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Synthesis, electrochemical properties and catalytic behavior for electrochemical hydrogen production of $[Ni(1,3-bis(diphenylphosphino) propane)((2-mercaptopyridinate)-\kappa N,S)]BF_4$



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ABSTRACT

A new nickel complex [Ni(1,3-bis(diphenylphosphino)propane)((2-mercaptopyridinate)- κN ,S)]BF₄ was synthesized and characterized by NMR spectroscopy, an X-ray crystallographic study, elemental analysis and electrospray ionization mass spectroscopy. The complex was synthesized under ambient conditions and was air-stable. Catalytic behavior for electrochemical production of hydrogen was investigated by cyclic voltammetry. The cyclic voltammogram with acetic acid as a proton source was very similar to the voltammogram without the complex; however, significant catalytic cathodic current was observed when trifluoroacetic acid was used as the proton source. Differences between the behavior of the complex with different acids in cyclic voltammetry was also observed in UV–Vis spectrum. The possible catalytic mechanism for hydrogen production is discussed.

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1. Introduction

One of the most serious problems the world faces is of the steady decline in the amount of energy available from conventional sources such as coal and petroleum [1]. Renewable energy such as solar and wind power is a very attractive alternative source of energy. The output of renewable sources is usually stored to a battery as electric power or as various kinds of fuels to store chemical energy because renewable sources of energy are not constant due to weather conditions [2]. Hydrogen is one of the most popular chemical energy storage fuels because it can make electric power without harmful waste [3]. Considerable research has been carried out world wide to make effective catalysis for electrochemical production of H_2 [4–9].

DuBois et al. have reported many bis-(1,5-R'-3,7-R-1,5-diaza-3,7-diphosphacyclooctane) Ni(II) complexes $([Ni(P_2^RN_2^R)]^{n+}$, hereafter) as efficient catalysts for electrochemical hydrogen production [10]. These complexes have nitrogen atoms in the ligand, and the nitrogen atoms serve as "pendant bases" to capture protons and transfer them to the Ni center. In this manner, the ligands enhance the catalytic behavior. Some drawbacks to the $P_2^RN_2^{R'}$ ligands is that they generally require anaerobic and anhydrous conditions.

We designed complex **1** shown in Scheme 1 as a potential catalyst for electrochemical hydrogen evolution. This complex has one 1,3-bis(diphenylphosphino)propane (dppp, hereafter) and two 2-mercaptopyridinate (2-pyS, hereafter). The two phosphorus atoms of dppp can stabilize Ni in low oxidation states. The nitrogen atoms of 2-pyS ligands do not coordinate to the Ni atom, and as such have the potential to serve as a pendant base. We attempted to obtain complex **1** as presented below, but an unexpected product was obtained instead. Here, we report the synthesis, characterization, and electrocatalytic activity for H₂ production of the [Ni(dppp)(2-pyS)]BF₄ (**2**).

2. Experimental

All materials were purchased from commercial suppliers (Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., and Tokyo Chemical Industry Co., Ltd.) and were used without further purification.

2.1. Measurements

¹H NMR (400 MHz) spectra were measured in dimethyl sulfoxide-d₆ and CD₃CN with a Bruker Avance III HD spectrometer using dimethyl sulfoxide-d₆ (δ = 2.50) and CD₃CN (δ = 1.94) as an internal standard. ³¹P NMR (161 MHz) spectra were measured in CD₃CN with a Bruker Avance III HD spectrometer using 85% H₃PO₄ in



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Scheme 1. Structures of complexes 1 and 2.

