

## Hydrogen Evolution Reaction Performance of Co(II) and Co(III) Complexes Based on pyridoxal (thio)semicarbazones

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**Summary:** Finding a renewable, cleaner and inexpensive source of energy has been a momentous challenge to the researchers. Among others, one intriguing solution is molecular H<sub>2</sub> which is considered as an ideal energy source for the future needs. Obtaining H<sub>2</sub> is extremely appealing but difficult to achieve. One of the most viable solutions is the electrocatalytic hydrogen evolution reaction (HER). In this paper, we presented electrocatalytic HER performances of pyridoxal-semicarbazone (PLSC) and pyridoxal *S*-methyl-iso-thiosemicarbazone (PLITSC) stabilized Co(II) and Co(III) complexes, i.e. ([Co(PLSC)(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>], **1**) and [Co(PLITSC-H)(PLITSC-2H)].CH<sub>3</sub>OH, **2**). Both complexes catalyzed the HER in acidic media while complex 2 was found to be more active than complex 1.

**Keywords:** Hydrogen evaluation reaction, Cobalt complexes, Pyridoxal-semicarbazone ligand (PLSC), Pyridoxal-*S*-methyl-isothiosemicarbazone (PLITSC).

### Introduction

Molecular hydrogen (H<sub>2</sub>) is the lightest molecule with well-known applications in the industrial production of ammonia, steel, and aluminum. In addition, owing to its highest energy content (per mole), H<sub>2</sub> has been suggested as an intriguing and alternative energy source to the carbon dioxide emitting fossil fuels. [1] Realizing its high importance and future demands, production of H<sub>2</sub> has become the most pursuing area of research in the last decade. [2] The electrocatalytic hydrogen evolution reaction (HER), which utilizes electricity to split water, is considered as one of the most promising technology to achieve this goal. [1-4]. This part of current demand and search has the target of creating and producing a suitable catalyst to efficiently perform electrocatalytic HER with a large yield and specificity. Several state-of-the-art homo- and heterogenous

electrocatalysts with variable activity and performance have been recently reported. [3] Among plethora of organic, inorganic and organic-inorganic hybrid compounds, complexes based on pyridoxal and carbazone units have attracted an immense interest due to its multi-dimensional applications including catalysis. One can judiciously modify the ligand backbone and lateral functionalities to create purpose-specific ligands (Fig. 1a). An additional benefit of such ligand systems is that they are able to coordinate to the metallic centers through different modes (Fig. 1b-c). For instance, it has been demonstrated that ligands like pyridoxal semi-carbazone (PLSC) [4-11] and pyridoxal *S* methyl iso-thiosemicarbazone (PLITSC) [12- 19] ligate to metal centers in three distinct modes namely neutral, monoanionic and dianionic forms (respectively (H<sub>2</sub>L), (HL<sup>-</sup>) (L<sup>2-</sup>) ) [4].

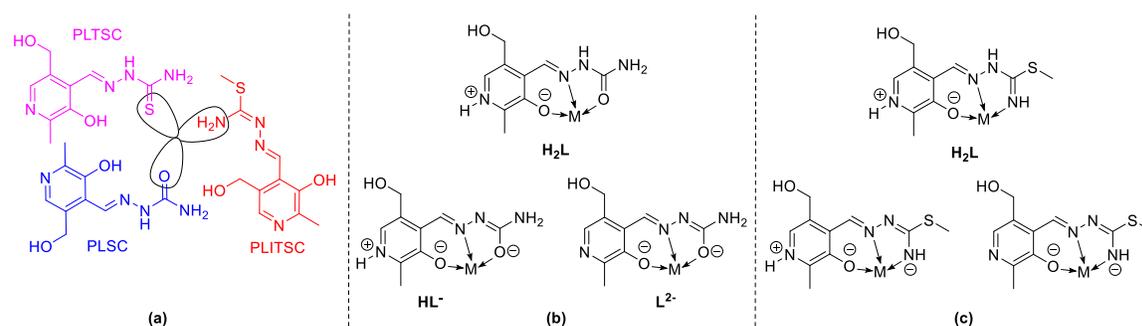


Fig. 1: General structural features for ligands base on pyridoxal-carbazone derivatives (pyridoxal semi-carbazone, pyridoxal thiocarbazon and pyridoxal-iso thiosemicarbazone (respectively PLSC, PLITSC, PLITSC) (a), different modes of coordination for PLSC (b) and PLITSC (c) ligands.

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Several works [20-23] on this topic have been published, in which it had been unequivocally shown that this group of complexes were catalytically active towards the  $H_2$  production. It also is worth mentioning that a majority of published research reported the synthesis and catalytic activities of Mo [23], Ru [22], Pd [21] and Ni [20] complexes stabilized by PLSC ligands. Despite its high usefulness, we noted that ligands such as pyridoxal-thiocarbazone (PLTSC), pyridoxal-*S*-methyl iso-thiosemicarbazone (PLITSC), and pyridoxal-semi-carbazones (PLSC) have not been tested yet for the electrocatalytic HER. To fill this gap, we present herein electrocatalytic HER performances of Co(II) and Co(III) compound stabilized by PLSC ( $[Co(PLSC)(SO_4)(H_2O)_2]$ ; **1**) and PLITSC ( $[Co(PLITSC-H)(PLITSC-2H)] \cdot CH_3OH$ ; **2**) (Chart 1). Based on our knowledge, this presented work is the first time that catalytic activity, including electrocatalytic HER, of a complex bearing PLITSC ligand(s) has been investigated.

