour of [Co(bpy)Cl₂]

The electrochemical behaviour of 2,2'-bipyridine is well documented and is usually pertinent at very negative potentials [54]. The profile of the cyclic voltammograms of [Co(bpy)₂Cl₂] did not show any variation between a CH₃CN-H₂O mixture at ratios of 1:1 or 4:1 v/v, respectively, however, the [nBu₄N]⁺ species have an enhanced solubility in the 4:1 mixture, and hence this was the preferred solvent. The cyclic voltammograms did, however, show a dependence on the supporting electrolyte. The cyclic voltammograms measured in 0.1 M NaCl (Figure 2), in 0.1 M [nBu₄N]Cl or [nBu₄N]ClO₄, showed a quasi-reversible wave for the Co^{II/I} redox couple (Figure S2-S4). The square wave voltammogram showed two closely spaced waves of equal electron count between -0.9 to -1.3 V. These are strongly suspected to be Co^{II/I} and Co^{I/0} reduction waves (see Table 2). Reversing the scan potential at -1.1 V *vs* AgCl/Ag (i.e. the end of the first cathodic wave), resulted in a retention of the anodic return wave. The retention of the return wave at this switching potential confirmed that it was associated with the Co^{II/I} redox couple. With either of the above supporting electrolytes, a product wave (at ca. +0.6 V) was observed more positive than the Co^{III/II} redox couple on a reductively initiated scan. However, on an oxidatively initiated scan, this wave was not observed. The current response of this product wave increases with repetitive cycling, and shifts to a more negative value (Figures S5-S7). Interestingly, this product wave is not observed on repetitive cycling when the scan direction is reversed at -1.1 V (*vs* AgCl/Ag) which is just beyond the Co^{II/I} redox couple (Figure S8). In the presence of the NaCl, [nBu₄N]Cl or [nBu₄N]ClO₄ supporting electrolyte, repetitive cycling did not cause any passivation of the electrode after 5 cycles, neither did it yield any additional peaks except for an anodic desorption/product wave, which occurred when the potential sweep goes beyond the potential of Co^{II/I} redox couple. These observations suggest that the product wave at ca. +0.6 V was the result of, or may be accelerated by the species produced at the Co^{I/0} redox couple. In a 2,2'-bipyridine cobalt(II) system, [Co(bpy)Br₂], reported by Polleux *et al.* [45], it was postulated that the irreversibility of that system, in acetonitrile, was due to the disproportionation of the Co(I) species to give Co(II) and metallic cobalt, and this they verified from the passivation of the working electrode when held at a constant potential of the Co^{II/I} couple. When 0.1 M [nBu₄N]Br was used as the supporting electrolyte, a similar behaviour to what was reported by Polleux *et al.* [45] was observed along with a stripping wave at -1.09 V in the cyclic voltammogram (Figure S9). In the presence of the 0.1 M bromide ions, supplied by the supporting electrolyte, it is expected that halide exchange will readily occur, and consequently the [Co(bpy)₂Br₂] species was formed *in situ* from [Co(bpy)₂Cl₂].

Figure 2. A cyclic voltammogram of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ measured in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1:1, v/v) at a scan rate of 100 mVs^{-1} on a glassy carbon working electrode vs AgCl/Ag ; inset square wave voltammogram. $[\text{Co}(\text{bpy})_2\text{Cl}_2] = 3.8 \text{ mM}$ and $I = 0.1 \text{ M}$ (NaCl).

Table 2. Effect of supporting electrolyte ($I = 1.0 \text{ M}$) on potentials of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ vs AgCl/Ag .

Solvent	Supporting electrolyte	$\text{Co}^{3+/2+} / \text{V}$	$\text{Co}^{2+/1+} / \text{V}$	$\text{Co}^{1+/0} / \text{V}$
$\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (1:1, v/v)	NaCl	0.22	-1.06	-1.17
$\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v)	$[\text{nBu}_4\text{N}]\text{Cl}$	0.25	-0.99	-1.13
$\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v)	$[\text{nBu}_4\text{N}]\text{ClO}_4$	0.27	-0.92	-1.12
$\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v)	$[\text{nBu}_4\text{N}]\text{Br}$	0.07	-1.26	-1.35

Potentials are determined by square wave voltammetry. There is an additional wave at ca -1.5 V that may be related to the $\text{Co}^{0/-}$ and the $\text{bpy}^{0/+}$ redox couples.

