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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, $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2]^{\cdot}23H_2O(4)$ ($ccdp^{5^-} = N,N^{\cdot}$ -Bis[2-carboxybenzomethyl]- N,N^{\cdot} -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 complex 1, 2 and 4 found to be redox active, complex 3 showed no redox activity in water.

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.^{1,2,3} 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).^{5,6,7} 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 3.5-3.7Å. 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 (H₅ccdp) is used to synthesize a series of systematically altered nickel(II) complexes. While the H₅ccdp ligand has two symmetric NO₃ 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.

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-visible Spectroscopy System in the spectrum/peak mode using a 1 cm Quartz cuvette. The ligand H₃ccdp, *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 CuSO₄5H₂O as a callibrant.

2.2. Synthesis

2.2.1. Synthesis of $K_2Ni[Hccdp]$ 8H₂O(1)

A green wet methanol solution (1:1 by volume, 6mL) of Ni(CH₃CO₂)₂'4H₂O (0.3720g, 1.495mmol) was slowly added into a stirring 6 mL methanolic solution (1:1 by volume) of H₅ccdp (0.500 g, 1.054 mmol) and KOH (0.3548g, 6.323 mmol). The reaction mixture was then stirred for 19 hrs 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 H₂O-MeOH filtrate solution. Yield: 0.2607g (34.9%)

Anal. Calcd. for $C_{23}H_{38}Ni_1N_2K_2O_{17}$: C, 36.75; H, 5.10; N, 3.73; Found: C, 36.17; H, 4.81; N, 3.05. UV λ_{max} (H₂O) nm (ϵ): 358 (23.9), 584 (14.8), 762 (7.8)

2.2.2. Synthesis of $Ni(H_2O)_6[Ni(Hccdp)(H_2O)_2]_2$ 12H₂O (2)

A wet methanol solution (1:1 by volume, 6mL) of Ni(NO₃)₂[•]6H₂O (0.1247g, 0.4288 mmol) was slowly added into a stirring 6 mL methanolic solution (1:1 by volume) of H₅ccdp (0.1500g, 0.3164 mmol) and (CH₃)₄NOH 5H₂O (0.1799g, 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: 0.0942g (42.8%) Anal. Calcd for C₄₆H₈₈Ni₃N₄O₄₀ : 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 $K_2[Ni_2(ccdp)(C_5H_7O_2)(H_2O)_2]$ 7 $H_2O(3)$

A wet methanol suspension (1:1 by volume, 6mL) of Ni(2,4-pentanedionate)₂ (0.5420g, 2.109 mmol) was slowly added into a stirring 6 mL water-methanol solution (1:1 by volume) of H₅ccdp (0.5000g, 1.054 mmol) and KOH (0.3551g, 6.329 mmol) at room temperature. The reaction mixture was left to react while stirring for 19 hrs 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 H₂O-MeOH filtrate solution. Yield: 0.3163g (37.6%) Anal. Calcd for C₂₈H₄₃Ni₂N₂O₁₈ : C, 37.72; H, 4.86; N, 3.14; Found: C, 37.64; H, 4.51; N, 2.59. UV λ_{max} (H₂O) nm (ϵ): 634 (35.8)

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

A green wet methanol solution (1:1 by volume, 6mL) of Ni(CH₃CO₂)₂'4H₂O (0.3720g, 1.495mmol) was slowly added into a stirring 6 mL methanolic solution (1:1 by volume) of H₅ccdp (0.250 g, 0.527 mmol) and Cs₂CO₃ (1.031g, 3.165 mmol). The reaction mixture was then stirred for 19 hrs 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 H₂O-MeOH filtrate solution. Yield: 0.5236g (61.4%) Anal. Calcd for C₄₈H₈₈Cs₆Ni₄N₄O₄₇ : C, 23.00; H, 3.54; N, 2.24; Found: C, 22.03; H, 2.87; N, 1.67. UV λ_{max} (H₂O) 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 α radiation (λ = 0.71073 Å). Data collection and unit cell refinement were performed using *Crystal Clear* software.²⁰ The data was measured in the range 2.20 < θ < 27.5° 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 $E_{1/2}^{\text{NHE}} = -0.45 \text{ V}$ Vs NHE in water)²⁴ or ferrocene (Cp₂Fe/Cp₂Fe⁺ literature value $E_{1/2}^{\text{NHE}} = 0.40 \text{ V}$ Vs NHE in DMF)²⁵ as an internal standards.