water ($\delta = 0.00$) as an external standard. Electrospray ionization mass (ESI-mass) spectral data were obtained on a JEOL JMS-T100CS spectrometer. The absorption spectrum was measured using a SIMADZU UV-3600 UV-Vis-NIR spectrophotometer. The optical path length was 1 cm. The concentration of the complex was 4.57×10^{-5} mol dm⁻³. Cyclic voltammetry was performed on BAS BAS100B/W using three electrode cells (glassy carbon electrode as working electrode, Pt coil electrode as counter electrode and homemade Ag⁺/Ag electrode as reference electrode). The medium was 0.1 mol dm⁻³n-Bu₄NPF₆/CH₃CN. The concentration of the complex was $1\times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$ and the amount was 10 ml. The stock solution of the acid were 4 mol dm^{-3} acetic acid/0.1 mol $dm^{-3}n$ -Bu₄NPF₆/CH₃CN and 2 mol dm^{-3} trifluoroacetic acid/0.1 mol dm⁻³*n*-Bu₄NPF₆/CH₃CN. *E*_{1/2} of the ferrocenium/ferrocene couple was 0.11 V versus Ag⁺/Ag. The scan rate was 100 mV s⁻¹. C, H and N analysis was furnished by Service center of the elementary analysis of organic compound of Kyushu University.

2.2. Synthesis

2.2.1. $[Ni(dppp)(2-pyS)]BF_4(2)$

A mixture of $[Ni(H_2O)_6](BF_4)_2$ (100 mg, 2.94×10^{-4} mol) and dppp (121 mg, 2.94×10^{-4} mol) in CH₃CN (10 ml) was stirred. The color of the solution turned to brown from blue. After 3 h, 2pySH (63.5 mg, 5.87×10^{-4} mol) was added and the solution was stirred overnight. The resulting red-brown solution was evacuated to dryness. The crude product was purified by recrystallization from H₂O/acetone. Orange plate crystals were recrystallized and were collected by filtration with a yield of 112 mg (50.9%). Anal. Calc. for C₃₂H₃₀NNiP₂SBF₄: C, 57.53; H, 4.53; N, 2.10. Found: C, 57.63; H, 4.47; N, 2.09%. ¹H NMR ((CD₃)₂SO, 400 MHz) δ 7.81 (d, Ar-H, 8H); 7.56-7.49 (m, Ar-H, 13H); 6.77 (d, Ar-H, 1H); 6.54 (t, Ar-H, 1H); 6.10 (d, Ar-H, 1H); 2.67 (br, PCH₂CH₂CH₂P, 4H); 1.85 (br, PCH₂CH₂CH₂P, 2H). ¹H NMR (CD₃CN, 400 MHz) δ 7.83–7.78 (m, Ar-H, 8H); 7.56-7.44 (m, Ar-H, 13H); 6.69 (d, Ar-H, 1H); 6.44 (t, Ar-H, 1H); 6.25 (d, Ar-H, 1H); 2.54 (m, PCH₂CH₂CH₂P, 4H) (The peak of PCH₂CH₂CH₂P could not be identified due to residual solvent or water.). ³¹P{¹H} NMR(CD₃CN, 161 MHz) δ 13.04 (br); 3.59 (br). UV–Vis (CH₃CN) λ_{max} , nm (ϵ , dm³ mol⁻¹ cm⁻¹) 274 (2.38 × 10⁴), 292sh (2.17 \times 10⁴), 326sh (9.13 \times 10³), 373 (3.2 \times 10³). ESI-Mass: m/z 580 (calc. for M-BF₄ = 580).

2.3. X-ray crystallography

Single crystals of **2** suitable for single-crystal X-ray analysis were obtained by slow recrystallization from a H_2O /acetone solution of complex **2** at room temperature. The data were collected on a RIGAKU R-AXIS RAPID II IP diffractometer. A multi-scan absorption correction was applied to the intensity data. The structure was solved by direct methods (*SIR-2011*) [11] and was refined by the full-matrix least-squares method on F^2 (SHELXL-2014/7) [12] using the Yadokari-XG software package [13]. All non-hydrogen