Cobalt(II)-containing complexes with chlorides as ligands are generally labile in the presence of water [50, 51], and it is likely that the complex is rapidly solvated. The overall cyclic voltammogram of the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species had a very similar profile to another polypyridyl cobalt(II) complex which had the halide ligand replaced with a water molecule [42], and gives merit to this preposition. However, the similarity of the complex in the NaCl , $[\text{nBu}_4\text{N}]\text{Cl}$ or $[\text{nBu}_4\text{N}]\text{ClO}_4$ supporting electrolyte compared to the $[\text{nBu}_4\text{N}]\text{Br}$ is suggesting that the case of the bromide, the halide may have remained coordinated to the complex. This can be inferred from the fact that if the halide was substituted by the solvent in all the cases explored above, the cyclic voltammogram would be expected to be similar irrespective of the supporting electrolyte (Figure 3). The electrochemical reactions occurring with the complex is summarized in (Scheme 2). Simulation of the cyclic voltammograms for the $\text{Co}^{\text{II/I}}$ and $\text{Co}^{\text{I/0}}$ redox couples as quasi-reversible couples using DigiSim® (Figure S10), estimated rate constants for the homogenous reactions

occurring to be 0.01 and 0.2 s⁻¹ at the Co(I) and Co(0) species, respectively. This quasi-reversibility is suspected to be related to (partial) deligation of the reduced metal centre [54, 55].

Scheme 2. Summary of the electrochemical behaviour of [Co(bpy)₂Cl₂] in [nBu₄N]ClO₄, [nBu₄N]Cl and NaCl supporting electrolytes.

Figure 3. Cyclic voltammograms of [Co(bpy)₂Cl₂] on a glassy carbon working electrode vs AgCl/Ag in CH₃CN-H₂O (4:1, v/v) in 0.1 M [nBu₄N]ClO₄ (red), 0.1 M [nBu₄N]Cl (black), and 0.1 M [nBu₄N]Br (green). [Co(bpy)Cl₂] = 2.6 mM.

The chemical reduction of cobalt species by borohydride salts are known to produce the corresponding cobalt(I) species [56, 57]. The addition of an excess (10 equivalences) of [nBu₄N]BH₄ in the CH₃CN-H₂O (4:1, v/v) solvent mixture produced the characteristic deep blue associated with cobalt(I) solutions with a λ_{max} = 600 nm in the visible spectrum and a tail into the NIR region [40]. The spectrum is given in Figure 4. The coordination number of Co(I) species can vary from 3 to 8 as reported in the literature [10, 57-60]. However, simpler species usually have coordination numbers from 3 and 5, and we suspect this species to be [nBu₄N][Co(bpy)₂(solv)], where the solv = CH₃CN and/or H₂O, and the spectrum is comparable to the radiolytic work of Sutin and co-workers [40]. Under inert atmosphere, this solution retained its deep blue colour over two days, but eventually faded to give an almost colourless solution along with a white precipitate within a week. Spectroelectrochemical reduction at -1.0 V (vs AgCl/Ag), in the presence of [nBu₄N]ClO₄ supporting electrolyte, gave the exact spectral characteristics to that obtained with

$[\text{Bu}_4\text{N}]\text{BH}_4$; which further confirmed the assignment of the $\text{Co}^{\text{II/I}}$ redox couple. The ^{59}Co NMR spectrum of the borohydride (reduced) solution gave a broad peak resonating at 2934 ppm with a peak width of ~ 550 ppm (ca 52,000 Hz), which is in the range typical of Co(I) species [61], and represents a first for this complex in the solution state (Figure 5). The broad nature of the peaks in the ^{59}Co NMR spectrum of Co(I) complexes is a common feature, and the paramagnetic nature presents a high degree of difficulty to acquire and interpret the spectrum in solution state [58, 62-64].

Figure 4. UV-visible-NIR spectra of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ (black line (1)), $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ in the presence of 10 equivalences of $[\text{Bu}_4\text{N}]\text{BH}_4$ (red line (3), 10 mm path length) and the resultant spectrum of the spectroelectrochemical reduction of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ (green line (2), 1 mm path length) at -1.1 V (vs AgCl/Ag) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v). $[\text{Co}(\text{bpy})_2\text{Cl}_2] = 1.9$ mM and 3.9 mM for the chemical and spectroelectrochemical reductions, respectively.

3.2.2 Electrochemical behaviour of quin and $[\text{Co}(\text{quin})\text{Cl}_2]$

It is evident from the structure of quin (Figure 1), that it is a non-innocent ligand due to: (i) the quinoline ring system, (ii) the α,β -unsaturated carbonyl moiety as well as (iii) the bridging nitrogen. An analysis of the MO diagram of the quin ligand and the $[\text{Co}(\text{quin})\text{Cl}_2]$ at the semi-empirical level (PM3) is suggestive that the quinoline moiety of the quin ligand is more accessible than the ketone group of the azo-bicyclic moiety for redox reactions (Figure 6). The complex electrochemical behaviour of quin and $[\text{Co}(\text{quin})\text{Cl}_2]$ required the use of different solvents to aid in interpreting the voltammograms, however, the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixture is emphasized.

