



The synthesis and characterization of new nickel complexes with unusual coordination modes



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ABSTRACT

Two mononickel complexes, $K_2[Ni(Hccdp)](CH_3OH) \cdot 8H_2O$ (**1**), and $[Ni(H_2O)_6][Ni(H_2ccdp)(H_2O)_2]_2 \cdot 12H_2O$ (**2**); a dinickel complex, $K_2[Ni_2(ccdp)(acac)(H_2O)_2] \cdot 7H_2O$ (**3**); and a tetranickel complex, $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2] \cdot 23H_2O$ (**4**) ($ccdp^{5-} = N,N'$ -Bis[2-carboxybenzomethyl]- N,N' -Bis[carboxymethyl]-1,3-diaminopropan-2-ol; $acac^- =$ acetylacetonato) have been synthesized and fully characterized using different techniques including single crystal X-ray crystallography and electrochemistry. The redox behavior of complexes **1–4** were studied using cyclic voltammetry either in water or DMF solution systems. Whereas complexes **1, 2** and **4** found to be redox active, complex **3** showed no redox activity in water.

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1. Introduction

Microorganisms have evolved to utilize nickel ions in several different enzymes. Examples of such enzymes include Ureases, Ni–Fe hydrogenase, CO dehydrogenase, methyl-coenzyme M reductase, etc [1–3]. Coordination environment around the metal centers in each of these enzyme's active sites are different. Furthermore, some of these metal centers are redox active; others are inactive and act as Lewis acid centers for enzymatic hydrolysis. Ureases are a class of enzymes that catalyze the hydrolysis of urea to carbon dioxide and ammonia. Urease has always generated a wide research interest since it was the first enzyme purified and isolated in crystalline form in 1926 [4]. Additionally, it was the first enzyme found to utilize nickel(II) as a cofactor, which was curious considering how other metallohydrolases typically utilize a strong Lewis acid, Zn(II) [5–7]. The first X-ray crystal structure for urease was determined by Karplus and group in 1995, from *Klebsiella aerogenes*, and since then many more have been solved for different types of ureases with greater resolution to produce further insight into the overall structure of the enzyme and its active site [8–14]. As shown in Scheme 1, the active site contains two nickel (II) ions bridged together by a carbamylated lysine residue and a bridging deprotonated water molecule [14–16]. The Ni(II)–Ni(II) internuclear distances in ureases of different bacterial sources

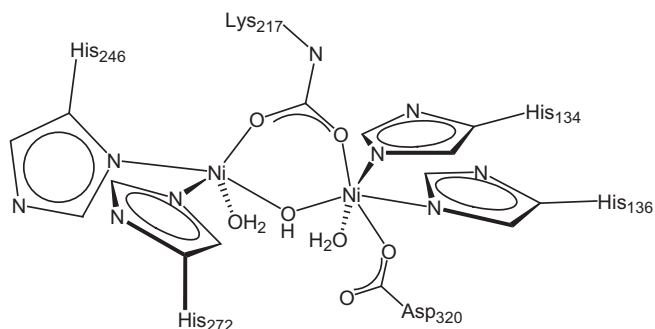
range from 3.5–3.7 Å. Although the reaction mechanism of the enzyme is still being debated, urease is considered to be one of the most efficient catalyst found in nature with a K_{cat}/K_M value of about 10^{14} times higher than the uncatalyzed reaction [16–18].

Although many dinucleating ligands have been synthesized in an effort to mimic urease, and other metalloenzymes, most of these turn out to be poor functional models as they lack catalytic activities. Hence, the interest for developing functional/structural mimics is pursued to help understand the catalysis and mechanism of reactions catalyzed by the enzyme.

