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Synthesis, characterization, magnetic anisotropy and catalytic behaviors of a cobalt complex of S,S'-bis(2-pyridylmethyl)-1,2-thiobenzene

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Abstract

S,S'-bis(2-pyridylmethyl)-1,2-thiobenzene (bptb) reacts with CoBr₂ to form a cobalt complex, [(bptb)CoBr₂]. Its structure has been determined by X-ray crystallography. Studies show that [(bptb)CoBr₂] can act as both a single-molecule magnet and a molecular catalyst. As a single-molecule magnet, magnetic anisotropy for [(bptb)CoBr₂] is revealed via the analyses of the direct-current magnetic data with a zero-field splitting (ZFS) parameter (D) of 69.88 cm⁻¹. Catalytic activities for hydrogen evolution from water are found. As an electrocatalyst, [(bptb)CoBr₂] can provide 870 moles of hydrogen per mole of catalyst per hour (mol H₂/mol catalyst/h) at an overpotential (OP) of 837.6 mV. As a photocatalyst, mixing with CdS nanorods (CdS NRs) as a photosensitizer, and ascorbic acid (H₂A) as a sacrificial electron donor, [(bptb)CoBr₂] can afford 19290 mol H₂ per mole of catalyst during 80 h irradiation. The highest apparent quantum yield (AQY) is ~24.30%.

Keywords: Cobalt complex; crystal structure; magnetic anisotropy; electro and photocatalytic activities for hydrogen evolution.

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1. Introduction

Considering that hydrogenase enzymes based on nickel or iron complexes can efficiently catalyze both the production and the oxidation of dihydrogen [1], researchers still focus their interests on the designs and studies of metal complexes, which have catalytic activities for hydrogen generation [2-5]. To a typical FeFe-hydrogenases supported by dithiolate ligands [2,6,7], the amine [8,9] cofactor is suggested to facilitate the cleavage/formation of the hydrogen-hydrogen bond and the transfer of protons to and from the distal metal center [9]. To mimic this natural performance, an approach is the design and preparation of unique ligands that impart novel chemistry when incorporated into the metal coordination sphere. These considerations have led to the development of catalysts based on complexes with varying ligands, and several complexes [10-13] have been developed as electrocatalysts for hydrogen production. Encouraged by that transition metal complexes supported by S atom ligands can serve as catalysts for photochemical driven hydrogen evolution [14,15], a new cobalt-based catalyst, [(bptb)CoBr₂] has been designed and synthesized in our lab. This cobalt complex acts as an efficient catalyst for H₂ production both in an electrocatalytic system and a photocatalytic system combining CdS NRs as a photosensitizer, and ascorbic acid (H₂A) as a sacrificial electron donor. Additionally, this mononuclear cobalt complex displays magnetic anisotropies. As new results, we present the synthesis, characterization, magnetic properties and catalytic behavior of the cobalt complex, [(bptb)CoBr₂].

2. Experimental Section

Physical measurements, crystal structure determination, and equations for the calculations of turnover frequency (TOF) and turnover number (TON) were showed in "Supplementary Materials". CdS nanorods (CdS NRs) were prepared by using the reported method [16].

2.1 Preparation of S,S'-bis(2-pyridylmethyl)-1,2-thiobenzene (bptb)

Based on the reported procedure [17], bptb was prepared, with the characterization via NMR measurements and analysis shown in Figs. S1 and S2. ¹H NMR (600 MHz, Chloroform-*d*): δ 8.51 (d, 2H), 7.54 (td, 2H), 7.27 (d, 2H), 7.23 – 7.20 (m, 2H), 7.11 (dd, 2H), 7.03 (dd, 2H), 4.25 (s, 4H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 157.28, 149.20, 136.62, 136.49, 129.99, 126.84, 123.16, 122.09, 39.76.

