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Electrocatalytic hydrogen evolution upon reduction of pyridoxal semicarbazone and thiosemicarbazone-based Cu(II) complexes

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Abstract: The growing global demand for renewable energy sources has pushed renewable, green energy sources to the forefront, among which the production of hydrogen gas from water occupies a significant place. To realize this goal, researchers across the globe are developing various systems that could swiftly catalyze the hydrogen evolution reaction (HER) in the highest possible yield. In the present work, the electrocatalytic HER performances of pyridoxal semicarbazone- and thiosemicarbazone-based Cu(II) complexes, *i.e.*, ([Cu(PLSC)Cl_2] and [Cu(PLTSC-H)H_2O]Br·H_2O) are reported. It has been unambiguously demonstrated that the complexes exhibit enviable level of HER catalytic activity. The catalytic activity of the complexes was not only the function of central metal but it was also controlled by the nature of the coordinating ligand.

Keywords: renewable energy; cyclic voltammetry; proton-coupled electron transfer.

INTRODUCTION

Molecular hydrogen is considered to be one of the best alternatives to non-renewable sources due to its high energy content and environment friendly nature.[1] Owing to its great potential and urgent demand towards a greener future, a plethora of research has been carried out on H_2 production. Among others, the electrocatalytic hydrogen evolution reaction (HER) has been extensively studied in the last decade.[1–4] One of the key challenges in this area of research is to design and develop suitable electrocatalysts with low kinetic barriers and to drive the reaction at high current densities.[5] In this context, a large number of organometallic and metal organic frameworks (MOFs) based electrocatalysts have been reported with variable performances.[5,6] However, it was found that high per-

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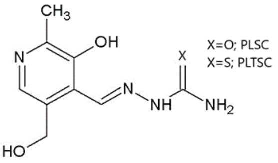
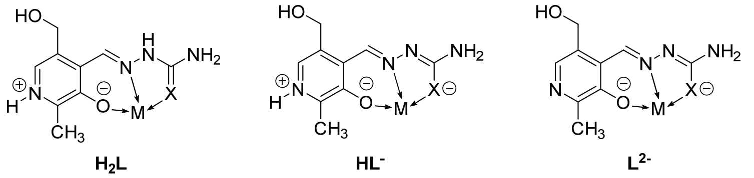
formance was often achieved with the use of catalysts based on expensive metals, such as platinum.[7] Therefore, realization of low-cost catalysts remains a challenge to the research community leading to the quest for new organic ligands and their earth abundant metal complexes with acceptable electrocatalytic activity.[8–10] Among varieties of organic ligands, mixed ligand systems based on semicarbazone/thiosemicarbazone and pyridoxal fragments (a form of vitamin B6, Scheme 1) have attracted interest of the researchers due to multi-dimensional applications.[11] Basically, PLSC and PLTSC are tridentate ligands that coordinate with metal ions through the phenolic oxygen, the hydrazine nitrogen and oxygen (in the case of PLSC) or sulfur (PLTSC; Scheme 2). Accordingly, these ligands are classified as ONO or ONS ligands. The three common coordination modes of such ligands are depicted in Scheme 2. A zwitterion (H_2L) in the neutral form with deprotonated phenolic $OH^–$ group and protonated "pyridine" N atom. Monoanionic form ($HL^–$) of the ligands PLSC and PLTSC is obtained through deprotonation of enol–thiol forms and dianionic form of ligands is obtained through further deprotonation of pyridine N atom ($L^{2–}$).



Scheme 1. Structural formulas and abbreviations of pyridoxal semicarbazone (PLSC; X = O) and thiosemicarbazone (PLTSC; X=S).



Scheme 2. Coordination modes and ligand forms for PLSC and PLTSC ligands.

A thorough literature survey indicated that, although a significant number of transition metals complexes with PLTSC and PLSC has been synthesized,[11–17] the catalytic activities of such complexes have rarely been studied.[18–21] Owing to this, it was envisioned that these complexes could be good candidates for cyclic voltammetry (CV) measurements and electrocatalytic hydrogen production (H_2) *via* proton reduction. Motivated by this, herein the electrocatalytic HER performances of pyridoxal semicarbazone- and thiosemicarbazone-based Cu(II) complexes, *i.e.*, ([Cu(PLSC)Cl_2] and [Cu (PLTSC-H)H_2O]Br·H_2O), are reported.

