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Conformational effects of $[Ni_2(\mu$ -SAr)₂] cores on their electrocatalytic activity

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Abstract: Two nickel complexes supported by tridentate *NS*₂ ligands [Ni₂(κ -*N*,*S*,*S*,*S*'-N^{*Ph*}(CH₂(MeC₆H₂R')S}₂)₂] (R' = 3,5-(CF₃)₂C₆H₃) (1) and [Ni₂(κ -*N*,*S*,*S*,*S*'-N^{*Bu*}(CH₂C₆H₄S}₂)₂] (2) were prepared as bioinspired models of the active site of [NiFe] hydrogenases. The solid-state structure of 1 reveals that the [Ni₂(μ -ArS)₂] core is bent, with the planes of the Ni centers at a hinge angle of 81.3(5)°, while 2 shows a coplanar arrangement between both Ni(II) ions in the dimeric structure. 1 electrocatalyzes proton reduction mcCF₃COOH at – 1.93 V (overpotential of 1.04 V with *i*_{cal}/*i*_p ≈ 21.8) and –1.47 V (overpotential of 580 mV with *i*_{cal}/*i*_p ≈ 5.9) vs Fc^{+/0}. The electrochemical behavior of 1 relative to 2 may be related to the bent [Ni₂(μ -ArS)₂] core that allows proximity of the two Ni···Ni centers at 2.730(8) Å, possibly favoring H⁺ reduction. In contrast, the planar [Ni₂(μ -ArS)₂] core of 2 results in a Ni···Ni distance of 3.364(4) Å, and is unstable in the presence of acid.

Introduction

Important efforts are currently underway to develop artificial systems for efficient hydrogen evolution reaction (HER), either by light- or electric-driven methods.^[1] In nature, some bacteria are provided with extremely efficient metalloenzymes named hydrogenases known to catalyze the reversible interconversion

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of protons and electrons with dihydrogen.^[2] [NiFe]-hydrogenase has interesting structural features in its heterobimetallic active site that include a $\{Ni(\mu-CysS)_2Fe\}$ -butterfly arrangement formed by the bridging cysteinyl ligands and a distorted square-planar geometry about the Ni center; this butterfly conformation leads to Ni…Fe distances from 2.9 to 2.5 Å that can accommodate a bridging hydride when the active site is reduced.^[21] In such systems, it has been observed that nickel is a crucial element that participates in this redox process, as it is believed to be the primary dihydrogen binding site due to its position at the end of the H₂ transfer channel in the enzyme, and its biochemical activity is favored by the sulfur rich environment provided by cysteine residues.^[2] Thus, understanding how these sulfur donors tune the redox potential at the metal center is key for the development of hydrogenase-inspired metal complexes. Considerable attention has been devoted to the development of discrete inorganic models with such electronic and structural features, [3],[4] and several types of chelating ligands featuring sulfur donor atoms have been reported. Nonetheless, the spectrum of tridentate NS2 ligands is composed primarily of thioethers and thioamides, likely due to their ease of preparation.^[5] In the case of multidentate thiolbased scaffolds, those reported to date are generally characterized by limited steric protection, which leads to aggregation and high sensitivity towards air oxidation.^[6] In this context, we have explored synthetic routes that lead to thiophenol-based multidentate ligands featuring bulkv substituents in the ortho-position relative to sulfur, starting from commercial salicylaldehydes (Scheme 1).^[7]

In the present work, we evaluate some of the steric and electronic factors that determine the conformation of $[Ni_2(\mu-ArS)_2]$ -type complexes with aminodithiophenolate ligands, and its relationship with the redox properties of the system. The steric effect evaluated is that of the substituent in the ortho-position of the thiophenolate ring (R¹ in Scheme 1). Furthermore, the electronic influence evaluated is that exerted by the substituent on the Natom of the central amine, by comparing the properties of aromatic vs aliphatic groups (R³ in Scheme 1). We have thus developed suitable ligands for the exploration of the properties of the corresponding earth-abundant metal complexes as hydrogen evolution electrocatalysts.^[8] With these considerations, we herein report the synthesis and characterization of Ni(II) complexes with the novel dianionic $(NS_2)^{2-}$ polytopic ligands obtained from L_n^{Stioc} (n = 1 o 2) precursors (Scheme 1), all of which provide geometric flexibility due to the methylene connectors between the central amine and the thiophenolate groups.





Scheme 2. Synthetic strategy for bis(S-arylthiocarbamate)amine ligand precursors from building group *o*-formyl-S-arylthiocarbamates: *i*) NaHB(OAc)₃, thf, 6 d, 60°C, *ii*) SOCl₂, CH₂Cl₂ r.t., 8 h, *iii*) primary amine (aniline or isobutylamine), K₂CO₃, Nal, thf, 8 d, 60°C.



Scheme 1. Synthesis of Ni(II) complex with (NS₂)²- ligands: i) MeONa, thf, 6 d, 65°C; ii) NiCl₂·6H₂O, r.t., overnight.

Results and Discussion

Synthetic procedures

To access $(NS_2)^{2^-}$ ligands, their preparation involves a Newman-Kwart thermal rearrangement (NKR) as the key step to obtain *o*formyl-S-arylthiocarbamates from the corresponding *O*arylthiocarbamates using *N*-methylpyrrolidinone (NMP) as solvent.^[7b] Treatment of the products through the route outlined in Scheme 1 produces the building blocks 2-chloromethyl-*S*arylthiocarbamates c for the subsequent reaction with one equiv. of aniline or isobutylamine (Scheme 1, see full characterization in Figures S1-S8),^[7] affording the bis(*S*-aryltiocarbamate) amine ligand precursors L₁^{Stioc} and L₂^{Stioc} in 83% and 81% yields, respectively (see Figures S9-S20 for spectroscopic data).

Synthesis of complexes

Preparation of the nickel complexes derived from L_1^{Stioc} and L_2^{Stioc} namely $[Ni_2(\kappa-N,S,S,S'-N^{Ph}\{CH_2(MeC_6H_2R')_s\}_2)_2]$ (R' = 3,5-

 $CF_{3}_{2}C_{6}H_{3}$ (1) and $[Ni_{2}(\kappa-N,S,S,S'-N^{iBu}\{CH_{2}C_{6}H_{4}S\}_{2})_{2}]$ **(2**), followed the same protocols; in both cases, treatment of $\mathsf{L}_n^{\text{Stioc}}$ with sodium methoxide (4 equiv.) in tetrahydrofuran (thf) under an inert atmosphere was required (Scheme 2). Complete deprotection of L_n^{Stioc} was determined by monitoring the disappearance of the peak arising from the carbamate group at m/z 72 by Electron Impact Mass Spectrometry (EI MS, Figure S16). After this time, slow addition of solid NiCl₂·6H₂O to a thf suspension of the in situ generated bis(thiophenolate)amines immediately change the color of the solution from yellow to brown and dark red, indicating the formation of the corresponding Ni(II) complexes 1 and 2, respectively (Scheme 2). Removal of sodium chloride and insoluble byproducts by filtration, followed by crystallization from saturated CHCl₃/CH₃CN solutions, afforded the analytically pure complexes.