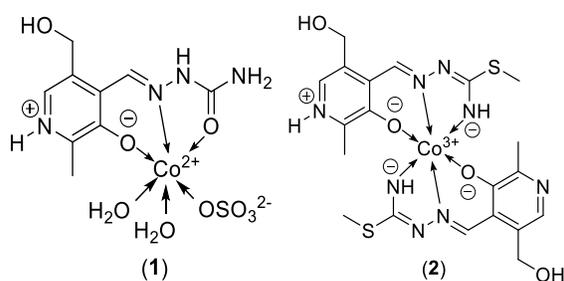


Chart 1: A perspective view of complex ( $[Co(PLSC)(SO_4)(H_2O)_2]$ ; **1**) and ( $[Co(PLITSC-H)(PLITSC-2H)] \cdot CH_3OH$ ; **2**) used in this study.

## Experimental

Ligands (PLSC and PLITSC) and their corresponding complexes **1** and **2** were synthesized and characterized according to the already described procedures [8,12]. Acetic acid ( $CH_3COOH$ ) is available from a commercial source, with appropriate purity. Analyses according to CV (Cyclic voltammetry) were completed by Autolab PGSTAT 128 potentiostat. The electrochemical cell comprising five mL of electrolyte tetrabutylammonium tetrafluoroborate  $[NBu_4][BF_4]$  into DMF solution (0.2 M  $[NBu_4][BF_4]$  and 2.5 mM of complexes) was purged with  $N_2$  gas. Was used a conventional three-electrode arrangement, including a glassy carbon as operating (CPE) (0.07  $cm^2$ ), and as a reference electrode was used platinum wire and as the secondary  $Ag/AgCl$ .

## Synthesis of $[Co(PLSC)(SO_4)(H_2O)_2]$ , **1**

0.15g (1 mmol) of  $CoSO_4$  was added into a warm  $H_2O$  (10 mL) solution that contained completely dissolved 0.26 g (1 mmol) of PLSC. Purple-colored mono-crystals for the X-ray examination was forming after few hours. The crystals were separated and rinsed off with ethanol. Yield: 0.19 g (78%). Elemental analysis: Calculated for  $C_9H_{16}CoN_4O_9S$ : C 26.03, H 3.88, N 13.49; Found: C 26.10, H 3.59, N13.50. IR data ( $cm^{-1}$ , KBr pellet): 2887, 1670, 1638, 1423.  $\lambda_{M(H_2O)}$ : 183  $Scm^2mol^{-1}$ .  $\mu_{eff} = 4.15$  BM.

## Synthesis of complex $[Co(PLITSC-2H)(PLITSC-H)] \cdot CH_3OH$ , **2**

0.27 g (1 mmol) of PLITSC and 0.28 g (1 mmol) of  $CoCl_2 \cdot 6H_2O$  were dissolved in about 10 mL MeOH by warming up the reaction mixture. The warm suspension was separated, cooled for approximately 10 hours, after which purple crystals formed. Crystals rinsed off with ethanol. Yield: 0.16 g (65%). Elemental analysis: Calculated for  $C_{21}H_{29}CoN_8O_5S_2$ : C 41, H 4.87, N 18.79. Found: C 40.79, H 4.65, N 18.65. IR data ( $cm^{-1}$ , KBr pellet): 3236, 1613, 1489, 832.  $\lambda_{M(H_2O)}$ : 165  $S cm^2mol^{-1}$ .  $\mu_{eff} = 0$  BM.

## Results and Discussion

Complexes **1** and **2**, ligands as well, were synthesized in satisfactory yield and purity by using reported procedure [8,12]. The composition of structures molecules of the complexes were confirmed by multi-spectroscopic analysis before the catalytic investigations.

It is evident that complex **1** ( $[Co(PLSC)(SO_4)(H_2O)_2]$ ) is a Co(II) complex, where the central metal is coordinated by a sulfate group and two water molecules. The octahedral environment is completed by the tridentate ligand PLSC (ONO), that adopted its neutral (zwitterionic/protonated) form ( $H_2L$ ). Confirmation of the ligand's coordination form was obtained from the IR spectrum given in Fig. 2a, in which the presence of a band around  $2850 cm^{-1}$  ( $\nu(NH^+)$  vibration) was clearly visible indicating the protonated form of this ligand [4]. The carbonyl  $\nu(C=O)$  band (noticeable by very high intensity) could be found at  $1670 cm^{-1}$  for semicarbazone ligand, i.e. about the same value characteristic for the majority of semicarbazones [24]. Existing a medium intense band in the spectrum at about  $620 cm^{-1}$  related to the coordinated  $SO_4^{2-}$  group [25]. Additionally, the macro analysis was consistent with the proposed molecular formula of the complex while the magnetic moment

measurements ( $\mu_{\text{eff}} = 4.15$  BM) confirmed that the reported complexes incorporated a Co(II)  $d^7$  (paramagnetic) center. The molar conductivity value for complex **1** ( $\lambda_M(\text{H}_2\text{O}) = 183 \text{ Scm}^2\text{mol}^{-1}$ ) was greater than for a 1:1 type of electrolyte, which was consequences by the cation which is double charged and anion in the solution of complex **1**.

The second complex is the Co(III) complex (a bis-ligand complex) in which both ligands are in deprotonated form. Confirmation of this is visible in Fig. 2b, by not presence of a usually band at about  $2850 \text{ cm}^{-1}$ . The value for  $\mu_{\text{eff}} = 0$  BM corresponded to a Co(III)  $d^6$  (diamagnetic) center. The molar conductivity value  $\lambda_M(\text{H}_2\text{O})$ :  $165 \text{ S cm}^2\text{mol}^{-1}$  for complex **2** was observed to be consistent a 1:1 electrolyte.