Figure 5. A ^{59}Co NMR spectrum of $[\text{nBu}_4\text{N}][\text{Co}(\text{bpy})_2(\text{solv})]$ (where solv = H_2O and/or CH_3CN) generated *in situ* from $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ in the presence of 10 equivalences of $[\text{nBu}_4\text{N}]\text{BH}_4$ in $\text{CD}_3\text{CN}-\text{D}_2\text{O}$ (4:1, v/v) at 28 °C.

Figure 6. A MO diagram of quin calculated at the PM3 level.

The quin species shows an irreversible anodic wave at +1.60 V (*vs* Ag) in DMF which is inaccessible in DMSO and the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v) solvents (Figures S11-S13). The electrochemical behaviour of the quin ligand is summarized in Table 3.

Table 3. The reduction potentials of quin vs Ag (Fc⁺/Fc) in various solvents.

Solvent	E_1 / V	E_2 / V	E_3 / V	E_4 / V
DMF	1.60 (0.75)*	-1.32 (-2.06)	-1.71 (-2.45)	-2.05 (-2.79)
DMSO	--	-1.30 (-2.07)	-1.77 (-2.54)*	-2.30 (-3.07)
CH ₃ CN-H ₂ O (4:1, v/v)	--	-1.18 (-1.52)*	-1.91 (-2.25)*	--

The potentials are determined from square wave voltammetry. *denotes irreversible redox couples.

A comparison of the peaks of the cyclic and square wave voltammograms of quin is suggestive the reduction at E_2 is a single step two-electron process, and the reduction(s) at E_3 (and E_4) appear to be single electron transfer(s). The MO analysis is suggestive that the reduction at E_2 is centred on quinoline moiety of the quin species. The behaviour of the base structure, quinoline, under chemical reduction has been established [65]. The (quasi-) reversibility displayed by the wave of the quin species at E_2 and the number of electrons involved seems consistent with an EE type mechanism [66], analogous to the chemical and electrochemical reductions of quinoline [67, 68]. Further evidence for such a reaction is obtained on the return sweep, where two closely spaced oxidation waves are observed in DMF and DMSO (Figures S11 & S12).

In the case of the [Co(quin)Cl₂] species, the presence of the metal centre results in the appearance of a redox wave more positive of the E_2 redox wave of the quin species (Figure 7 and Figures S11-S13). The additional waves (in comparison to quin) are assigned to cobalt metal centre (Table 4). The Co^{III/I} redox couple was observed at -0.68, -0.95, and -0.63 V vs Ag in DMF, DMSO, and CH₃CN-H₂O (4:1, v/v), respectively. In CH₃CN-H₂O, a strong desorption wave is observed at +0.9 V vs Ag on a reductively initiated scan (Figure 7, 3b). This wave is absent on an oxidatively initiated scan, and as such is not related to the Co^{III/II} redox couple. Indeed, this desorption wave is likely due to “free” cobalt(II) resulting from the electrochemical decomposition of the complex, as a similar wave was observed in the cyclic voltammogram of cobalt(II) in the solvent (Figure S13). Similar to the [Co(bpy)₂Cl₂] species, the cyclic voltammogram of [Co(quin)Cl₂] showed a dependence on the supporting electrolyte, however, the variation is a lot more subtle. The variation is best observed by square wave voltammetry, however, from the cyclic voltammograms (Figure S15), it can be seen that the Co^{I/0} redox couple is resolved from the reduction of the ligand based on the choice of the supporting electrolyte (

Table 5). The behaviour of the cobalt metal centre is similar to the [Co(bpy)₂Cl₂] species shown in Scheme 2, however, the quin ligand shifts the redox potential of the cobalt couples to more positives values relative to the bpy ligand.

Table 4. The reduction potentials vs Ag (Fc⁺/Fc) of [Co(quin)Cl₂] in the various solvents.

Solvent	Co ^{+3/+2} / V	Co ^{+2/+1} / V	E_2 / V
DMF	+1.69 (+0.95)	-0.68 (-1.42)	-1.13 (-1.87)
DMSO	--	-0.95 (-1.72)	-1.10 (-1.87)
CH ₃ CN-H ₂ O (4:1, v/v)	+1.35 (+1.01)	-0.63 (-0.97)	-1.10 (-1.44)

Potentials are determined from square wave voltammetry.

