available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue of Photocatalysis for Solar Fuels)

New tricks for an old dog: Visible light-driven hydrogen production from water catalyzed by *fac*- and *mer*- geometrical isomers of tris(thiosemicarbazide) cobalt(III)

Yang Zhao ^{a,†}, Yongheng Wang ^{c,†}, Qiaoyu Wu ^a, Jinqing Lin ^a, Shenghui Wu ^a, Wenjuan Hou ^b, Ruibo Wu ^c, Genggeng Luo ^{a,*}

^a College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, Fujian, China

^b Instrumental Analysis Center, Huaqiao University, Xiamen 361021, Fujian, China

^c School of Pharmaceutical Sciences, East Campus, Sun Yat-sen University, Guangzhou 510006, Guangdong, China

ARTICLE INFO

Article history:

Received 28 September 2017

Accepted 19 October 2017

Published 5 March 2018

Keywords:

Thiosemicarbazide

Cobalt complexes

Molecular catalysis

Geometric isomers

Photocatalysis

ABSTRACT

Increasing interest has been paid to the development of earth-abundant metal complexes as promising surrogates of platinum for the electrocatalytically and photocatalytically driven hydrogen evolution reaction. In this work, we report on molecular H₂-evolving catalysts based on two octahedral complexes of cobalt thiosemicarbazide, *fac*-[Co(Htsc)₃]Cl₃·3H₂O (**C1**, Htsc = thiosemicarbazide) and *mer*-[Co(Htsc)₃]Cl₃·4H₂O (**C2**), which have facial (*fac*) and meridional (*mer*) geometry, respectively. Electrochemical studies confirmed that both **C1** and **C2** are active electrocatalysts in MeOH solution using acetic acid as the proton source, with the same overpotential of ~ 640 mV and TOF of ~ 210 s⁻¹. The complex **C1** also exhibits electrocatalytic activity for hydrogen evolution reaction in aqueous media free of organic solvent with a moderate overpotential (560 mV). Visible light-driven hydrogen evolution experiments were carried out in combination with fluorescein as photosensitizer and triethylamine as sacrificial reductant in homogeneous environments. Our studies showed that both **C1** and **C2** can be used as efficient proton-reduction catalysts in purely aqueous solution and have the same photocatalytic activities. A TOF of 125 h⁻¹ with a TON of 900 for photocatalytic H₂ generation using **C1** and **C2** in water were achieved for the noble-metal-free homogeneous system. It should be noted that this is the first reported study investigating the effect on the catalytic hydrogen production performance of using *fac*- and *mer*-isomers of molecular catalysts.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen (H₂) is a promising fuel source for future energy use. Reduction of water into H₂ using visible light is one of the most promising scenarios for a sustainable energy supply. In

this arena, molecular reaction systems can provide a high degree of tunability toward the optimization of this reductive half-reaction. An efficient homogeneous molecular system for photochemical reduction of protons to H₂ generally requires at least three basic components: a photosensitizer (PS), a pro-

* Corresponding author. Tel/Fax: +86-592-6162225; E-mail: ggluo@hqu.edu.cn

† These authors contributed equally to this work.

This work was supported by the National Natural Science Foundation of China (21641011, 21773313), the Natural Science Foundation of Fujian Province (2015J01053, 2016J01060), Program for New Century Excellent Talents in Fujian Province University, and Promotion Program for Young and Middle-aged Teacher in Science, Technology Research of Huaqiao University (ZQN-PY104).

DOI: 10.1016/S1872-2067(17)62940-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

ton-reduction catalyst (PRC), and a sacrificial electron donor. Among the PRCs, molecular species based on earth-abundant cobalt centers have received considerable attention [1–4]. It is noted that these cobalt-based PRCs often feature square planar or pyramidal structures with labile axial ligands (typically aqua or halide) [1–5], whereas cobalt complexes with octahedral geometries remain unexplored. Furthermore, in these reported homogeneous H₂-evolving systems, most cobalt PRCs usually operate in mixtures of organic solvents and water because of their poor solubility and aqueous activity [1–4]. Thus, the search for efficient cobalt-based molecular catalysts that can function in purely aqueous solution remains a great challenge [6–8].

In contrast, compounds based on thiosemicarbazide (NH₂–NH–C(=S)–NH₂, denoted as Htsc), which belong to the group of thiourea derivatives, can form stable complexes with many transition and main-group metal ions [9]. In the past, Htsc-containing complexes have attracted much attention because of their highly desirable biological and pharmaceutical properties, such as antioxidant, antibacterial, antiviral, or anti-malarial activities [10–12]. However, the use of such thiosemicarbazide-based complexes as H₂-evolving molecular catalysts remains unexplored. Herein, we report a pair of octahedral geometric isomers with *fac*- and *mer*-geometry of tris(thiosemicarbazide) cobalt(III), i.e., *fac*-[Co(Htsc)₃]Cl₃·3H₂O (**C1**) and *mer*-[Co(Htsc)₃]Cl₃·4H₂O (**C2**). They are confirmed to be active molecular PRCs for electrocatalytic and photocatalytic reduction of protons.