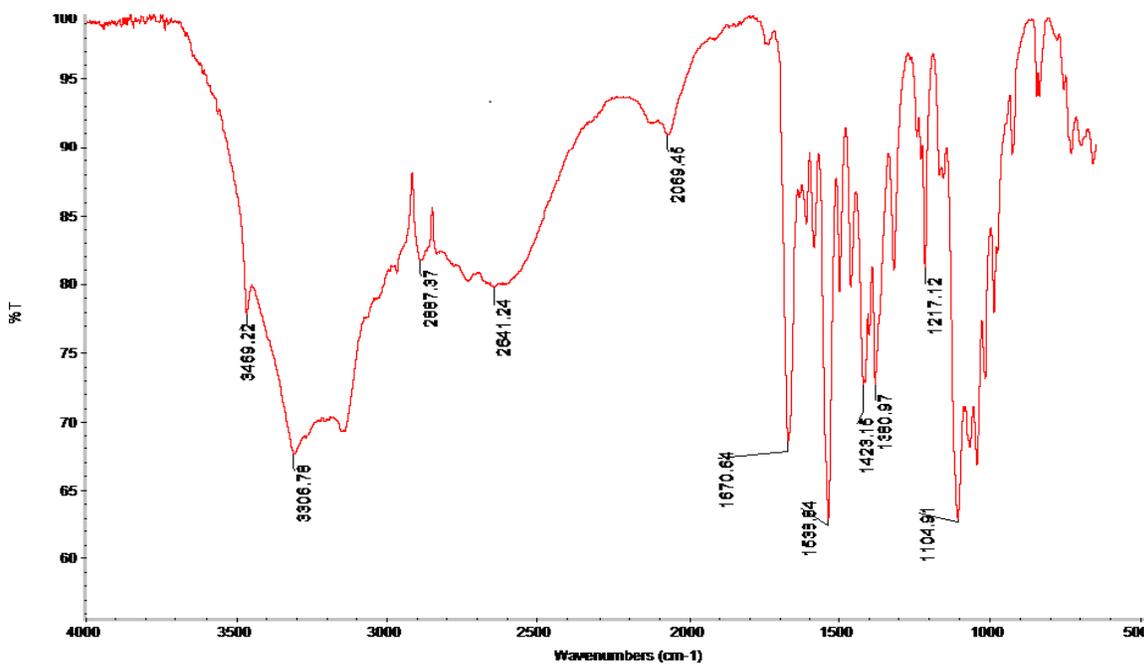
The nature (neutral, monoanionic and dianionic) of the respective ligands in these complexes (Fig. 3) is earlier studied by X-ray analysis [8, 12]. For completeness, we include a part of this discussion in this work. The PLSC ligand in complex **1** adopted neutral (i.e. zwitterionic) form as evident by the double bond feature of C1-O2 ( $1.257(5) \text{ \AA}$ ) and the single bond feature of N3-N4 ( $1.374(4) \text{ \AA}$ ) fragments as well as the value for the C5-N6-C7 angle of  $124.3(3)^\circ$  of suggesting N-protonation of the pyridine ring. One of the PLITSC ligands in complex **2** adopted the mono-anionic form while the other ligand the di-

anionic form [12]. First of all, values for the C1-N2 ( $1.334(5) \text{ \AA}$ ) and C'-N2 ( $1.326(6) \text{ \AA}$ ) bond distances confirmed the first deprotonation for both PLITSC ligands. However, vastly different values for the angle around the pyridine N atom for the two ligands ( $118.7(4)^\circ$  for C6-N4-C8 and  $124.3(4)^\circ$  for C6'-N4'-C8') clearly indicated that only one ligand underwent second deprotonation.

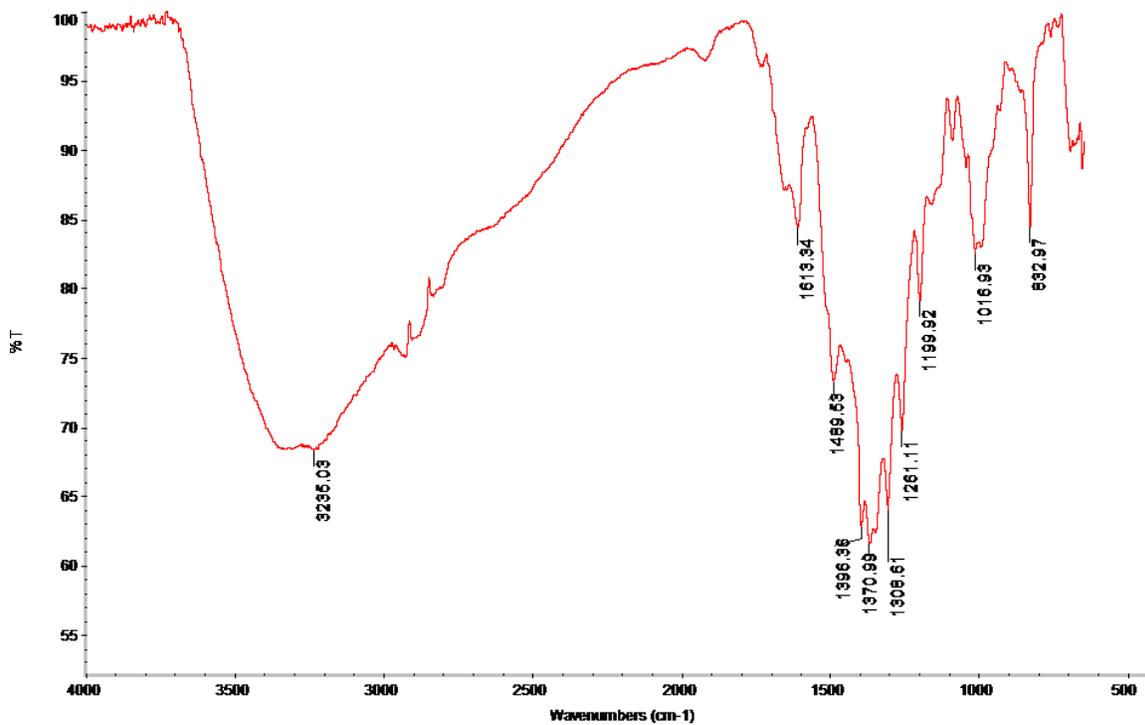
Based on the analyses presented above, it can be concluded that the purity of the complexes used for the current electrochemical tests (hydrogen evaluation reactions) was quite high and that the coordinative nature of all ligands was precisely determined in the presented cobalt complexes.