Table 5. Effect of supporting electrolyte ($I = 1.0\text{ M}$) on potentials of $[\text{Co}(\text{quin})\text{Cl}_2]$ vs AgCl/Ag in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v).

Supporting electrolyte	$\text{Co}^{+3/+2} / \text{V}$	$\text{Co}^{+2/+1} / \text{V}$	$\text{Co}^{+1/0} / \text{V}$	$\text{Quin}^{0/2-}$
$[\text{nBu}_4\text{N}]\text{BF}_4$	1.38	-0.63	-1.08 ^a	
NaCl	--	-0.62	-1.12 ^a	
$[\text{nBu}_4\text{N}]\text{Cl}$	--	-0.63	-0.97	-1.11
$[\text{nBu}_4\text{N}]\text{Br}^{\text{b}}$	--	-0.62	-0.84	-1.11

Potentials are determined from square wave voltammetry. ^a Represents a broad multi-electron peak in which the metal centre reduction is superimposed on the ligand reduction. ^b A suspension is formed when the complex was added to this electrolyte.

Figure 7. Cyclic voltammograms of quin (a) and $[\text{Co}(\text{quin})\text{Cl}_2]$ (b) measured in (1) DMSO, (2) DMF, and (3) $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v) on a glassy carbon working electrode vs Ag quasi-reference electrode. $[\text{quin}] = 3.8\text{ mM}$, $[\text{Co}(\text{quin})\text{Cl}_2] = 3.8\text{ mM}$, $I = 0.1\text{ M}$ ($[\text{nBu}_4\text{N}]\text{ClO}_4$), and scan rate = 100 mV s^{-1} .

In the presence of 0.1 M $[\text{nBu}_4\text{N}]\text{Br}$ as the supporting electrolyte, precipitation was observed, and here also we suspect that halide exchange occurred *in situ* to form the bromide analogue. The cyclic and square wave voltammograms of the suspension indicated that the potentials couple of the $\text{Co}^{I/0}$ couple were shifted to more a positive value compared to the chloride species (

Table 5). From the results, it is clear that the $\text{Co}^{\text{II/I}}$ redox couple of $[\text{Co}(\text{quin})\text{Cl}_2]$ can be resolved from quin ligand in all the supporting electrolytes and solvents employed. The additional cathodic waves observed in the cyclic voltammograms of the complex beyond those of the cobalt redox couples, have been assigned to the ligand. Generally, the potentials were more positive relative to the free quin. The shift in the values of the redox potentials of the ligand upon complexation to the cobalt metal centre clearly indicated that the cyclic voltammograms of $[\text{Co}(\text{quin})\text{Cl}_2]$ is not a simple addition of the cyclic voltammograms of the metal centre and quin ligand (Figure S13) [69, 70]. The non-additive nature of the cyclic voltammogram also indicated that the $[\text{Co}(\text{quin})\text{Cl}_2]$ species does not undergo complete solvolysis in the $\text{CH}_3\text{CN-H}_2\text{O}$ mixture, i.e. the nitrogen coordinated ligand was retained. The shifts in the reduction potential of the quin ligand in the $[\text{Co}(\text{quin})\text{Cl}_2]$ species, in addition to the strong adsorption on the electrode, makes simulation of the complete cyclic voltammogram extremely complex and challenging. A simulation of the $\text{Co}^{\text{II/I}}$ redox couple at four scan rates using DigiSim® was met with good success, when the $\text{Co}^{\text{II/I}}$ redox couple was treated in a similar manner to the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species (Figure S18). From the simulations, the rate constant for the homogeneous reaction for Co(I) species generated from $[\text{Co}(\text{quin})\text{Cl}_2]$ was estimated to be $2 \text{ M}^{-1} \text{ s}^{-1}$ which is about 200 times greater than that of the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species. It is interesting that both the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Co}(\text{quin})\text{Cl}_2]$ species produced a desorption/product wave when subjected to reduction, and from the simulation of the cyclic voltammograms there appears to be a homogenous reaction that followed the reduction. As will be discussed below, it is likely that the homogenous step at the Co(I) oxidation state of the $[\text{Co}(\text{quin})\text{Cl}_2]$ species is related to a reaction between Co(I) and the quin ligand. Reduction to the Co(0) state most likely resulted in (partial) deligation as was noted with the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species. The deligation may occur at an enhanced rate for the $[\text{Co}(\text{quin})\text{Cl}_2]$ species due to the prevalence of the strong desorption wave, and it also appeared that the deligation and metal deposition processes are enhanced in the presence of the bromide supporting electrolyte for both species.