We chose the two cobalt complexes according to the following considerations: (1) There is no report of using octahedral geometric isomers for catalytic hydrogen production. Thus, the catalytically H₂-evolving activity of the two cobalt complexes with *fac*- and *mer*-configuration will be compared. (2) The two ionic complexes have sufficient solubility in water, which will facilitate the evaluation of their catalytic properties in H₂O without organic additives. (3) The amino nitrogens of Htsc can, in principle, serve as internal proton transfer sites, as previously hypothesized for a pendant nitrogen base in nickel bis(diphosphine) for protonation. (4) The results may represent a new paradigm for the construction of noble-metal-free photocatalytic systems using thiosemicarbazide-containing complexes for solar hydrogen generation.

2. Experimental

2.1. Materials

All chemical reagents used in the syntheses were of analytical grade and used without further purification, unless otherwise indicated. Water was purified using a Milli-Q system. Triethylamine (TEA) and all solvents were dried by standard literature methods [13]. The elemental analyses (C, H, and N contents) were determined on a Vario EL III analyzer. Co was analyzed on a PLASMA-SPEC ICP atomic emission spectrometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Photoluminescence (PL) spectra were obtained using a Thermo Scientific Lumina fluorescence

spectrophotometer. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet iS50 FT-IR spectrometer as KBr pellets in the frequency range of 4000–400 cm^{−1}. Mass spectra (MS) experiments were carried out on an Agilent Infinity II QTOF G6545.

2.2. Synthetic procedures

The syntheses of *fac*-[Co(Htsc)₃]Cl₃·3H₂O (**C1**) and *mer*-[Co(Htsc)₃]Cl₃·4H₂O (**C2**) were achieved using literature methods [14] and the products were characterized by electronic absorption spectroscopy, elemental analysis, FT-IR spectroscopy, and single-crystal X-ray diffraction (SCXRD) to determine their actual molecular structures.

fac-[Co(Htsc)₃]Cl₃·3H₂O (**C1**). MS (*m/z*): 332.3, corresponding to the cationic unit. UV/Vis, λ_{max}/nm (ε/L mol^{−1}·cm^{−1}), (H₂O): 257 nm (6261), 414 nm (97), 547 nm (93). IR (KBr): ν(cm^{−1}) = 3387 (s), 3144 (s), 1625 (s), 1401 (s), 1328 (m), 1219 (s), 1154 (m), 1011 (w), 754 (w), 703 (s), 613 (s), 575 (s), 520 (m). Anal. Calcd. (found) for CoC₃H₂₁O₃N₉S₃Cl₃: C, 7.31 (7.43); H, 4.30 (4.36); N, 25.58 (25.66); Co, 11.96 (12.28).

mer-[Co(Htsc)₃]Cl₃·4H₂O (**C2**). MS (*m/z*): 332.3, corresponding to the cationic unit. UV/Vis, λ_{max}/nm (ε/L mol^{−1}·cm^{−1}), (H₂O): 248 nm (4179), 420 nm (309), 575 nm (79). IR (KBr): ν(cm^{−1}) = 3272 (s), 3100 (s), 1634 (s), 1434 (m), 1393 (m), 1253 (m), 1152 (w), 1012 (w), 760 (w), 700 (m), 589 (w), 439 (w). Anal. Calcd. (found) for CoC₃H₂₃O₄N₉S₃Cl₃: C, 7.05 (7.16); H, 4.54 (4.61); N, 24.68 (24.76); Co, 11.54 (11.82).

Two other cobalt complexes, [Co(dmgH)₂pyCl] (**C3**, where dmgH = dimethylglyoximate monoanion and py = pyridine) and [Co(bpy)₃Cl₂] (**C4**, where bpy = 2,2'-bipyridine), were prepared according to the literature procedures [15,16].

2.3. Electrochemical experiments

Electrochemical experiments were performed using a CHI 650E electrochemical analyzer. Cyclic voltammograms (CVs) were recorded in an electrolytic cell with a 3 mm glassy-carbon working electrode, saturated calomel electrode (SCE) as reference electrode, and a platinum-wire counter electrode as auxiliary electrode. The glassy-carbon working electrode was polished with alumina (1.0 μm, 0.3 μm, and 0.05 μm) on a polishing cloth before each measurement. The solution was purged with Ar gas and dried by standard literature methods prior to measurements. The measurements were performed in methanol with 0.1 mol/L tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) as a supporting electrolyte. Controlled potential coulometry was done in an electrolytic cell with a glassy-carbon working electrode, SCE reference electrode, and a platinum-wire counter electrode. After electrolysis, a sample of the headspace was injected into a gas chromatograph (GC).

2.4. General procedure for photocatalysis

The photocatalytic water splitting experiments were performed according to the previous work [17,18]. In a typical experiment, 10 mL of a 5% TEA aqueous solution containing

fluorescein (FL) (1×10^{-3} M) and either **C1** or **C2** (1×10^{-5} mol/L) was added to a Schlenk bottle. The solution was then freeze-pump-thaw degassed three times and irradiated using a xenon light source (300 W, Beijing Perfectlight Co., Ltd.), with an optical filter employed to cut off light with wavelengths below 420 nm, under constant stirring. The pH of the solution was adjusted to the desired value using hydrochloric acid or sodium hydroxide as required and determined by an OHAUS ST5000 pH meter. During irradiation, the gas phase of the reaction system was analyzed by a GC (Shimadzu GC-2014C) with a thermal conductivity detector, a 5 Å molecular sieve column, and with N₂ as carrying gas. The amounts of hydrogen were quantified by the external standard method.