3. Results and discussion

3.1. Synthesis

As shown in **Scheme 2**, the ligand H_5 ccdp was synthesized in two pot reactions. The synthesis of the precursor reduced Schiff base, H₃cdp, was accomplished by the condensation of stoichiometric amounts of 2-carboxybenzaldehyde and 1,3-diaminopropan-2-ol in presence of NaOH in methanol under refluxing conditions for 4 hrs, followed by the subsequent reduction using NaBH₄. Acidification of the resulting solution by addition of HCl to pH of 5 yielded a precipitation of white solid product. The product was characterized to be a reduced Schiff base, H₃cdp·H₂O, by different analytical techniques such as elemental analysis, FTIR and NMR spectroscopy. Alkylation of the secondary amines of H₃cdp with stoichiometric quantities of iodoacetic acid produced the dinucleating ligand, H₅ccdp, in good yield. The reaction of Ni(II) salt with H₅ccdp in several different molar ratio in presence of mild bases, such as (CH₃)₄NOH, NEt₃ or K₂CO₃, or strong bases such as NaOH in methanol at room temperature conditions for several hours afforded different complexes, which were crystallized into a range of monoto tetra-nickel complexes, K₂Ni[Hccdp][•]8H₂O (1), $Ni(H_2O)_6[Ni(Hccdp)(H_2O)_2]_2 \cdot 12H_2O$ (2), $K_2[Ni_2(ccdp)(C_5H_7O_2)(H_2O)_2] \cdot 7H_2O$ (3) and $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2]^2 23H_2O$ (4). Details of the synthesis are given in the experimental section.

3.2. Crystal structures

Cell parameters and data collection summaries for all complexes are given in Table 1. The molecular structures for complexes 1 - 4 are shown in Fig.s 1, 2, 4 and 5, respectively; selective bond angles and bond lengths are given in Table 2.

$3.2.1. K_2 Ni[Hccdp]^{\circ} 8H_2 O(1)$

Crystal structure of the mononuclear complex, 1 consists of one dianionic $[Ni(Hccdp)]^{2}$ species, two potassium counter cations along with eight water molecules of crystallization. A view of the anion of 1 is depicted in Fig. 1. The crystallographic summary and selected metric data are given in Tables 1 and 2, respectively. The molecular structure contains a nickel(II) coordinated to the Hccdp⁴⁻ ligand and two noncoordinated potassium counter cations. The coordination geometry around the nickel ion is best described as a distorted octahedral geometry with an N₂O₄ environment where there are two aliphatic carboxylate oxygens, two aromatic carboxylate oxygen and two tertiary amine nitrogens of the ligand. The nickel ion is coordinated to N(1) and N(2)from the tertiary amines and to O(3) and O(6) from the aliphatic carboxylate oxygens to form the equatorial plane. Both the amines and the carboxylate oxygens are coordinated to the nickel center in *cis*- fashion of the plane. The O(1) and O(8) from the aromatic carboxylate oxygen atoms reside *trans* to each other occupying the axial positions of the octahedron. The major geometrical distortion of the originates from the large bite angle $[O(3)-Ni-O(6) = 101.68^{\circ}]$ as well as in the small bite angles $[O(3)-Ni-N(1) = 82.57^{\circ}]$; $[O(6)-Ni-N(2) = 81.20^{\circ}]$; and $[O(3)-Ni-O(8) = 84.00^{\circ}]$ of the dinucleating ligand. One interesting feature of the crystal structure of complex 1 is that, although the pendant alcoholic part of the ligand is expected to act as a bridging alkoxo group, it is turned out of the coordination environment. The H-bond network systematically distributed through the crystal lattice, as shown in the packing diagram, has contributed towards the overall stability of the crystal lattice. The extended network of H-bonding is constructed through the water molecules, alcoholic-OH, aliphatic-COO-, and aromatic-COOH groups of the ligands. The bond distances and bond angles for complex 1 are in well within the range of metric values of similar nickel(II) complexes reported in the literature.²⁶⁻³⁹