3.2.3 Electrochemical behaviour of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Co}(\text{quin})\text{Cl}_2]$ in the presence of *p*-cyanoanilinium tetrafluoroborate

Numerous cobalt-containing species have been associated with the electrocatalytic reduction of protons [23]. The electrochemical behaviour of both complexes in the presence of *p*-cyanoanilinium tetrafluoroborate as an acid source were investigated for electrocatalytic activity. In the $\text{CH}_3\text{CN-H}_2\text{O}$ (4:1, v/v) solvent system, *p*-cyanoanilinium tetrafluoroborate did not display any electroactivity within the vicinity of the $\text{Co}^{\text{II/I}}$ redox couple (Figure 8 and 9). In the presence of the acid source a reduction wave is observed more positive than the $\text{Co}^{\text{II/I}}$ redox couple and the peak current increased with the concentration of the added *p*-cyanoanilinium tetrafluoroborate towards saturation (Figure 10, Figures S19 & S20). The peak current was also dependent on the concentration of the cobalt species (Figure S21) and in both cases showed scan rate dependence.

Figure 8. Cyclic voltammograms of $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ in the absence (red broken line) and presence (5.15, 10.3, 15.2 and 25.8 mM) of $p\text{-cyanoanilinium}$ tetrafluoroborate (**pcatfb**) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v), at a scan rate of 100 mV s^{-1} in 0.1 M $[\text{nBu}_4\text{N}]\text{Cl}$ at a glassy carbon working electrode vs AgCl/Ag (15.0 mM of $p\text{-cyanoanilinium}$ tetrafluoroborate only shown with black broken line).

Figure 9. Cyclic voltammograms of a) [*p*-cyanoanilinium tetrafluoroborate] = 7.9 mM, b) [Co(quin)Cl₂] = 3.6 mM, c) [HClO₄] = 7.0 mM, d) 3.6 mM of [Co(quin)Cl₂] and 7.9 mM *p*-cyanoanilinium tetrafluoroborate, e) 3.6 mM of [Co(quin)Cl₂] and 7.0 mM HClO₄ measured in CH₃CN-H₂O (4:1, v/v) on a glassy carbon working electrode at a scan rate of 100 mV s⁻¹.

Figure 10. Cyclic voltammograms of [Co(quin)Cl₂] = 3.6 mM in the absence (a) and presence of 1.9 (b), 4.4 (c), 6.9 (d), 8.9 (e) and 12 mM (f) *p*-cyanoanilinium tetrafluoroborate in CH₃CN-H₂O (4:1, v/v), at a scan rate of 100 mV s⁻¹ (0.1 M [ⁿBu₄N]BF₄) at a glassy carbon working electrode vs AgCl/Ag.

Interestingly, the cyclic voltammograms of the [Co(quin)Cl₂] species in the presence of an acid source (Figure 9 and 10) shows a cathodic wave appearing ca 300 mV more positive than the Co^{II/I} redox couple, and ca 1000 mV more positive than the reduction of proton source. Similar behaviours in the presence of the acid were observed irrespective of the supporting electrolyte for the respective cobalt(II) complexes. Even more interesting was that the suspension observed for [Co(quin)Cl₂] in [ⁿBu₄N]Br dissolved in the presence of the acid source.

The retention of a peak-like shape as the acid concentration was increased in the presence of [Co(bpy)₂Cl₂], or the two-wave system that developed for the [Co(quin)Cl₂] species are suggestive of diffusion controlled processes at electrode surface [10, 12, 22, 71]. Indeed, the electrochemical behaviour of the systems in the presence of acid displayed some of the characteristics of a free-diffusing catalyst [71-73]. For the [Co(quin)Cl₂] species, the consumption of the catalyst at the first wave of the two-wave system that developed is then governed by the diffusion of the substrate and the position of the peaks are altered by the concentration of the acid (Figure 10). The saturation of the peak current at higher acid concentrations could imply a change in rate determining step and is more obvious in the case of the [Co(quin)Cl₂] system, and further evidenced by changes in the profile of the cyclic voltammograms. As the concentration of the acid is increased, there are three cathodic waves close to the cobalt redox couples

that are altered by the concentration of the acid, suggesting a complex mechanism for the $[\text{Co}(\text{quin})\text{Cl}_2]$ (Figure 11). These data may be interpreted as evidence for electrocatalytic behaviour for the reduction of proton.