2.2 Synthesis of the cobalt complex, [(bptb)CoBr₂]

Addition of a 10 mL methanol solution of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (0.16 g, 0.5 mmol) to a solution of S,S'-bis(2-pyridylmethyl)-1,2-thiobenzene (bptb) (0.16 g, 0.5 mmol) in 10 mL ethanol, a red solution was formed. Under room temperature, slow evaporation afforded pink needle-shaped crystals (0.21 g, 77%). Elemental measurements and analysis, calcd for C₁₈H₁₆Br₂CoN₂S₂: C: 46.67; H: 3.38; N: 6.05. Found: C: 46.51, H: 3.40, N: 6.09.

3. Results and discussion

3.1 General characterizations for CdS NRs and [(bptb)CoBr₂]

As shown in Scheme 1, the cobalt complex, [(bptb)CoBr₂] was obtained by the reaction of CoBr₂ and bptb. The result is consistent with the following structural and ESI-MS analysis. According to the reported method [16], CdS nanorods (CdS NRs) was prepared, with the characterizations by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) shown in Fig. S3.



Scheme 1 Synthesis of the ligand, bptb and [(bptb)CoBr₂].

To determine the structure of [(bptb)CoBr₂], X-ray crystallography was employed, giving the results listed in Tables S1-S2 and Fig. 1. In solid, the cobalt atom is coordinated by two nitrogen atoms, two sulfur atoms from bptb, and two Br atoms. Two Br⁻ ions are positioned in *cis* type. The bond lengths of Co–N are 2.150(7) and 2.151(8) Å, and the Co-S distances are 2.494(2) and 2.501(2) Å, respectively. The distances between Co and Br are 2.5101(12) and 2.5438(12) Å, respectively. Moreover, using powder X-ray diffraction to check the purity of [(bptb)CoBr₂] sample, with the results shown in Fig. S4. The peak positions of the simulated patterns were consistent with the experimental ones, indicating the [(bptb)CoBr₂] sample is in good purity.

To characterize the structure of $[(bptb)CoBr_2]$ in solution, ESI-MS spectrum of $[(bptb)CoBr_2]$ was measured in CH₃CN, with the result shown in Fig. S5. ESI-MS spectrum of $[(bptb)CoBr_2]$ showed one peak at a mass-to-charge ratio (*m/z*) of 463.9224 in CH₃CN, which is assigned to the species of $[(bptb)CoBr]^+$. The dissociation of a Br ion leaves an empty position on the cobalt center, amenable to binding to H⁺ or H₂O and hydrogen production. Such results prompted possible usage of this cobalt complex as a catalyst for hydrogen generation.

3.2 Magnetic behavior of the cobalt complex, [(bptb)CoBr₂]

Magnetic behaviors of [(bptb)CoBr₂] were investigated in the temperature range 2-300 K, with the results shown in Fig. 2. The $\chi_M T$ value was 2.91 cm³Kmol⁻¹ at 300 K, much higher than the spin-only value of 1.875 cm³Kmol⁻¹ for a mononuclear high-spin Co^{II} (S = 3/2, g = 2.0). This value is in the reported range of 2.1–3.4 cm³Kmol⁻¹ for the anisotropic high-spin Co^{II} center [18], attributed to the orbital contribution [19]. Moreover, the $\chi_M T$ values slowed down with decreasing temperature from 300 K to 130 K, then decreased quickly below 130 K, and the minimum 1.82 cm³Kmol⁻¹ was reached at 2 K. The downturn of the $\chi_M T$ value at low

temperatures can be attributed to the inherent magnetic anisotropy of the Co^{II} ion.

To further understand the magnetic anisotropy, the measurements for variable-field magnetization of [(bptb)CoBr₂] were carried out in the range from 0 to 7 T at temperatures of 2.0, 3.0 and 5.0, respectively. As shown in Fig. 2-inset, the values of magnetization of [(bptb)CoBr₂] at 7 T were lower than the theoretical saturation value ($3 N\mu B$), suggesting the presence of the magnetic anisotropy.