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Characterization of 1. Complex 1 was isolated as a black crystalline material in 45% yield by crystallization from a 9:1 CHCl₃/CH₃CN mixture. 1 was formulated as a dimeric species based on Fast Atom Bombardment Mass Spectrometry measurements (FAB MS, Figure S21), with the molecular ion [M]⁺ giving rise to a peak at *m*/*z* 1692; the assignment was further confirmed through NMR spectroscopy, and structural determination by X-ray diffraction (XRD). The ¹H NMR spectrum and additional characterization allowed to establish the identity of 1 (Figures S22-25). This complex is stable under air and moisture both in the solid state, and in CH₂Cl₂, CHCl₃, ethyl acetate, or diethyl ether solutions.

Characterization of 2. The reaction of in situ generated aminodithiolate ligand derived from L2^{Stioc} (see FAB MS in Figure S26) and NiCl₂·6H₂O afforded the analytically pure red microcrystalline complex 2 in 52% yield. This complex is an air stable species that is insoluble in most common organic solvents, including hot DMF, toluene, or DMSO, so that informative NMR spectra could not be recorded. The infrared spectroscopic analysis allowed us to confirm the presence of the ligand through the characteristic stretches of the organic fragment in the complex, (such as aromatic C-H stretch 3051 and 3008 cm⁻¹, Figure S27). Combustion and XRD analysis confirmed that 2 is a dimer of the form [Ni₂(κ-N, S, S, S'-N^{iBu}{CH₂C₆H₄S}₂)2]. Additionally, indirect characterization of 2 by derivatization to a more soluble species was envisioned. Thus, suspensions of 2 in CH₂Cl₂ were treated with 2-naphthylisocyanide, which resulted in the dark green product 3 (Scheme 3); this new complex is soluble in common organic solvents except for hexane or toluene, and is also air

stable for extended periods of time in the solid state and in CHCl₃, CH₂Cl₂, ethyl acetate and diethyl ether solutions. **3**, which was formulated as C₂₉H₂₈N₂NiS₂ by combustion analysis, was obtained in 67% yield and characterized by ¹H and ¹³C{¹H} NMR, IR, FAB MS (Figures S28-S32) and XRD (Figure S33), all this corresponding to the formation of the monomeric complex [Ni(κ -N,S,S'-N^{iBu}{CH₂C₆H₄S}₂)(C=NC₁₀H₇)] (**3**) with a 1:1 metal/ligand stoichiometry.



Scheme 3. Reaction of 2 with 2-naphthylisocyanide: *i*) 2-naphthylisocyanide, CH₂Cl₂, r.t., overnight.

Solid-state structures

Slow evaporation of a solution of **1** in CHCl₃/CH₃CN (9:1) yielded black single crystals, red crystals of **2** were obtained by slow cooling of a hot CHCl₃ solution (70°C) in a sealed vial, while slow evaporation of CH₂Cl₂/MeOH (1:1) solution of complex **3** leads to formation of dark green microcrystals. All of the above crystals were suitable for structural elucidation by XRD (Figures 1, S33,



Figure 1. Top: Mercury diagrams of 1 and 2 at the 50 % probability level showing the coordination environments defined by the N and S donors around the Ni(II) ions; H and minor-occupancy atoms are omitted for clarity; colour code: C, grey; F, lime; S, yellow; N, blue; Ni, green. Bottom: hinge angles of 1 and 2.

Tables S1 and S2). Both complexes 1 and 2 crystallize in the monoclinic space group P21/c (Table 1 lists selected bond distances and angles). In the dimeric structures, each Ni center is tetracoordinated by the tridentate ligand via the N-atom of the central amine and the thiophenolate sulfur donors; the coordination environment of the Ni(II) ions is completed by a bridging sulfur donor of a second monomeric unit, resulting in the observed dinuclear structure (Figure 1). For each Ni center in 1 the average S-Ni-S_{bridge} trans angle is 164.82(5)°, whereas the corresponding N-Ni-S_{bridge} angle is $171.31(11)^{\circ}$; for 2 the corresponding angles are 168.04(3)° and 171.13(5)° respectively. Thus, the coordination geometry of Ni(II) in compounds 1 and 2 can be described as distorted square planar. Those planes around the Ni centers in 1, defined by N1, S1, S2, and S4 (N1, S1, S2, and S1_{bridge} for 2) are joined along one edge by means of S1 and S2 (S1 and S1_{bridge} for **2**, see Table 1 and Figure 1); therefore, for both complexes each monomeric unit has a terminal thiophenolate ligand that may be considered electron-rich (S4 and S3 atoms for 1 and S2 for 2 in Figure 1).^[9] Additionally, the two coordination planes around the Ni centers in 1 define a dihedral angle (θ) of 81.3(5)° (hinge angle) leading to a Ni…Ni distance of 2.7295(8) Å, comparable with previously reported [Ni₂(κ -N.S.S.S'- N^{iBu} {CH₂(MeC₆H₂R')S}₂] (R' = 3,5-(CF₃)₂C₆H₃, **4**, with Ni···Ni distance of 2.702(8) Å, and $(\theta) = 85.5(4)^{\circ}$).^[7c] On the other hand, in **2** the hinge angle is θ = 180(2)° (Table 1 and Figure 1), resulting in a coplanar arrangement with considerably longer Ni…Ni distance of 3.364(4) Å.

Table 1.	Selected bond	distances (Å) and	angles (°	°) for 1 and 2	
					1	

Bonds	1	Bonds	2
Ni1…Ni2	2.7295(8)	Ni1…Ni1*	3.364(4)
Ni1-S1	2.2251(1)	Ni1-S1	2.2136(6)
Ni1-S4	2.1803(1)	Ni1-S2	2.1697(6)
Ni1-S2	2.2062(1)	Ni1-S1*	2.1969(5)
Ni1-N1	1.997(4)	Ni1-N1	1.9928(2)
S1-Ni1-S4	164.82(5)	S1-Ni1-S2	168.04(3)
N1-Ni1-S2	171.31(11)	N1-Ni1-S1*	171.13(5)
N1-Ni1-S1	96.63(1)	N1-Ni1-S1	95.53(5)
N1-Ni1-S4	97.96(1)	N1-Ni1-S2	96.43(5)
S4-Ni1-S2	90.48(5)	S2-Ni1- S1*	87.54(2)
S2-Ni1-S1	74.80(5)	S1*-Ni1-S1	80.57(2)
Ni1-S1-Ni2	76.12(4)	Ni1-S1-Ni1*	99.43(2)

Structural analysis of these dimers reveals a bent-endo **1** and planar-anti **2** conformations of the [Ni₂(μ -ArS)₂] frameworks. In this context, Aullón and co-workers have reported that in molecules with a strongly bent ($\theta < 150^{\circ}$) [L₂M(μ -SR)₂ML₂] fragment, the shorter Ni…Ni distances observed reflect a high degree of intermetallic overlap between 3dz²-4pz orbitals of each