atoms were refined with anisotropic parameters. H atoms were included in the calculated positions and were refined by a riding model. Crystallographic diagrams were created with the *ORTEP* program [14]. The selected crystallographic data were as follows: formula $C_{32}H_{30}B_1F_4N_1Ni_1P_2S_1$, formula weight 668.09 g mol⁻¹, crystal size $0.49 \times 0.12 \times 0.10$ mm³, orthorhombic, *P*ca2₁, *a* = 18.7410(10) Å, *b* = 9.6065(5) Å, *c* = 16.7669(9) Å, *V* = 3018.6(3) Å³, *Z* = 4, *T* = 120(2) K, *D*_{calc} = 1.470 mg m⁻³, 26799 reflections collected, 6851 independent reflections, *R*_{int} = 0.0552, *R*₁ = 0.0346 (*I* > 2 σ (*I*)), w*R*₂ = 0.0738 (all data), absolute structure parameter -0.009(9), Goodness-of-fit on *F*² 1.030. CCDC 1578156.

3. Results and discussion

3.1. Synthesis and characterization

Complex **2** was synthesized in two steps under ambient conditions. The first step was the reaction of Ni^{2+} ion and dppp ligand, that produced $[Ni(dppp)(solvent)_2]^{2+}$ as a precursor complex. The second step was the reaction of the precursor complex and the 2-pySH ligand. The complex was purified by recrystallization. The complex was air-stable in solid form and in solution, and was characterized by ¹H NMR, ³¹P NMR, elemental analysis and ESI-mass (Figs. S1–4).

The crystal structure of **2** is shown in Fig. 1. A nickel(II) center is coordinated by the dppp ligand and bidentate 2-pyS ligand. The deviation of Ni from the least square mean plane of P1/P2/S1/N1 is 0.09 Å. The dihedral angle between the least square mean plane of P1/P2/Ni1 and the least square mean plane of S1/N1/Ni1 is 9.57°. These data indicate that the Ni(II) ion has a square planar geometry.

In other bidentate-2-pyS octahedral Ni(II) complex [15–17], the bond distances of Ni–S and Ni–N range in 2.475(1)–2.5517(7) Å and 2.034(4)–2.083(5) Å, respectively. The bond angle of N–Ni–S ranges in 67.27(4)–68.53(4)°. Therefore, compared with similar reported species [15–17], complex **2** has shorter bond distances of Ni–S and Ni–N and a wider bond angle of N–Ni–S. On the other hand, the Ni–P distance and P–Ni–P angle are almost same values



Fig. 1. Crystal structure of complex **2** showing the cation. The counter anion and hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ni1–S1 = 2.2320(10), Ni1–N1 = 1.966(3), Ni1–P1 = 2.1901(10), Ni1–P2 = 2.1663(9), N1–Ni1–S1 = 74.15 (9), P1–Ni1–P2 = 91.56(4).

as those of [Ni^{II}(dppp)(dithiocarbamate)]⁺ [18–21] (Ni–P distance: 2.1652(7)–2.192(2) Å; P–Ni–P angle: 93.75(8)–97(1) °).

3.2. Electrochemical behavior

Fig. 2 is the cyclic voltammogram of complex **2** in *n*-Bu₄NPF₆/ CH₃CN. **2** exhibits two irreversible one-electron cathodic peaks at $E_{1/2} = -1.13$ and -1.56 V (all potentials are shown vs. the Ag⁺/Ag redox couple), and are assigned to Ni(II)/Ni(I), Ni(I)/Ni(0), respectively. Two anodic peaks at $E_p = -0.79$ and -0.12 V are results of the irreversibility of the Ni(II)/Ni(I) and/or Ni(I)/Ni(0) redox couples. The reversible couple ($E_{1/2} = 0.11$ V) is assigned to ferrocenium/ferrocene couple as an internal reference.