To further quantify the anisotropy of [(bptb)CoBr₂], the Hamiltonian (1) and *PHI* program [20] were employed to fit the experimental data, with the results plotted in Fig. 2.

$$H=D(\widehat{S}_{z}^{2}-S(S+1)/3)+E(\widehat{S}_{x}^{2}-\widehat{S}_{y}^{2})+\mu_{B}g\widehat{S}\cdot H$$
(1)

Where D, E, S, H and μ_B represent the axial zero field splitting (ZFS) parameter, the rhombic or transverse ZFS parameter, the spin projection, magnetic field vector, and the Bohr magneton, respectively.

According to the data listed in Fig. 2, D= 69.88 cm⁻¹, E= 8.19, $g_x=g_y=2.62$, $g_z=2.39$. The similar magnetic properties were also observed in the reported cobalt complexes [21,22].

3.3 Electrocatalytic behavior of [(bptb)CoBr₂]

Encouraged by that cobalt complexes can serve as electrocatalysts for hydrogen generation via an unstable hydride intermediate [5,23], we first investigated electrochemical behaviors of [(bptb)CoBr₂]. With 0.10 M [(n-Bu)₄N]ClO₄ as a supporting electrolyte, cyclic voltammograms (CVs) of CoBr₂, the ligand (bptb) and

the cobalt complex, [(bptb)CoBr₂] were measured in CH₃CN, respectively, giving the results shown in Fig. S6 and Fig. 3. As shown in Fig. 3a, [(bptb)CoBr₂] showed one reduction peak at -1.26 versus Ag/AgNO₃, which can be assigned to the Co^{II/I} couple.

As shown in Fig. 3b, voltammetric currents emerging at -1.26 V versus Ag/AgNO₃ exhibited a systematic increase with addition of varied content of acetic acid from 0.0 to 4.69 mM. This rise in current can be attributed to the catalytic evolution of dihydrogen from acetic acid [5,23]. Additionally, upon addition of 3.35 mM acetic acid, a new reduction wave was observed near -1.61 V versus Ag/AgNO₃. Further addition of acetic acid led to an increase in the current, consistent with a catalytic process [24].

Together literature precedents [25-27], with above observations and analysis, a catalytic cycle for H₂ evolution from acid mediated by [(bptb)CoBr₂] was depicted in Scheme 2. First, a cobalt(I) species, [(bptb)Co^I-Br] was formed via an one-electron reduction of [(bptb)Co^I-Br]⁺. Upon addition of hydrogen proton (H⁺) led a Co^{III}-H species, [H-Co^{III}(bptb)-Br]⁺ to be formed. Next, one-electron reduction of the Co^{III}-H species resulted in the formation of a Co^{II}-H species, [H-Co^{II}(bptb)-Br]. Further addition of hydrogen proton to [H-Co^{II}(bptb)-Br] afforded a H₂ molecule.



Scheme 2 Possible electrocatalytic mechanism for proton reduction to hydrogen by [(bptb)CoBr₂].

Next, the electrocatalytic activity of [(bptb)CoBr₂] was investigated via bulk electrolysis, with the results listed in Fig. S7. Under -1.45 V versus Ag/AgNO₃, the addition of [(bptb)CoBr₂] led to the presence of 139 mC charge used 2 min of electrolysis, with accompanying generation of H₂, which was confirmed by gas chromatography. However, only a charge of 8 mC was afforded without [(bptb)CoBr₂] (Fig. S7b), indicating that [(bptb)CoBr₂] can serve as an electrocatalyst for hydrogen generation. The electrocatalytic efficiency (turnover frequency (TOF)) of [(bptb)CoBr₂] also can be estimated by equation 2 [28], and equation 3 [29] was used to calculate overpotential (OP), with the results listed in Fig. S8. For instance, at an OP of 941.6 mV, [(bptb)CoBr₂] can afford 103 moles of hydrogen per mole of catalyst per hour (mol H_2 /mol catalyst/h).

$$TOF = \Delta C / (F^* n_1 n_2 t)$$
 (2)

Overpotential = Applied potential $-E^{\odot}_{HA}$

= Applied potential –
$$(E^{\odot}_{H^+}-(2.303RT/F)pK_{aHA})$$
 (3)

Next, electrocatalytic behavior of [(bptb)CoBr₂] was characterized in aqueous media, with the results shown in Fig. S9. The strength of the reduction of [(bptb)CoBr₂] wave increased with decreasing pH values from 7.0 to 4.5 and the onset of the catalytic wave were shifted to higher potentials, which are attributed to a catalytic process [30].