3.2.2. $Ni(H_2O)_6[Ni(Hccdp)(H_2O)_2]_2$ 12H₂O (2)

Crystal structure of complex **2**, consists of two monoanionic $[Ni(H_2ccdp)]^{-1}$ species, a $Ni(H_2O)_6^{2+}$ counter cation and eleven cocrystallized water molecules engaged in stabilizing the crystal lattice. An ORTEP that shows the anion part of complex **2** is presented in Fig. 2, and crystallographic summary and selected metric data for the structure are listed in Tables 1 and 2, respectively. The monoanionic species of complex

contain a nickel(II) center coordinated to the dinucleating ligand H₂ccdp³⁻ and two water molecules. The coordination geometry around the nickel ion is best described as a distorted octahedral geometry formed by the alcoholic oxygen, acetate oxygen, benzoate oxygen and tertiary amine nitrogen of the ligand in addition to the two oxygen atoms form water molecules. Whereas the O(8) and O(6) from the respective benzoate and the acetate carboxylates groups of the ligand are coordinated to the nickel(II) center in a trans fashion, the O(10) and O(11) of the two water molecules are *cis*- to each other. The major distortion of the resulting octahedral coordination sphere originates in the large bite angles for the O(10)-Ni-N(2) = 100.6° and O(10)-Ni-O(8) = 97.6° as well as in the small bite angles for the O(6)-Ni-N(2) = 76.14°, O(6)-Ni-O(10) = 83.5° and O(5)-Ni-N(2) = 83.1° of the ligand. One interesting feature of the crystal structure of complex 2 is that the pendant alkoxo arm of the ligand and that one of the tertiary amines (N2) is protonated and thus only one Ni(II) cation is incorporated into the coordinating pocket of the unprotonated side of the dinucleating ligand. The stability of this structure is assumed due to the eleven waters of crystallization which stabilize the system by forming a strong H-bond network systematically distributed through the lattice, Fig. 3. The extended network of the H-bonding is constructed through the coordinates and free water molecules, alcoholic –OH, aliphatic –COO⁻, aromatic –COOH and ammonium groups of the vacant site of the ligand as well as the hexa-aqua nickel cation that sits in the crystallographic center if symmetry. Previously, we have reported literature similar network of H-bonding that stabilized Zn(II) complexes.¹⁹ The rest of the bond distances and bond angles observed for complex 2 are consistent with values reported in the literature.³⁰⁻⁴¹

3.2.3. $K_2[Ni_2(ccdp)(acac)(H_2O)_2]^{-}7H_2O(3)$

The crystal structure of the dinuclear complex **3** consists of one dianionic $[Ni_2(ccdp)(acac)(H_2O)_2]^{2-}$ specie, and two potassium counter cations. A view of the dianion portion of complex **3** is depicted in Fig. 4, and selected metric data are presented in Table 2. The dianionic complex consists of two Ni(II) ions bridged by the alkoxo group, the ccdp⁵⁻ ligand, two water molecules coordinated to Ni(1), and exogenous acetylacetonato ligand coordinated to the Ni(2) center in a bidentate fashion is

