



Synthesis and characterization of a heteroleptic nickel paddlewheel complex

Tomohiko Hamaguchi^{*}, Ryoma Shimazaki, Isao Ando

Department of Chemistry, Faculty of Science, Fukuoka University 8-19-1 Nanakuma, Jonan-ku, Fukuoka, 814-0180, Japan

ARTICLE INFO

Article history:

Received 12 May 2018

Received in revised form

4 July 2018

Accepted 4 July 2018

Available online 5 July 2018

Keywords:

Ni complex

Heteroleptic paddlewheel complex

2-Pyridinethiolate

1,2-bis(diphenylphosphino)ethane

ABSTRACT

A heteroleptic paddlewheel Ni complex of formula $[\text{Ni}_2(\mu_2(N,S)\text{-}2\text{-pyS})_3(\mu_2\text{-dppm})](\text{BF}_4)$ (2-pyS: 2-pyridinethiolate; dppm: 1,2-bis(diphenylphosphino)ethane) was synthesized and characterized by X-ray diffraction, elemental analysis, and electrospray ionization mass spectroscopy. A single-crystal X-ray diffraction study revealed that the complex has $\mu_2(N,S)\text{-}2\text{-pyS}$ bridging ligands. Furthermore, spectroscopic and electrochemical studies were performed, and the corresponding results were confirmed by computational chemistry.

© 2018 Elsevier B.V. All rights reserved.

Paddlewheel complexes are interesting molecules not only for their basic properties such as magnetism [1–4] but also for their application as catalysts [5–7] and as building blocks for the construction of supramolecules [8–11]. In general, these complexes are constructed from two metal ions and four bridging ligands. Paddlewheel complexes can be classified into two categories according to the bridging ligands: “homoleptic” paddlewheel complexes, in which the four bridging ligands are the same, and “heteroleptic” paddlewheel complexes, which are constructed from two or more kinds of bridging ligands ($[\text{M}_2\text{L}_4]^{n+}$ and $[\text{M}_2\text{L}_m\text{L}'_{(4-m)}]^{n+}$, respectively, in Fig. 1).

In contrast with the abundant number of reports for homoleptic paddlewheel complexes that can be found in the SciFinder search with “paddlewheel complex” as a key word, we can find only 4 reports in the case of similar search with “heteroleptic paddlewheel complex” as a key word [12–15]. Considering that the properties of the paddlewheel complexes can be regulated by the substituent effects of the bridging ligands [16], we envisage heteroleptic paddlewheel complexes as particularly attractive because their properties can be tuned by changing the bridging ligands. In this study, we describe the synthesis and properties of a new heteroleptic nickel paddlewheel complex **1** of formula $[\text{Ni}_2(\mu_2(N,S)\text{-}2\text{-pyS})_3(\mu_2\text{-dppm})](\text{BF}_4)$ (2-pyS: 2-pyridinethiolate; dppm: 1,2-

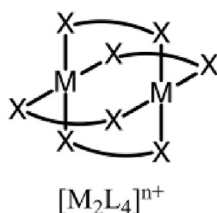
bis(diphenylphosphino)ethane).