2.5. X-ray structural determination

Single crystals of **C1** and **C2** with appropriate dimensions were chosen and mounted on a glass fiber for data collection. Data were collected on an Oxford Diffraction Gemini A with a CCD area detector, and the CrysAlisPro and CrysAlis RED software packages were used for data collection and data integration. The collected data were corrected for absorbance by an analytical numeric absorption correction using a multifaceted crystal model based on expressions derived from the Laue symmetry using equivalent reflections [19]. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 [20] and SHELXL-97 [21] program packages, respectively. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically and refined with isotropic temperature factors. The hydrogen atoms attached to nitrogen and oxygen for **C1** and **C2** were located in the difference Fourier maps and refined with all other atoms fixed. Selected crystallographic data for **C1** and **C2** are summarized in Table S1. Selected bond lengths and angles for **C1** and **C2** are listed in Table S2. CCDC-1576996 (**C1**) and 1577003 (**C2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.6. Computational details

All the theoretical calculations were performed with the Gaussian 09 package [22]. For the purpose of accordance with the experimental results, the geometric parameters taken from our SCXRD analysis were used as the starting points for the geometry optimizations. Ground-state geometries were fully optimized in the framework of density functional theory (DFT) using the hybrid functional B3LYP, which combines Becke's 3-parameter exchange functional [23] and Lee, Yang, and Parr's correlation functional [24]. The split-valence and triple-zeta basis set TZVP [25] and the polarizable continuum model (PCM) [26] of water solvent were employed in all calculations. All geometries were deemed to be energy minima, as no negative frequencies were found. Time-dependent DFT (TD-DFT) [27] was applied to compute the vertical transition energies.

3. Results and discussion

3.1. Synthesis and structural characterization

The complexes of cobalt thiosemicarbazide (**C1** and **C2**) were synthesized as reported in the literature [14]. Their structures were characterized by elemental analyses, MS, IR spectroscopy, and UV/Vis spectroscopy in the solution and solid state, as well as X-ray crystallography in the solid state. Single crystals of **C1** and **C2** suitable for X-ray diffraction were grown through the diffusion of concentrated hydrochloric acid into aqueous solutions of **C1** and **C2**. Single-crystal X-ray diffraction (SCXRD) analysis revealed that **C1** is composed of a $[\text{Co}(\text{Htsc})_3]^{3+}$ cation, three Cl^- anions, and three lattice water molecules, while **C2** consists of a $[\text{Co}(\text{Htsc})_3]^{3+}$ cation, three Cl^- anions, and four lattice water molecules (see Fig. S1 in the Supporting Information (SI)). In **C1** and **C2**, the cation $[\text{Co}(\text{Htsc})_3]^{3+}$ is a six-coordinate Co^{III} complex with a distorted octahedral geometry. The cobalt center is ligated by three bidentate Htsc ligands through the sulfur and hydrazinic nitrogen atoms. The average Co–N distance of 1.988 Å in **C1** is close to the 1.980 Å observed in **C2**, whereas the average Co–S distance of 2.220 Å in **C1** is slightly less than the corresponding distance of 2.251 Å observed for **C2**. In the case of complexes of general formula $[\text{Co}(\text{N}_2\text{S})_3]$, there are two possible geometric isomers: facial (*fac*)- and meridional (*mer*)-isomers. Symmetry considerations show that in the *fac*-isomer the three ligands are equivalent, which is not the case in the *mer*-isomer. As can be seen from Fig. 1, the $[\text{Co}(\text{Htsc})_3]^{3+}$ unit in **C1** adopts a *fac*-arrangement, which is distinct from the *mer*-geometry of **C2** (Fig. 1).

The UV/Vis absorption spectra of **C1** and **C2** measured in water are shown in Fig. 2. The electronic absorption spectra of the Co^{III} complexes contain two visible bands at 545 and 425 nm for **C1** and at 585 and 410 nm for **C2**. These bands are characteristic of low-spin Co^{III} complexes in which the metal is in an octahedral environment [28]. The first of these bands is assigned to the transition $^1A_{1g} \rightarrow ^1T_{1g}$, and the second to the $^1A_{1g} \rightarrow ^1T_{2g}$ transition. In addition, the third, strong, high-energy absorption band at ~255 nm is attributed to the ligand-to-metal charge transfer. The diffuse reflectance spectra of **C1** and **C2** bear very similar features to the solution spectra of the ionic complexes in water (Fig. S2), indicating that the same species

Fig. 1. ORTEP drawing of the cations *fac*- $[\text{Co}(\text{Htsc})_3]^{3+}$ (a) and *mer*- $[\text{Co}(\text{Htsc})_3]^{3+}$ (b) showing the numbering scheme.

Fig. 2. UV/Vis absorption spectra of **C1** and **C2** in water. Inset: close-up of the region between 400 and 800 nm.

with *fac*- and *mer*-configuration exist in the solid state and in solution. The frontier molecular orbitals of **C1** and **C2** were also analyzed by DFT. The optimized geometric parameters for the lowest-energy conformer are comparable to those determined crystallographically for **C1** and **C2** (Fig. S3). The main contribution to the highest occupied molecular orbital (HOMO) calculated for the optimized complex **C1** or **C2** is from the thiosemicarbazide ligands (Fig. 3), while the lowest unoccupied molecular orbital (LUMO) is an antibonding combination of a Co-centered orbital (of d symmetry) with the orbitals of the thiosemicarbazide ligands. A time-dependent DFT study was also performed to calculate the electronic transition in water. The calculated spectra of **C1** and **C2** are similar to the experimental spectra (Fig. S4).