Figure 11. Dependence of the catalytic peak current (i_{pc}) of $[\text{Co}(\text{quin})\text{Cl}_2]$ on the concentration of p -cyanoanilinium tetrafluoroborate in $\text{CH}_3\text{CN-H}_2\text{O}$ (4:1, v/v) measured at a scan rate of 100 mV s^{-1} on a glassy carbon working electrode vs AgCl/Ag . $[\text{Co}(\text{quin})\text{Cl}_2] = 4.1 \text{ mM}$ $I = 0.1 \text{ M}$ $[\text{nBu}_4\text{N}]\text{Cl}$ (◆: $E_{pc,1} = -0.4$ to -0.5 V ; ▲: $E_{pc,2} \approx -0.9 \text{ V}$ and; □: $E_{pc,3} \approx 1.03 \text{ V}$).

In the presence of a Brønsted acid, it is also likely that the $[\text{Co}(\text{quin})\text{Cl}_2]$ species is protonated and this may reduce the effective concentration of the p -cyanoanilinium tetrafluoroborate (**pcatfb**). The spectroelectrochemical reduction of $[\text{Co}(\text{quin})\text{Cl}_2]$ showed that band at $\sim 410 \text{ nm}$ for the $[\text{Co}(\text{quin})\text{Cl}_2]$ species is absent in the presence of the acid source (Figure 12). This band at 410 nm coincides with the absorbance of the quin ligand, and it therefore appears that the ligand is indeed protonated. In the absence of the acid, a new band develops at about 530 nm when the complex is reduced at a constant potential of -0.7 V vs AgCl/Ag (Figure 12 a). This band we believe, is associated with the Co(I) species, however the reduction of $[\text{Co}(\text{quin})\text{Cl}_2]$ by $[\text{nBu}_4\text{N}]\text{BH}_4$ did not result in the stable formation of this band. The addition of $[\text{nBu}_4\text{N}]\text{BH}_4$ resulted in the pale yellow brown solution of $[\text{Co}(\text{quin})\text{Cl}_2]$ rapidly turning blue green, then quickly transformed to a yellow brown mixture with a pale green precipitate. Indeed in the presence of BH_4^- the α,β -unsaturation is also likely to be reduced, and the resulting species is likely to react very quickly with the Co(I) species [74]. This reaction is also the most likely source of the homogenous reaction suggested in the simulation of the cyclic voltammogram of the $[\text{Co}(\text{quin})\text{Cl}_2]$ species *vide supra*.

Controlled-potential electrolysis (CPE) measurements for the production of hydrogen were conducted in a sealed two-chambered H-cell on unstirred solutions for one hour. The production of hydrogen on glassy carbon electrode was confirmed for both the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Co}(\text{quin})\text{Cl}_2]$ species and the results are

summarized in Table 6. The results of the controlled potential electrolysis experiments confirm that the species are indeed electrocatalysts for the reduction of protons to hydrogen. The general scheme for the electrocatalytic reduction of protons by cobalt complexes is given Scheme 1. A plausible mechanism consistent with our observations for the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and the $[\text{Co}(\text{quin})\text{Cl}_2]$ species is given in Scheme 3. In Scheme 3, it can be seen that there is a subtle difference in the proposed (simplified) mechanism for both species, and this difference lies in the fact the $[\text{Co}(\text{quin})\text{Cl}_2]$ species is easily protonated in the presence of the acid source as discussed *vide supra*. For both CoL_nCl_2 species (see Figures S26-S28 for e.g.), when a heterolytic mechanism was assumed for the formation of hydrogen from the $\text{Co}^{\text{III}}\text{-H}$, it was not possible to use a common set of parameters to simulate the cyclic voltammogram for a given concentration of catalyst in the presence of incremental amounts of **pcatfb**. The simulated currents increased with **pcatfb** much more rapidly than that observed experimentally. From this, it is evident that the electrocatalytic hydrogen evolution is not dominated by a heterolytic pathway. Likewise, when a homolytic mechanism/pathway was assumed the simulated cyclic voltammograms gave a more satisfactory comparison though not ideal to the experimental data for a given concentration of **pcatfb**. From the nature of the experimental cyclic voltammograms, it is possible that the mechanism is a combination of both pathways. It is also likely that a particular mechanism may be favoured based on the concentration of the acid source. A pathway involving the $\text{Co}^{\text{II}}\text{-H}$ may also be involved based on the enhancement of the peak current within the vicinity of the $\text{Co}^{\text{III/I}}$ redox couple. However, the inclusion of a $\text{Co}^{\text{II}}\text{-H}$ pathway in the mechanism resulted in the simulated cyclic voltammograms being incomparable to the experimental cyclic voltammograms.