The one-pot reaction of $[\text{Ni}(\text{H}_2\text{O})_6](\text{BF}_4)_2$, dppm, 2-mercaptopyridine, and triethylamine afforded a red-brown crude product, from which complex **1** was obtained by recrystallization [17]. The purity of the bulk sample was confirmed by powder X-ray analysis (Fig. S1 in supporting information) and elemental analysis. Crystals suitable for a single-crystal X-ray diffraction study were obtained by slow recrystallization from an acetonitrile (CH_3CN) solution of **1** and diethyl ether vapor. The corresponding crystal structure of complex **1** is shown in Fig. 2 [18]. The structure of **1** consists of one complex cation and one BF_4^- counter anion. The cation has a dinickel core bridged by three 2-pyS ligands and one dppm ligand, which form the heteroleptic paddlewheel structure. Because the complex cation has one positive charge and each 2-pyS ligand has one negative charge, it can be inferred that the Ni atoms are divalent. The ligands 2-pyS act as $\mu_2(N,S)$ -bridging ligands. A search in the CCDC database (updated to May 2017) reveals that there are only three reports of complexes containing two Ni ions connected by $\mu_2(S,S)\text{-}2\text{-pyS}$ or $\mu_2(S,S)\text{-}2\text{-pyS}$ -derivative [19–21], which contrasts with the numerous reports on related complexes with other metal ions. As far as we know, our complex is the second Ni complex that contains the $\mu_2(N,S)\text{-}2\text{-pyS}$ moiety, following that reported by Chaudhury et al. [22]. In complex **1**, Ni1 and Ni2, which are coordinated by the S1/S2/P1/N3 and S3/P2/N1/N2 atoms, respectively, exhibit square-planar coordination geometry. The two square-planar metal centers are not eclipsed, as shown in Fig. 2(b). The Ni–N and Ni–S bond lengths, 1.93 and 2.20 Å in average,

^{*} Corresponding author.

E-mail address: thama@fukuoka-u.ac.jp (T. Hamaguchi).

homoleptic



heteroleptic

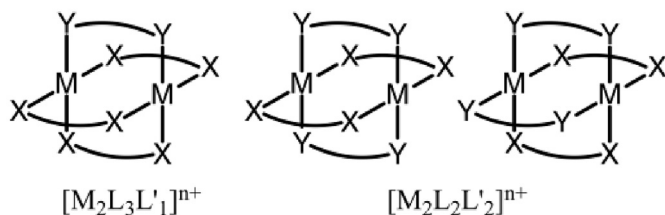


Fig. 1. Homoleptic and heteroleptic paddlewheel complexes.

respectively, are shorter than those of a related Ni complex containing the $\kappa^2(N,S)$ -2-pyS moiety (2.02–2.16 Å for Ni–N and 2.26–2.55 Å for Ni–S) [21,23–27], which stems most likely from the less tight coordination in complex **1**. The ligand dpmm acts as μ_2 -bridging ligands. A search in the CCDC database reveals that there are more than fifty reports of complexes containing two Ni ions connected by dpmm; however, they are mainly Ni(I) or Ni(0) complexes and/or octahedral-coordinated Ni complexes. There are only eight reports of complexes containing two square-planar coordinated Ni(II) ions connected by μ_2 -dpmm [28–33]. The Ni–P bond length, 2.21 Å in average, falls within the range of those of a related Ni complex (2.11–2.22 Å) [29,33]. The distance between the two Ni ions of 2.533(1) Å falls within the range of 2.38–2.65 Å that Parkin et al. reported in 2009 for paddlewheel Ni complexes [34], and within the slightly expanded range that results from a search in the CCDC database (2.33 [35] to 2.77 Å [36,37]). This Ni–Ni distance suggests the existence of a bond between the two Ni ions. However,

because the absence of net bonding interaction between the two Ni centers was reported in the case of other Ni(II) paddlewheel complexes [38], we believe that there is no bonding interaction in complex **1**.

Only the $[Ni_2(2\text{-pyS})_3(dppe)]^+$ complex was obtained, and other heteroleptic complexes (such as $[Ni_2(2\text{-pyS})_2(dppe)_2]^{2+}$ or $[Ni_2(2\text{-pyS})_1(dppe)_3]^{3+}$) could not. In fact, attempts at the synthesis of $[Ni_2(\mu_2(N,S)\text{-}2\text{-pyS})_n(\mu_2\text{-dppe})_{(4-n)}]^{(4-n)+}$ ($n = 1, 2$) by changing the mole ratio of Ni:dppe:2-pySH resulted in failure.