#### Cyclic voltammetry (CV) of complexes **1** & **2**

The studied compounds examined by CV in DMF solvent comprising 0.2 M tetrabutylammonium tetrafluoroborate,  $[\text{NBu}_4][\text{BF}_4]$  and 2.5 mM of complexes **1** or **2**, as depicted in Fig. 4. Complex **1** shows 2 peaks of reduction with  $E_p^{\text{red}} = -0.60 \text{ V}$  and  $-1.58 \text{ V}$  attributed to  $\text{Co}^{2+}/\text{Co}^+$  and  $\text{Co}^+/\text{Co}$  couples, respectively. The CV study of complex **2** showed three reduction peaks with  $E_p^{\text{red}} = -0.62 \text{ V}$ ,  $-0.9 \text{ V}$  and  $-1.28 \text{ V}$  for three couples  $\text{Co}^{3+}/\text{Co}^{2+}$ ,  $\text{Co}^{2+}/\text{Co}^+$  and  $\text{Co}^+/\text{Co}$ , furthermore to a peak at about  $-1.5 \text{ V}$  corresponding to the ligand reduction.



(a)



(b)

Fig. 2: IR spectra of Cobalt complexes  $[\text{Co}(\text{PLSC})(\text{SO}_4)(\text{H}_2\text{O})_2]$  (a) and  $[\text{Co}(\text{PLITSC-H})(\text{PLITSC-2H})]\cdot\text{CH}_3\text{OH}$  (b)

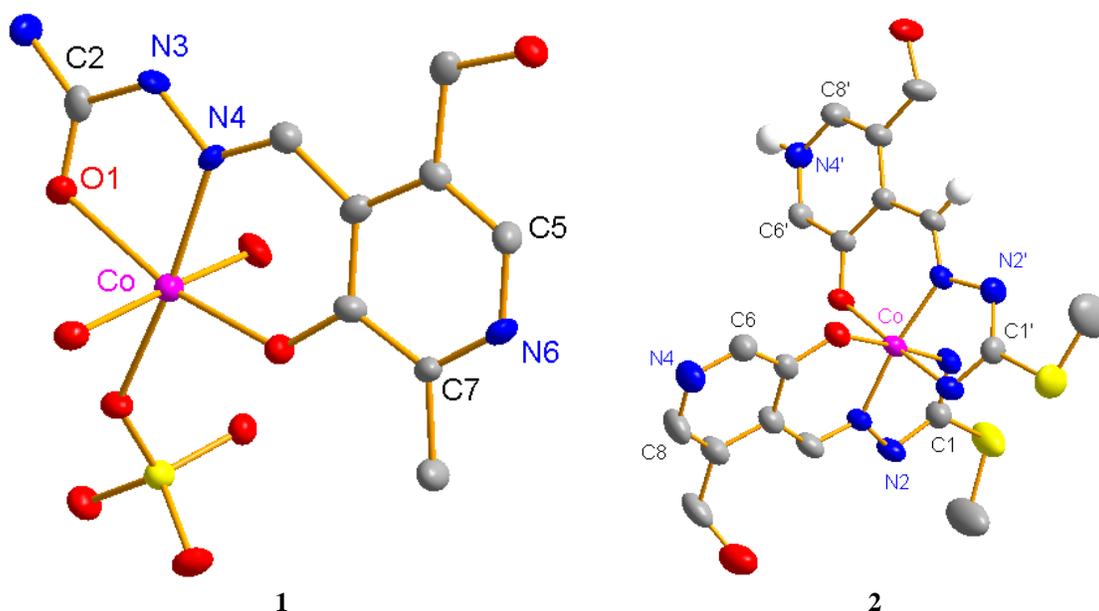


Fig. 3: Molecular structures for complexes **1** and **2** as drawn with a probability of 50%. Most H atoms as well as non-coordinating solvent molecules are not presented for better overview. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) (selected) for **1**: C1-O2 1.257(5), N3-N4 1.374(4), C5-N6-C7 124.3(3); for **2**: C1-N1 1.334(5), C1'-N1' 1.326(6), C6-N4-C8 118.7(4), C6'-N4'-C8' 124.3(4).