crystallized in $P\overline{1}$ space group. Despite the fact that ccdp⁵⁻ is a symmetrical dinucleating ligand, the coordination environments around each of the Ni(II) centers are not symmetrical. The crystal structure of the complex indicates that the coordination of the binucleating ccdp⁵⁻ ligand to the two Ni(II) centers is best described as octahedral geometries with each metal center missing *cis*--sites. The missing *cis*--sites are, then, taken with two water molecules and acetylacetonate ion around Ni (1) and Ni(2) center, respectively. While the equatorial plane around Ni(1) is defined by the bridging alkoxo, the tertiary amine and the two water molecules, the equatorial plane around the Ni(2) has the bridging alkoxo, tertiary amine and the acetylacetonate group coordinated in a bidentate fashion. While the acetate and the benzoate carboxylate arms on one end of the ccdp^{5-} ligand take the axial positions around Ni(2), the acetate and the benzoate carboxylate on the other end of the ligand take equatorial positions on a *cis*—fashion to each other around Ni(1). The two acetate and two benzoate arms of the ligand appear at the opposite sides of the plane defined by the propyldiamine backbone and the two nickel centers. Recently, we have reported similar configuration of the ccdp⁵⁻ ligand around a polynuclear cobalt complex.⁴² The degree of distortion around the Ni(1) center is pronounced by the large bite angle of O(13)-Ni(1)-N(1) = 107.5° as well as in the small bite angles for the O(5)-Ni(1)-N(1) = 82.0° , O(13)-Ni(1)-O(12) = 82.1° and O(3)-Ni(1)- $N(1) = 82.3^{\circ}$. Despite the fact that the Ni(2) is coordinated to the ccdp⁵⁻ ligand in a similar manner to the Ni(1) center, the octahedral distortions are not as severe as around Ni(1). Slight distortions are observed in the O(6)-Ni(2)- $O(11) = 93.72^{\circ}$ and O(6)-Ni(2)- $N(2) = 79.79^{\circ}$ bite angles. Another interesting structural feature of the complex is the 133.4° for the Ni(1)-O(5)-Ni(2) bond angle. The degree is wider than expected for a tetrahedral oxygen but is slightly smaller to values observed for similar complexes reported in the literature.²⁹ The average Ni-O_{water}, Ni-O_{benzote}, Ni-O_{acetate}, Ni-O_{alkoxo}, Ni-O_{acac} and Ni-N_{amine} bond distances are 2.110, 2.076, 2.081, 2.042, 2.029 and 2.075 Å, respectively. The observed bond lengths are comparable to values reported for similar complexes in the literature. ^{19, 26-50}

The internuclear Ni(1)---Ni(2) distance in complex **3** is 3.75 Å. While this distance is at the long end range of distances observed in the active site of the urease, it is

comparable to distances in enzyme model dinickel complexes reported in the literature.^{29,38,39,44-50} Moreover, the nickel coordinated water molecules present an opportunity as a good leaving group for substrate binding and/or protonation of urea in hydrolysis. The fact that one of the water molecules has an extended bond length to the nickel is a testament to its candidacy for a good leaving group in presence of substrates. Hence, Complex **3** is an suitable structural model for the active site of urease, which contains two nickel(II) ions bridged together by a carbamylated lysine residue and deprotonated water molecule, histidine and carboxylate ligands, Scheme 1.6

3.2.4. $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2]^2 3H_2O(4)$

The unit cell of the crystal structure contains a tetranuclear Ni(II) complex anion, 4, consists of two trianionic $[Ni_2(ccdp)(\mu-\eta^2-\eta^2-CO_3)]^{3-1}$ fragments, and six cesium counter cations, along with 23 water molecules of crystallization. While the ORTEP of the molecular structure of the complex 4 anion is shown in Fig. 5, selected metric data for the structure are summarized in Table 2. The X-ray characterization of 4 reveals that the complex is terta-nickel cluster produced as a result of self-assembly of two [Ni₂(ccdp)]⁻ units and two bridging CO_3^{2} ions coordinated to the nickel centers in the rare *anti-anti*, *pseudo-oxo*, μ - η^2 - η^2 -carbonato fashion. The coordination geometries around each Ni(II) center is best described as a distorted octahedral geometry defined by NO₅ coordination environments. All the nickel centers are coordinated to the μ -alkoxo, the acetate oxygen, the benzoate oxygen, the tertiary amine nitrogen of the $ccdp^{5}$ ligand and two oxygens from the bridging carbonato ligand. The octahedral geometry around Ni(1) is defined by the O(10), O(11), O(5), and N(1) atoms at the equatorial positions and the O(1) and O(3)at the axial positions. While the benzoate and the acetate arms of $ccdp^{5-}$ ligand take the distorted axial positions, the amine, the alkoxo and the carbonate groups occupy the equatorial positions of the octahedral. The bond angles for O(1)-Ni(1)-O(3), O(5)-Ni(1)-O(10), O(10)-Ni(1)-O(11), O(10)-Ni(1)-N(1) and O(5)-Ni(1)-N(1) are 169°, 105°, 63°, 105°, 87°, respectively. Similar coordination behaviors were observed around other three Ni(II) centers of the complex. These metric values indicate the severity of distortion of