Assuming the simplified mechanism is valid, the overall rate constant for H_2 evolution was estimated from the height of the catalytic plateau current (Eq. 1) [6, 10, 71]. The reaction rate, k , can be estimated from Eq. 1, where n is the number of electrons, i_c is the plateau current (mA), i_p is the peak current in the absence of acid, F is the Faraday's constant (96485 C mol^{-1}), $[\text{H}^+]$ is the bulk concentration of the *p*-cyanoanilinium tetrafluoroborate (**pcatfb**), and k is the reaction rate constant ($\text{M}^{-1} \text{ s}^{-1}$) can be determined from $1/(\sqrt{v})$ vs the slopes of plots of i_c/i_p vs $\sqrt{[\text{H}^+]}$ (Figure S23) [6]. Comparing the chloride-containing supporting electrolytes, k is calculated to be 6.2 ± 1.2 and $5.9 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Co}(\text{bpy})\text{Cl}_2]$ in 0.1 M NaCl and $[\text{nBu}_4\text{N}]\text{Cl}$, respectively, where as a value of $1467 \pm 440 \text{ M}^{-1} \text{ s}^{-1}$ was obtained for $[\text{Co}(\text{quin})\text{Cl}_2]$ in 0.1 M $[\text{nBu}_4\text{N}]\text{Cl}$, compared to the $7000 \text{ M}^{-1} \text{ s}^{-1}$ reported for $[\text{Co}(\text{dmgBF}_2)(\text{H}_2\text{O})_2]$ in CH_3CN [22].

$$\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk[\text{H}^+]^2}{Fv}} \quad (1)$$

Figure 12. Absorbance changes of CH₃CN-H₂O of (4:1, v/v) solution of [Co(quin)Cl₂] = 3.6 mM (a) in the absence of **pactfb** and (b) in the presence of 12.5 mM **pactfb**, at -0.70 V (vs Ag), I = 0.1 M ([ⁿBu₄N]BF₄).

Table 6. Summary of the effect of the supporting electrolyte (SE) on the apparent rate constant, and the turn over number (TON) for the electrocatalytic production of hydrogen in the presence of *p*-cyanoanilinium tetrafluoroborate.

Entry	complex	Solvent ratio (CH ₃ CN:H ₂ O)	SE	TON (1 hour)
1	[Co(bpy) ₂ Cl ₂]	4:1, v/v	[ⁿ Bu ₄ N]Cl	0.51 ± 0.1
2	[Co(quin)Cl ₂]	4:1, v/v	[ⁿ Bu ₄ N]Cl	0.40 ± 0.02
3	[Co(bpy) ₂ Cl ₂]	4:1, v/v	[ⁿ Bu ₄ N]Br	1.1 ± 0.2
4	[Co(quin)Cl ₂]*	4:1, v/v	[ⁿ Bu ₄ N]Br	0.25 ± 0.04
5	[Co(quin)Cl ₂] [†]	4:1, v/v	[ⁿ Bu ₄ N]ClO ₄	0.034 ± 0.004
6	[Co(dmgbF ₂) ₂ (H ₂ O) ₂] [§]	4:1, v/v	[ⁿ Bu ₄ N]ClO ₄	1.8 ± 0.2
7	[Co(bpy) ₂ Cl ₂]	4:1, v/v	[ⁿ Bu ₄ N]ClO ₄	0.06 ± 0.03
8	[Co(bpy) ₂ Cl ₂]	1:1, v/v	NaCl	0.88 ± 0.14

CPE at: -1.3, -1.2, -1.1 and -1.1 V using [ⁿBu₄N]Br, [ⁿBu₄N]Cl, NaCl, and [ⁿBu₄N]ClO₄ respectively as supporting electrolyte and [Co(bpy)₂Cl₂] as pre-catalyst. CPE at: -1.1 V using [ⁿBu₄N]Br, and -0.75 V with [ⁿBu₄N]Cl, NaCl, and [ⁿBu₄N]ClO₄ as supporting electrolyte and [Co(quin)Cl₂] as pre-catalyst. *Observed colloidal metal on the working electrode at the end of the experiment. [Co(dmgbF₂)₂(H₂O)₂]: CPE at -1.0 V. [†]Nearly identical results were obtained with [ⁿBu₄N]BF₄ as supporting electrolyte. [§]The axial water molecules are readily substituted by halides and other strongly coordinating ligands, hence the ClO₄⁻ supporting electrolyte.