EXPERIMENTAL

All chemicals were obtained from Sigma–Aldrich or Across Organics and used as received. Solvents were dried according to available literature methods.[22] Cyclic voltammetry

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experiments were realized using an Autolab PGSTAT 128 potentiostat. The electrochemical cell containing 5 ml of a solution of electrolyte $[NBu_4]$ $[BF_4]$, 0.2 M in DMF, was degassed with nitrogen gas A conventional three-electrode arrangement was employed, consisting of a vitreous carbon working electrode (GCE, 0.07 cm^2), a platinum wire as the auxiliary electrode and Ag/AgCl as the reference electrode. All potentials in the paper are referred to Ag/AgCl scale. Ligands (PLSC and PLTSC) and corresponding Cu(II) complexes were synthesized following a reported procedure.[11]

Synthesis of PLSC ligand (PLSC·HCl·H_2O)

To a warm mixture of pyridoxal hydrochloride (3.10 g, 15 mmol) and semicarbazide hydrochloride (1.60 g, 15 mmol) in 30 mL water, $Na_2CO_3\cdot 10H_2O$ (4.5 g, 25 mmol) was added in portions. After stirring for 5 h, the obtained microcrystalline yellow deposit was filtered off, washed with H_2O and dried to realize the final product. Yield: 3.70 g (95 %).

Synthesis of PLTSC ligand (PLTSC·$3H_2O$)

To a mixture of pyridoxal hydrochloride (2.03 g, 10 mmol) and thiosemicarbazide (0.91 g, 10 mmol) dissolved in 20 mL of methanol, LiOAc (0.70 g, 10 mmol) was added and refluxed for 45 min. The yellow deposit of the ligand was isolated very fast and washed with MeOH. Yield: 2.42 g (82 %).

Synthesis of complex Cu(PLSC)Cl_2

PLSC·HCl·H_2O ligand (0.10 g, 0.35 mmol) was dissolved in 10 mL of MeOH. To this solution, 0.15 g (0.88 mmol) $CuCl_2\cdot 2H_2O$ was added and warmed. The resulting green solution was filtered off and the obtained gleaming small crystals were washed with MeOH after 25 h. Yield: 0.10 g (79.8 %).

Synthesis of complex [Cu(PLTSC-H)H_2O]Br·H_2O

A mixture of PLTSC·$3H_2O$ (0.20 g, 0.7 mmol) and $CuBr_2$ (0.22 g, 1 mmol) in 30 mL of H_2O was heated until complete dissolution of the reactants. The resulting green solution was left at room temperature for 50 h. The obtained crystals were filtered off and dried under vacuum. Yield: 0.24 g (88 %).

RESULTS AND DISCUSSION

The ligands and their corresponding Cu(II) complexes, *i.e.*, [Cu(PLSC)Cl_2] and [Cu(PLTSC-H) H_2O] Br·H_2O), were obtained in good yields and purities following a reported procedure.[8] The molecular compositions of the complexes were determined using various analytical techniques prior to the catalytic studies. It has been reported that the PLSC ligand adapted its neutral form while PLTSC its monoanionic form upon coordination with Cu(II) ion and the formation of the title compounds.[11]

Cyclic voltammetry of ([Cu(PLSC)Cl_2] and [Cu(PLTSC-H) H_2O] Br·H_2O)

The studied complexes were further characterized by cyclic voltammetry in DMF solution with 0.2 M tetrabutylammonium tetrafluoroborate, $[NBu_4][BF_4]$ and 2.5 mM [Cu(PLSC)Cl_2] or [Cu(PLTSC-H)H_2O]Br·H_2O. The Cu(II) complex of the *O*-containing ligand exhibited two reduction peaks with E_p^{red} of –0.10 and -1.48 V for Cu^{2+}/Cu^+ and Cu^+/Cu, respectively. The corresponding

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oxidation peaks appear at –0.7 V (retarded because of the resistivity) and 0 V. In addition, a third oxidation peak appeared at –0.25 V that may be attributed to the ligand.[23] However, the two reduction peaks of the copper complex of the PLTSC ligand appeared at –0.50 (Cu^{2+}/Cu^{+}) and –1.25 V (Cu^{+}/Cu), in addition to the reduction peak of the ligand at –0.81 V. Note that the latter reduction peak was attributed to the ligand based on cyclic voltammetry of the free ligand (Fig. 1).[23] The differences in electrochemical behavior between [Cu(PLSC)Cl_2] and [Cu(PLTSC-H)H_2O]Br·H_2O are attributed to the presence of sulfur atom in the PLTSC ligand. The corresponding oxidation peaks appeared at –1.0, –0.7 and –0.45 V.