To further understand the electrocatalytic activity of $[(bptb)CoBr_2]$ in aqueous media, bulk electrolysis was carried out in buffer, with the results plotted in Fig. S10. Under -1.45 V versus Ag/AgCl, only 312 mC of charge was provided from a neutral buffer used 2 min of electrolysis (Fig. S10a). Surprisingly, the introduction of $[(bptb)CoBr_2]$ led to the formation of 1454 mC of charge under the same conditions (Fig. S10b). According to Fig. S11a, 48 mL of H₂ was afforded during 1 h electrolysis, and the Faradaic efficiency was 98% (Fig. S11b). Based on equations (2) and (4) [31], TOFs and OPs were estimated, with the results listed in Fig. S12. For example, at an OP of 837.6 mV, $[(bptb)CoBr_2]$ can electro-catalyze hydrogen evolution with a TOF of 870 mol H₂/mol catalyst/h.

Overpotential = Applied potential- E(pH) = Applied potential- (-0.059pH) (4)

The result that [(bptb)CoBr₂] is responsible indeed for the electrocatalytic hydrogen evolution was also supported by other pieces of evidence: 1) CVs of the free ligand (bptb), acetic acid and CoBr₂ were each measured under identical conditions. From Figs. 3, S6, S13, the catalytic competency achieved with the cobalt complex was not matched by just bptb, acetic acid and CoBr₂. 2) Controlled-potential electrolysis (CPE) of an aqueous buffer solution, bptb, CoBr₂ and [(bptb)CoBr₂] were each measured under the same conditions. According to Fig. S14, a neutral buffer (pH 7.0) only afforded 313 of charge during 2 min of electrolysis under -1.45 V versus Ag/AgCl. The use of solely bptb or CoBr₂ as a catalyst afforded hydrogen with 336 mC and 386 mC of charge, respectively. However, when [(bptb)CoBr₂] was used as a catalyst, bulk electrolysis provided H₂ with 1347 mC of charge. Thus, the formation of [(bptb)CoBr₂] is essential for catalytic activity in above catalytic system. This can be attributed to the ligand, bptb, that coordinates to the cobalt center and can stabilize the low oxidation state of cobalt (such as Co⁺) well.

Under the same conditions, the catalytic activity of $[(bptb)CoBr_2]$ (870 mol H₂/mol catalyst/h at an OP of 837.6 mV) is higher than some reported molecular catalysts based on cobalt complexes for electrocatalytic H₂ production from a neutral water. For example, a cobalt complex with N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene (bpbH₂), Co(bpbH₂)Cl₂ (810 mol

 H_2 /mol catalyst/h at an OP of 837.6 mV) [23] (Table 1) and a cobalt complex, [CoA₂(H₂O)₂] (A: picolinic acid ion) that can afford 722 mol of hydrogen per mole of catalyst per hour at an OP of 837.6 mV [32]. Under -1.45 V versus Ag/AgCl, the electrocatalytic activity of [(bptb)CoBr₂] is lower than that of [(phen)₂Co(CN)₂]·ClO₄ (phen: 1,10-phenanthroline; TOF: 1113 mol H₂/mol catalyst/h) [5] (Table 1). It is not easy to make a comparison for the catalytic activity among different electrocatalytic systems in term of TOF values, because of possible differences in the experimental conditions conducted and calculated methods. The catalytic efficiencies of some reported catalysts based on cobalt complexes [33-35] were listed in Table 1.