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nickel ion.^[10a] This may stabilize these conformations relative to the coplanar ones, where such overlap is much less effective, resulting in no possibility for a cooperative effect of electron delocalization between the two metal centers. To establish the factors that determine whether the structure will be bent or coplanar, the influence of the terminal and bridging ligands on the Ni…Ni interactions in the bent molecules can be analyzed. Thus, ligands capable of accepting metal charge transfer on their π^* orbitals (π -acidic ligands) tend to strengthen the Ni \cdots Ni interaction, while π -basic ligands tend to weaken it.^[10a] In both 1 and 2, the same type of bridging and terminal donor atoms are present (except for the N-phenyl or N-isobutyl substituents), but the main difference is a steric one: the choice of bulky 3,5-(CF₃)₂C₆H₃ substituents at the thiophenolate moieties and steric repulsion between these terminal ligands at the two metal atoms may be the governing factor for the large degree of bending observed, highlighting the importance of the substituents in the orthoposition relative to the sulfur donor to stabilize a particular conformation.^[10]

Optical Spectroscopy

The electronic absorption spectrum of **1** (Figure 2, blue trace) in CH₂Cl₂ solution exhibits intense bands at 360 (2.66 x 10⁴ M⁻¹cm⁻ ¹) and 443 nm (9.18 x 10³ M⁻¹cm⁻¹), assigned as LMCT bands according to previous reports.^{[1g],[11],[12]} The other bands observed for 1 were assigned to an intraligand transition at 289 nm (shoulder, 2.92 x 10^4 M⁻¹cm⁻¹, L \rightarrow L), and a S_{bridge} \rightarrow Ni transition at 533 nm (3.09 x 10^3 M⁻¹ cm⁻¹). On the other hand, for 2 all electronic transitions are shifted to higher energies (Figure 2, red trace). The absorption maxima were observed at 263 nm (3.45 x $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) for L \rightarrow L transitions, together with LMCT at 301 nm $(3.90 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}, \text{ S}\sigma \rightarrow \text{Ni}), 369 \text{ nm} (1.48 \times 10^4 \text{ M}^{-1}\text{cm}^{-1},$ $S\pi \rightarrow Ni$) and 416 nm (shoulder, 1.05 x 10⁴ M⁻¹ cm⁻¹, $S_{bridge} \rightarrow Ni$). Finally, the monomeric complex 3 featuring a naphthylisocyanide ligand, ^[13] displays only the L \rightarrow L transition at 235 nm (6.4 x 10⁴ $M^{-1}cm^{-1}$), and a $S\sigma \rightarrow Ni$ transition at 313 nm (3.90 x 10⁴ $M^{-1}cm^{-1}$) without evidence of a $S_{\text{bridge}} {\rightarrow} Ni$ band, as expected (Figure 2, green trace).



Figure 2. UV-vis spectrum of 1 (blue trace), 2 (red trace), and 3 (green trace) in CH_2Cl_2 solution ca. 0.04 mM.

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Electrochemical Studies

Electrochemical analysis for complexes **1**, **2**, and **3** in 0.1 M NBu₄PF₆/CH₂Cl₂ was performed under a N₂ atmosphere. Cyclic voltammograms of **1** [1 mM] are characterized by a reversible redox couple attributed to reduction processes of one of the two nickel centers, Ni₂^{(II,II)/(II,I)} at $E_{1/2}$ = -1.65 V versus the ferrocenium/ferrocene couple (Fc^{+/0}) as internal standard (scan rate 100 mV s⁻¹, ΔE_p = 100 mV, see Figure 3, blue trace). This peak separation is comparable to the maximum separation observed for the Fc^{+/0} couple under the same conditions (Figure S34).^[14a]



Figure 3. Cathodic CV of complexes 1 (blue trace), 2 (red trace), and 3 (green trace) at a scan rate of 100 mV s⁻¹ (1 mM in 0.1 M Bu₄NPF₆-CH₂Cl₂, glassy carbon electrode).

Surprisingly, neither the substituent on the nitrogen atom of the central amine (compare CVs of 1 with related systems 4),^[7c] nor the conformation of the $[Ni_2(\mu-ArS)_2]$ framework seem to have an effect on the potentials values for the cathodic processes. Thus, for the previously reported complex 4,[7c] the Ni2(II,II)/(II,I) redox couple was determined at $E_{1/2}$ = -1.65 V versus Fc^{+/0}, for 2 the same process is characterized by a reversible redox couple at $E_{1/2}$ = -1.67 V ($\Delta E_{\rm p}$ = 118 mV, Figure 3, red trace), while an irreversible wave at -1.75 V is observed for monomeric complex 3 (Figure 3, green trace). When the scanning direction is reversed, 1 reveals two reversible redox processes; the first one is assigned to $Ni_2^{(II,II)/(II,III)}$ at $E_{1/2} = 0.32$ V vs Fc^{+/0}, (Figure 3 blue trace and Figure S35), a feature that is analogous to that observed for the isobutylamine-based analogue 4, but 150 mV less positive.[7c] The second redox process, attributed to Ni2(III,III)/(III,III), is observed at E1/2 = 0.91 V (ΔE_p = 100 mV, Figure 3, blue trace). In contrast, the planar **2** revealed irreversible processes at E_{1a} = 0.20, and E_{2a} = 0.90 V (the anodic CV and inversion potentials allowed us to assign the reduction of these species, Figures S36 and S37). One possible explanation for this difference is that in the anodic processes, the Ni2^{(II,II)/(II,III)} couple could be stabilized by Ni(d⁷)-Ni(d⁸) electronic delocalization, which is favored in bent molecules (see DFT studies below). In this context, the oxidations at 0.20 and 0.90 V in 2 correspond to an electron transfer followed by a chemical reaction EiCi.[14],[15] Thus, fast conversion from the electrochemically generated Ni(III) complex to an oxidation product Z may occur. In contrast, oxidation of **3** is most likely a ligand-centered redox process (Figure 3, green trace).^[14b, c]

Electrocatalytic dihydrogen generation

The most common method to evaluate the catalytic activity of artificial hydrogenases is through cyclic voltammetry in the presence of increasing concentration of a proton source.^[15] Previous studies have evaluated the activity of this type of catalysts using acids of varying strength: perchloric,[16a] tetrafluoroboric,^[16b] p-toluenesulfonic,^[16c] acetic,[16d] and trifluoroacetic (TFA) acids.[16e] The catalytic activity is thus gauged by changes in the reduction peak (i_{cat}) in the presence of acids, with the best catalysts producing a larger increase in current.^[15] Figure 4 shows the CV of 1 after successive additions of TFA. Noticeably, the catalytic wave does not grow directly at the same potential as the reversible couple for Ni₂(II,II)/(II,I) but is observed at $E_{cat/2}$ = -1.93 V, a value that is displaced cathodically by 280 mV relative to the reversible couple; this behavior has been observed in the presence of strong acids.^{[1g],[17]} In addition, at concentrations greater than 4.0 mM of TFA, a new wave at $E_{cat/2} = -1.47$ V emerges: this suggests that an intermediate that can be reduced more easily than 1 may be formed.^[1g] A protonated species proposed as 1-H. from protonation at the electron-rich terminal sulfur, arising in a CE mechanism (with C corresponding to a chemical step, in this case protonation, follow by E representing an electron transfer process) in which the reduction of the protonated species 1-H occurs at a less cathodic potential than the direct reduction of 1 (see Figure 9 and DFT studies below). Although this proposal is tentative until more evidence can be obtained to support this mechanism, it seems a reasonable hypothesis to explain the dependence of HER processes on the nature of the acid. Additionally, following the method of Barton and Rauchfuss,^[17d] overpotential (η) values for **1** were determined at 1.04 V (-1.93) and 580 mV (- 1.47 vs. Fc^{+/0}, see Figure 5 for indication of $E_{cat/2}$ and the overpotential).