3.2. Electrocatalytic proton reduction

CVs of **C1** recorded in a solution of *n*-Bu₄NPF₆ in CH₃OH (0.1 mol/L) show the coupled Co^{III}/Co^{II} and Co^{II}/Co^I reduction process at ~ -0.68 and ~ -0.096 V (vs SCE) [29,30], respectively (Fig. 3a). The Co^{II}/Co^I potential falls within the range of that of

Fig. 3. Isodensity contours of the HOMOs and LUMOs calculated by DFT for **C1** and **C2**.

proton reduction, indicating that the reduced state of **C1** may be capable of directly reducing protons. To investigate whether **C1** is a potential electrocatalyst for proton reduction, acetic acid (AcOH, $pK_{aMeOH} = 9.7$) [31] was employed as a very inexpensive proton source. As displayed in Fig. 4(a), upon successive addition of AcOH to CH₃OH solutions of **C1**, the cathodic current at -1.28 V increases, indicative of electrocatalytic reduction. At the concentration of 40 equivalents of AcOH, the observed catalytic current has a linear correlation with the added AcOH concentration at a scan rate of 200 mV/s (Fig. 4(b)). Beyond this acid concentration, the current is acid-independent, indicating that the PRC **C1** is acid-saturated. Control experiments using AcOH or Co(NO₃)₂ in AcOH in the absence of **C1** showed no hydrogen evolution activity within the potential window. The catalytic wave grew out of the Co^{II}/Co^I redox couple at a more cathodic potential in these control experiments, implying that the first step for H₂ evolution involves sequential electrochemical reductions to Co(I) species, which is followed by protonation events. Electrodeposits as potential heterogeneous catalysts are excluded on the basis of negative standard rinse experiments (Fig. S5). Controlled potential electrolysis was performed at -1.28 V (vs SCE) to con-

Fig. 4. (a) Cyclic voltammograms of **C1** (1.0 mmol/L) in the absence (gray curve) and the presence (black curves) of varying concentrations of AcOH (2.0–8.0 mmol/L) recorded in a CH₃OH solution of *n*-Bu₄NPF₆ (0.1 mol/L) on a glassy-carbon electrode at 200 mV/s. (b) Dependence of normalized catalytic current, i_{cat} , on concentration of acetic acid. Currents were extracted from voltammograms.

firm the identity of the gaseous product as hydrogen. **C1** consumed more charge than the blank during the bulk-electrolysis experiment, which supports that the complex is responsible for catalysis (Fig. S6).

To evaluate the electrocatalytic property of **C1**, the turnover frequency (TOF) and the overpotential (η) of the reaction were determined. Using data in this acid-independent regime, the rate constant for hydrogen evolution (k) can be calculated from the expression:

$$\frac{i_{\text{cat}}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk}{Fv}}$$

in which v is the scan rate in V/s, n is the number of electrons transferred (two for hydrogen evolution), R is the gas constant, T is the temperature in K, and F is the Faraday constant. The i_{cat}/i_p value of 23 in the acid-independent region (for a scan rate of 200 mV/s) indicates that the TOF, which is also the observed rate constant, is 210 s^{-1} . Using the method of Appel and Helm [32], η is determined to be 640 mV (–1.28 V vs SCE). Under identical experimental conditions, hydrogen evolution using the other PRC, **C2**, yielded an equivalent TOF of 208 s^{-1} and η of 636 mV (Fig. S7), demonstrating that the two geometric isomers of **C1** and **C2** have the same electrochemical behavior.

As shown in Fig. 5, electrochemical hydrogen evolution reaction catalyzed by **C1** was further evaluated in a phosphate buffer solution (pH = 7.0; 0.1 mol/L), which also showing distinct flow of cathodic current. The overpotential $\eta(E_{\text{cat}/2})$ in the aqueous solution is defined by the difference between the standard electrode potential for electrochemical hydrogen evolution reaction defined by the equation 1 (equation 1: $E_{1/2}(2\text{H}^+/\text{H}_2) = -0.241 - 0.059 \text{ pH/V vs. SCE}$) and the potential ($E_{\text{cat}/2}$) at which the catalytic current becomes exactly the half of the maximum catalytic current. From $E_{\text{cat}/2}$ value determined for the catalytic current, the $\eta(E_{\text{cat}/2})$ value for electrochemical hydrogen evolution reaction catalyzed by **C1** at pH = 7.0, is measured to be 560 mV.

Fig. 5. CV for aqueous phosphate buffer solution (pH = 7.0; 0.1 mol/L) of **C1** (0.5 mmol/L) containing NaCl (0.1 mol/L) on a glassy-carbon electrode at room temperature under N_2 atmosphere, recorded at a sweep rate of 200 mV/s.