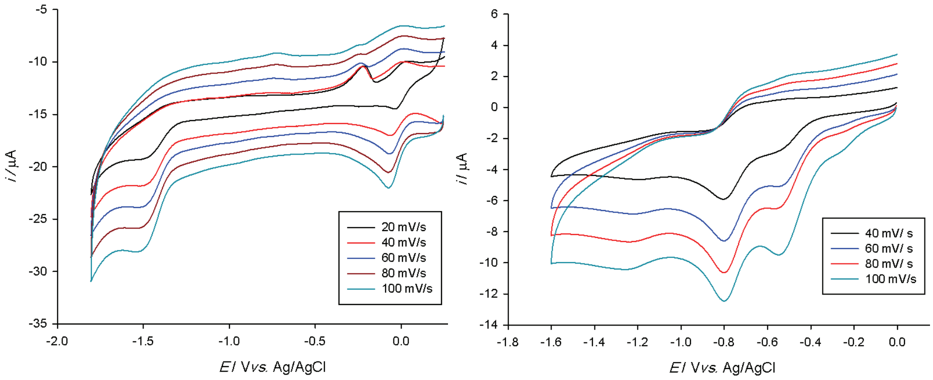

Fig. 1. Cyclic voltammetry of 2.5 mM [Cu(PLSC)Cl_2] (left) and 2.5 mM [Cu(PLTSC-H) H_2O]Br H_2O (right) DMF solutions containing 0.2 M [NBu_4][BF_4] at a carbon electrode *vs*. Ag/AgCl with different scan rate under nitrogen.

Hydrogen evaluation reaction (HER) studies

Both Cu(II) complexes were studied as electrocatalysts for proton reduction into molecular hydrogen using acetic acid as the proton source. The proton reduction occurred at the second reduction peak, where a clear increase of the current at –1.53 and –1.25 V for [Cu(PLSC)Cl_2] and [Cu(PLTSC-H) H_2O]Br·H_2O, respectively, were noticed (Fig. 2). It is noteworthy that these two voltages were marked, respectively, with shifts of 320 and 600 mV compared to the electrocatalysts-free medium (Fig. 3, Table I). Remarkably, the current increased with the number of acid equivalents. The highest electrocatalytic activity was observed in the presence of twelve equivalents of acetic acid (relative to the catalyst mole number) for the complex with the S-containing ligand, while for the complex with O-containing ligand, the highest activity was achieved in the presence of eight equivalents (Fig. 4). These results confirm the beneficial effect of using S-containing complexes instead of O-containing ones. Evidently, better activity was highlighted for the S-containing copper complex with maximum current 4.5 time higher than the acid-free medium, while a maximum current of 3.5 time

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higher was observed in the presence of [Cu (PLSC)Cl_2] (Fig. 5). Moreover, the current density *vs.* acetic acid concentration relationship obtained at potentials of –1.53 and –1.25 V for [Cu(PLSC)Cl_2] and [Cu(PLTSC-H)H_2O]Br·H_2O, respectively, have been plotted. The highest electrocatalytic activity was observed in the presence 20 mM acetic acid, which corresponds to 12 equivalents of acid with respect to the catalyst concentration (Fig. 4).

