# 利用钴–氨基硫脲类配合物作为氧化还原催化剂光分解水制备氢气

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**摘要**：通过将磷配体与氨基硫脲结合进一步增加螯合配体的配位能力,并引入磺酸根增强其水溶性,合成了一个钴配合物 Co-NSP(配体 HNSP：4-[2-(2-二苯基膦-苯烯基)-氨基硫脲腙]苯甲酸),利用其氧化还原特性开展均相体系的光驱动从水中制备氢气的研究。新的 NSP 三齿配体能够稳定低价的金属中心,有助于提升催化剂的催化性能。利用其与荧光素所构筑的光催化体系,在电子牺牲剂三乙胺存在下显示出良好的性能,光照 6 h 其 TON(turnover number)可达 2 000 mol H$_2$ 每摩尔催化剂。为了研究和比较其性能特点,对这一光催化体系的 荧光滴定和氧化还原性能也进行了较细致的研究。

**关键词**：氨基硫脲；金属钴配合物；光催化制备氢气；氮硫磷三齿配体
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# Photocatalytic Hydrogen Production from Water Using Cobalt-Thiosemicarbazone Complex as Redox Catalyst

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**Abstract:** By incorporating a phosphine donor within a thiosemicarbazone moiety to enhance the coordinated ability of the chelators, a cobalt complex Co-NSP　(HNSP: 4-[2-(2-diphenylphosphino-benzylidene) thiosemicarbohydrazone]benzenesulfonate) was obtained as the proton reduction catalyst for light driven H$_2$ evolution in homogeneous environment with fluorescein as the photosensitizer. The presence of NSP tridentate chelator benefits the formation of low oxidized species to increase the catalytic efficiency，and the incorporation of a sulfonate group enhances the water solubility of the catalyst. The amount of H$_2$ generation in 12 h photolysis maximizes in the presence of sacrificial reagent NEt$_3$ at pH value of 11.0. The initial TOF (turnover frequency) is about 200 mol H$_2$ per mole catalyst per hour with the turnover number　(TON) about 2 000 mol H$_2$ per mole of catalyst. CCDC: 1039240.

**Key words**: thiosemicarbazone; cobalt complex; photocatalytic hydrogen ecolution; nsp tridentate chelator

## 0　Introduction

Solar energy conversion of water into the environmentally clean fuel hydrogen offers one of the best long-term solutions for meeting future energy demands[1-3]. Inspired by the highly evolved, finely tuned molecular systems that exquisitely manage photon capture and conversion processes to drive oxygenic water-splitting[4], current solar fuel research involves developing these molecular based systems containing a chromophore or photo-sensitizer for light absorption, a catalyst for H$_2$ generation, an electron

source for proton reduction and a means of electron transfer to the catalyst[5]. Of these promising examples reported in photocatalytic hydrogen evolution using transition metal complexes as catalysts, the highly active systems incorporating environmentally friendly organic dye as the sensitizer are highly desirable[6].

Thiosemicarbazones (TSCs) are strong chelating ligands for the transition metals that have received considerable attention due to the great variety of pharmacological properties depending on the parent aldehyde and ketone as well as metal ions[7]. They are well known for the conventional proton immigration path through the thiolate/thioamide resonance equilibrium[8]. Since the proton transformation in the transition metal catalysts and the interactions between the active hydrogen atom and the metal ions are the important factors influencing the catalytic efficiency of the proton reduction, these metal TSCs complexes might be one of the promising candidates for the proton reduction[9].

Through incorporating a triphosphine moiety as an additional donor to modify the redox potential of the metal centres[10], and a sulfonate group to enhance the water solubility of the complex, we report herein a new thiosemicarbazone complex Co-NSP as a catalyst for the hydrogen production in a homogeneous system with fluorescein(Fl) as the photosensitizer and triethy-lamine (NEt$_3$) as the sacrificial electron donor[11]. We envision that the strong coordinating ability of the NSP chelator would enhance the stability of these metal complexes, the presence of S and P donors benefits the formation of low oxidized species to increase the catalytic efficiency for the H$_2$ evolution[12].