3.3. Visible light-driven hydrogen evolution

Since the primary motivation for H_2 -producing photocatalysis is to reduce protons from water, organic additives and their waste by-products should be minimized or completely eliminated. The ionic complexes **C1** and **C2** have sufficient solubility ($> 40 \text{ mg/mL}$ at 20°C) in water for their catalytic light-assisted proton reduction activity to be suitably evaluated in fully aqueous solution. Toxic solvents like acetonitrile or methanol commonly used in other homogeneous H_2 -evolving systems are not required in our system [1–4]. The visible light-driven catalytic activity of **C1** and **C2** for H_2 production was investigated using a three-component artificial photosynthesis system: fluorescein (FL) as PS, TEA as sacrificial electron donor, and **C1** (or **C2**) as PRC. Quantitative determination of the generated H_2 was conducted by GC analysis, as described in the Experimental Section. We chose FL as the PS because its excited state and reduced state provide a high driving force ($^1\text{FL}^* \sim -1.7 \text{ V}$ and $\text{FL}^{\cdot-} \sim -1.3 \text{ V}$ vs SCE [33]) for successive reduction of the catalyst **C1** or **C2**. When employing TEA as the sacrificial reductant, the net reaction being driven photochemically can be expressed by the equation: $\text{NEt}_3 + \text{H}_2\text{O} \rightarrow \text{HNEt}_2 + \text{H}_2 + \text{CH}_3\text{CHO}$. Thermochemical data indicate that the overall reaction is thermodynamically unfavorable and must be driven by light energy. During initial observations using the PRC **C1**, the pH of the reaction solution had a marked effect on hydrogen production from an aqueous solution of TEA (Fig. 6). The amount of H_2 generated in 15 h photolysis maximized at pH = 11.5 and quickly decreased below pH = 9 and above pH = 13. For the photolysis, the component concentrations were $1 \times 10^{-3} \text{ mol/L}$ FL, $1 \times 10^{-5} \text{ mol/L}$ **C1**, and 0.36 mol/L TEA in water. The pH value of each run was adjusted by addition of HCl or NaOH. Below pH 9 and above pH 13, the amounts of H_2 produced were moderate (less than 15% of that obtained at pH = 11.5 during the same period of irradiation). The great decrease in production of hydrogen at lower pH values was probably because of the protonation of TEA, which resulted in poor elec-

Fig. 6. Influence of pH on the photogeneration of H_2 from a system composed of **C1** + FL + TEA in water after 15 h of irradiation ($\lambda > 420 \text{ nm}$).

Fig. 7. Photocatalytic H₂ production profiles of the three-component systems containing 1×10^{-3} mol/L FL, 1×10^{-5} mol/L **C1** or **C2**, and 0.36 mol/L TEA in water at pH = 11.5 upon xenon irradiation ($\lambda > 420$ nm).

tron-donating ability. At higher pH values, the decreased concentrations of protons impair the efficiency of photogeneration of hydrogen.

The photocatalytic efficiencies of **C1** and **C2** were compared under the optimized pH condition. As shown in Fig. 7, the systems composed of either catalyst **C1** or **C2** produced copious amounts of H₂ with a turnover number (TON) of 900 for **C1** and 890 for **C2**, corresponding to an estimated initial TOF of 128 h^{-1} with respect to catalyst **C1** and 125 h^{-1} for **C2**. The very similar values of both TON and TOF indicate that the *fac*-**C1** and *mer*-**C2** have approximately the same photocatalytic activity in our system. Control experiments revealed that the absence of light activation or deletion of any single molecular constituent resulted in negligible H₂ production under the same conditions. In all of the hydrogen production experiments that did yield H₂, induction periods of about 0.5–1 h were observed before substantial amounts of hydrogen evolved. These induction phases may be ascribed to the formation of Co^I species or cobalt nanoparticles from the photodecomposition of cobalt complexes. A

Fig. 8. Hg poisoning experiment using FL (1 mmol/L), TEA (5%, v/v), and **C1** (1×10^{-5} mol/L) in H₂O at pH = 11.5 under visible-light irradiation ($\lambda > 420$ nm).

Fig. 9. Regeneration of photocatalytic activity resulting from the addition of one equivalent of **C1**. Experimental conditions: 1×10^{-5} mol/L **C1**, 1×10^{-3} mol/L FL, and 0.36 mol/L TEA at pH = 11.5.

similar result was observed by Eisenberg and co-workers for cobaloxime-based molecular catalysts [34]. The homogeneity of the photocatalytic system utilizing **C1** or **C2** was ascertained through the Hg poisoning test. When a large excess of Hg was added to the system, the catalytic activity was unaffected and remained stable throughout the photolysis process (Fig. 8 and Fig. S8). This finding suggests a molecular catalyst for the photocatalytic hydrogen production in each of the **C1**- and **C2**-based systems.

After approximately 8 h of irradiation, the rate of hydrogen evolution began to noticeably decrease, indicating that at least one of the system components had been consumed. The addition of fresh FL or TEA produced a negligible restoration of activity. However, upon addition of **C1**, the initial activity was nearly fully restored, indicating that the system was mainly limited by the decomposition of the PRC (Fig. 9). Two other known cobalt complexes, cobaloxime **C3** and the tris(2,2'-bipyridine)cobalt(II) complex **C4** (Scheme 1), were reported to be efficient photocatalysts both in basic solutions of organic solvents and in water [35,36]. We also studied the cat-

Scheme 1. Structures of **C1**, **C2**, **C3**, **C4**, and FL used in this work.

Fig. 10. Photocatalytic hydrogen production for a system containing FL (1×10^{-3} mol/L), TEA (5%, v/v), and **C1–C4** (1×10^{-5} mol/L) at pH = 11.5.

alytic performance of those cobalt complexes for photoinduced hydrogen generation under our conditions. However, under the same conditions specified in Fig. 6, **C3** and **C4** gave TONs of 151 and 20, respectively, much lower than **C1**, after 15 h irradiation. In summary, **C1** and **C2** displayed efficient photocatalytic hydrogen evolution activity in pure water solution (Fig. 10).