the octahedral geometry around the nickel centers. Furthermore, the crystal structure indicates displacement of the nickel centers from their respective equatorial planes by 0.08 Å and 0.11 Å for Ni(1) and Ni(2), respectively.

One other interesting feature of the structure is the 142° bond angles between the two nickel centers bridged by the alkoxo moiety of ccdp⁵⁻ ligand, Ni(1)-O(5)-Ni(2). The rather large bond angles observed in this structure is rare among similar complexes reported in the literature.^{26,46,51-61} This bond angle indicates that the alkoxo oxygens take a curious closer to sp² than sp³ hybridization. This hybridization on oxygen is quite interesting, with the lone pair on the p_z orbital overlapping with the partially filled $d_x^2-y^2$ orbital from Ni(II) ion. When compared to the Ni-O-Ni bond angle observed in complex **3**, it is interesting to note that the angles are larger in complex **4**. The observed large bond angle is attributed to the highly flexible nature of the ccdp⁵⁻ ligand to open up the angle upon binding to the carbonato bridges in making complex **4**.

The average Ni-O_{benzoate}, Ni-O_{acetate}, Ni-O_{alkoxo} and Ni-N_{amine} bond distances are 2.045, 2.116, 2.038 and 2.060 Å, respectively. These bond lengths are comparable to values reported for similar complexes in the literature but longer than other reported phenoxo-O bridged dinuclear Ni(II) complexes.^{27,28,44,45,49,50} Whereas the alkoxo bridged average Ni---Ni internuclear distance is 3.86 Å, a longer carbonato bridged Ni---Ni average distance of 4.28 Å is observed. While the former Ni---Ni internuclear distance is slightly longer than observed in complex 3 and other alkoxo bridged dinuclear nickel complexes in the literature, the latter is shorter than distances reported for similar complexes reported in the literature.^{27,28,44,45} As the result of this rather rare coordination ability the carbonato ligand, a cluster with a distorted octagonal shape cavity defined by Ni(1)-O(5)-Ni(2)-O(12)-Ni(2a)-O(5a)-Ni(1a)-O(10) atoms is formed. The front and side of the cavity are depicted in Fig. 6. The Ni(1)---Ni(2a) internuclear distance, 5.75 Å, can be considered as reasonable approximation of the diametric size of the cavity. The Ni(1)-O(10)-Ni(1A) and Ni(2)-O(12)-Ni(2A) bond angles of 173 and 170°, respectively, constructs an interesting slightly distorted irregular hexagon out of the octagonal The other observed bond distances and bond angles for complex 4 are geometry. consistent with values reported in the literature.^{19,26-50,56,57,60,61}

Several coordination modes of carbonato ligands with polynuclear nickel complexes have been reported in the literature.^{27,28,62} However, the observed μ - η^2 - η^2 -cabonato coordination, as shown in Fig. 6, to produce the tetranuclear nickel complex has not been previously reported. The coordination modes described in the literature for the carbonate ion as a bridge in polynickel complexes is summarized in Scheme 3.^{27,28,62}

3.3. Electrochemical Study

The electrochemical behavior of complexes 1-4 were studied using cyclic voltammetry at room temperature in water or DMF solutions containing 0.1 M KCl and $(Bu)_4NPF_6$ supporting electrolytes, respectively. The electrochemical data are presented in Table 3. All potentials are referenced to NHE using either ferrocene or methyl viologen as internal standards. Except complex 3, all show some form of redox behavior within water and DMF potential windows. Under similar experimental conditions, the electrochemical studies of the free ligand using the cyclic voltammetry showed no electrochemical activity within the scanned potential window. Thus, the electrochemical waves observed in the cyclic voltammagrams of the complexes are metal based.