Figure 4. CVs of **1** in CH₂Cl₂ with increasing trifluoroacetic acid [TFA]. Experimental conditions: 1.0 mM **1** with 0.1 M NBu₄PF₆ collected at scan rate of 0.1 V s⁻¹ with 0.0, 0.1, 0.5, 1.0, 2.0, 4.0, 8.0, 12.0, 20.0 and 30.0 mM (bottom) TFA concentrations; Fc as internal standard. Inset: i_{car}/i_p dependence with increasing [TFA] at 100 mVs⁻¹ near to cathodic processes at -1.93 V (purple triangles) and -1.47 V (blue squares).



Figure 5 Experimental CVs for proton reduction. $E_{cat/2}$ denotes the half-peak potential of the catalytic wave. Conditions: 1 mM 1 in a 0.1 M NBu₄PF₆ solution in CH₂Cl₂, 100 mV s⁻¹ scan rate, glassy carbon electrode. The red trace was run in the absence of acid, then blue trace with 30 mM TFA.

In contrast, successive additions of TFA during electrochemical experiments to solutions of 2 resulted in the appearance of several reduction waves with different current responses, as shown in Figure 6. Only a very small current increase is observed at -1.67 V (η = 780 mV) related to the Ni₂^{(II,II)/(II,I)} redox couple, a process attributed to the direct reduction of 2 at lower TFA concentrations. However, significant current enhancement is observed at -1.53 V (η = 640 mV) and -1.08 V (η = 190 mV) upon increasing the amount TFA. These irreversible processes are associated with ligand protonation in different binding sites and subsequent dissociation (see Figure 10 and DFT studies below). Thus, while 1 shows chemical stability under these conditions (Figures S38 and S39), complexes 2 and 3 (Figures. S40 and S41) appear to be degraded at concentrations above 8 mM TFA, since fast extinction of the S→Ni charge transfer bands is evident as the concentration of TFA is increased. The choice of acid is related to its reduction potential at the glassy carbon (GC) electrode, since a larger potential window where TFA is not reduced is available compared with other acids. This leads to proton reduction catalyzed by the complex, and not directly at the electrode surface. [16e] This was experimentally verified by measuring the CV of TFA in supporting electrolyte solution, effectively demonstrating that in the working potential window for the nickel complexes there are no redox processes at the glassy carbon electrode (Figure S42). On the other hand, the catalytic current obtained with TFA as the proton source is higher when compared with trichloroacetic (TCA) and acetic (HOAc) acids, indicating that the catalytic reaction depends on the nature of the acid (Figures S43 and S44), a characteristic that reinforces the proposed CE mechanism. [17b]





Figure 6 CVs of **2** in CH₂Cl₂ with increasing [TFA]. Experimental conditions: 1.0 mM 1 with 0.1 M NBu₄PF₆ collected at scan rate of 0.1 V s⁻¹ with 0.0, 0.1, 0.2, 0.4, 0.8, 1.6, 2.4, 3.2, 4.0, 5.0, 6.0, 7.0 and 8.0 mM (bottom) TFA concentrations; Fc as internal standard. Inset: i_{cal}/i_p dependence with increasing [TFA] at 100 mV s⁻¹ near to cathodic process at -1.67 V.

Kinetic Studies

Analysis of the three redox processes observed for 1 (Figure 3, S45 and S46), and 2 (the process centered at $E_{1/2}$ = -1.67 V in Figure 3, red trace and S47) at different scan rates determined that the electrochemically reversible electron transfer processes involve freely diffusing species. [18] Kinetic studies have been carried out for HER catalyzed by 1, directly from CVs by comparing the ratio of catalytic current in the presence of TFA (i_{cat}) to the peak current for the reduction of 1 in the absence of acid (i_p) , with the linear relationship between i_{cat}/i_p and [TFA] indicating a second-order dependence on proton concentration (see eq. 1 and Figure 4).^[20] Although eq. 1 is typically applicable to catalysts that employ simple first-order E_rC_i (Reversible electron transfer followed by an irreversible chemical reaction) mechanisms, there are several reports in which it has been used in the analysis of more complex systems for comparative purposes.^{[1g],[17]} Therefore, linear plots of (i_{cat}/i_p) vs [TFA] are observed in a wide range of TFA concentrations (0.1 to 30 mM) and for scan rates between 0.10 and 0.30 V s⁻¹ for 1 (Figure S48). By contrast, in the case of 2, decomposition of the catalyst occurs at a lower acid concentration, leading to deviation from linearity (Figure 6 inset).

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \left(\frac{RTk[H^+]^2}{Fv}\right)^{1/2} (1)$$

On the other hand, at higher concentrations of TFA, the ratio i_{cal}/i_p tends to plateau at a maximum value. Since the current reaches saturation at high concentrations of TFA, in **1** the maximum value of i_{cal}/i_p was found at 21.8 (at -1.93 V). Thus, using the relation in eq. 1, a value of k_{obs} (TOF) = 45.6 s⁻¹ can be derived. For **2** degradation occurs at lower acid concentrations (Figure 6); this is

true for all the scan speeds at which the study was conducted, so that TOF and i_{cat}/i_p values cannot be extracted due to the unknown nature of the active species under these conditions. This contrasts with the observations for 1, where the metal is supported by an auxiliary ligand with bulky substituents ortho to sulfur that confer steric protection and a bent conformation to the bimetallic complex. Therefore, the poor catalytic behavior of 2 compared to that of 1 can be related to its planar conformation and instability in acidic medium, both features attributed to the lack of steric hindrance in L_2^{Stioc} . Thus, **1** is active with $i_{cat}/i_p = 21.8$ in CH₂Cl₂, which is among the highest values reported for these types of systems, ranging from $i_{cat}/i_p = 7.8$,^[19a] through $i_{cat}/i_p = 4.0$,^[21b] to i_{cat}/i_p = 2.0.^[21] Nonetheless, this value corresponds to a modest TOF of 45.6 s⁻¹ at a TFA concentration of 30 mM, which is compatible with a 1.0 mM catalyst concentration in terms of stability.

