



A heptadentate ligand possessing two phenol groups: Its diverse coordination chemistry and the catalytic behaviors of its transition complexes towards benzene oxidation



Xiuli You^{a,c}, Zhenghong Wei^{a,*}, Beibei Xu^a, Xiaoming Liu^{a,b,*}

^a Department of Chemistry, Nanchang University, Nanchang 330031, China

^b College of Biological, Chemical Sciences and Engineering, Jiaying University, Jiaying 314001, China

^c Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, China

ARTICLE INFO

Article history:

Received 4 June 2014

Accepted 14 July 2014

Available online 1 August 2014

Keywords:

Transition metal complex

Multidentate ligand

Phenolate derivatives

Electrochemistry

Benzene hydroxylation

ABSTRACT

Reacting the heptadentate ligand 2,2'-(((pyridine-2,6-diylbis(methylene))bis((pyridin-2-ylmethyl)-azanediyl))bis(methylene))diphenol (**H₂L**) with one equivalent of CuCl₂·6H₂O, NiCl₂·6H₂O and FeCl₃·6H₂O, followed by anion exchange with PF₆⁻, BPh₄⁻ and ClO₄⁻ formed three mononuclear complexes [Cu(**H₂L**)](Cl)(PF₆) (**1**), [Ni(**HL**)](BPh₄) (**2**) and [Fe(**L**)](ClO₄) (**3**), respectively. Their structures in the solid state were determined by X-ray crystallography. The three metal centers in complexes **1–3** adopt distorted tetragonal pyramidal (Cu²⁺), octahedral (Ni²⁺) and pentagonal bipyramidal (Fe³⁺) geometries, respectively. In addition, the electrochemistry and their catalytic activity in the oxidation reaction of benzene to phenol by H₂O₂ were investigated.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

In recent decades, multidentate ligands and their transition metal complexes have been one of the intensely investigated areas owing to their diverse potential applications in many aspects, such as in catalysis [1,2], solar cells [3,4], molecular devices [5–7], mimics of metalloenzymes [8–10], and so on [11,12]. The properties or functionalities of the obtained complexes depend very much on the coordinated geometries and donor atoms, as well as the metal centres. In catalytic reactions catalyzed by transition metal complexes, an unsaturated coordinating site or an easy leaving group on the metal centre is essential [13–21].

In nature, the required structural features are achieved via the tertiary structure imposed by protein folding. Through such a structural design, natural catalytic systems can make some reactions proceed under mild conditions, otherwise harsh conditions are necessary. For example, methane mono-oxygenases (MMO) which are categorized into two types, soluble MMO (sMMO) and particulate MMO (pMMO) can selectively oxidize the very stable C–H bond in methane to methanol at ambient temperature and pressure [22]. The former is an iron enzyme and the latter a copper

enzyme [23]. Thus, exploring the functional features of a complex focuses largely on ligand design and synthesis, as well as the selection of suitable metals. In this sense, the chemistry of multidentate organic ligands and their transition metals have always been the focus for manipulation.

Herein, we report a heptadentate ligand, 2,2'-(((pyridine-2,6-diylbis(methylene))bis((pyridin-2-ylmethyl)azanediyl))bis(methylene))diphenol (**H₂L**), and its transition metal complexes. The ligand possesses two phenol and three pyridinyl groups. The coordinating capability of the phenolic oxygen atoms can be tuned by their deprotonation [24–30]. Reaction of the ligand with Cu²⁺, Ni²⁺ and Fe³⁺ salts produced three mononuclear complexes, [Cu(**H₂L**)](Cl)(PF₆) (**1**), [Ni(**HL**)](BPh₄) (**2**) and [Fe(**L**)](ClO₄) (**3**), respectively, in which the two phenol groups vary from fully coordinated to fully uncoordinated. The electrochemistry and catalytic efficiency on the direct oxidation of benzene to phenol by H₂O₂ were also investigated.

2. Experimental

2.1. Instrument and materials

The reactions were performed under an argon atmosphere using standard Schlenk techniques when necessary. Solvents were freshly distilled by using appropriate drying agents prior to use.

* Corresponding authors. Address: Department of chemistry, Nanchang University, Nanchang 330031, China. Tel./fax: +86 (0)573 83643937.

E-mail addresses: weizh@ncu.edu.cn (Z. Wei), xiaoming.liu@mail.zjxu.edu.cn (X. Liu).