electrocatalytic performance of [(bptb)CoBr₂] To investigate the in heterogeneous medium, electrochemical measurements were carried out by using a modified electrode with [(bptb)CoBr₂] as the working electrode. As shown in Fig. S15, in 0.5 M Na₂SO₄ aqueous solution (pH 7.0), [(bptb)CoBr₂] could electrocatalyze hydrogen evolution with a current density of -3.10 at an overpotential of 877 mV. Similar electrocatalytic behaviors were found in the reported samples [36,37]. A modified gold electrode with [Co-P] (cobalt^{II}-5,10,15,20-tetrakis[3-(p-acetylthiopropoxy)phenyl]porphyrin) could afford hydrogen with a current density of -1.6 at an overpotential of 700 mV [36]. To a modified glassy carbon with a cobalt-tetraimine complex, at pH 2.0, onset of catalysis occurred at 0.24 V overpotential, and bulk electrolysis at 0.54 V overpotential operated at ~1 mA/cm² with 80 \pm 10% Faradaic efficiency [37].

3.4 Heterogeneous photocatalytic system with $[(bptb)CoBr_2]$ for H_2 generation

Inspired by that transition metal complexes supported by S atom ligands often serve as catalysts for photochemical driven hydrogen evolution [14,15], a photocatalytic system containing ascorbic acid (H₂A) as an electron donor, [(bptb)CoBr₂] as a catalyst and CdS NRs as a photosensitizer was designed. From Figs. S3a, S16 and S17, CdS NRs were dispersed on the surface of [(bptb)CoBr₂] particle.

To get an optimal photocatalytic system for hydrogen production, a series of measurements were carried out. First, impact of pH of media on the photocatalytic activity of H_2 production was investigated, with the results listed in Fig. S18. At pH 4.5, the highest catalytic activity for hydrogen evolution was found with a TON of 3190 mol of H_2 (mol of cat)⁻¹ used 2 h of irradiation.

To investigate the impact of the amount of photosensitizer on the photocatalytic H_2 generation, photocatalytic systems containing 0.10 M ascorbic acid, [(bptb)CoBr₂] (0.010 mM) and a varying content of CdS NRs were designed. As shown in Fig. S19, upon increasing the amount of CdS NRs, the TON increased until a highest value of 3720 mol of H_2 (mol of cat)⁻¹ was obtained at 0.14 mg.mL⁻¹ used 2 h of irradiation. Then, when the amount of CdS NRs was more, the TON decreased (Fig. S19). Next, photocatalytic systems containing CdS NRs (0.14 mg·mL⁻¹), [(bptb)CoBr₂] (0.010 mM) and varying contents of ascorbic acid were assembled to investigate the effect of an amount of ascorbic acid on the catalytic activity, with the results listed in Fig. S20. The TON increased with increasing the amount of ascorbic acid until a highest value

of 6000 mol of H_2 (mol of cat)⁻¹ was got at 0.28 M used 2 h of irradiation. Then, the TON decreased when the amount of ascorbic acid was more.

Based on the above observation and analysis, an optimal three-component system containing 0.14 mg·mL⁻¹ CdS NRs, 0.28 M ascorbic acid and [(bptb)CoBr₂] (0.010 mM) was obtained. As shown in Fig. 4, upon light irradiation, the photocatalytic system afforded H₂ and could work for about 100 h. More details, H₂ evolution started immediately and the rate increased sharply for about 40 h. Then the build-up of H₂ slightly increased until H₂ formation ceased after about 100 h. For instance, during 60 h irradiation, the photocatalytic system with [(bptb)CoBr₂] can afford 18350 mol of H₂ (mol of cat)⁻¹.

Remarkably, [(bptb)CoBr₂] exhibits higher efficiency for hydrogen evolution than [(bpte)CoCl₂] (bpte: S,S'-bis(2-pyridylmethyl)-1,2-thioethane; TON: 6740 mol of H₂ (mol of cat)⁻¹) [38], indicating that bptb can constitute the better active catalyst for hydrogen generation than bpte. This result can be attributed to the electronic properties of the ligands (bptb and bpte). The introduction of phenyl makes the electron distribution more uniform in the cobalt complex, letting it easier to form the Co^{III} -H species, further promoting the formation of hydrogen [39-41].