Computational Studies

The electronic properties of dimeric complexes 1, 2, and monomeric 3 were analyzed computationally by density functional theory (DFT). Complex 2B was also considered, corresponding to optimization of 2 with a bent geometry between the two Ni coordination planes: all attempts to achieve a planar geometry for 1 failed. Figure 7 shows the optimized geometries of dimeric 1 (a), 2 (b), the hypothetical 2B (c) and monomeric 3 (d). For 2B the energy calculated with an angle of 102° between the coordination planes is 2.3 kcal mol⁻¹ higher than that of planar 2. The small energetic difference allows us to postulate the possibility of interconversion of planar and bent conformations in solution. Moreover, the predicted geometry of 2B agrees with a previous report by Alvarez et al., [10b] where the ligands generate six membered rings that can favor the Ni coordination planes to adopt an endo conformation. Square planar geometry was observed around the metals centers, with a Ni…Ni distance calculated at 3.45 Å for 2, in contrast with the weak metal-metal interaction that may be present in bent 1 and 2B, characterized by distances of 2.90 Å.^[20] This configuration may be aided by H-bonds from the N-Ph moiety to the CF₃ groups at C-H. F distances of 2.602 and 2.739 Å at 119.9° and 130.3° respectively.



Figure 7 DFT-optimized structures of dimeric complexes 1 (a), 2 (b), hypothetical 2B (c), and monomeric 3 (d). H-atoms are omitted for clarity.

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Electronic population analysis provides valuable information about the electronic structure of the complexes: the low charges calculated for the atoms in the $[Ni_2(\mu-ArS)_2]$ core shows a higher degree of covalency in these Ni-S bonds than for those involved in the terminal Ni-S interactions, see Table S4. Negligible charge changes are calculated for the N-aromatic vs N-aliphatic substituents, despite the difference of 150 mV in the electrochemical properties observed for 1 vs 4. However, the different Ni-N distances obtained, larger for N-Ar than for N-/Bu, suggests inferior donor ability of the N-atom in the aniline-based 1, destabilizing the oxidized Ni(III) complex. A time-dependent DFT study was performed to calculate the electronic transitions of the complexes in dichloromethane solution, see Figures S49 and S50. In most cases the spectra are dominated by intense bands between 250 nm and 450 nm. Complex 1 shows a strong electronic transition at 357 nm that is mainly attributed to S→Ni ligand-to-metal charge transfer (LMCT); according to the experimental results and previous reports at 446 nm a LMCT band is observed. ^{[1g], [11]} For 2, three main bands were calculated at 274, 316, and 407 nm assigned to $S \rightarrow L$, and $S \rightarrow Ni$ transitions. For the bent analogue **2B**, the corresponding $S \rightarrow L$ and $S \rightarrow Ni$ transitions were calculated at 264 and 368 nm. The similar shape of the UV-vis bands observed for the coplanar 2, and for the folded **2B** may be rationalized by the vibrational modes allowed by the geometry of the compounds, which have small energetic differences and may interconvert in solution. Only one Ar→Ar* (Ar* = antibonding orbital in the aromatic group) excitation is predicted for 3 at 268 nm. These results agree with the experimental data, where the general observation are high intensity electronic absorptions (typical for charge transfer transitions), with relatively low energies that reflect good orbital overlap between the sulfur donors and the Ni(II) ions, while also attesting to the high degree of covalency of the Ni-S bonds. In addition, it is confirmed that the conformations of the $[Ni_2(\mu-ArS)_2]$ frameworks significantly affect the electronic structure of the complexes, leading to high intensity and low energy S→Ni charge transfer transitions for the bent complexes relative to the planar ones, presumably because the interaction of the nickel centers in bent complexes leads to greater orbital delocalization.

Figure 8 shows the HOMO and LUMO orbitals for the calculated Ni(II) complexes. The ligand- *vs* metal-centered redox processes can be analyzed from the calculated frontier molecular orbitals of the complexes and specifically for the highest-occupied molecular orbital (HOMO), which presumably loses an electron upon oxidation. Likewise, the LUMO level must be involved during reduction. For complex **3**, the LUMO is predicted to be too high in energy to allow a reversible reduction process, as determined experimentally. The energetic proximity of the orbitals close to HOMO (HOMO-2 at ca. -0.220 a.u.) in complexes **1** and **2**, with contributions of more than 62% of Ni atom could be the involved in the generation of the proposed Ni(III) species generated electrochemically.

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Figure 8 Simplified diagrams of the frontier HOMO and LUMO of the Ni(II) complexes 1, 2, 2B, and 3.

Finally, in an effort to explain the electrocatalytic results and the different chemical stabilities between 1 and 2, DFT calculations were performed to explore the possible protonation step prior to electrochemical H₂ formation process. Calculations indicate that the terminal sulfur in 1 (see β -sulfur in Figure 9) is the energetically favorable site for protonation in the gas phase and in CH₂Cl₂ as Polarization Continuum Model (PCM), whereas for α -S and γ -N the relatively high barriers of 17.0 and 16.0 kcal mol⁻ ¹ respectively, render the protonation at such positions less likely. Additionally, the Ni-Ni distance is not affected during β -sulfur protonation and 1 does not undergo major structural changes. On the other hand, two possible protonation sites are energetically accessible for 2: at the terminal sulfur atom (see β -sulfur in Figure 10), where no significant structural changes are observed. The second possibility is at the tertiary amine (*p*-nitrogen in Figure 10), where drastic geometric changes occur, including the loss of the Ni-N bond upon protonation.







Figure 9 Calculated protonation free energies of **1**. The values in red correspond to the free energy difference between the most stable protonation site and the other two options in the gas phase; blue values correspond to the free energy change estimated in dichloromethane as PCM.



Figure 10 Calculated protonation free energies of 2. The values in red correspond to the free energy difference between the most stable protonation site and the other two in the gas phase; blue values correspond to the free energy change estimated in dichloromethane as PCM.

Conclusions

Among the three nickel complexes with sulfur-rich environments reported herein, the dimeric complex $[Ni_2(\kappa-N,S,S,S'-N^{Ph}CH_2(MeC_6H_2R')S]_2]_1$ was found to be active for electrocatalytic proton reduction; in contrast, the related $[Ni_2(\kappa-N,S,S,S'-N^{iBu}\{CH_2C_6H_4S\}_2)_2]_2$ shows poor stability under catalytic conditions. 1 reduces protons at $E_{cat/2} = -1.93$ V (vs Fc^{+/0}) with $i_{cat}/i_p = 21.8$ and at $E_{cat/2} = -1.47$ V with $i_{cat}/i_p = 5.9$, making it a better catalyst than 2, which undergoes degradation at low acid concentrations. The good activity of 1 is likely a result of the bulky nature of the ligand due to the presence of the bis(trifluromethyl)aromatic substituent group ortho to the S-atom, which not only protects the metal centers in $[Ni_2(\mu-ArS)_2]$, but also provides a hinge angle that allows the nickel ions to approach and stabilize the different oxidation states necessary for HER. In contrast, the poor catalytic activity of 2 can be attributed to the

negligible steric protection provided by the ligand, and to the planar conformation of the $[Ni_2(\mu -ArS)_2]$ core. In both cases, a significant degree of covalency of the Ni-S bonds is predicted by DFT calculations. The theoretical studies also establish that the proximity of the Ni(II) ions in the bent complexes (1, the calculated **2B**, and the previously reported **4**) favor a weak interaction between the metal centers, which appears to be crucial for electrocatalytic proton reduction.

