

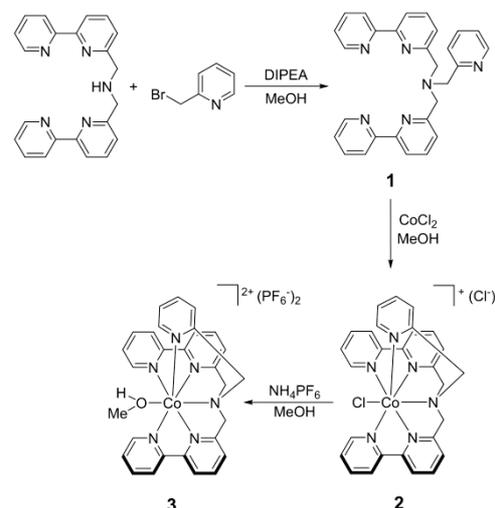
Heptacoordinate Co(II) complex: a new architecture for photochemical hydrogen production.

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Abstract: The first heptacoordinate cobalt catalyst for light-driven hydrogen production in water has been synthesized and characterized. Photochemical experiments using [Ru(bpy)₃]²⁺ as photosensitizer gave a turnover number (TON) of 16300 mol H₂ (mol cat.)⁻¹ achieved in two hours of irradiation with visible (475 nm) light. This promising result provides a path forward in the development of new structures to improve the efficiency of the catalysis.

The production of clean and sustainable energy represents a great challenge to tackle both problems of decreasing the use of fossil fuels and increasing energy demands. Photocatalytic water splitting constitutes a promising strategy to convert solar energy into chemical energy, generating hydrogen, a highly energetic and environmental friendly fuel.^{[1],[2]} Generally speaking, photocatalytic systems for hydrogen production contain a photosensitizer, a sacrificial electron donor and a catalyst.^[3] In particular the development of active and stable catalysts has been a subject of intense study to improve the efficiency of the hydrogen evolution process. The most studied catalysts are based on earth-abundant materials as cobalt and nickel because of their low cost and high activity.^[4] Recently, polypyridine cobalt complexes have gained great attention compared to cobaloxime complexes, because of their superior stability and catalytic activity.^[3a, 5] Some of these systems reported by Zhao, Webster and co-workers and by Alberto and co-workers achieved remarkable turnover numbers (TONs) of 4000 mol H₂ (mol cat.)⁻¹ and 11000 mol H₂ (mol cat.)⁻¹ respectively.^{[5a], [5b]} The common feature in the design of such complexes consists in hexacoordinate compounds with a distorted octahedral structure based on tetradentate or pentadentate polypyridine ligands, with the remaining coordination sites occupied by labile ligands (e.g. water). The increased reactivity of cobalt complexes in distorted

octahedral structures proves the importance of taking into account the architecture of the complexes to improve their efficiency.^[4a, 5e] To further investigate the effect of coordination geometry on the catalytic activity, we designed a new hexadentate polypyridyl ligand that leads to the formation of an unusual heptacoordinate Co(II) (Figure 1). Seven-coordination is quite rare for Co complexes, representing less than 1% of the known structures. Furthermore such heptacoordinate complexes have never found practical applications to date.^[6] In this work we present the synthesis, characterization and photocatalytic studies of the first example of a heptacoordinate cobalt catalyst and we demonstrate that, under visible light irradiation in fully aqueous medium, this complex can efficiently catalyze the production of H₂ reaching a TON of 16300 mol H₂ (mol cat.)⁻¹ within 2 h of irradiation with visible light (475 nm). Ligand **1** was synthesized from *N,N*-Bis-(6-(2,2'-bipyridyl)methyl)amine^[7] and 2-(Bromomethyl)pyridine (Scheme 1, see Supporting Information for synthetic details). Reaction of **1** with CoCl₂ in methanol at room temperature gave the heptacoordinate complex **2**. Derivative **3** with PF₆⁻ as counterion was also prepared to perform electrochemical studies in CH₃CN.



Scheme 1. Synthesis of the ligand **1** and complexes **2** and **3**.

Single crystals of compounds **2** and **3** suitable for X-ray diffraction were obtained respectively by layering a methanol solution of **2** with diethyl ether and by slow diffusion of hexane in a solution of **3** in methanol. The solid state structures are shown in Figure 1 and the crystallographic parameters are described in the Supporting Information (Tables S2 and S3).