# 1 Experimental

## 1.1 Materials and instruments

All chemicals were of reagent grade obtained from comercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Vario EL III elemental analyzer. $^1$H NMR spectra were measured on a Varian INOVA 400 M spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a HPLC-Q-Tof MS

spectrometer using methanol as mobile phase. UV-Vis spectra were recorded on a HP 8453 spectrometer. Solution fluorescent spectra were measured on JASCO FP-6500. Both excitation and emission slit widths were 2 nm. The solution of these compounds was prepared in 1:1($V/V$) EtOH/water solutions, and the emission of fluorescein ($1.0 \times 10^{-5}$ mol·L$^{-1}$) was excited at 460 nm.

Electrochemical measurements were carried out under nitrogen at room temperature on ZAHNER ENNIUM Electro-chemical Workstation with a conventional three-electrode system with a homemade Ag/AgCl electrode as the reference electrode, a platinum silk with 0.5 mm diameter as the counter electrode, and a glassy carbon electrode as the working electrode. Cyclic voltamograms were obtained with the solution concentrations of $ca$. 1.0 mmol·L$^{-1}$ for the cobalt-based compounds and 0.1 mol·L$^{-1}$ for the supporting electrolyte, ($n$-Bu$_4$N)PF$_6$. The addition of NEt$_3$HCl (0.1 mmol·L$^{-1}$ in CH$_3$CN) was carried out with syringe[13].

Photoinduced hydrogen evolution was performed in a 40 mL flask. The flask was sealed with a septum, pre-degassed by bubbling nitrogen for 15 min under atmospheric pressure at room temperature. In the experiment for various amounts of the catalyst, the 1:1 ($V/V$) EtOH/H$_2$O solution containing Fl and NEt$_3$ was added with a total volume of 5.0 mL. The pH value of the solution was adjusted by adding HCl or NaOH to a suitable value. Then the samples were irradiated by a 500 W Xenon lamp, the reaction temperature was 293 K by using a water filter to absorb heat. The generated photoproduct of H$_2$ was characterized by GC 7890T instrument using a 5 molecular sieve column (0.6 m ×3 mm), thermal conductivity detector, and nitrogen as carrier gas. The amount of H$_2$ generated was determined by the external standard method. Hydrogen in the resulting solution was not measured and the slight effect of the hydrogen gas generated on the pressure of the flask was neglected for calculation of the volume of hydrogen gas.

## 1.2 Synthesis of HNSP

2-(diphenylphosphino)benzaldehyde (0.58 g, 2

mmol) and 4,4-dimethyl thiosemicarbazide (0.27 g, 2 mmol) were mixed in 10 mL methanol. After refluxing for 4 h, the formed yellow solid was isolated, washed with methanol and dried under vacuum. Then the products (2-(diphenylphosphino)benzylidene)-4,4-dimethylthiosemicarbazide (0.24 g, 0.6 mmol) and 4-aminobenzenesulfonic acid (0.10 g, 0.6 mmol)) were refluxed in the dry acetonitrile for 12 h under nitrogen atmosphere. Total yield (based on 4,4-dimethyl thiose-micarbazide): 48%. The white precipitate was colle-cted by vacuum filtration. Anal. Calcd. for $C_{26}H_{22}N_3O_3PS_2$(%): C.60.10; H.4.27; N. 8.09. Found: C, 59.81; H, 4.34; N, 7.98. $^1H$ NMR (CDCl$_3$, 400 MHz):12.01 (s, 1H), 10.03 (s,1H), 8.8 (d,1H), 8.37 (m,1H), 8.0~8.3 (s, 2H), 7.5~7.6(d,2H), 7.1~7.5(m,15H), 6.8(m,1H). API-MS $m/z$: 518([M-H$^+$]).

### 1.3　Synthesis of Co-NSP

The ligand HNSP (0.5 mmol, 0.25 g) and Co(BF$_4$)$_2$·6H$_2$O (0. 25 mmol, 0.094 g) was mixed in 15 mL methanol. The dark brown mixture was filtered. By slow evaporation of the solvent from the filtrate, red-black crystals were obtained. Yield: 75%. Anal. Calcd. for $C_{40}H_{35}N_6P_2S_2Co$ BF$_4$·2H$_2$O(%): C 52.91, H 4.33, N 9.26; Found: C: 53.33; H 3.79; N 9.32. $^1H$ NMR (MeOD, 400 MHz): 8.57 (d, 1H, H$_4$, $J$=7.2 Hz), 7.93 (t, 2H, NH$_2$), 7.64 (s, 1H, H5), 7.44(m, 7H, H, H, H$_1$), 7.39 (t, 1H, H$_3$ $J$=7.2Hz), 7.22 (m, 4H, H, $J$=4.2 Hz ), 6.86(t, 1H, H$_2$, $J$=7.2 Hz); ESI-MS $m/z$: 783.18([M$^+$]).