Experimental Section

General remarks

Unless otherwise indicated, all manipulations were carried out without taking precautions to exclude air and moisture. Specific synthetic operations were performed under a dry dinitrogen atmosphere by Schlenk techniques. Et₂O, thf, and dimethoxyethane (DME) were obtained oxygenand moisture free by distilling from sodium benzophenone under N_2 . MeOH was obtained free of oxygen and moisture by distillation on sodium and under N_2 atmosphere using standard Schlenk techniques. N-methyl-2-pyrrolidone (NMP) was distilled at reduced pressure and used immediately. All chemicals and solvents were used as received without further purification unless mentioned otherwise. Unsubstituted O- and S-(2-formylphenyl)-N,N-dimethylthiocarbamates (a, R¹ = H, R² =H) are easily accessible from the corresponding phenol. [21] The synthesis of the precursors 2.4- disubstituted N.N-dimethylthiocarbamates (a, $R^1 = C_6H_4$ -(CF₃)₂, R² = CH₃) has been reported in previous work. ^[7d] ¹H (400 MHz) and ¹³C{¹H} (100 MHz) NMR spectra were recorded on a Bruker 400 MHz Ultrashield[™] NMR spectrometer using the residual protiated solvent signal or tetramethylsilane (TMS) as internal references (TMS δ = 0.00, CHCl₃ δ = 7.26 ppm) at room temperature; subsequently they were processed through the MestReNova software of Mestrelab Research. Electron Impact mass spectrometry (EI MS) experiments were performed a Shimadzu GCMS-QP2010 spectrometer. Positive ion FAB⁺ MS were acquired with a JEOL JMS-SX-102A mass spectrometer operated at an accelerating voltage of 10 kV from a nitrobenzyl alcohol matrix by using xenon atoms at 6 keV.

X-ray crystallography

Suitable single crystals of 1-3 mounted on a glass fiber were studied with Oxford Diffraction Gemini "A" diffractometer with a CCD area detector $(\lambda_{Mox\alpha} = 0.71073 \text{ Å}, \text{ monochromator: graphite})$ source equipped with a sealed tube X-ray source at 130 K. Unit cell constants were determined with a set of 15/3 narrow frame/runs with 1° in ω scans. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans ^[22] were used for data collection and data integration. Analysis of the integrated data did not reveal any decay. Final cell constants were determined by a global refinement of 6758 for 1, 4150 for 2 and 2956 reflections for 3 with $4.0390 < \theta < 29.6612^{\circ}$. Collected data were corrected for absorbance by using analytical numeric absorption correction ^[23] Structure solution and refinement were carried out with the SHELXS-2014 ^[24] and SHELXL-2014 ^[25]; wingx v2014.1 ^[26] and Mercury CSD 4.1.0 software [27] was used to prepare material for publication. Full-matrix leastsquares refinement was carried out by minimizing (Fo2-Fc2)2. All nonhydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C-H = 0.95- 1.0 Å and with Uiso(H) = 1.2Ueq(C) for aromatic, methine and methylene groups and Uiso(H) = 1.5Ueq(C) for methyl groups. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary material number CCDC 1862077 (1), 1862079 (2), 1862078 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail:deposit@ccdc.cam.ac.uk.

Computational details

Unrestricted calculations were carried out using the Gaussian09 package.^[28] The hybrid density functional method known as B3LYP was applied.^[29] Effective core potentials (ECP) were used to represent the innermost electrons of the transition atoms and the basis set of valence double- ζ quality for associated with the pseudopotentials known as LANL2DZ.^[30] The basis set for the light elements as S, C, N, and H was 6-31G*.^[31] Energies in solution were taken into account by PCM calculations (dichloromethane, ϵ = 8.93), ^[32] keeping the geometry optimized for gas phase (single-point calculations).

Electrochemical details

Cyclic voltammetry measurements were made under N₂ in anhydrous CH₂Cl₂ with a potentiostat–galvanostat, CH Instruments 600E, with a glassy carbon working electrode and a platinum wire auxiliary electrode. Potentials were recorded versus a pseudo-reference electrode of AgBr(s)/Ag(wire) immersed in a 0.1 M NBu₄Br CH₂Cl₂ solution. All voltammograms were started from open circuit potential (OCP) and were scanned in both directions, positive and negative, and obtained at a scan rate from 0.050 to 0.400 V s⁻¹. In agreement with IUPAC convention, the voltammogram of the ferrocenium–ferrocene (Fc^{+/0}) system was obtained to establish the values of half wave potentials (*E*_{1/2}) from the expression *E*_{1/2} = (*E*_a + *E*_c)/2.

Synthesis of ligands precursors

S-2-(Hydroxymethyl)phenyl-N,N-dimethylthiocarbamate

Unsubstituted salicylaldehyde ($R^1 = H, R^2 = H$ in scheme 1), (1.24 g, 5.93 mmol) was dissolved in dry thf (50 mL) under nitrogen at room temperature. NaBH(OAc)₃ (3.77, 17.79 mmol) was added to the stirring solution, generating a white suspension; this mixture was refluxed for 24 hours. After this time, the resulting suspension was cooling down to room temperature, so disappearance of starting material was confirmed by thin layer chromatography (hexane/EtOAc 9:1) together with conversion to one major product. The solution was evaporated to dryness under reduced pressure, and the resulting white solid residue was collected by filtration and dissolved in CHCl₃ (25 mL). The organic layer was washed with water (3 x 15 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The product was purified by column chromatography (SiO₂ 70:230, hexane:EtOAc 8:2 to 60:40). Light yellow oil 1.02 g, (81%). Rf = 0.12 in 70:30 hexane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃, r. t.): δ 7.63 (d, 1H, J = 7.6, Hz, Ar), 7.53 (d, 1H, J = 7.6 Hz, Ar), 7.49 (t, 1H, J = 7.6 Hz, Ar), 7.33 (t, 1H, J = 7.6, Ar), 4.69 (s, 2H, Ar-CH₂-OH), 3.25 (br, 1H, ArCH₂-OH), 3.11 (s, 3H, ArS(CO)N(CH₃)₂), 3.03 (s, 3H, ArS(CO)N(CH₃)₂) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃, room temperature): δ 168.02 (1C), 145.46 (1C, Ar), 137.09 (1C, Ar), 130.76 (1C, Ar), 130.51 (1C, Ar), 128.44 (1C, Ar), 127.25 (1C, Ar), 64.23 (1C), 37.22 (2C) ppm. *m/z* (rel. Int.): 212 (30) [M⁺]. IR (ATR, cm⁻¹): 3404 (v_{C-OH}), 1256 (v_{C-O}). Anal. Calcd (%) for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.17. Found: C, 56.54; H, 6.11; N, 6.35; S, 14.05.