In this study, the ligand N,N' -Bis[2-carboxybenzomethyl]- N,N' -Bis[carboxymethyl]-1,3-diaminopropan-2-ol (H_5ccdp) is used to synthesize a series of systematically altered nickel(II) complexes. While the H_5ccdp ligand has two symmetric NO_3^- coordination pockets suitable for binding to metal ions in close proximity, its flexibility and reactivity has yielded various coordination products when reacted with nickel(II) under different reaction conditions. Herein, we report two mononickel complexes, $K_2[Ni(Hccdp)](CH_3OH) \cdot 8H_2O$ (**1**), and $[Ni(H_2O)_6][Ni(H_2ccdp)(H_2O)_2]_2 \cdot 12H_2O$ (**2**); a dinickel complex, $K_2[Ni_2(ccdp)(acac)(H_2O)_2] \cdot 7H_2O$ (**3**); and a tetranickel complex, $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2] \cdot 23H_2O$ (**4**). Of particular interest are the binuclear and tetranuclear nickel complexes, **3** and **4**, in which the nickel centers have unsymmetrical donor and coordination environments, provided by the ligand $ccdp^{5-}$, H_2O , $acac^-$ and CO_3^{2-} ligands. All the complexes have been characterized by crystal structure analyses and spectroscopic methods. Moreover, the redox properties of the complexes are studied in detail.

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Scheme 1. Schematic depiction of the structure of the active site of *Klebsiella aerogenes* urease [6].

2. Experimental

2.1. Materials and methods

All starting materials were purchased from commercial sources and were used without further purification. UV–Vis spectrometry was performed using an Agilent 8453 UV–Vis Spectroscopy System in the spectrum/peak mode using a 1 cm Quartz cuvette. The ligand H_5ccdp , N,N' -Bis[2-carboxybenzomethyl]- N,N' -Bis[carboxymethyl]-1,3-diaminopropan-2-ol, has been prepared using the reported procedure [19]. Magnetic susceptibility of complexes **3** and **4** was measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as a callibrant.

2.2. Synthesis

2.2.1. Synthesis of $K_2Ni[Hccdp] \cdot 8H_2O$ (**1**)

A green wet methanol solution (1:1 by volume, 6 mL) of Ni $(CH_3CO_2)_2 \cdot 4H_2O$ (0.3720 g, 1.495 mmol) was slowly added into a stirring 6 mL methanolic solution (1:1 by volume) of H_5ccdp (0.500 g, 1.054 mmol) and KOH (0.3548 g, 6.323 mmol). The reaction mixture was then stirred for 19 h at room temperature. The dark green solution was collected and set for crystallization. Dark blue X-ray-quality single crystals were grown by slow acetone diffusion into the H_2O –MeOH filtrate solution. Yield: 0.2607 g (34.9%) *Anal. Calc.* for $C_{23}H_{38}NiN_2K_2O_{17}$: C, 36.75; H, 5.10; N, 3.73; Found: C, 36.17; H, 4.81; N, 3.05%. UV λ_{max} (H_2O) nm (ϵ): 358 (23.9), 584 (14.8), 762 (7.8).

2.2.2. Synthesis of $Ni(H_2O)_6[Ni(Hccdp)(H_2O)_2] \cdot 12H_2O$ (**2**)

A wet methanol solution (1:1 by volume, 6 mL) of Ni $(NO_3)_2 \cdot 6H_2O$ (0.1247 g, 0.4288 mmol) was slowly added into a stirring 6 mL methanolic solution (1:1 by volume) of H_5ccdp (0.1500 g, 0.3164 mmol) and $(CH_3)_4NOH \cdot 5H_2O$ (0.1799 g, 0.9939 mmol). The reaction mixture was then left stirring overnight at room temperature. A light blue solution was obtained, filtered and portions of it were set for crystallization. The light green X-ray-quality single crystals were grown by slow diethyl ether diffusion into the light blue filtrate. Yield: 0.0942 g (42.8%) *Anal. Calc.* for $C_{46}H_{88}Ni_3N_4O_{40}$: C, 36.49; H, 5.82; N, 3.70; Found: C, 35.75; H, 5.72; N, 3.46%. UV λ_{max} (DMSO) nm (ϵ): 395 (50.0), 661 (26.8).