To investigate the apparent quantum yields (AQYs), a photocatalytic system was irradiated under monochromic light with a band-pass filter (λ = 469 nm), giving the results listed in Fig. 5. Based on equation 5 [42], the AQYs of the photocatalytic system for H₂ generation were calculated, with the results shown in Fig. 5. The AQY was ~19.90% used the first 2 h irradiation, and then it increased until 24.30% at 6 h irradiation.

AQY (%) =
$$(2 \cdot \eta_{H2} \cdot N_A \cdot h \cdot c)/(t_{irr} \cdot \lambda \cdot I \cdot A) \cdot 100$$
 (5)

To find factors responsible for the photocatalytic H_2 evolution in the above photocatalytic system, bptb, $CoBr_2$ or [(bptb)CoBr_2] was employed as a catalyst to assembly three component systems with ascorbic acid and CdS NRs, respectively. As shown in Fig. S21, as a catalyst, bptb or $CoBr_2$ only gave 5.9 and 19 µmol H_2 , respectively. However, when [(bptb)CoBr_2] was used as a catalyst, the photocatalytic system could afford 321 µmol H_2 . Thus, the formation of [(bptb)CoBr_2] is essential for catalytic activity in above photocatalytic system.

3.5 Study for photocatalytic mechanism

In order to find the photocatalytic procedure, several measurements and analysis were carried out. First, we measured electronic spectra of [(bptb)CoBr₂] and the related components, with the results shown in Fig. S22. Based on CdS NRs, the introduction of [(bptb)CoBr₂] into CdS NRs led to red shift of the absorption onset and reduction of Eg of CdS NRs, indicating that the range and ability of visible light absorption of CdS NRs are improved.

Next, measurements and analysis of photoluminescence (PL) spectra of [(bptb)CoBr₂] and the related components were carried out, giving the results shown in Fig. S23. With the excitation of 450 nm, CdS NRs exhibited two emission peaks at 559 and 681 nm, respectively. However, with the immobilization of [(bptb)CoBr₂], the peak intensity of CdS NRs at 681 nm decreased, showing a lower possibility of

Journal Pre-proofs

electron-hole pair recombination due to the fast electron transfer from CdS NRs to [(bptb)CoBr₂] [43]. Therefore, as an electron acceptor loaded on the CdS NRs surfaces, [(bptb)CoBr₂] can trap efficiently photo-generated electrons and promoted their combination with H⁺ to form H₂. Based on the above investigations and analysis, it is reasonable to speculate that a cobalt(I) species is generated via the reduction of [(bptb)CoBr₂], which was found in the reported samples [44]. The results are also consistent with the following orbital calculation.

To carry out orbital calculation of [(bptb)CoBr₂], "Gaussian B3LYP/6-31G" was employed. According to Fig. 6, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of [(bptb)CoBr₂] were -4.492 and -1.662 eV, respectively. Considering that E_{LUMO} (-1.662 eV) of [(bptb)CoBr₂] is higher than the conducting band of CdS (-3.8 eV) [45], the photogenerated electrons transfer from CdS to [(bptb)CoBr₂] is energetically favorable.

Next, electrochemical impedance spectra of [(bptb)CoBr₂] and the related components were measured, with the results shown in Fig. 7. Compared with CdS NRs, the mixture of CdS NRs and [(bptb)CoBr₂] showed much smaller arc radius, indicating that the introduction of [(bptb)CoBr₂] makes interfacial charge transfer faster, and separation efficiency of photogenerated charge carriers much higher [8,46].