The turnover numbers (TON) were compared to a noted electrocatalyst [Co(dmgbF₂)₂(H₂O)₂] [10, 22] under similar conditions (Table 6, entry 6). One of the disadvantages to the macrocyclic cobalt(II)-containing complexes based on the dimethylglyoxime (dmg) derivatives as equatorial ligands, is that these complexes may be destroyed by hydrogenation or acid catalyzed hydrolysis under the acidic

conditions [10-12, 75, 76]. We have observed that both the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ and $[\text{Co}(\text{quin})\text{Cl}_2]$ were stable in the acid medium over a few days based on absorption measurements. The CoL_nCl_2 species while not as efficient as the macrocyclic oxime system, may offer the advantage of acid stability in the acidic media (and in some cases air) compared to the dmg systems [37, 42, 43]. Despite the large disparities in the apparent rate constants (based on the assumptions of the mechanism involved), from the comparison given in Table 6 (entries 1-6), the CoL_nCl_2 species (where $\text{L} = \text{bpy}$ or quin) offered a respectable TON with an appropriate supporting electrolyte compared to the $[\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})_2]$ species in the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v) solvent mixture. It can also be seen that the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species did the catalysis at a more negative potential (at -1.1 to -1.3 V) than the $[\text{Co}(\text{quin})\text{Cl}_2]$ which typically operated at -0.75 V. It is interesting to note that although the $[\text{Co}(\text{quin})\text{Cl}_2]$ species operated at a more positive potential and had a much larger apparent rate constant, this species consistently produced a lower TON than the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species. This may further point to the complexity of the mechanism [73] involving the $[\text{Co}(\text{quin})\text{Cl}_2]$ species, as illustrated by the changes in the cyclic voltammogram as the acid concentration varies (Figure 10). For the $[\text{Co}(\text{quin})\text{Cl}_2]$ species it seemed there are two factors working to its disadvantage: (i) the enhanced homogenous reaction at the $\text{Co}(\text{I})$ species relative the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ species and; (ii) the reaction of the $\text{Co}(\text{I})$ species with the α,β -unsaturation (which may have also contributed to the enhanced homogenous rate constant determined in the simulations of $[\text{Co}(\text{quin})\text{Cl}_2]$ relative to $[\text{Co}(\text{bpy})_2\text{Cl}_2]$).

It is also apparent that the bromide analogue of the $[\text{Co}(\text{bpy})_2\text{Cl}_2]$ complex that was formed *in situ* was more efficient than chloride species, where as in the $[\text{Co}(\text{quin})\text{Cl}_2]$ species the opposite effect was observed (Table 6, entries 3 and 4). This behaviour of the bpy species, in the presence of the bromide supporting electrolyte, might be the result of cobalt colloidal or nanoparticles (stabilized by the “softer” bromide ions) that can be formed from the electrochemical decomposition [77] of bromide species $[\text{Co}(\text{bpy})_2\text{Br}_2]$, resulting from the deligation of the complex and subsequent metal deposition as indicated by its electrochemical properties [45] as shown above. The presence of any such colloidal or nanoparticles, would in no doubt alter the mechanism for the proton reduction. In the case of the $[\text{Co}(\text{quin})\text{Cl}_2]$ species, the deposition of metal particles on the surface may have been too rapid and prevented electrocatalysis.

4 Conclusions

In concluding we have shown that the two CoL_nCl_2 species (where $\text{L} = \text{bpy}$ and $n = 2$ or $\text{L} = \text{quin}$ and $n = 1$) produced $\text{Co}(\text{I})$ species of very different stabilities in the $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixed solvent system of various ratios. These systems also produce hydrogen in the presence of *p*-cyanoanilinium tetrafluoroborate in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixed solvents, and the choice of the supporting electrolyte influences the turn over number for the production of hydrogen. A complex mechanism may be involved, however a simplified mechanism was proposed.

Acknowledgements

AAH would like to thank the NSF for an NSF CAREER Award as this material is based upon work supported by the National Science Foundation under CHE-1431172 (formerly CHE – 1151832). AAH would also like to thank Old Dominion University for the start-up package that allowed for the successful completion of this work. The authors would like to thank Ms. Celina Franklin, a former undergraduate

student of AAH from The University of the West Indies, Cave Hill Campus, Barbados, for preparing [Co(quin)Cl₂], Dr. James Hall for his assistance with the ⁵⁹Co NMR spectral acquisitions, and Dr. Stephen Feldberg of Brookhaven National Laboratory for insightful discussions and suggestions. The authors are also very grateful for the helpful comments of the reviewers.

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The stability of the Co(I) species of two mononuclear dichlorocobalt(II) compounds bearing 2,2'-bipyridine and *trans*-2-(2'-quinolyl)methylene-3-quinuclidione ligands was assessed via ^{59}Co NMR spectroscopy, electrochemical, and catalyzed proton electroreduction studies.