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Co(II) displays a heptacoordinate geometry, best described as faced capped octahedron, with six positions occupied by the hexadentate ligand and one of the axial positions occupied by labile ligands as Cl⁻ or MeOH. The closest to linear angles are indeed Cl1–Co1–N2 with 164.1(1)° in **2** and O1–Co1–N4 with 162.0(1)° in **3**. Co–N bond lengths are in the range of 2.09–2.41 Å, thus in line with typical normal to long Co–N lengths observed in cobalt polypyridine complexes (see Section 14 of Supporting Information for more details).^[5a, 5c, 8] Interestingly, the Co–Cl bond in **2** (2.468(1) Å) is much longer than the Co–O(MeOH) bond length (2.254(3) Å) in **3**. Using the bond valence sum method (BVS)^[9] to evaluate the efficiency of binding of Co(II) by the ligands, values of 1.84 for **2** and 1.89 for **3** indicate in both cases an insufficient coordination of the metal ion by the ligand sphere, most likely due to the strains and sterics of the N-donor ligand. Magnetic properties of complex **2** were studied using the Evans method. A magnetic moment $\mu_{\text{calcd}} = 5.3$ BM (Figure S1) was obtained, which matches the literature value reported for a high-spin Co(II) system with three unpaired electrons.^[10] B3LYP electronic structure calculations of both complexes **2** and **3** predicted the high spin state (⁴Co(II)) to be significantly lower in energy (ca. 0.7 eV) than the low spin state (²Co(II)), with a resulting spin density of 2.8 localized on the metal center (see Figure S15). The heptacoordination is also found in the optimized structures of the high-spin states of complexes **2** and **3**, with calculated distances for the Co–N bonds close to the experimental ones and going from ca. 2.18 to 2.46 Å and ca. 2.13 to 2.39 Å in complex **2** and **3**, respectively. The C–OHMe and Co–Cl distances are instead calculated to be 2.44 and 2.34 Å, respectively, hence slightly longer than the experimental ones.

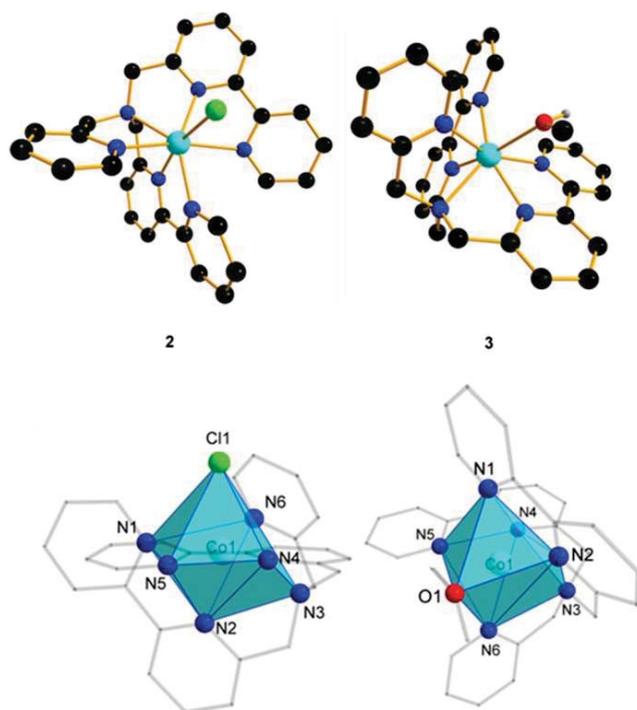


Figure 1. Crystal structures of **2** and **3** (top) and labelling scheme of first coordination sphere (bottom). Color code: Co (turquoise), N (blue), O (red), C (black), Cl (green) and H (grey); counterions of **2** (Cl⁻), of **3** [2(PF₆)⁻], methanol molecules and other H atoms have been omitted for clarity.