Combined these observation, analysis and literature precedents [47-49], a possible mechanism for the photocatalytic H_2 production was schemed. As outlined in Scheme 3, the conduction band (CB) of CdS NRs provided electrons via irradiation;

then the introduction of the photoexcited electron into $[(bptb)CoBr_2]$ led to the formation of a reduced cobalt(I) species, a high reactive intermediate. The accumulation of the Co(I) species will undergo oxidative addition of a proton to afford the Co^{III} hydride species. Further introduction of hydrogen proton to the Co^{III}-H species provided H₂ and regenerated the starting cobalt complex.

$$CdS \longrightarrow h^{+} + e^{-}$$

$$[(bptb)Co^{II}-Br]^{+} + e^{-} \longrightarrow [(bptb)Co^{I}-Br]$$

$$[(bptb)Co^{I}-Br] + H_{3}O^{+} \longrightarrow [(bptb)BrCo^{III}-H]^{+} + H_{2}O$$

$$h^{+} \longrightarrow [(bptb)BrCo^{III}-H]^{+} + e^{-} \longrightarrow [(bptb)BrCo^{II}-H]$$

$$[(bptb)BrCo^{II}-H] + H_{3}O^{+} \longrightarrow H_{2} + [(bptb)BrCo^{II}]^{+} + H_{2}O$$

Scheme 3 Possible mechanism for H₂ production by the photocatalytic system with [(bptb)CoBr₂].

4. Conclusions

This paper presents the synthesis and characterization of a new cobalt(II) complex, [(bptb)CoBr₂], coming from the reaction of bptb and cobalt salt. As a single-molecule magnet, this cobalt complex exhibits magnetic anisotropy with a zero-field splitting (ZFS) parameter (D) of 69.88 cm⁻¹. As a molecular catalyst, [(bptb)CoBr₂] shows catalytic activity for both electrochemical and photochemical driven hydrogen evolution from water. Mixing with CdS NRs and ascorbic acid (H₂A), [(bptb)CoBr₂] can photocatalyze hydrogen evolution under blue light and can work for about 100 h.

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			TOF	TON	
Catalysts	Electrolyte solution	Applied potential	mol H ₂ /mol	mol H ₂ /mol	Ref
			catalyst/h	catalyst	
[(bptb)CoBr ₂]	0.25 M phosphate buffer	-1.45 V vs Ag/AgCl	870	/	This work
	solution, pH 7.0				
[(phen) ₂ Co(CN) ₂]·ClO ₄	0.25 M phosphate buffer solution,	-1.45 V vs Ag/AgCl	1113	/	[5]
	рН 7.0				
[Co(bpbH ₂)Cl ₂]	0.25 M phosphate buffer solution,	-1.45 V vs Ag/AgCl	810		[23]
	рН 7.0				
[(PY5Me ₂)Co(OH ₂)](CF ₃ SO ₃) ₂		-1.30 V vs SHE	917	5.5×10 ⁴	[33]
	2.0 M phosphate buffer solution,				
	рН 7.0				
cobalt(II) porphyrins	A solution of 160 mM	-1.6 V vs NHE	9.12	104	[34]
with -SO ₃ H	AcOH in DMSO				
cobalt(II) porphyrins	A solution of 160 mM	-1.6 V vs NHE	0.23	1.9	[34]
with -COOMe	AcOH in DMSO				
cobalt(II) porphyrins	A solution of 160 mM	-1.6 V vs NHE	4.54	51.8	[34]
with -COOH	AcOH in DMSO				
cobalt(II) porphyrins	A solution of 160 mM	-1.6 V vs NHE	0.56	6.4	[34]
with -H	AcOH in DMSO				
cobalt(II) porphyrins	A solution of 160 mM	-1.6 V vs NHE	4.04	46	[34]
with -COONH ₂	AcOH in DMSO				
cobalt(II) porphyrins	A solution of 160 mM	-1.6 V vs NHE	0.31	1.5	[34]
with -OH	AcOH in DMSO				
[Co(bpyPY2Me)(CH ₃ CN)(CF ₃	0.3 M ascorbate, pH 7.0	-1.20 V vs SHE	/	40	[35]
SO ₃)](CF ₃ SO ₃)					

Table 1. Electrocatalytic activities of some cobalt-based catalysts for H₂ generation

PY5Me₂: 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine; bpyPY2Me: polypyridyl ligand.