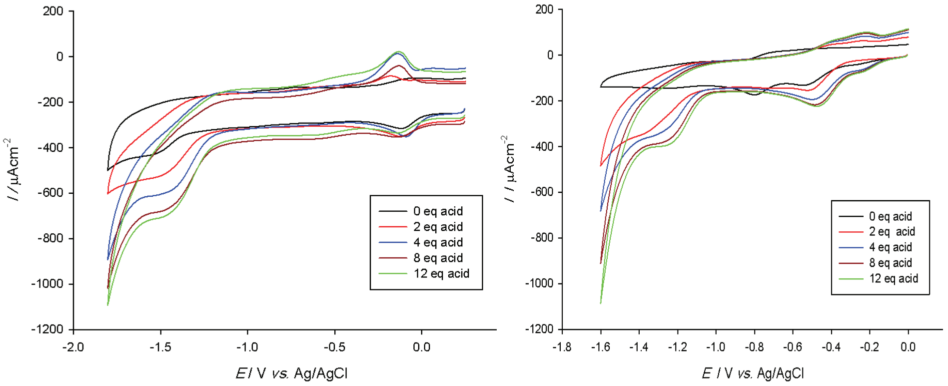

Fig. 2. Cyclic voltammetry of 2.5 mM [Cu (PLSC)Cl_2] (left) and 2.5 mM [Cu(PLTSC-H) H_2O]Br.H_2O (right) DMF solutions containing 0.2 M [NBu_4][BF_4], scan rate 100 mV s^{-1} at a vitreous carbon electrode under N_2, in the presence of 2-12 equivalents of acetic acid.

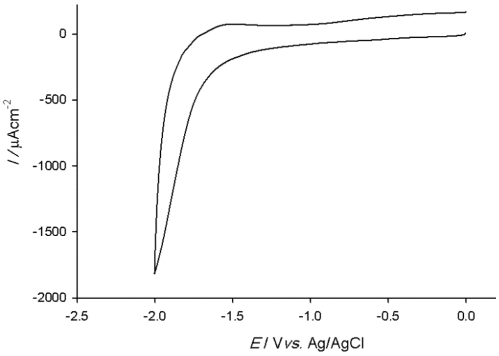

Fig. 3. Cyclic voltammetry obtained in a catalyst-free solution containing 20 mM acetic acid in [Bu_4N][BF_4]-DMF, scan rate 100 mV s^{-1} at a vitreous carbon electrode under N_2.

TABLE I. Potentials of the reduction wave of CH_3COOH *vs.* Ag/AgCl in the absence or presence of the different complexes and the second reduction peak shift of the studied complexes

DMF solution of CH_3COOH	*E* / V *vs.* Ag/AgCl	Shift[a], mV
Electrocatalysts-free	–1.85	0
In the presence of [Cu(PLSC)Cl_2]	–1.53	320
In the presence of [Cu(PLTSC-H)H_2O]Br·H_2O	–1.25	600

[a] Compared to the proton reduction potential in electrocatalyst free medium

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The rate constants were estimated using the approach of Dubois and co-worker and the i_{cat}/i_0 data, based on Eq. (1):

$$k_{obs} = 0.1992(Fv/RTn^2)(i_{cat}/i_0)^2 \quad (1)$$

where F, v, R, T, i_{cat} and i_0 are the Faraday constant, the scan rate, the gas constant, the temperature, the peak catalytic current and the peak current in the absence of acetic acid, respectively, and n is the number of electrons.[24]

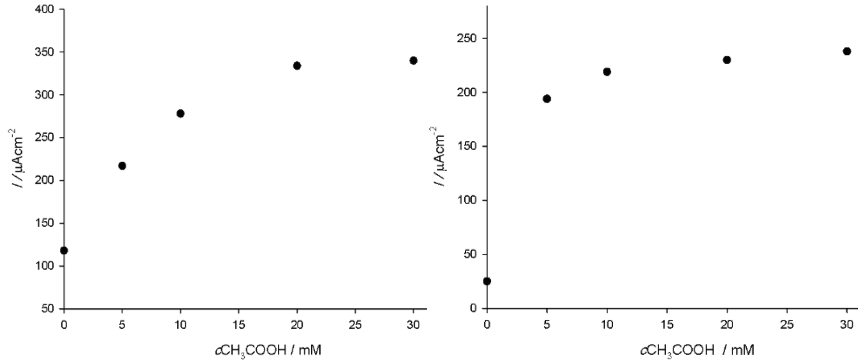

Fig. 4. The current density *vs.* acetic acid concentration relationship for [Cu(PLSC)Cl_2] obtained at a potential of –1.53 V (left) and for [Cu(PLTSC-H)H_2O]Br·H_2O obtained at a potential of –1.25 V (right).