Cyclic voltammetry (CV) performed on a solution of **3** in CH₃CN (Figure 2) displays two successive reversible electron transfer waves, which can be tentatively assigned to a metal centered Co(II)/Co(I) process ($E_{1/2} = -1.1$ V, all potentials vs. Ag/AgCl) and to a ligand centered reduction ($E_{1/2} = -1.61$ V).^[8, 11] Noteworthy, in contrast to all known Co polypyridine complexes, no Co(III)/Co(II) wave was observed until +2.0 V (i.e. in the range of the solvent electrochemical window).^[5e] Addition of increasing amounts of acetic acid to a solution of **3** in CH₃CN leads to the evolution of catalytic waves attributed to the catalytic reduction of protons (Figure 2, for control experiments see Figure S2). On the basis of these catalytic waves, an overpotential requirement of ca. 420 mV was calculated at the first possible catalytic wave and of ca. 730 mV at the second one (see Section 4 of Supporting Information for calculations details).^[8, 11-12]

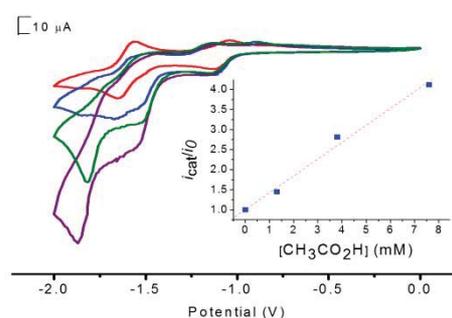


Figure 2. Cyclic voltammograms of 4 mM solutions of **3** in CH₃CN, 0.1 M TBAPF₆ at 0.1 V s⁻¹ with 0 (red), 1.3 (blue), 4 (green) 8 (purple) mM of acetic acid. Inset: catalytic enhancement i_{cat}/i_0 (current in the catalytic wave over the current of the mono-electronic wave observed in the absence of acid) as a function of acid concentration. Glassy carbon working electrode, Ag/AgCl (3.5 M KCl) reference electrode and glassy carbon auxiliary electrode.

Photocatalytic experiments were performed in 1 M solutions of acetate buffer with ascorbic acid (0.1 M) and [Ru(bpy)₃]²⁺ (0.5 mM, bpy = 2,2'-bipyridine) as sacrificial electron donor and as photosensitizer, respectively. In order to optimize the conditions for hydrogen production, a series of experiments was conducted varying catalyst concentration, pH and temperature. Results from the catalytic concentration dependence given in Figure 3 show that the activity, in terms of TONs, increases significantly at lower concentration of the catalyst. A TON of 16300 (±1600) mol H₂ (mol cat.)⁻¹ and turnover frequency (TOF) of 5000 (±280) mol H₂ (mol cat.)⁻¹ h⁻¹ were obtained using a catalyst concentration of 0.1 μM. It is worth to notice that these values represent, to our knowledge, the highest values obtained so far for a Co-based molecular catalyst in the presence of ascorbic acid and [Ru(bpy)₃]²⁺. The quantum yield values obtained using 0.1 μM and 10 μM of catalyst are estimated to be 3% and 11% respectively (see Section 15 of Supporting Information). According to literature, the linear dependence between the amount of hydrogen produced and the catalyst concentration in the investigated range (see Figure S4), together with the absence of an induction period, suggest a molecular process.^[5c] This evidence was further corroborated by dynamic light scattering measurements (see Figure S5) that showed no noticeable formation of nanoparticles larger than 2 nm.^[13] Moreover, photochemical experiments conducted in the presence of 1 mL Hg(0) did not show any change in the activity, as expected for

a homogeneous catalysis.^[14] However, according to the results it is not possible to exclude with certainty the formation of nanoparticles smaller than 2 nm.

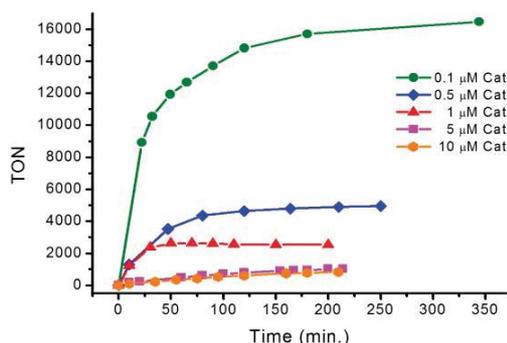


Figure 3. Photocatalytic hydrogen production over time in 1.0 M acetate buffer at pH 4.0 with 0.1 M ascorbic acid, 0.5 mM $[\text{Ru}(\text{bpy})_3]^{2+}$ and different concentrations of catalyst at 20°C irradiated with LED light (475 nm).