^1H and ^{13}C NMR spectra were recorded on an AVANCE DRX 400 (Bruker) spectrometer in CDCl_3 . UV–vis spectra were collected on a Shimadzu UV-2550 spectrophotometer. Infrared spectroscopic data were recorded on an FT-IR spectrometer (Scimitar 2000, Varian). Micro-analysis was performed on a Heraeus CHN–O–Rapid instrument. The catalytic reactions were analyzed by GC (gas chromatography) using an Agilent instruments model 6890N network GC system equipped with a DB–WAX capillary column (column length: 30 m; internal diameter: 0.32 mm). Electrochemical measurements were performed on an Echo Chemie Autolab PGSTAT 30 in dry acetonitrile using $[\text{NBu}_4][\text{BF}_4]$ as a supporting electrolyte; platinum and Ag/AgCl were used as working and reference electrodes [31], respectively. The compounds 2,6-bis(bromomethyl)pyridine [32], and 4-methyl-2-((pyridin-2-ylmethyl)amino)methylphenol [33] were synthesized using literature procedures.

2.2. Synthesis

2.2.1. The ligand **H₂L**

2,6-Bis(bromomethyl)pyridine (265 mg, 1.0 mmol), 4-methyl-2-((pyridin-2-ylmethyl)amino)-methylphenol (684 mg, 3.0 mmol) and K_2CO_3 (690 mg, 5.0 mmol) were mixed in acetonitrile (80 mL) in a flask (250 mL). After being refluxed for 36 h, the reaction was filtered, and the filtrate was concentrated using a rotary evaporation to give the crude product. Further purification was performed by flash chromatography on a silica gel column with ethyl acetate/petroleum ether (10:1) as the eluent to give a white solid (340 mg, 61%). Element Anal. Calc. for $\text{C}_{35}\text{H}_{37}\text{N}_5\text{O}_2$ (FW = 559.7): C, 75.11; H, 6.66; N, 12.51. Found: C, 75.58; H, 6.93; N, 12.64%. ^1H NMR (δ , ppm, 400 M, CDCl_3): 10.71 (s, 2H, OH), 8.57 (d, $J = 4.8$ Hz, 2H, Py), 7.62 (m, 2H, Py), 7.56 (m, 1H, Py), 7.32 (d, 2H, Py), 7.26 (m, 2H, Py), 7.16 (m, 2H, Py), 6.98 (d, $J = 8.1$ Hz, 2H, Ph), 6.86 (s, 2H, Ph), 6.79 (d, $J = 8.1$ Hz, 2H, Ph), 3.86 (s, 8H, CH_2), 3.75 (s, 4H, CH_2), 2.23 (s, 6H, CH_3). ^{13}C NMR: 158.2, 157.8, 155.1, 148.9, 137.4, 136.7, 130.6, 129.4, 127.9, 123.2, 122.4, 122.2, 121.7, 116.2, 59.2, 59.0, 57.1, 20.4. UV–Vis (DMF, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol L}^{-1} \text{cm}^{-1}$)): 219 (24360), 267 (28690).

2.2.2. Complex **1**

To a solution of the ligand **H₂L** (559 mg, 1 mmol) in methanol (10 mL) was added $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (242 mg, 1 mmol) to give a blue solution. After being stirred for five minutes, NH_4PF_6 (163 mg, 1 mmol) was added to produce a blue precipitate, which was collected *via* filtration, washed with methanol and dried in vacuum. Recrystallisation of the solid in a MeCN/MeOH/ Et_2O system gave blue crystals of **1** after two weeks (522 mg, 65%). Anal. Calc. for $\text{C}_{35}\text{H}_{37}\text{N}_5\text{O}_2\text{PF}_6\text{ClCu}$ (Mw = 803.6): C, 52.26; H, 4.60; N, 8.71. Found: C, 52.58; H, 4.33; N, 8.64%. IR (cm^{-1}): 3400 (s), 3101 (w), 2919 (w), 2865 (w), 1608 (s), 1489 (s), 1445 (m), 1265 (s), 1132 (s), 1108 (s), 1087 (s), 843 (s), 758 (m), 667 (m), 551 (m). UV–Vis (DMF, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol L}^{-1} \text{cm}^{-1}$)): 223 (21360), 261 (20690), 289 (7900), 323 (4356), 650 (434).