Statements

I am Shu-Zhong Zhan, a corresponding author, from South China University of Technology. My work focuses on the design and studies of new catalysts for hydrogen generation. Now I'd like to report some new results to readers via *Inorg*.

Chim. Acta.

Shu-Zhong Zhan: Writing- reviewing and editing of the manuscript.

Wei-Xia Liu: Synthesis and characterization of the cobalt complex, [(bptb)CoBr₂].

Zhen-Lang Xie: Investigation for catalytic activities of [(bptb)CoBr₂]; revision of the

manuscript.

Jun-Zheng Zhan: Synthesis and characterization of the ligand, bptb.

Song-Ping Wu: Design of this subject.

Statements

I am Shu-Zhong Zhan, a corresponding author, from South China University of Technology. My work focuses on the design and studies of new catalysts for hydrogen generation.

No conflict of interest.



Fig. 1. ORTEP drawing of the $[(bptb)CoBr_2]$ with thermal ellipsoids on the 50% probability level (hydrogen atoms are not shown) (up). Two-dimensional layer of compound $[(bptb)CoBr_2]$ along the ab plane (down).



Fig. 2. Temperature dependence of the $\chi_M T$ product for [(bptb)CoBr₂] under temperature range of 2-300 K in the field of 1 kOe. The inset shows the M vs. B/T plots in the temperature range 2.0-5.0 K. The solid lines are the best-fit curves using the *PHI* program.



Fig. 3. (a) Cyclic voltammogram (CV) of $[(bptb)CoBr_2]$ (1.59 mM) in 0.10 M of $[n-Bu_4N]ClO_4$ CH₃CN solution at a glassy carbon electrode and a scan rate of 100 mV·s⁻¹. (b) CVs of a solution of $[(bptb)CoBr_2]$ (1.59 mM) with varying amounts of acetic acid. Conditions: 0.10 M $[n-Bu_4N]ClO_4$ as supporting electrolyte, scan rate: 100 mV·s⁻¹, glassy carbon working electrode (1 mm diameter), Pt counter electrode, Ag/AgNO₃ reference electrode.



Fig. 4. Hydrogen evolution kinetics obtained upon continuous visible irradiation (λ = 469 nm) of a pH 4.5 buffer solution containing 0.14 mg·mL⁻¹ CdS NRs, 0.28 M ascorbic acid, and [(bptb)CoBr₂] (0.01 mM).



Fig. 5. Photocatalytic H₂ production of [(bptb)CoBr₂] under visible light (λ = 469 nm) and an apparent quantum yield (AQY) of [(bptb)CoBr₂] under monochromatic light (λ = 469 nm). The reaction system contained 0.14 mg mL⁻¹ CdS NRs, 0.010 mM [(bptb)CoBr₂], 0.28 M ascorbic acid (pH 4.5). 19.9, 19.9, 24.3, 23.0, 22.7



Fig. 6. Calculated molecular orbital energy levels of [(bptb)CoBr₂] with the molecular orbital maps of the HOMO and LUMO.



Fig. 7. Electrochemical impedance spectroscopy Nyquist plots of CdS NRs and CdS NRs/[(bptb)CoBr₂] in 0.010 M K₃Fe(CN)₆/K₄Fe(CN)₆ electrolyte in the dark.



[(bptb)CoBr₂], a catalyst for electrochemical and photochemical driven hydrogen evolution with high efficiency.

> The cobalt complex, [(bptb)CoBr₂] is formed by the reaction of CoBr₂ and S,S'-bis(2-pyridylmethyl)-1,2-thiobenzene (bptb).

> [(bptb)CoBr₂] exhibits magnetic anisotropy with a zero-field splitting (ZFS) parameter (D) of 69.88 cm⁻¹.

Together with CdS NRs and ascorbic acid, [(bptb)CoBr₂] can provide 19290 moles
H₂ per mole of catalyst during 80 h irradiation.