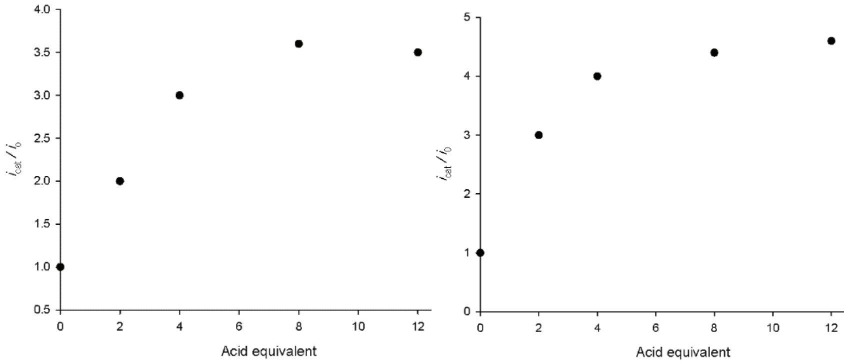

Fig. 5. Effect of the acid concentration on the i_p/i_0 ratio at a vitreous carbon electrode of [Cu(PLSC)Cl_2] (left) and [Cu(PLTSC-H)H_2O]Br·H_2O (right) recorded at –1.53 and –1.25 V, respectively (catalytic reduction of the proton peak).

The electrocatalytic rate constants (k_{cat}, 25 °C) in the presence of these complexes at a vitreous carbon electrode are reported in Table II from the magnitude of i_{cat}/i_0 in the acid independent regime.

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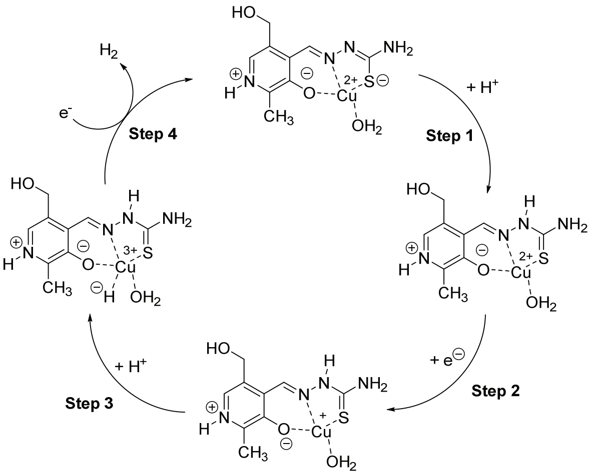
TABLE II. The rate constant (k_{obs}, 25 °C) for catalysis at vitreous carbon (8 eq. acid)

Complex	i_{cat}/i_0	k_{obs} / s^{-1}
[Cu(PLSC)Cl$_2$]	3.6	10.10
[Cu(PLTSC-H)H$_2$O]Br H$_2$O	9.4	68.50

Possible mechanism of HER

As electrochemical analysis has shown, copper in which the PLSC ligand was in its neutral form was much less catalytically active than copper in which the PLTSC ligand was coordinated in the deprotonated form HL$^-$. Hence, it is proposed that the catalytic abilities of the complexes primarily depend on the nature and the coordinated form of the ligand, as observed by the CV measurements. Thus, the complex that contains the PTLSC ligand in its mono-anionic form will initially accept a proton at one of the N atoms found at the ligand backbone (Step 1, Scheme 3). This process will then be followed by sequential electron (Step 2) and proton (Step 3) transfers or these two steps could occur in a concerted step, *i.e.*, *via* proton-coupled electron transfer (PCET).[25,26] Simultaneous heterolytic cleavages of the N–H and Cu–H bonds and electron transfer steps (Step 4, Scheme 3) were proposed to occur to generate a molecule of hydrogen. On the other hand, as the PLSC-containing complex contains the ligand in the neutral form, it is proposed that its electrocatalytic activity occurs primarily at the metal center without involving the ligand and hence lessening its overall activity (Scheme 4). In this case, PCET is depicted for the first step followed by homolytic cleavage of the Cu–H bond, *via* reductive elimination, involving two independent complexes to form molecular hydrogen.[26]



Scheme 3. Proposed electrochemical generation of H_2 as catalyzed by [Cu(PLTSC-H)·H_2O] Br·H_2O. Formal charges for several atoms, including the central metal ion, are depicted for clarity.