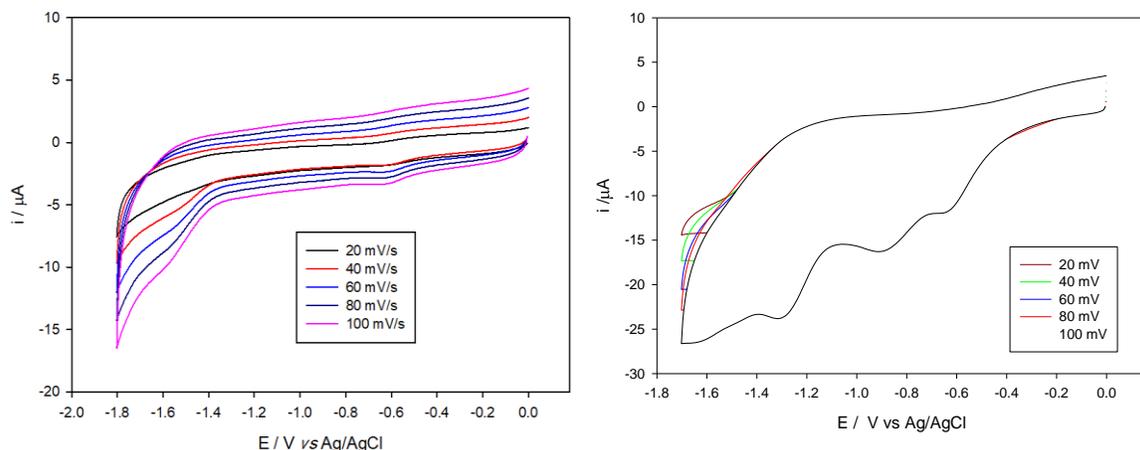


Fig. 4: Cyclic voltammety of DMF solvent comprising 0.2 M  $[\text{NBu}_4][\text{BF}_4]$  and 2.5 mM of complex 1 (left) or 2 (right) at carbon electrode vs Ag/AgCl at various scan movements below nitrogen.

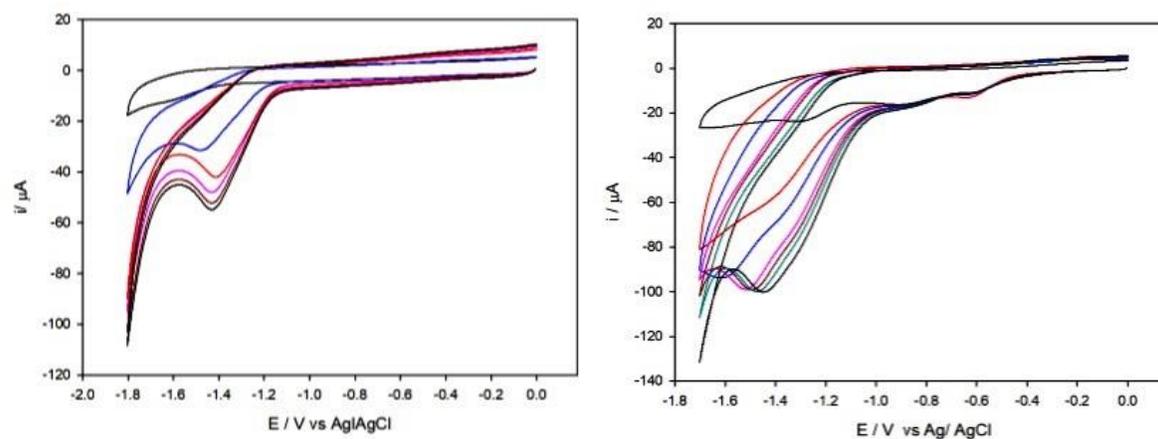


Fig. 5: Cyclic voltammety of 2.5 mM of complex 1 (left) and 2 (right) in DMF solvent comprising 0.2 M  $[\text{NBu}_4][\text{BF}_4]$  in the appearance of 2-16 equivalent of acetic acid.

#### Hydrogen evolution reaction (HER) studies

Comparing to the earlier reported copper complexes ( $[\text{Cu}(\text{PLSC})\text{Cl}_2]$  and  $[\text{Cu}(\text{PLTSC-H})\text{H}_2\text{O}]\text{Br}\cdot\text{H}_2\text{O}$ ) [26], the electrocatalytic performance of the complexes 1 and 2 was noticeably better in the behavior of acetic acid (2-16 equivalent). The proton reduction takes place at the second (-1.58 V for complex 1) and third peaks (-1.28 V for complex 2) with a shift of 270 mV and 500 mV comparing to the catalysts-free medium (Fig. 5). The different potentials at which the proton reduction occurs are listed in the (Table 1). It is worth noting that the proton reduction was evidenced by an obvious increase of the present density including the amount of acid equivalent. For both the complexes, powerful activities were identified in the

appearance of 12 equivalent of acetic acid and the maximum current was observed to be 4.5 and 10.5 times higher compared to the acid-free medium for complexes 1 and 2, respectively (Fig. 6).

Table 1: Reduction potentials of  $\text{CH}_3\text{COOH}$  in a function of Ag / AgCl. based on the appearance of several complexes and the shifting compared to a reduction of the secondary peak of examined complexes.