Photocatalytic experiment performed with the same concentrations of catalyst (20 mM) and photosensitizer (20 mM) showed a decreased activity (Figure S6). This evidence proves that the system needs low concentrations of catalyst and ca. 5000 equivalents of photosensitizer to reach the highest efficiency. Control experiments performed in the absence of $[\text{Ru}(\text{bpy})_3]^{2+}$, ascorbic acid or catalyst showed no significant formation of H_2 (Figure S7), proving the photocatalytic nature of the process. Hydrogen evolution ceased after around two hours with nearly 90% of H_2 evolved within the first hour of irradiation. HPLC studies of the reaction mixture before and after photocatalysis indicated that the catalyst remains stable during the H_2 evolution (Figure S8).^[5c] To investigate the factors contributing to the cessation of H_2 evolution, three independent experiments were performed. $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$ and ascorbic acid, ascorbic acid followed by catalyst were added to the reaction mixture after 2 hours of irradiation. Upon addition of $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.5 mM) a resumed production of hydrogen (19% of the amount produced in the pristine system) was observed upon irradiation (Figure S10). Conversely, addition of ascorbic acid (0.1M) led to the formation of only 10% of H_2 upon irradiation and further addition of catalyst (0.5 μM) to this solution did not show any increase of produced H_2 (Figure S11). The best results were obtained upon addition of $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.5 mM) and ascorbic acid (0.1M), which gave a further generation of H_2 of 40% (Figure S12). These results suggest that $[\text{Ru}(\text{bpy})_3]^{2+}$ and ascorbic acid mainly contribute to the end of hydrogen formation during the photocatalytic experiment. Hydrogen evolution efficiency shows a pronounced pH dependence in the range of 3 - 5.6 (Figure S13), the highest TON being observed at pH = 4.^[15] Moreover, an increase of the amount of evolved hydrogen was observed upon temperature decrease in the range of 30°C - 5°C with a concomitant decrease of the TOF (Figure S14). This effect can be attributed to an inversely proportional relationship between temperature and hydrogen evolving kinetics. The decrease of TON at higher temperature is due to a detrimental effect of temperature on the catalyst (Figure S9). Therefore, in our system the operating temperature of 20°C represents the best compromise between system stability and hydrogen evolution rate.

In conclusion we have presented the first example of a

heptacoordinate cobalt complex capable of catalyzing light-driven hydrogen evolution in fully aqueous medium. The high TONs achieved in two hours of irradiation and the stability of the system observed during the irradiation period at 20°C suggest that heptacoordinate cobalt complexes represent a promising architecture for the development of highly active and stable photocatalysts. Furthermore the oxidation potential of the couple $\text{Co}(\text{III})/\text{Co}(\text{II})$ higher than +2 V could enable the use of this complex in conjugated water splitting systems. Mechanistic studies of the process and modifications of the ligand to improve the activity towards H_2 evolution are currently in progress.

Experimental Section

All chemicals were purchased from usual suppliers and used as delivered. *N,N*-Bis-(6-(2,2'-bipyridyl)methyl)amine was synthesized according to literature procedure.^[7] Syntheses of **1**, **2** and **3** are described in the Supporting Information. Copies of crystallographic data can be obtained on quoting the depository numbers CCDC-1531898 (**2**) and 1531899 (**3**) (E-Mail: deposit@ccdc.cam.ac.uk). Cyclic voltammetric measurements were conducted in CH_3CN (0.1 M of NBu_4PF_6) using a glassy carbon working electrode, Ag/AgCl (3.5 M KCl) as reference electrode and glassy carbon auxiliary electrode. All solutions were purged with Ar for 5 minutes before CVs were recorded. Photocatalytic experiments were performed in 6 mL solutions of 1 M acetate buffer with ascorbic acid (0.1 M) and $[\text{Ru}(\text{bpy})_3]^{2+}$ (0.5 mM) respectively used as sacrificial electron donor and as photosensitizer. The system was irradiated with a 1.1 W LED light (475 nm) in a water jacketed flask under constant stirring. H_2 evolution was monitored by GC TCD detector (column molecular sieve 5 A of 30 m x 0.53 mm) during photocatalysis by periodically sampling 50 μL of headspace. Gas chromatography calibration curves were made by sampling known amounts of H_2/Ar mixtures with a Hamilton sample lock syringe from gas sampling bags.

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Keywords: cobalt • heptacoordinate complex • hydrogen • photocatalysis • polypyridyl ligand

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