To investigate the catalytic activity for H₂ production of the complex 2, electrochemical measurements with acid were carried out. Fig. 3(a) shows the electrochemical behavior of complex 2 with acetic acid as a proton source. A large cathodic peak is observed at \sim -2.2 V: however, a very similar response is observed without the complex (Fig. S5 and Ref. [22]). Any additional cathodic peaks are not observed, and the result reveals that complex 2 does not perform the electrochemical production of H₂ in the presence of acetic acid. In the case of trifluoroacetic acid, the electrochemical behavior changes significantly as shown in Fig. 3(b). Compared with no acid conditions, an enhancement of the cathodic current around -1.8 V is observed by the addition of trifluoroacetic acid. The cathodic current at the potential is also observed under acid condition without complex 2; however, the cathodic current with the complex is at least 1.6 times larger than the cathodic current without the complex shown in Fig. S5. The cathodic current increases with an increase in the amount of acid. Therefore, complex 2 does act as a catalyst for electrochemical hydrogen production in the presence of trifluoroacetic acid. Unfortunately, a detection of hydrogen by a gas chromatography was not carried out because the potential at which complex 2 showed catalytic behavior was partly overlapped by the potential at which trifluoroacetic acid was reduced without catalyst.

3.3. Mechanism of H₂ production

Complex **2** does not show electrochemical catalytic behavior with acetic acid ($pKa^{CH3CN} = 22.3$ [23]) but it does with trifluoroacetic acid ($pKa^{CH3CN} = 12.7$ [24]) Dubois et al. have improved catalysts for electrochemical hydrogen production by the introduction of pendant amines which act as proton relays. The 2-pyS ligand of complex **2** could not act as a proton relay in the isolated state due to the bidentate coordination of this ligand. However, Henderson et al. reported that [Ni(2-pyS){PhP(CH₂CH₂PPh₂)₂]]⁺ is protonated by 2,6-dimethylpyridinium tetraphenylborate followed by dissociation of the nitrogen of 2-pyS [25]. Therefore, the difference of the electrochemical behavior could be affected by whether the 2-pyS ligand was protonated by the acid. To check the assumption, UV–Vis spectrum of complex **2** with acids was measured



Fig. 2. Cyclic voltammogram of 2. The arrow indicates the direction of the scans.



Fig. 3. Catalytic behavior of **2** for electrochemical hydrogen production with varying concentrations of (a) acetic acid and (b) trifluoroacetic acid. Acid stock solution were 4 mol dm⁻³ (acetic acid) and 2 mol dm⁻³ (trifluoroacetic acid). The equivalents are denoted in parentheses.



Fig. 4. UV–Vis spectra of complex **2** with different concentrations of (a) acetic acid and (b) trifluoroacetic acid.

(Fig. 4). The spectrum of a solution of complex **2** changes upon addition trifluoroacetic acid, whereas adding acetic acid does not affect the spectrum. The results show that complex **2** is stable in acetic acid/CH₃CN solution and that complex **2** does show structural change due to protonation in trifluoroacetic acid/CH₃CN solution.

Based on the above results and the literature of $[Ni^{II}(P_2^R N_2^{T'})_2]^{n+}$ [10,26,27], we propose the mechanism of H₂ production as in Scheme 2. The first protonation makes the 2-pyS ligand monodentate in its coordination to the S atom. In this intermediate species, the N atom is protonated and the complex has additional solvent.



Scheme 2. Possible catalytic mechanism for hydrogen production by complex 2.

The consecutive two one-electron reductions make $[Ni(H)(dppp)((2-pyS)-\kappa S)(solv.)]^0$. Following intermediate species is generated by further protonation, then H₂ and the initial complex are produced.

4. Conclusions

In this study, new nickel complex [Ni (1,3-bis(diphenylphosphino)propane)((2-mercaptopyridinate)- κN ,S)]BF₄ was prepared, characterized and investigated electrochemically. The complex does not act as a catalyst for electrochemical hydrogen production with acetic acid; however, it does in the presence of trifluoroacetic acid. Based on the UV–Vis spectroscopy and the literature, the mechanism of H₂ production is proposed.

Complex **2** shows catalytic behavior for strong acid, but does not for weak acid. Furthermore, turnover frequency and current efficiency could not be estimated. Our studies for improved catalysts based on new proton relay ligands are currently under examination.

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Appendix A. Supplementary data

CCDC 1578156 contains the supplementary crystallographic data for complex **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10. 1016/j.poly.2017.12.006.

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