2.2.3. Synthesis of $K_2[Ni_2(ccdp)(C_5H_7O_2)(H_2O)_2] \cdot 7H_2O$ (**3**)

A wet methanol suspension (1:1 by volume, 6 mL) of Ni(2,4-pentanedionate)₂ (0.5420 g, 2.109 mmol) was slowly added into a stirring 6 mL water–methanol solution (1:1 by volume) of H_5ccdp (0.5000 g, 1.054 mmol) and KOH (0.3551 g, 6.329 mmol) at room temperature. The reaction mixture was left to react while stirring for 19 h at room temperature. A pale green precipitant was formed

and was removed after filtration. Dark green X-ray-quality single crystals were grown by slow diethyl ether diffusion into the dark green H_2O –MeOH filtrate solution. Yield: 0.3163 g (37.6%) *Anal. Calc.* for $C_{28}H_{43}Ni_2N_2O_{18}$: C, 37.72; H, 4.86; N, 3.14; Found: C, 37.64; H, 4.51; N, 2.59%. UV λ_{max} (H_2O) nm (ϵ): 634 (35.8)

2.2.4. Synthesis of $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2] \cdot 23H_2O$ (**4**)

A green wet methanol solution (1:1 by volume, 6 mL) of Ni $(CH_3CO_2)_2 \cdot 4H_2O$ (0.3720 g, 1.495 mmol) was slowly added into a stirring 6 mL methanolic solution (1:1 by volume) of H_5ccdp (0.250 g, 0.527 mmol) and Cs_2CO_3 (1.031 g, 3.165 mmol). The reaction mixture was then stirred for 19 h at room temperature. The dark green solution was collected and was set for crystallization. Green X-ray-quality single crystals were grown by slow acetone diffusion into the H_2O –MeOH filtrate solution. Yield: 0.5236 g (61.4%) *Anal. Calc.* for $C_{48}H_{88}Cs_6Ni_4N_4O_{47}$: C, 23.00; H, 3.54; N, 2.24; Found: C, 22.03; H, 2.87; N, 1.67%. UV λ_{max} (H_2O) nm (ϵ): 388 (78.35), 644 (36.41), 659 (35.49). Room temperature magnetic study.

2.3. X-ray crystallography

The data were collected at 98(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and unit cell refinement were performed using *Crystal Clear* software [20]. The data was measured in the range $2.20 < \theta < 27.5^\circ$ using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with *Crystal Clear* [20] and *ABSCOR* [21], respectively. The structure, using *SHELXL-97*, was solved by direct methods and refined (on F^2) using full-matrix, and least-squares techniques [22,23]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. Electron density peaks were used to identify oxygen bound hydrogen atoms and the displacement parameters were set to 1.5 times the displacement parameters of the bonded atoms.

2.4. Electrochemical measurement

Electrochemical measurements were made on a BAS-CV50 electroanalyzer controlled with a Pentium III computer and utilizing three-electrodes: glassy carbon working electrode, platinum wire counter electrode, and a Vycor-tipped Ag/AgNO₃ reference electrode. Working electrodes were polished to a mirror finish on a microcloth of diamond or alumina (1.0 and 0.05 mm particles, respectively) and were cleaned electrochemically. Cyclic voltammograms were obtained from 1.0 mM analyte concentration in either water or DMF, using 0.1 M KCl or $[n-Bu_4N][PF_6]$ supporting electrolytes, respectively. Data were analyzed using the software provided with this instrumentation. Solutions were degassed with a purge of N₂ for 10 min and a blanket of N₂ was maintained over the solution while making the measurements. The *iR* compensation between the working and reference electrodes was accomplished by applying the positive feedback from the BAS-CV50 current follower. All potentials were measured at room temperature and scaled to NHE using either methyl viologen (MV^{2+}/MV^+ literature value is $E_{1/2}^{NHE} = -0.45 \text{ V}$ versus NHE in water) [24] or ferrocene (Cp_2Fe/Cp_2Fe^+ literature value $E_{1/2}^{NHE} = 0.40 \text{ V}$ versus NHE in DMF) [25] as an internal standards.

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