### 1.4　Crystallography

Intensity data were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda$=0.071 073 nm) using the SMART and SAINT programs [14]. The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares methods with SHELXTL version 5.1[15]. In both of the two structural refinements, except several partly occupied solvent water molecules, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms, whereas no hydrogen atoms corresponding to the solvent molecules were added and refined. One of the benzene rings was disordered into two parts with the S.O.F. (site occupied factor) of each part being fixed as 0.5, and the geometrical constraints of idealized regular polygons were used for the disordered rings, the C-C bond distance of the phenyl ring being 0.139 nm and the diagonal C-C distance of the phenyl ring being 0.278 nm. Six oygen atoms in two sulfonate groups were disordered into two parts with with the S.O.F. of each part being refine by free variable. SQUEEZE program was used with the number of 18.

### 1.5　Crystal data of Co-NSP

CoC$_{57}$H$_{58}$N$_6$O$_{10}$P$_2$S$_4$ $M_r$=1 236.20, Monoclinic, space group $C2/c$, red black block, $a$=5.246 3(4) nm, $b$=1.529 7(1) nm, $c$=4.226 3(5) nm, $\beta$=125.68(1)°, $V$=27.730(4) nm$^3$, $Z$=16, $D_c$=1.184 g·cm$^{-3}$, $\mu$(Mo $K\alpha$)=0.467 mm$^{-1}$, $T$=296(2) K. 24 393 unique reflections ($R_{int}$=0.126 8). Final $R_1$ (with $I>2\sigma(I)$)=0.081 9, $wR_2$ (all data)=0.134 7.

CCDC: 1039240.

## 2　Results and discussion

Ligand HNSP (4-[2-(2-(diphenylphosphino)benzylidene)thiosemicarbohydrazone] benzenesulfonate) is synthesized by refluxing a methanol solution containing 2-(diphenylphosphino)benzaldehyde and thiosemicarbazide for 4 h, and the product is further reacted with 4-aminobenzenesulfonic acid, with a total yield of 48%. Reaction of the ligand HNSP and Co(BF$_4$)$_2$·6H$_2$O in a methanol solution gives Co-NSP in a yield of about 75%. Elemental analyses indicate the pure phase of its bulky sample. Single crystal structural analysis reveals the presence of a +1 charged cation and a BF$_4^-$ within an asymmetric unit. The metal centre is octahedrally coordinated by two NSP chelators from two different ligands. These two ligands bind to a cobalt(II) in a *mer* configuration (with pairs of S atoms and P atoms each bearing a cis relationship, whereas the thiocarbazone N atoms are *trans* to each other) as found in the related cobalt thiocarbazone complexes (Fig.1)[16]. The C-S, C-N and N-N bond distances are all within the normal range of single and double bonds, pointing to the extensive electron delocalization over the ligand skeleton [17].

Accordingly, the proton would easily immigrate on the suitable position during the proton reduction processes, beneficial to the high efficiency of the catalytic system[18].
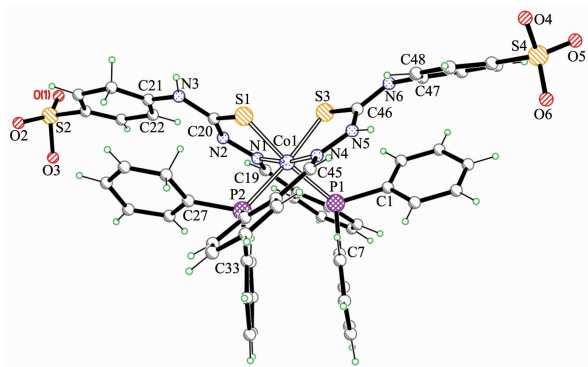