The metal based reduction potential data for the complexes is summarized in Table 3. As presented in the table, complex **1** showed one quasi reversible reduction at 1.29 V ($\Delta E_p = 100 \text{ mV}$). The values of ΔE_p and peak current ratio of the wave at 1.29 V are slightly bigger than what is expected for one-electron transfer processes. This redox event for complex **1** and its $E_{1/2}$ value is constant with different scan rates (25-500 mV/s). Due to poor water solubility, the electrochemical measurement of complex **2** was performed in dry DMF. The complex showed a persistent irreversible reduction peak at - 0.92 V with in the potential window. Whereas complex **3** didn't display any redox activity in water, under the same electrochemical conditions, complex **4** showed two irreversible waves centered at potential of 1.15 and 1.00 V. The large anionic charge of the complex **4** is partly responsible for the considerably resistance to reduction as indicated to by the E_{pc} potential value of 1.15 V when compared to the rest of the complexes in this report.

3.4. Magnetic Study

Whereas the dinickel complex **3** shows an effective magnetic moment, μ_{eff} , of 4.01 µB, the tetranickel complex **4** shows a room temperature magnetic moment value of 4.62 µB. These values are lower than that expected for two and four noninteracting nickel(II) centers in an octahedral geometry. These indicate that the nickel(II) centers in complexes **3** and **4** are antiferromagnetically coupled. The measured magnetic moments for complex **1** and **2** are 2.96 and 2.98 µB, respectively. These values are expected for mononickel(II) complexes in octahedral geometries as two unpaired electrons are responsible for the overall magnetic moment.

4. Conclusion

Four new nickel complexes of the ligands H₅ccdp with interesting coordination chemistry have been synthesized and fully characterized. The nickel centers exhibited different coordination numbers and several coordination modes with the carboxylate and carbonato groups of the ligands. Whereas, the nickel center of complex 1 is in a N₂O₄ octahedral environment involving a single ligand wrapping around Ni(II), the other single mononickel complex, 2, has a NO₅ coordination sphere utilizing a single coordination pocket of the ligand and two waters to complete the octahedral environment. For complex 3, an asymmetric dinickel(II) complex was realized as the two Ni(II) centers acquire a NO₅ coordination environments with Ni(1) coordinated with two water molecules and Ni(2) with a single acetylacetonate exogenous ligands. On the other hand, a highly symmetrical tetranickel complex 4 with four NO₅ Ni(II)s with a rare μ_4 carbonato bridging motif has been characterized. With the exception of complex 3, all complexes showed fairly accessible redox activities in water. The unusually larger anionic charge of the complex 4 is partly responsible for the considerably accessible oxidation potential when compared to the rest of the complexes in this report. Room temperature magnetic study of complex 3 and 4 suggested that the metal centers are antiferromagnetically coupled. Overall, these studies indicates that H_5 ccdp is a highly flexible ligand that provides a highly versatile and tunable coordination scaffold for nickel(II).

Acknowledgements

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Supporting Information: The cyclic voltammograms in aqueous solution or DMF of complexes 1 - 4 in 0.1 M KCl or (Bu)₄NPF₆ with platinum or GC working electrodes at scan rate ranges of 100 mV/s are reported in Figs 1S-5S.

Scheme 1



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

m

1

Scheme 2





Scheme 3 Cast of carbonato coordination modes in polynuclear nickel complexes reported in the literature.



Scheme 4. Schematic representation of the synthesis of complexes 1-4, shown are only the anioinc complexes.

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Fig 1. Thermal ellipsoid plot (50% probability) of the core dianionic complex ion, [Ni(Hccdp)]²⁻ (1).