S-2-(Chloromethyl)phenyl-N,N-dimethylthiocarbamate (c). To a solution of S-2-(hydroxymethyl)phenyl-N,N dimethylthiocarbamate (b) (2.12 g, 10.02 mmol) in 60 mL of CH₂Cl₂, 2.19 mL of thionyl chloride was added. The resulting Light-yellow solution was stirred at room temperature for 5 h. after this time volatile materials were evaporated under vacuum.

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(b).

The resulting yellow solid residue was collected by filtration and dissolved in CHCl₃ (30 mL). The organic layer was washed with water (3 x 20 mL), dried with Na₂SO₄ and concentrated under reduced pressure. The product was purified by recrystallization (toluene/CHCl₃ 8:2). Colorless crystals 1.94 g, (84%). R_f = 0.45 in 71:29 hexane/ethyl acetate. melting point: 85-87°C. ¹H NMR (400 MHz, CDCl₃, r. t.): δ 7.60 (*dd*, 1H, *J* = 7.7, 1.5 Hz, Ar), 7.58 (*dd*, 1H, *J* = 7.7, 1.4 Hz, Ar), 7.47 (*td*, 1H, *J* = 7.5, 1.5 Hz, Ar), 7.38 (*td*, 1H, *J* = 7.6, 1.6 Hz, Ar), 4.80 (s, 2H, Ar-CH₂-Cl), 3.18 (s, 3H, ArS(CO)N(CH₃)₂), 3.05 (s, 3H, ArS(CO)N(CH₃)₂) ppm. RMN ¹³C {¹H} NMR (100 MHz, CDCl₃, room temperature): δ 165.06 (1C), 140.95 (1C, Ar), 137.20 (1C, Ar), 129.82 (1C, Ar), 129.77 (1C, Ar), 128.47 (1C, Ar), 127.81 (1C, Ar), 45.06 (1C), 37.38 (2C, ArS(CO)N(CH₃)₂) ppm. El MS *m*/*z* = 229 [M⁺]. IR (ATR, cm⁻¹): 766 (ν C-cl). Anal. Calcd (%) for C₁₀H₁₂ClNOS: C, 52.28; H, 5.27; N, 6.10. Found: C, 52.07; H, 5.18; N, 6.01.

Proligand L $_1^{\text{Stioc}}$. In a 100 mL Schlenk flask, approximately 50 mL of DME were transferred under N $_2$ atmosphere, then (1.00 g, 2.19 mmol) of 2-(chloromethyl)-4-methyl-6-[3,5-bis(trifluoromethyl)phenyl]-S-

phenylthiocarbamate (c in Scheme 1) [7d] was added, followed by Nal (0.33 g, 2.19 mmol); after 1 hour of stirring at room temperature, anilinium chloride (0.13 g, 0.10 mmol) and K₂CO₃ (0.55 g, 3.99 mmol) were added; the solution was stirred at 80°C for 7 days (monitoring by thin-layer chromatography). After the reaction was complete, DME was evaporated and an extraction was carried out in diethyl ether/water. Finally, the product obtained was crystallized in a methanol/CHCl3 mixture as a colorless solid, yield: 83%; melting point: 157°C. ¹H NMR (400 MHz, CDCl₃, room temperature): 57.91 (s, 2H, CF₃Ar), 7.86 (s, 4H, CF₃Ar), 7.31 (s, 2H, SAr*), 7.29 (t, 2H, m-NAr), 7.20 (s, 2H, SAr*), 6.79 (3H, o and p (NAr)), 4.90 (s, 4H, PhN-CH2), 3.02 (s, 6H, NCH3*), 2.97 (s, 6H, ArS(CO)N(CH3)2), 2.43 (s, 6H, ArS(CO)N(CH₃)₂) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃, room temperature): δ 24.43 (s), 39.50 (s), 39.61 (s), 56.68 (s), 114. 26 (s), 118.61 (s), 122.64 (q, $3J_{C-F}$ = 3.4 Hz ArCF₃), 124.21 (s), 125.25 (q, 1J = 268.6 Hz CF₃), 129.97 (s), 131.07 (s), 131.4 (s), 132.51 (q, 2J_{C-F} = 32.7 Hz ArCF₃), 138.06 (s), 142.44 (s), 145.23 (s), 145.76 (s), 147.22 (s), 149.97 (s), 167.04 (s) ppm. IR (ATR, cm⁻¹): 1656 (v_{C=0}), 1122 (v_{C-F}), 1276 y 1375 ($\nu_{C\text{-N}}).$ Anal. Calcd (%) for $C_{44}H_{37}F_{12}N_3O_2S_2$: C, 56.27; H, 3.84; N, 4.58; S; found: C, 55.12; H, 3.78; N, 4.32.

 $Proligand \ L_2{}^{Stioc}.$ In a 250 mL round bottom Schlenk flask under N_2 atmosphere the S-2-(chloromethyl)phenyl-N.N-dimethylthiocarbamate (c) (0.80 g, 3.48 mmol) was added followed by Nal (0.58 g, 3.87 mmol), isobutylamine (174 $\mu\text{L},~1.73$ mmol) and K_2CO_3 (0.97 g, 7.02 mmol); this mixture was stirred 4 days at 65°C and the solvent evaporated to dryness, the solid residue was dissolved in CH₂Cl₂. The organic layer was washed with (3 x 25 mL) sodium thiosulfate aqueous solution, dried with Na₂SO₄ and concentrated under reduced pressure. The product was purified by crystallization for slow evaporation (CH₂Cl₂/MeOH 1:1). Colorless crystals, 0.65 g, 81% yield. melting point: 137°C. Rf = 0.21 in 2:1 hexane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃): δ 7.64 (*d*, 2H, *J* = 7.5 Hz, Ar), 7.45 (*d*, 2H, J = 7.5 Hz, Ar), 7.35 (t, 2H, J = 7.5 Hz, Ar), 7.22 (t, 2H, J = 7.2 Hz, Ar), 3.68 (s, 4H, ^{iBu}N(CH₂)Ar), 3.04 (d, 12H, J = 7.1 Hz, ArS(CO)N(CH₃)₂, 2.15 (d, 2H, J = 7.2 Hz, ^{iBu}N), 1.84 (m, 1H, J = 6.7 Hz, ^{iBu}N), 0.85 (d, 6H, J = 7.2 Hz, $^{iBu}N)$ ppm. ^{13}C {1H} NMR (100 MHz, CDCl3, room temperature): δ 166.70 (2C), 143.88 (2C), 137.12 (1C), 130.53 (2C), 129.36 (2C), 128.43 (2C), 127.04 (2C), 63.06 (2C), 57.44 (2C), 36.96 (2C), 26.23 (1C), 21.04 (2C) ppm. EI MS m/z 459 [M⁺]. IR (ATR, cm-1): 1281 (vc-o), 1186 (vc-o-c). Anal. Calcd (%) for C24H33N3O2S2: C, 62.71; H, 7.24; N, 9.14; S, 13.95. Found: C, 62.88; H, 7.20; N, 8.82; S, 12.27.