Selected bond distance (nm): Co(1)-S(1) 0.224 9(2), Co(1)-S(3) 0.226 4(2), Co(1)-P(1) 0.230 4(2), Co(1)-P(2) 0.230 7(2), Co(1)-N(1) 0.193 6(5), Co(1)-N(4) 0.192 3(5)

Fig.1　Structures of Co-NSP showing the coordinated geometry of the metal ion, Solvent molecules and the hydrogen atoms are omitted for clarity

Cyclic voltammogram of Co-NSP in an acetontrile solution exhibits one reversible $Co^{II}/Co^{I}$ redox process at −1.03 V (vs Ag/AgCl). Addition of $Et_3NH^+$ with increasing amounts triggers the appearance of a new irreversible cathodic wave near the $Co^{II}/Co^{I}$ response. Increasing the concentration of $Et_3NH^+$ raises the height of the new wave and shifts it to more negative potentials (Fig.2). The wave is potentially attributed to the proton reduction, suggesting that Co-NSP is able to reduce proton with a catalysis process[19]. Co-NSP is also an efficient quencher for the photosensitizer Fl,
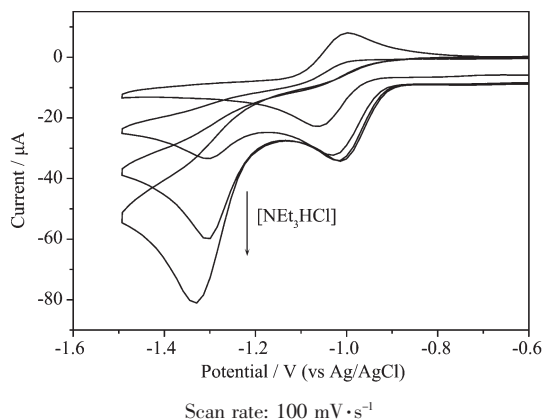


Scan rate: 100 mV·s⁻¹

Fig.2　Cyclic Voltammogram of Co-NSP (1 mmol·L⁻¹) in $CH_3CN$ with 0.1 mol·L⁻¹ TBAPF₆ upon addition different concentrations of Et₃NHCl

the titration curve follows the linear Stern-Volmer behaviour with a quenching constant $k_{SV}$ of $1.09 \times 10^4$ L·mol⁻¹. The quenching behaviour is also considered as a photoinduced electron transfer process from the excited state of Fl* to Co-NSP, providing the possibility for the excited state Fl to activate Co-NSP for the $H_2$ production in solution[20].

Photolysis for solution of F1 (2.0 mmol·L⁻¹) and Co-NSP (10 μmol·L⁻¹) in a solvent mixture containing NEt₃ (10% V/V) in 1:1 H₂O/EtOH at 25C results the direct $H_2$ generation. The volume of $H_2$ was quantified at the end of the photolysis by GC analysis of the headspace gases[21]. The amount of $H_2$ generation in 6 h photolysis maximizes at pH value of 11.0 (Fig.3a). The increase of pH values really decreases the efficiency, due to the lower proton concentration in solution and the fact that the $H_2$ generation becomes more thermodynamically unfavorable with increasing pH value. Whereas at lower pH value, the potential protonation of NEt₃ diminishes its ability to function as an electrondonor, and the NEt₃ decomposition becomes less facile. The light induced $H_2$ evolution depends on the concentration of sacrificial reagent NEt₃, the optimal concentration is 10% with a decrease in activity at both lower and higher concentration(Fig. 3b). The initial TOF (turnover frequency) calculated is about 200 mol $H_2$ per mole catalyst per hour with TON (turnover number) about 2 000 mol $H_2$ per mole of catalyst in the system containing F1 (2.0 mmol·L⁻¹) and Co-NSP (10 μmol·L⁻¹) in a solvent mixture conta-ining NEt₃ (10% V/V) in 1:1 H₂O/EtOH at 25 ℃ at pH=11.0. These values are comparable to the highest value reported in fluorescein/cobalt systems[20].