Fig 2. Thermal ellipsoid plot (50% probability) of the core monoanionic complex ion, [Ni(H₂ccdp)]⁻, (2).



Fig 3. Thermal ellipsoid plot (50% probability) showing the extensive H-bonding network among the three monoanionic complex ions, $[Ni(H_2ccdp)]^-$ (2), twelve molecules of water of crystallizations and the $[Ni(H_2O)_6]^{2+}$ ion.



Fig 4. Thermal ellipsoid plot (50% probability) of the core dianionic complex ion of $[Ni_2(ccdp)(acac)(H_2O)_2]^2$, (3).



Fig 5. Thermal ellipsoid plot (50% probability) of the anionic complex ion of $[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2]^{6-}$, (4).



Fig 6. (a) Thermal ellipsoid plot (50% probability) of the core anionic complex of **4**, $[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2]^{6^-}$, demonstrating the μ_4 -cabonato and the octagonal cavity defined by Ni(1)-O(5)-Ni(2)-O(12)-Ni(2a)-O(5a)-Ni(1a)-O(10). (b) Side view of the cavity.

Complex	1	2	3	4
Empirical formula	$C_{48.40}H_{61.20}K_4N_4$	$C_{46}H_{84}N_4Ni_3O_{40}$	$C_{28}H_{45}K_2$	C ₄₈ H ₄₀ Cs _{5.3}
-	Ni_2O_{27}		$N_2Ni_2O_{19}$	N ₄ Ni ₄ O _{34.2}
Formula weight	1404.83	1509.30	908.6	2159.30
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	$P 2_1/m$
$a(\text{\AA})$	9.1881(16)	10.3408(9)	12.063(2)	13.597(3)
b(A)	12.795(2)	12.6088(16)	12.876(2)	22.209(4)
$c(\text{\AA})$	13.942(2)	14.1077(17)	13.704(2)	14.446(3)
$\alpha(^{\circ})$	108.373(3)	88.854(8)	63.940(7)	90
$\beta(^{\circ})$	99.105(2)	71.459(7)	81.347(7)	109.327(3)
$\gamma(^{\circ})$	106.5194(13)	66.063(5)	89.942(9)	90
Volume(Å ³)	1434.9(5)	1581.3(5)	1885.2(5)	4116.5(15)
Ζ, Ζ'	2,1	2,1	2,1	2,1
$\rho(calc.)$	1.623	1.585	1.513	1.742
λ	0.71073	0.71073	0.71073	0.71073
Temp.(K)	98(2)	98(2)	98(2)	98(2)
F(000)	728	792	880	2052
$\mu(\text{mm}^{-1})$	1.038	0.991	1.291	3.119
T_{min}, T_{max}	0.6458, 1.000	0.8142, 1.000	0.8641, 1.000	0.5763, 1.000
$2\theta_{range}(^{\circ})$	2.43 to 27.50	2.20 to 26.50	2.59 to 27.50°	2.37 to 26.50°
Reflections	10313	11622	14754	19833
Collected				
Independent	6528	6492	8620	8555
reflections	[R(int) = 0.0217]	[R(int)=0.0302]	[R(int)=0.0245]	[R(int)=0.0245]
Data / restraints /	6528 / 0 / 415	6492 / 0 / 490	8620 / 0 / 505	8555 / 0 / 496
parameters				
$wR(F^2 \text{ all data})$	0.0791	0.0995	0.1550	0.1788
<i>R</i> (<i>F</i> obsd data)	0.0396	0.0464	0.0616	0.0783
GOOF on F^2	1.008	1.017	1.04	1.074
Observed data	6210	6019	7796	7447
$[I] > 2\sigma(I)$				
Largest and mean	0.001/ 0.000	0.006/ 0.000	0.000/ 0.000	0.001/ 0.000
shift / s.u.				
Largest diff. peak	1.69/ -0.66	1.01/ -0.63	2.53/ -0.76	4.46/-2.45
and hole, $e/Å^3$				
		2 1/2		

 Table 1 Crystal data and structure refinement for complexes 1, 2, 3 and 4

 $wR2 = \{ \Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{1/2}; R1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$