Complex **1** was subjected to UV–vis analysis in CH₃CN, and the corresponding spectrum is shown in Fig. 3(a). The two weak broad bands that appear in the visible region and the two intense sharp bands in the UV region were tentatively assigned to ligand-to-metal charge transfer (LMCT) and ligand-centered $\pi\text{-}\pi^*$ transition, respectively. To verify this assignment, a TD-DFT calculation was carried out [39], and the result is summarized in Tables S1 and S2 and Fig. S2. Accordingly, the two weak broad bands in the visible region could be attributed to LMCT (mainly 2-pyS to nickel) or metal-to-metal charge transfer. However, the origin of the two intense sharp bands in the UV region is difficult to predict owing to the complexity of the transition.

Lin et al. recently reported the electrochemical hydrogen production catalyzed by $[Ni_2(dppe)_2(CN)_4]$ [33]. Even though their Ni₂ complex is not a paddlewheel complex, its structure resembles that of complex **1**. Thus, each dimer has two Ni centers with square-planar coordination geometry, and the two planes are almost parallel to each other. Moreover, the Ni planes are bridged by dppe ligands in the μ_2 coordination mode. The authors concluded that apical vacant positions play an important role in catalytic behavior [33]. Motivated by this, we tested the catalytic behavior of our complex by performing an electrochemical study. The corresponding cyclic voltammogram in *n*-Bu₄NPF₆/CH₃CN is depicted in Fig. 4.

The cathodic scan from 0.1 V (all potentials are shown versus the ferrocenium/ferrocene couple) exhibits four irreversible cathodic peaks at $E_p = -1.23, -1.60, -2.09,$ and -2.40 V. Considering that the X-ray crystallographic study revealed that the two nickel centers are electronically distinct, with an S/S/P/N coordination environment around one nickel center and an S/P/N/N around the other, these four cathodic peaks can be assigned to one-electron reduction of the moieties Ni₂(II,II)/Ni₂(I,II), Ni₂(I,II)/Ni₂(I,I), Ni₂(I,I)/

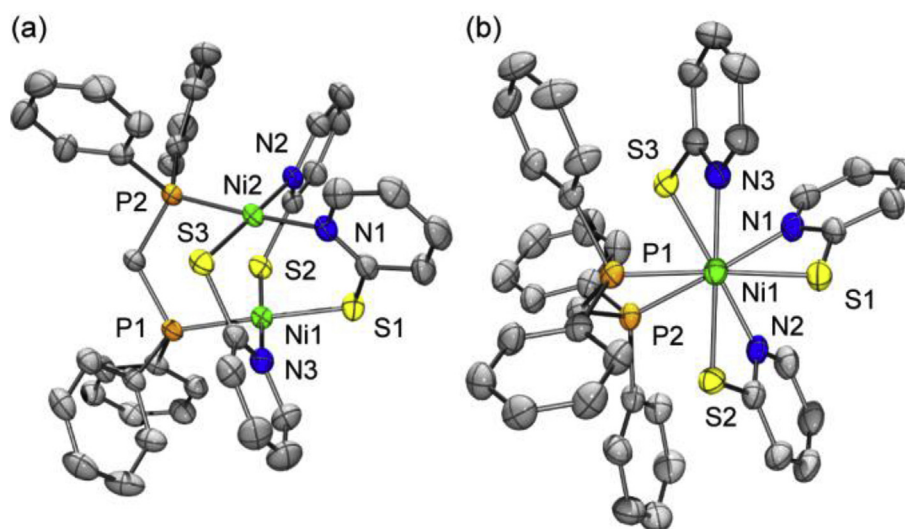


Fig. 2. (a) Crystal structure of the cation of complex **1**. The counter anion and hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. (b) View along the Ni...Ni axis.

Download English Version:

<https://daneshyari.com/en/article/7806704>

Download Persian Version:

<https://daneshyari.com/article/7806704>

[Daneshyari.com](https://daneshyari.com)