3.4. Fluorescence quenching of FL* and proposed catalytic mechanism for H_2 evolution

In the three-component photodriven catalytic systems, the PS excited state can function as either an oxidant or a reductant, and can be quenched by an electron donor or an acceptor [37]. To decide between these two possibilities in our system, the luminescence of the excited FL*, in deaerated H_2O at pH = 11.5, was monitored as a function of both TEA and, separately, **C1** concentration (Fig. 11 and 12). Stern-Volmer analyses yielded the quenching constants for the system. The rate constants for reductive quenching of FL* by TEA and oxidative quenching by **C1** are 1.1×10^7 and 1.2×10^{10} mol L^{-1} s^{-1} , respectively. These results show that the excited state of FL* can be both oxidatively quenched by the catalyst and reductively quenched by TEA, and the corresponding quenching processes are diffusion-controlled. Although the rate constant for oxidative quenching is about 10^3 times larger than that of reductive quenching, the reductive quenching process is still dominant given the much higher concentration of TEA (0.36 mol/L) relative to **C1** (0.01 mmol/L). It should be noted that **C2** also shows similar quenching constants on the basis of the Stern-Volmer plots (Fig. S9).

Based on the preceding electrochemical and photochemical

Fig. 11. (a) Emission spectra of FL (0.01 mmol/L) as a function of added **C1** in H_2O at pH = 11.5. (b) Stern-Volmer plot of quenching by **C1**.

Fig. 12. (a) Emission spectra of FL (0.01 mmol/L) as a function of added TEA in H_2O at pH = 11.5. (b) Stern-Volmer plot of quenching by TEA.

Scheme 2. Postulated mechanism for photocatalytic hydrogen evolution with the PRCs **C1** and **C2**.

observations, a possible, although still ambiguous, catalytic mechanism can be postulated (Scheme 2). After irradiation by visible light, FL is promoted to its excited state FL*, and then quenched by TEA to generate its anionic form FL^{•-}. The mechanism for the reduction of protons to H₂ by **C1** or **C2** involves two-electron reduction from FL^{•-} or FL*, which is followed by two protonation events, most likely protonation at an amino nitrogen atom of the thiosemicarbazide ligand, accompanied by dechelation. Protonation of a pendant nitrogen base would be consistent with the proposed mechanism for the hydrogen-evolving catalysts nickel bis(diphosphine) [38] and nickel tri(pyridine-2-thiolate) [33]. After the above steps, H₂ is released from the system through the heterocoupling between Co–H⁻ and N–H⁺, though a homolytic pathway cannot be ruled out. Further studies including theoretical calculations are needed to describe the mechanism in detail.

4. Conclusions

In summary, two geometric isomers, *fac*- and *mer*-tris(thiosemicarbazide) cobalt(III) (**C1** and **C2**), have been synthesized and characterized by X-ray single-crystal diffraction. The two cobalt complexes were tested for activity in electrocatalytic H₂ production by employing acetic acid as a very inexpensive proton source in CH₃OH. Electrocatalytic experiments in CH₃OH showed that both **C1** and **C2** are active electrocatalysts having the same activity, providing a TOF of 210 s⁻¹ with a moderate overpotential of 0.64 V when using glassy carbon as electrode material. **C1** also exhibits electrocatalytic activity for hydrogen evolution reaction in aqueous media (pH = 7.0) with a moderate overpotential (560 mV). The photocatalytic water reduction properties of **C1** and **C2** were further evaluated in purely aqueous solution using FL as the PS with

TEA as the sacrificial reductant. Efficient H₂ evolution (up to 900 turnovers vs catalyst) was achieved under visible-light irradiation. **C1** and **C2** showed similar electrocatalytic and photocatalytic H₂ evolution activities, indicating that *fac/mer* isomerism does not affect the H₂ evolution activity of this complex.

Acknowledgments

Yang Zhao thanks Subsidized Project for Cultivating Post-graduates' Innovative Ability in Scientific Research of Huaqiao University. The Instrumental Analysis Centre of Huaqiao University for analytical characterization is also acknowledged.