Control results without either the Co-NSP, the F1 or the NEt₃ show that the absence of any one yields unobservable amount of $H_2$, demonstrating that all of Co-NSP, F1 and NEt₃ are essential for $H_2$ generation. These artificial photosynthetic systems could not work well in the absence of the light. With the fixed concentration of Fl (2 mmol·L⁻¹), the initial rate of $H_2$ generation has a first-order dependence on the concentration of the redox catalyst Co-NSP. At higher concentration of the catalyst, the TON does not scale
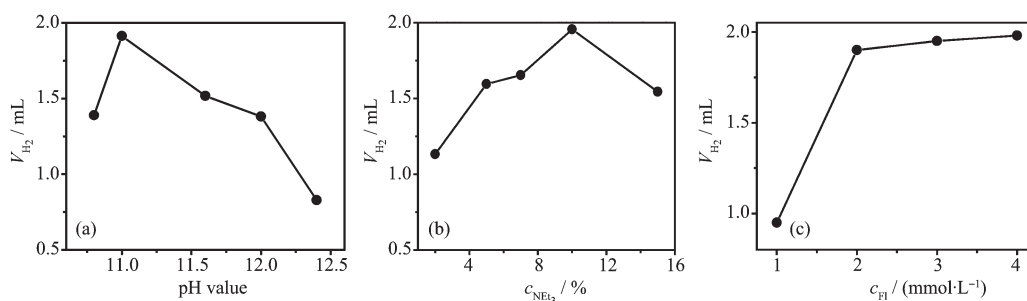
Fig.3　Hydrogen production of the systems containing Co-NSP (10 $\mu mol \cdot L^{-1}$), Fl (2.0 $mmol \cdot L^{-1}$) and $NEt_3$ (10%) with various pH values (a); of the systems containing Co-NSP (10 $\mu mol \cdot L^{-1}$), Fl (2.0 $mmol \cdot L^{-1}$) at pH=11.0 with various concentrations of $NEt_3$ (b) and of the systems containing Co-NSP (10 $\mu mol \cdot L^{-1}$) and $NEt_3$ (10%) at pH=11.0 with various concentrations of Fl (c)

linearly with the catalyst concentration; even through a larger amount of $H_2$ is evolved (Fig.4). When concentration of the redox catalyst Co-NSP (10 $\mu mol \cdot L^{-1}$) is fixed, the TOF and TON reach the platform value when the concentration of Fl varies to 3.0 $mmol \cdot L^{-1}$, further addition of Fl causes a very little TON enhancement corresponding to the catalyst (Fig. 3c). These results suggest both the Co-NSP and Fl are decomposed during the photolysis, similar to these related systems containing Fl and $NEt_3$, similar to these related systems containing photosensitizer Fl and TEA as sacrificial electron donors[22].
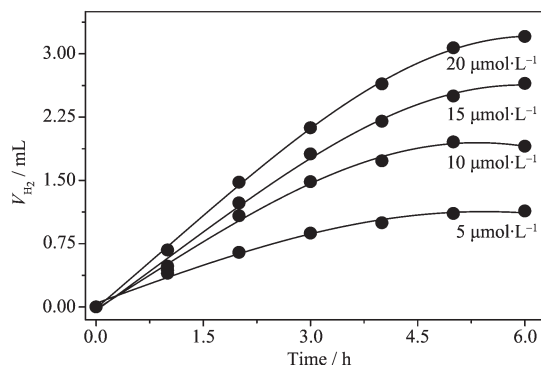


Fig.4　Hydrogen production of the systems containing Fl (2.0 $mmol \cdot L^{-1}$), $NEt_3$ (10%) in 50% $EtOH/H_2O$ at pH=11.0 in 5 mL solution with various concentrations of the redox catalyst Co-NSP

## 3　Conclusions

In summary, by incorporating a phosphine donor within a thiosemicarbazone moiety to enhance the coordinated ability of the chelators, a cobalt complex Co-NSP as proton reduction catalysts for light driven $H_2$ evolution in homogeneous environment with fluorescein as photosensitizer. The presence of new NSP tridentate chelator benefits the formation of low oxidized species to increase the catalytic efficiency, and the incorporation of a sulfonate group enhances the water solubility of the catalyst. With the presence of sacrificial reagent $NEt_3$, the amount of $H_2$ generation in 12 hours photolysis maximizes at pH value of 11.0. The initial TOF is about 200 mol $H_2$ per mole catalyst per hour with the turnover number (TON) about 2 000 mol $H_2$ per mole of catalyst. These values are comparable to the highest value reported in fluorescein/cobalt systems[20].

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