Synthesis of Complexes

$$\label{eq:constraint} \begin{split} & [\text{Ni}_2(\textit{x-N},\textit{S},\textit{S},\textit{S}'-\text{N}^{\text{Ph}}\{\text{CH}_2(\text{MeC}_6\text{H}_2\text{R}')\text{S}\}_2)_2] \ (\text{R}'=3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3) \ (1). \ \text{In a} \\ & 100 \ \text{mL} \ \text{round bottom Schlenk flask, 50 mL of anhydrous thf were} \\ & \text{transferred, subsequently} \ (\text{L}_1^{\text{Stoc}}) \ (0.25 \ \text{g}, \ 0.27 \ \text{mmol}) \ \text{was added under} \end{split}$$

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constant stirring, then a NaOMe/MeOH (25 % 0.25 mL, 1.08 mmol) solution was transferred to this mixture; immediately after this addition, the solution turned yellow. This mixture was kept at 65 °C under constant stirring for 6 days (monitoring the progress by mass spectrometry), once confirmed complete deprotection of all the precursor, NiCl₂·6 H₂O (0.07 g, 0.27 mmol), is added, immediately the dispersion changed to a dark brown color; This mixture was left overnight to ensure complete reaction. Finally, the solution was evaporated and an extraction was carried out in diethyl ether/water. The product was crystallized in ether (slow evaporation), obtaining crystals in the shape of black needles. Yield: 45%; black crystals; melting point: 278 °C; ¹H NMR (400 MHz, CDCl₃, room temperature): δ 1.95 (s, 6H, CH₃), 2.19 (s, 6H, CH₃*), 3.81 (d, 2H, CH₂), 4.56 (d, 2H, CH₂), 5.15 (d, 2H, CH₂), 6.15 (s, 2H, CH₂), 6.51-7.66 (30 H, Ar) ppm. 13C{1H} NMR (100 MHz, CDCl3, room temperature): δ 20.60, 21.18, 67.26, 72.84, 119.80, 121.28, 122.47, 122.94, 127.74, 128.26, 129.93, 131.29, 132.31, 134.26, 135.53, 135.71, 137.82, 138.41, 140.14, 141.80, 142.85, 144.39 ppm. UV-vis λ nm (ε M⁻¹cm⁻¹) 238 (7.3 x 10⁴), 289 (3.0 x 104), 360 (2.66 x 10⁴), 443 (9.18 x 10³), 533 (3.09 x 10³), 775 (7.7 x10²). IR (ATR, cm⁻¹): 2914 (v_{C-H}), 1584 (v_{C=C}), 1124 (v_{C-F}). Anal. Calcd (%) for C₇₆H₅₀F₂₄N₂Ni₂S₄: C, 53.92; H, 2.98; N, 1.65; S, 7.58; found: C, 52.03; H, 3.02; N, 1.70; S, 7.53; FAB-MS m/z 1692 [M]+.

[Ni2(x -N,S,S,S'-N^{iBu}{CH2C6H4S}2)2] (2). In a 100 mL Schlenk flask under N_2 atmosphere (L2^{Stioc}) (0.265 g, 0.56 mmol) was dissolved in anhydrous thf, then solution of NaOMe/ MeOH was added and this mixture was stirred 8 days at 65°C. Then, solid NiCl₂.6H₂O (0.13 g, 0.56 mmol) was added, this mixture was stirred 6 hours at room temperature. The solvent was evaporated to dryness, the solid was washed with ethyl acetate, diethyl ether and water. The red, sparingly soluble microcrystals were added CH₂Cl₂ and placed in a sealed vial and warmed up, allowing for slow cooling to room temperature. The solid obtained was insoluble in most solvents and very sparingly soluble in CHCl3 and CH2Cl2, 0.11 g, 51 % yield. R_f = 0.44 in 3:1 hexane/ ethyl acetate M.p. > 250 (dec. 140°C). El MS m/z 746 [M⁺]. UV-vis λ nm (ϵ M⁻¹cm⁻¹) 263 (3.4 x 10⁴), 301 (3.90 x 10⁴), 369 (1.48 x 10⁴), 416 (1.05 x 10⁴), 524 (2.9 x 10³), 775 (3.2 x10²); IR (ATR, cm⁻¹): 3443 (vo-н), 2958 (vc-н), 1586 (vc=c). Anal. Calcd (%) for $C_{36}H_{42}N_2Ni_2S_4(CHCI_3)$: C, 51.21; H, 5.00; N, 3.23; S, 14.78. Found: C, 51.63; H, 5.18; N, 3.65; S, 14.53.

[Ni(ĸ-N, S, S-N^{/Bu}{CH₂C₆H₄S}₂)(C=NC₁₀H₇)] (3). In a 100 mL Schlenk flask under N_2 atmosphere, complex **2** (37 mg, 0.07 mmol) was dissolved in CH₂Cl₂ at 40 °C and 2-naphthylisocyanate was added (11 mg, 0.07 mmol), this mixture was stirred 90 minutes at 40°C and concentrated under reduced pressure. The product was purified by crystallization by slow evaporation (CH₂Cl₂/MeOH 1:1). Dark green microcrystals (32 mg) were obtained in 67 % yield. Rf = 0.55 in 3:1 hexane/ ethyl acetate. M.p. > 250 (dec. 132 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.92 (s, 1H, Ar), 7.88 (t, 3H, Ar), 7.62 (m, 4H, Ar), 7.48 (s, 1H, Ar), 7.30 (s, 1H, Ar), 7.20 (s, 1 H, Ar), 7.06 (m, 4H, Ar), 4.69 (dd, 4H, ^{iBu}N(CH₂)), 2.70 (m, 1H, J = 7.1 Hz, ^{iBu}N), 2.63 (d, 2H, ^{iBu}N), 1.39 (d, 6H, ^{iBu}N) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃, room temperature): § 166.90 (1C), 165.58 (2C), 152.02 (1C), 141.67 (2C), 137.90 (2C), 131.38 (2C), 130.25 (2C), 127.58 (2C), 127.20 (2C), 126.86 (2C), 118.22 (1C), 111.51 (2C), 60.08 (1C), 53.50 (2C), 37.06 (4C), 14.48 (1C) ppm. EI MS *m*/z 552 [M⁺]. UV-vis λ nm (ε M⁻¹cm⁻¹) 235 (6.4 x 10⁴), 313 (3.90 x 10⁴), 366 (3.67 x 10⁴), 775 (1.1 x10²); IR (ATR, cm⁻¹): 2958 (v_{C-H}), 2162 (v_{C=H}), 1584 (v_{C=C}). Anal. Calcd (%) for C₂₉H₂₈N₂NiS₂: C, 66.05; H, 5.35; N, 5.31; S, 12.16. Found: C, 66.57; H, 5.11; N, 5.36; S, 11.15.

Conflicts of interest

There are no conflicts to declare

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Keywords: Nickel complexes • Hydrogenase • Biomimetic Model • Hydrogen evolving reaction • Electrocatalyst

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