References

- [1] V. Artero, M. Chavarot-Kelidou, M. Fontecave, *Angew. Chem. Int. Ed.*, **2011**, 50, 7238–7266.
- [2] G. G. Luo, K. Fang, J. H. Wu, J. Mo, *Chem. Commun.*, **2015**, 51, 12361–12364.
- [3] G. G. Luo, K. Fang, J. H. Wu, J. C. Dai, Q. H. Zhao, *Phys. Chem. Chem. Phys.*, **2014**, 16, 23884–23894.
- [4] A. Xie, X. L. Liu, Y. C. Xiang, G. G. Luo, *J. Alloys Compd.*, **2017**, 717, 226–231.
- [5] N. Kaeffer, M. Chararot-Kerlidou, V. Artero, *Acc. Chem. Res.*, **2015**, 48, 1286–1295.
- [6] Y. Sun, J. P. Bigi, N. A. Piro, M. L. Tang, J. R. Long, C. J. Chang, *J. Am. Chem. Soc.*, **2011**, 133, 9212–9215.
- [7] W. M. Singh, T. Baine, S. Kudo, S. L. Tian, X. A. N. Ma, H. Y. Zhou, N. J. DeYonker, T. C. Pham, J. C. Bollinger, D. L. Baker, B. Yan, C. E. Webster, X. Zhao, *Angew. Chem. Int. Ed.*, **2012**, 51, 5941–5944.
- [8] R. S. Khnayzer, V. S. Thoi, M. Nippe, A. E. King, J. W. Jurss, K. A. El Roz, J. R. Long, C. J. Chang, F. N. Castellano, *Energy Environ. Sci.*, **2014**, 7, 1477–1488.
- [9] A. K. Singh, S. Sharma, *Coord. Chem. Rev.*, **2000**, 209, 49–98.
- [10] M. M. Aly, Y. A. Mohamed, K. A. M. El-Bayouki, W. M. Basyouni, S. Y. Abbas, *Eur. J. Med. Chem.*, **2010**, 45, 3365–3373.
- [11] D. Banerjee, P. Yogeeswari, P. Bhat, A. Thomas, M. Srividya, D. Sriram, *Eur. J. Med. Chem.*, **2011**, 46, 106–121.
- [12] J. Haribabu, K. Jeyalakshmi, Y. Arun, N. S. P. Bhuvanesh, P. T. Perumal, R. Karvembu, *J. Biol. Inorg. Chem.*, **2017**, 22, 461–480.
- [13] J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents*, 4th ed., New York: Wiley-Interscience, **1986**.
- [14] K. K. W. Sun, R. A. Haines, *Can. J. Chem.*, **1970**, 48, 2327–2333.
- [15] G. N. Schrauzer, *Inorg. Synth.*, **1968**, 11, 61–70.
- [16] J. I. Goldsmith, W. R. Hudson, M. S. Lowry, T. H. Anderson, S. Bernhard, *J. Am. Chem. Soc.*, **2005**, 127, 7502–7510.
- [17] G. G. Luo, Y. H. Wang, J. H. Wang, J. H. Wu, R. B. Wu, *Chem. Commun.*, **2017**, 53, 7007–7010.
- [18] G. G. Luo, X. C. Li, J. H. Wang, *ChemistrySelect*, **2016**, 1, 425–429.
- [19] R. C. Clark, J. S. Reid, *Acta Crystallogr. A*, **1995**, A51, 887–897.
- [20] G. M. Sheldrick, *SHELXS-97: Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.
- [21] G. M. Sheldrick, *SHELXL-97: Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.
- [22] A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M.

Graphical Abstract

Chin. J. Catal., 2018, 39: 517–526 doi: 10.1016/S1872-2067(17)62940-1

New tricks for an old dog: Visible light-driven hydrogen production from water catalyzed by *fac*- and *mer*- geometrical isomers of tris(thiosemicarbazide) cobalt(III)Yang Zhao[†], Yongheng Wang[†], Qiaoyu Wu, Jinqing Lin, Shenghui Wu, Wenjuan Hou, Ruibo Wu, Genggeng Luo^{*}
Huaqiao University; Sun Yat-sen University

A pair of water-soluble octahedral complexes of cobalt(III) thiosemicarbazide with geometric isomers show efficient activity of photo-catalyzing H_2 production. This is the first example of investigating the effect on catalyzing H_2 production using geometric isomers.

- Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010. *Gaussian09 Rev. B.01*, Gaussian, Inc., Wallingford CT, **2010**.
- [23] A. D. Becke, *J. Chem. Phys.*, **1993**, 98, 5648–5652.
- [24] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, 37, 785–789.
- [25] A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.*, **1994**, 100, 5829–5835.
- [26] E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.*, **1997**, 107, 3032–3041.
- [27] L. Goerigk, S. Grimme, *J. Chem. Phys.*, **2010**, 132, 184103/1–184103/9.
- [28] A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn., **1984**.
- [29] X. Jing, C. He, Y. Yang, C. Y. Duan, *J. Am. Chem. Soc.*, **2015**, 137, 3967–3974.
- [30] C. Baffert, V. Artero, M. Fontecave, *Inorg. Chem.*, **2007**, 46, 1817–1824.
- [31] B. G. Cox, *Org. Process Res. Dev.*, **2015**, 19, 1800–1808.
- [32] A. M. Appel, M. L. Helm, *ACS Catal.*, **2014**, 4, 630–633.
- [33] Z. J. Han, W. R. McNamara, M. S. Eum, P. L. Holland, R. Eisenberg, *Angew. Chem. Int. Ed.*, **2012**, 51, 1667–1670.
- [34] P. Du, R. Eisenberg, *Energy Environ. Sci.*, **2012**, 5, 6012–6021.
- [35] T. M. McCormick, Z. Han, D. J. Weinberg, W. W. Brennessel, P. L. Holland, R. Eisenberg, *Inorg. Chem.*, **2011**, 50, 10660–10666.
- [36] J. F. Dong, M. Wang, P. Zhang, S. Q. Yang, J. Y. Liu, X. Q. Li, L. C. Sun, *J. Phys. Chem. C*, **2011**, 115, 15089–15096.
- [37] G. G. Luo, H. Lu, X. L. Zhang, J. C. Dai, J. H. Wu and J. J. Wu, *Phys. Chem. Chem. Phys.*, **2015**, 17, 9716–9729.
- [38] M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, D. L. DuBois, *Science*, **2011**, 333, 863–866.