2.2.3. Complex **2**

To a solution of the ligand **H₂L** (559 mg, 1 mmol) in methanol (10 mL) was added Et_3N (0.2 mL). After being stirred for five minutes, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (474 mg, 2 mmol) was added to give a green solution. The reaction was further stirred for five minutes and $\text{Na}[\text{BPh}_4]$ (342 mg, 1 mmol) was added to produce a light-green precipitate which was collected *via* filtration, washed with methanol and dried in vacuum. Recrystallisation of the product in DMF/ Et_2O gave light-green crystals of **2** after four days (402 mg, 43%). Anal. Calc. for $\text{C}_{59}\text{H}_{56}\text{N}_5\text{O}_2\text{BNi}$ (Mw = 936.6): C, 75.59; H, 5.98; N, 7.47. Found: C, 75.18; H, 5.53; N, 7.64%. IR (cm^{-1}): 3405 (s), 3051 (m), 2919 (w), 2865 (w), 1607 (s), 1578 (s), 1489 (s), 1449 (s), 1422 (m),

1270 (s), 732 (s), 704 (s), 610 (m). UV–Vis (DMF, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol L}^{-1} \text{cm}^{-1}$)): 227 (27300), 267 (22640), 318 (8600).

2.2.4. Complex **3**

To a solution of the ligand **H₂L** (559 mg, 1 mmol) in methanol (10 mL) was added Et_3N (0.5 mL). After being stirred for five minutes, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (270 mg, 1 mmol) was added into the solution to give a deep purple solution. The reaction was further stirred for five minutes and LiClO_4 (106 mg, 1 mmol) was added to accrue a purple precipitate, which was collected *via* filtration, washed with methanol and dried in vacuum. Recrystallisation of the product in dichloromethane gave purple crystals of **3** after one week (413 mg, 58%). Anal. Calc. for $\text{C}_{35}\text{H}_{35}\text{N}_5\text{O}_6\text{ClFe}$ (FW = 713.0): C, 58.91; H, 4.91; N, 9.82. Found: C, 58.58; H, 4.93; N, 9.64%. IR (cm^{-1}): 3403 (s), 3011 (w), 2921 (2), 2861 (w), 1605 (s), 1486 (s), 1442 (m), 1270 (s), 1154 (s), 1083 (s), 1015 (s), 795 (m), 639 (m), 545 (m). UV–vis (DMF, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol L}^{-1} \text{cm}^{-1}$)): 220 (24360), 260 (21460), 356 (1495), 585 (890).

2.3. X-ray crystallography [34]

The procedures for the data collection of X-ray single crystal diffraction data were the same as described in our previous work [35]. All non-hydrogen atoms were modeled anisotropically. Except for the hydroxyl hydrogen atoms, which were added from a Fourier map, all other hydrogen atoms were placed in idealized positions and treated as riding atoms. Details of the data collection and refinement are given in Table 1.

2.4. Catalytic oxidation of benzene with H_2O_2 in acetonitrile

A typical procedure for the catalytic oxidation of benzene has been reported in previous work [21]. To a solution of the catalyst (20 μmol), benzene (10 mmol) and CH_3CN (3 mL) in a reaction flask (25 mL), an aqueous solution of H_2O_2 (2 mL, 30%) was added. The reaction mixture was heated to 80 °C and stirred vigorously for 3 h. After being cooled to room temperature, the reaction mixture was filtered, and the filtrate formed into two layers. The sample taken from the upper organic layer was analyzed by gas chromatography.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of the ligand with Cu^{2+} , Ni^{2+} and Fe^{3+} is summarized in Scheme 1. In our work, we found its reaction with three equivalents of Cu^{2+} in the presence of excess Et_3N afforded a hexanuclear cluster, $[\text{Cu}_6\text{L}_2(\text{OH})_4](\text{ClO}_4)_4$, in which the six Cu^{2+} centres were bridged by the oxygen atoms of the phenolate groups of the ligand and four OH^- groups. However, when no base was added, the reaction of the ligand **H₂L** with either one or two equivalents of CuCl_2 produced only a mononuclear complex, $[\text{Cu}(\text{H}_2\text{L})](\text{Cl})(\text{PF}_6)$ (**1**), in which the two phenol groups were pendant, without being deprotonated. Under similar conditions, only oily products, which were unsuitable for further characterization, were obtained when both Ni^{2+} and Fe^{3+} were employed. When a base such as Et_3N was used, the reaction of **H₂L** with either one or two equivalents of Ni^{2+} and Fe^{3+} gave rise to two mononuclear complexes, $[\text{Ni}(\text{HL})](\text{BPh}_4)$ (**2**) and $[\text{Fe}(\text{L})](\text{ClO}_4)$ (**3**), respectively. In complex **2**, only one phenol group was deprotonated and subsequently coordinated to Ni^{2+} , whereas in complex **3**, both phenol groups were completely deprotonated and coordinated to the Fe^{3+} ion to form a seven-coordinated complex.

Download English Version:

<https://daneshyari.com/en/article/1334489>

Download Persian Version:

<https://daneshyari.com/article/1334489>

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