DMF solution of $\text{CH}_3\text{COOH}$	Potential / V vs Ag/AgCl	Shift / mV more positive
Electrocatalysts-free	-1.85	0
In the appearance of complex 1	-1.58	270
In the appearance of complex 2	-1.28	500

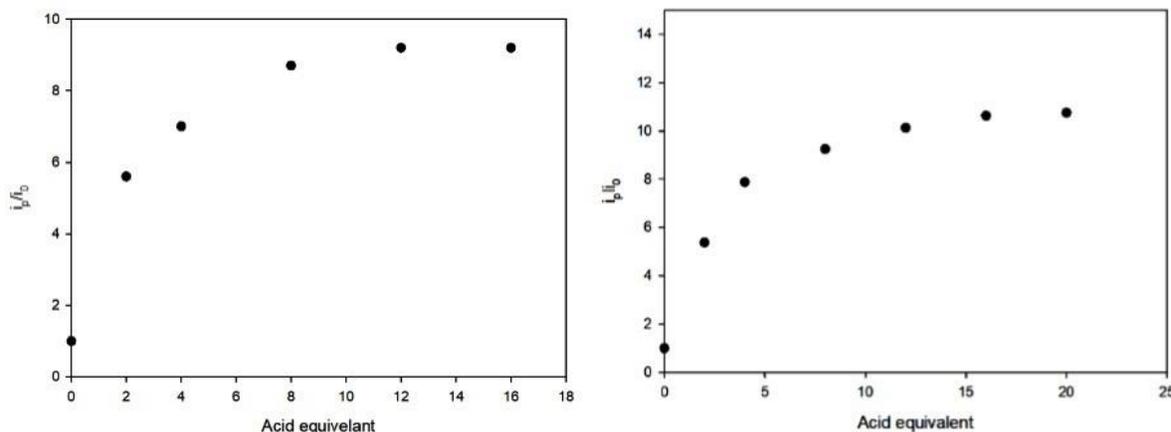


Fig. 6: Influence of the acid concentration on  $i_p/i_o$  ratio at a glassy carbon electrode. 2.5 mM of complex **1** (left) and **2** (right) in DMF solvent comprising 0.2 M  $[\text{NBu}_4][\text{BF}_4]$ .

Fig. 6 shows the influence of acid concentration on  $i_p/i_o$  ratio at a glassy carbon electrode.  $i_p$  is the peak of catalytic current at 100 mVs<sup>-1</sup> and  $i_o$  is the peak current in the absence of acetic acid for the one-electron reduction step. From these figures, we can conclude the noticeable of cobalt complexes. In addition, the maximum activity was observed for the cobalt complex coordinated to S-containing ligand for the different acid equivalent.

Using the approach developed by Dubois [27] the rate constants were predicted and the  $i_p/i_o$  data, based on the equation below (F is the Faraday constant, R is the gas constant, T is the temperature,  $i_p$  is the peak catalytic current,  $i_o$  is the peak current in the nonexistence of acetic acid and n is the number of electrons).

$$k_{\text{obs}} = 0.1992(Fv/RTn^2)(i_p/i_o)^2$$

The rate constants ( $k_{\text{cat}}$ , 25 °C) of the catalysis of the different electrocatalyst complexes, at glassy carbon electrode is estimated in Table-2, the extent of  $i_p/i_o$  in the acid sovereign mode.

Table-2: The rate constant ( $k_{\text{obs}}$ , 25 °C) for catalysis at glassy carbon (8 eq acid).

Complex	$i_p/i_o$	Rate constant ( $k_{\text{obs}}$ ) / s <sup>-1</sup>
1	9.40	68
2	10.50	85.5

It is well established that the catalytic activity of a complex is in relation with central metal, its oxidation state, as well as the way of coordination and coordination number of central metals [28]. In addition to this, we noted that the type of coordinated ligands also plays a significant role, i.e. the form of their coordination to the central metal, Co (II) and Co

(III) in this case. In Co (II) complex **1**, the PLSC ligand is in its neutral form, while in Co (III) complex **2** the ligands are in mono- and di-deprotonated forms. Considering also that the two complexes contain the central metal in different oxidation states, it would be realistic to assume that complex **2**, which contains the central metal in a higher oxidation state, would show a better catalytic activity. Indeed, the measurements have shown that there is a significant difference in activity of these two complexes. Is apparent in Table 2, the rate constant ( $k_{\text{obs}}$ ) worth off complex **2** (85.5 s<sup>-1</sup>) was observed to be *ca.* 1.25 times higher as compared to complex **1** (68s<sup>-1</sup>). This observation was attributed to complex **2** containing both PLITSC ligands in the deprotonated forms as well as the central metal in a higher oxidation state.

#### Possible mechanism of HER

Based on the above information, we compiled the HER mechanism route for complexes (1) and (2). It is well known that for a given metal complex, metal undergoes multi electron reduction process to realize catalytically active low valent state which then get protonated and forms metal hydrides. [29]. The resulting metal hydride finally produces H<sub>2</sub> via homolytic or heterolytic pathways. [30] Literature survey suggests that the catalytic mechanism, among others, depends on the strength of the acid used.[31] As depicted in Fig. 4 and 5, complex **2** exhibit two reduction peaks attributed to Co (II)→Co(I) and Co(I)→Co (0) couples, while complex **3** showed three reduction peaks attributed to Co (III)→Co (II), Co (II)→Co(I) and Co (I)→Co (0) couples. In both the systems, H<sup>+</sup> reduction takes place near to Co(I)→Co (0) potential indicating Co(0) as the catalytically active species (Fig. 7). Therefore, we assume that oxidative protonation of Co(II)-Ln (Ln = PLSC or

PLITSC) species yielded hydride intermediate H-Co(II)-L<sub>n</sub> which reacts with a proton (protonolysis) to produce the metal complex and dihydrogen..