面式、经式异构体的钴-氨基硫脲配合物作为催化剂应用于可见光催化分解水产氢赵阳^{a,†}, 王永恒^{c,†}, 吴莽宇^a, 林金清^a, 吴升晖^a, 侯文娟^b, 巫瑞波^c, 骆耿耿^{a,*}^a华侨大学材料科学与工程学院, 福建厦门361021^b华侨大学分析测试中心, 福建厦门361021^c中山大学药学院, 广东广州510006

摘要: 近年来, 作为替代贵金属铂催化剂的铁、钴和镍等非贵金属配合物分子催化剂, 由于合成容易、结构调控方便以及具有良好的催化活性等特点, 成为均相光催化分解水产氢领域的研究热点. 其中, 钴配合物具有结构简单、成本低廉、容

易合成以及具有理想的氧化还原电位等优势,更是光催化分解水产氢领域的优先研究对象。由于稳定性及溶解度的问题,在已报道的研究工作中,大部分钴配合物测试环境均在有机溶剂或有机溶剂/水混合溶剂中。因此,寻找水溶性良好的钴配合物催化剂成为了目前的均相光催化分解水产氢领域的研究焦点之一。在此之前,氨基硫脲配合物已经广泛用于生物和制药等研究,例如:抗氧化、抗菌以及抗病毒等领域。而在人工光合产氢领域采用氨基硫脲配合物作为催化剂的例子则比较罕见。在该项研究中,我们报道了一对水溶性较好($> 40 \text{ mg mL}^{-1}$, 20°C)且具有几何异构特征的八面体钴-氨基硫脲配合物作为光、电催化质子还原产氢的分子催化剂。这对几何异构体分别为:面式异构体 $[\text{Co}(\text{Htsc})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ (**C1**, Htsc = 氨基硫脲配体)和经式异构体 $[\text{Co}(\text{Htsc})_3]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ (**C2**)。我们将几何异构体**C1**和**C2**作为水还原分子催化剂,与有机光敏剂荧光素一起构筑了不含贵金属成分的光催化分解水产氢体系。在三乙胺作为牺牲剂及纯水环境中,体系展现出了良好的光催化制氢性能。可见光照15 h后,体系产氢相对于催化剂的TON接近900。对比实验结果表明,具有这对几何异构的**C1**和**C2**具有相似的光催化产氢性能,暗示其催化机理的相似性。汞中毒实验结果表明,光催化分解水产氢过程中并没有钴纳米胶体形成,可以确定这是一个均相光催化分解水产氢体系。在纯水环境下,我们将**C1**和**C2**与传统的钴配合物(钴酞配合物: $[\text{Co}(\text{dmgH})_2\text{pyCl}]$ (dmgH = 丁二酮肟, py = 吡啶); 联吡啶钴配合物: $[\text{Co}(\text{bpy})_3\text{Cl}_2]$ (bpy = 2,2'-联吡啶))的催化活性进行对比。结果表明,催化剂**C1**和**C2**展现出了较强的光催化产氢活性。此外,电催化实验表明,在乙腈中且乙酸作为质子源的情况下,**C1**和**C2**具有相同的电催化活性,过电位接近640毫伏,催化转化频率(TOF)为每秒210。同时,在 $\text{pH} = 7$ 的磷酸盐缓冲溶液中,**C1**和**C2**也同样表现出对水分子的电催化产氢性能,过电势为560毫伏。

这是当前第一例具有几何异构体的分子催化剂对光、电催化产氢体系影响的工作。

关键词: 氨基硫脲; 钴配合物; 分子催化; 几何异构体; 光催化

收稿日期: 2017-09-28. 接受日期: 2017-10-19. 出版日期: 2018-03-05.

*通讯联系人. 电话/传真: (0592)6162225; 电子信箱: gglo@hqu.edu.cn

[†]共同第一作者.

基金来源: 国家自然科学基金(21641011, 21773313); 福建省自然科学基金(2015J01053, 2016J01060); 福建省高校新世纪优秀人才项目; 华侨大学研究生科研创新能力培育计划资助项目。

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

《催化学报》进入中科院 JCR 期刊分区工程技术大类2区

近日,中国科学院文献情报中心发布 2016 年版中科院JCR期刊分区, *Chinese Journal of Catalysis* (《催化学报》)在工程技术类 1845 种期刊中排名第 354位,居工程技术大类2区。中科院 JCR 期刊分区按照学术影响力作为划分方式,将每个学科的所有期刊按照学术影响力(3年平均JCR影响因子(IF))由高到低降序排列,依次划分为4个区,使每个分区期刊影响力总和相同。由于学科内期刊的3年IF的偏态分布,这使得1区期刊数量极少。为保证期刊1区期刊数量,1区期刊取整个学科数量总数的5%,即3年平均IF最高的5%的期刊为1区期刊。2–4区期刊使用3年平均IF总和相同的方式划分(分区方法详见<https://www.fenqubiao.com>)。

近年,《催化学报》的学术质量及影响力不断提升,这是中国化学会催化委员会委员、《催化学报》编委、审稿专家、作者和读者长期不懈努力和共同支持的结果。衷心感谢各位老师、投稿原创性高质量稿件、学术质量把关以及组约优秀稿件、组办高水平专刊等方面所给予的持续的、巨大的支持!

(《催化学报》编辑部)