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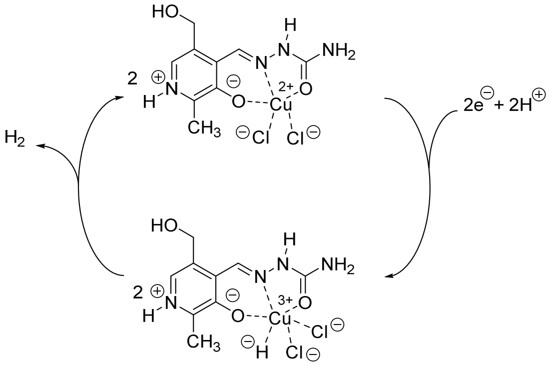
Actually, according to the proposed mechanisms depicted in Schemes 3 and 4, it could be assumed that the catalytic ability of [Cu(PLTSC-H)H_2O] Br·H_2O would be twice as high in comparison to that of [Cu(PLSC)Cl_2]. The ligand protonation would allow for the formation of a single H_2 molecule per catalytic cycle for the former complex, while only half of H_2 per proposed catalytic cycle involving the latter complex. Indeed, if the results of the CV measurements in Table I are examined, it could clearly be observed that the second reduction peak shift is twice as large for the PLTSC-containing complex (600 *vs.* 320 mV). Similarly, the value for i_{cat}/i_0 (Table II) is also significantly higher for [Cu(PLTSC-H) H_2O]Br·H_2O (9.4) in comparison to [Cu(PLSC)Cl_2] (3.6). These observations strongly suggest that in order to create more efficient catalysts based on transition metal complexes incorporating semicarbaone- and thiosemicarbazone pyridoxal ligands, one should strive to synthesize complexes in which the ligands would be coordinated in mono- or di-deprotonated forms.



Scheme 4. Proposed electrochemical generation of H_2 as catalyzed by [Cu(PLSC)Cl_2]. Formal charges for several atoms, including the central metal ion, are depicted for clarity.

This could possibly be achieved by modifying the pH medium of the solution used in the synthesis of these complexes. Acidic medium during synthesis would favor neutral coordination forms of PLSC and PLTSC ligands.[8] Certainly, the role of the central metal (in this case copper) is also not completely insignificant. The challenge would be to synthesize complexes containing PLSC and PLTSC ligands with metals such as Ru, Ir or Rh, as these metals have already exhibited excellent activity in numerous catalytic processes (*e.g.*, Wilkinson, Grubbs and Schrock complexes).

CONCLUSIONS

This work presented captivating possibilities that a targeted design of coordination systems could lead to efficient electrocatalysts for the hydrogen evolution reaction. The cyclic voltammetry measurement performed on a couple of Cu(II) compounds coordinated by either the O-containing PLSC or the S-containing PLTSC ligand showed their undoubted ability to electro-catalyze reduction of the CH_3COOH acidic proton and convert it into molecular hydrogen. The better activity for the complex containing the deprotonated form of the coordinated ligand should also be highlighted. This valuable information would be considered in the future as an extremely useful guideline for the synthesis of electrocatalysts based on PLSC or PLTSC ligands.

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ИЗВОД

ЕЛЕКТРОКАТАЛИЗА ИЗДВАЈАЊА ВОДОНИКА НАКОН РЕДУКЦИЈЕ КОМПЛЕКСА БАКРА (II) НА БАЗИ ПИРИДОКСАЛНИХ ПОЛУ- И ТИОСЕМИКАРБАЗОНА

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Растућа глобална потражња за обновљивим изворима енергије довела је у први план обновљиве, зелене изворе енергије, међу којима производња водоника из воде заузима значајно место. Да би остварили овај циљ, истраживачи широм света развијају катализатор који би могао брзо да катализује реакцију издвајања водоника (HER) у највећем могућем приносу. У овом раду извештавамо о електрокаталитичким HER перформансама комплекса Cu (II) на бази пиридоксалних семи- и тиосемикарбазона, тј. ([Cu(PLSC)Cl_2] и [Cu (PLTSC-H) H_2O]Br·H_2O). Недвосмислено смо показали да комплекси показују завидан ниво HER каталитичке активности. Каталитичка активност комплекса није била само функција централног метала већ и контролисана врстом координирајућег лиганда.

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