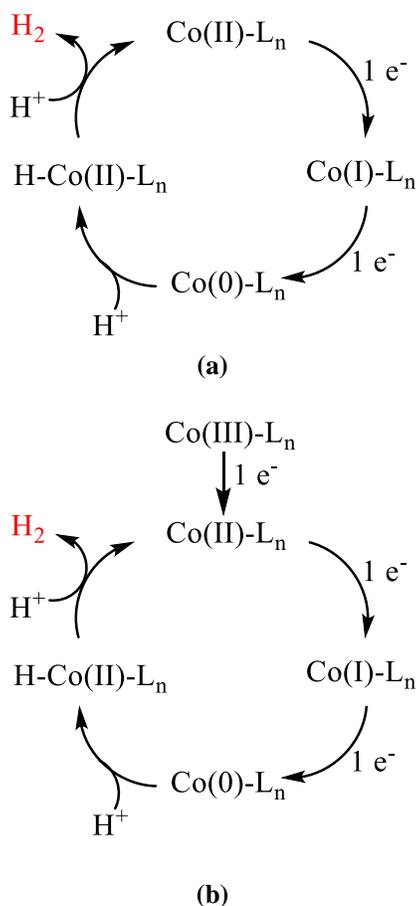


Fig. 7: Possible mechanism of HER by (a) Co(II) and (b) Co(III) complexes.

## Conclusion

We have shown here that complexes **1** and **2** are interesting catalysts for the protons reduction into molecular hydrogen at the carbon electrode in DMF-[Bu<sub>4</sub>N][BF<sub>4</sub>] solution at room temperature. The CV of complex **1** two consecutive reduction peaks are shown with  $E_p^{\text{red}} = -0.60$  V and  $-1.58$  V vs Ag/AgCl and complex **2** shows two reduction peaks with  $E_p^{\text{red}} = -0.62$  V and  $-1.50$  V vs Ag/AgCl. There is a direct reduction of acetic acid (CH<sub>3</sub>COOH) on the glassy carbon electrode at  $E_p -1.85$  V vs Ag/AgCl in [Bu<sub>4</sub>N][BF<sub>4</sub>]-DMF, while the reduction potential slides towards  $-1.58$  V and  $-1.28$  V vs Ag/AgCl in the appearance of complexes **1** and **2**, respectively. For complex **1**, which contains the neutral form of PLSC ligand, ligand protonation cannot be expected and, consequently, the electrocatalytic activity was

assigned solely on the activity of the central metal. For complex **2**, the catalytic ability was observed to be about twice as high than in complex **1**. Further studies to delineate the effect of ligand and metal centers on the mechanistic pathways are underway.

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## References

1. I. Staffell, D. Scamman, A. Abad, P. Balcombe, P. Dodds, P. Ekins, N. Shah and K. Ward, The role of hydrogen and fuel cells in the global energy system, *Energy Environ. Sci.*, **12**, 463 (2019).
2. N. Dubouis and A. Grimaud, The hydrogen evolution reaction: from material to interfacial descriptors, *Chem. Sci.*, **10**, 9165 (2019).
3. J. Zhu, L. Hu, P. Zhao, L. Lee and K. Yin-Wong, Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles. *Chem. Rev.* **120**, 851 (2020)
4. V. Jevtovic, *Cu, Fe, Ni and V Complexes with Pyridoxal Semicarbazones*, Lap Lambert Publication, Saarbrücken, (2010).
5. V. Jevtovic, G. Pelosi, S. Ianeli, M. Leovac, R. Kovacevic and S. Kaisarevic, Synthesis, Structural Studies and Biological Activity of a Dioxovanadium(V) Complex with Pyridoxal Semicarbazone, *Acta Chimica Slovenica*, **57**, 363 (2010).
6. V. Jevtovic and D. Vidovic, Bis [4-(2-carbamoylhydrazin-1-ylidene-κ N, O)-5-hydroxymethyl-2-methylpyridinium-3-olato-κ O] cobalt (II) dinitratedihydrate, *Acta Crystallographica*, **E-66**, m408 (2010).
7. D. Vidovic, A. Radulovic and V. Jevtovic, Synthesis, characterization and structural analysis of new copper (II) complexes incorporating a pyridoxal-semicarbazone ligand, *Polyhedron*, **30**, 16 (2011).
8. V. Jevtovic, Syntheses, characterisation and structural analysis of new cobalt (II, III) complexes incorporating a pyridoxal-semicarbazone ligand, *IJSET*, **2**, 591 (2015).
9. V.M. Leovac, Lj.S. Jovanović, V.S. Jevtović, G. Pelosi and F. Bisceglie, Transition metal complexes with thiosemicarbazide-based ligand – Part LV: Synthesis and X-ray structural study of novel Ni(II) complexes with pyridoxal semicarbazone and pyridoxal thiosemicarbazone. *Polyhedron*, **26**, 2971 (2007)

10. D. Poleti, Lj. Karanović, V. Leovac and V. Jevtović, Di-bromo(pyridoxal-semicarbazone  $\kappa^3N1,O3,O3'$ )copper(II). *Acta Cryst.*, **C-59**, 73 (2003).
11. N.Z. Knežević, V. M. Leovac, V.S. Jevtović, M. Grgurić-Šipka and S.T. Sabo, Platinum(IV) complex with pyridoxal semicarbazone, *Inorg. Chem. Comm.*, **6**, 561 (2003).
12. V. Jevtovic, D. Cvetkovic and D. Vidovic, Synthesis, X-Ray characterization and antimicrobial activity of iron(II) and cobalt(III) complexes with the Schiff base derived from pyridoxal and semicarbazide or S-methylisothiosemicarbazide, *Journal of Iranian Chemical Society*, **8**, 727 (2011).
13. S. Novaković, Z.D. Tomić, V.S. Jevtović and V.M. Leovac, Transition metal complexes with thiosemicarbazide-based ligands. XLIII. Chlorobis(3-methylisothiosemicarbazide- $\kappa^2(2)N(1),N(4)$ )zinc(II) chloride, *Acta Crystallographica Section C Crystal Structure Communications*, **58**, m358 (2002).
14. V.M. Leovac, V.S. Jevtović and G.A. Bogdanović, Transition metal complexes with thio-semicarbazide-based ligands. XLIV.1. Aqua (3-hydroxy-5-hydroxymethyl-2-methylpyridine-4-carboxaldehyde 3-methylisothiosemicarbazone- $\kappa^3O, N1, N4$ ) nitratocopper (II) nitrate, *Acta Crystallographica Section C Crystal Structure Communications*, **58**, m514 (2002).
15. V.S. Jevtovic, Lj.S. Jovanović, V.M. Leovac and L.J. Bjelica, Transition metal complexes with thiosemicarbazide-based ligands. Part 49. New complexes of iron (III) with deprotonated tridentate Schiff base - Pyridoxal derivatives, *J. Serb. Chem. Soc.*, **70**, 187 (2005).
16. V. Jevtovic and D. Vidovic, D. Synthesis, Characterization and X-Ray Crystal Structure of the Tri-Aqua(3-Hydroxy-5-Hydroxymethyl-2-Methylpyridine-4-Carboxaldehyde Methylisothiosemicarbazone:  $\kappa^3, O3, N7, N10$ ) Ni(II) Nitrate, *J. Chem. Cryst.*, **40**, 794 (2010).
17. V. Jevtovic, Synthesis, Characterization and X-ray Crystal Structure of the Dimer Complex [Cu (PLITSC-2H) (NH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O], *American Journal of Chemistry*, **3**, 148 (2013).
18. J. Mirkovic and V. Jevtovic, A Series of Co (II) and Co (III) Complexes Incorporating Pyridoxal-S-methylisothiosemicarbazone: Synthesis, Physico-chemical Characteristic and Biological Activity, *American Journal of Chemistry*, **4**, 131 (2014).
19. V. Jevtovic, Synthesis and Structural Analysis of a Cu (II) Complex Incorporating Pyridoxal-S-Methylisothiosemicarbazone (PLITSC) Ligand, *American Journal of Chemistry*, **4**, 47 (2014).
20. R. Manikandan, P. Anitha, G. Prakash, P. Vijayan, P. Viswanathamurthi, Synthesis, spectral characterization and crystal structure of Ni (II) pyridoxal thiosemicarbazone complexes and their recyclable catalytic application in the nitroaldol (Henry) reaction in ionic liquid media, *Polyhedron*, **81**, 619 (2014).
21. R. Manikandan, P. Anitha, P. Viswanathamurthi and J. Grzegorz-Maleck, Palladium(II) pyridoxal thiosemicarbazone complexes as efficient and recyclable catalyst for the synthesis of propargylamines by a three-component coupling reactions in ionic liquids, *Polyhedron*, **119**, 300 (2016).
22. R. Manikandan, P. Anitha, G. Prakash, P. Vijayana, P. Viswanathamurthi, R. Jay-Butcher and J. Grzegorz -Malecki, Ruthenium(II) carbonyl complexes containing pyridoxal thiosemicarbazone and trans-bis(triphenylphosphine/arsine): Synthesis, structure and their recyclable catalysis of nitriles to amides and synthesis of imidazolines, *Journal of Molecular Catalysis A: Chemical*, **398**, 312 (2015).
23. J. Pisk, B. Prugovečki; D. Matković-Čalogović, R. Poli, D. Agustin and V. Vrdoljak, (VI) complexes with pyridoxal thiosemicarbazone ligands as molybdenum(V) precursors in oxygen atom transfer process and epoxidation (pre)catalysts, *Polyhedron*, **33**, 441 (2012).
24. T. S. Wang, Infrared Absorption of the Carbonyl Group of Semicarbazides, Semicarbazones, and Pyrazolecarboxamides, *Appl. Spectrosc.*, **22**, 167 (1968).
25. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, (1997).
26. S. A. Al-Zahrani, V. Jevtovic, K. M. Alenezi, H. El Moll, A. Haque and D. Vidovic, Electrocatalytic hydrogen evolution upon reduction of pyridoxal semicarbazone and thiosemicarbazone-based Cu (II) complexes, *J. Serb. Chem. Soc.* (2021) <https://doi.org/10.2298/JSC210520050A>
27. T. D. Liu, L. Du-Bois and R.M. Bullock, Synthetic Models for the Active Site of the [FeFe]-Hydrogenase: Catalytic Proton Reduction and the Structure of the Doubly Protonated Intermediate, *Nat. Chem.*, **5**, 228 (2013).
28. V. Jevtovic, K. Alenezi, H. El Moll, A. Haque, J. Humaidi, S. Al-Zahrani and D. Vidovic, Pyridoxal (thio) Semicarbazone Ligands and Their Fe(III) Complexes as Potential Electrocatalysts for Hydrogen Evolution Reaction,

- Int. J. Electrochem. Sci.*, **16**, (2021) Article ID: 210731, doi: 10.20964/2021.07.61
29. X. Li, H. Lei, X. Guo, X. Zhao, S. Ding, X. Gao, W. Zhang and R. Cao, Graphene-Supported Pyrene-Modified Cobalt Corrole with Axial Triphenylphosphine for Enhanced Hydrogen Evolution in pH 0–14 Aqueous Solutions, *ChemSusChem*, **10**, 22 (2017).
30. L. Tong, L. Duan, A. Zhou and R. Thummel, First-row transition metal polypyridine complexes that catalyze proton to hydrogen reduction, *Coordination Chemistry Reviews*, **402**, 213070 (2020)
31. B. Beyene and C. Hunga, Recent progress on metalloporphyrin-based hydrogen evolution catalysis, *Coordination Chemistry Reviews*, **410**, 213234 (2020).