	1 able 2. 5	elected bond len	guis [A] and	angles [] for col	inplexes 1, 2,	5 anu 4	
1		2		3		4	
Bond Length [Å]							
Ni-O1	2.056(2)	Ni-O5	2.106(2)	Ni1 Ni2	3.750(1)	Ni1A Ni2A	3.857(2)
Ni-O3	2.060(2)	Ni-O6	2.071(2)	Ni1-N1	2.071(3)	Ni1A […] Ni1	4.279(2)
Ni-O6	2.058(1)	Ni-O8	2.050(2)	Ni1-O1	2.067(5)	Ni1A […] Ni2	5.750(2)
Ni-08	2.067(2)	Ni-O10	2.083(2)	Ni1-O3	2.063(4)	Ni1-O5	2.039(6)
Ni-N1	2.093(2)	Ni-011	2.066(3)	Ni1-05	2.016(3)	Ni1-O1	2.052(6)
Ni-N2	2.103(2)	Ni-N2	2.088(3)	Ni1-O12	2.059(3)	Ni1-O10	2.1459(13)
				Ni1-O13	2.161(4)	Ni1-O11A	2.131(7)
				Ni2-N2	2.079(3)	Ni1-O3	2.115(6)
				Ni2-O5	2.067(3)	Ni1-N1	2.055(7)
				Ni2-06	2.098(3)	Ni2-05	2.038(6)
				Ni2-09	2.085(4)	Ni2-O12	2.1339(14)
				Ni2-O10	2.033(5)	Ni2-09	2.043(6)
				Ni2-O11	2.024(3)	N12-013A	2.111(7)
						Ni2-N2	2.066(7)
			D			Ni2-06	2.117(6)
			Boi	nd Angle [°]			
02 N: 06	101.69(7)	010 N:1 N2	100 < 1(0)	NEL OF NEC	122 4(1)	N:2 012 N:24	160.0(5)
$O_3 \text{ N}$: N1	101.08(7) 82.57(7)	O_{10} - N_{11} - N_2	100.01(9) 76 14(0)	012 Ni1 012	133.4(1) 82 14(12)	NIZ-UIZ-NIZA	109.9(3) 142.1(3)
O_5 -INI-INI	82.37(7) 81.20(7)	O6 Ni1 O10	70.14(9) 83 47(0)	013 - N11 - 012 013 Ni1 N1	1075(2)	$\frac{111}{100} \frac{100}{100} 10$	142.1(3) 171 2(5)
$O_{3}N_{1}O_{8}$	81.20(7) 84.00(7)	00-Ni1-010 05-Ni1-N2	83.47(9)	O_{1} -Ni1-N1	107.3(2) 81.96(13)	05-Ni1-01	922(3)
03-Ni-N2	174.17(7)	0.03 - Ni1 - Ni2	97.58(9)	0.12-Ni1-01	92.78(13)	05-Ni1-010	104.9(3)
01-Ni- 08	174.17(7) 174.63(7)	011-Ni1-010	95 31(11)	012-111-01 03-Ni1-N1	82 28(15)	05-Ni1-010	95 4(3)
N1-Ni-O8	89 78(7)	011 101 00	<i>ys</i> . <i>si</i> (11)	05-Ni1-013	88 19(12)	05-Ni1-N1	87 0(3)
08-Ni-N2	90.80(7)			011-Ni2-05	90.68(12)	01-Ni1-010	95.2(3)
06-Ni-O1	85.75(7)			09-Ni2-N2	93.30(14)	01-Ni1-011A	89.1(3)
01-Ni-O3	91.02(7)			06-Ni2-O10	88.81(12)	01-Ni1-N1	92.8(3)
				O6-Ni2-O11	93.72(13)	O10-Ni1-O11	62.5(3)
				O6-Ni2-N2	79.79(13)	010-Ni1-O3	90.7(3)
					~ /	011A-Ni1-03	85.3(3)
						O11A-Ni1-N1	105.3(3)
						O3-Ni1-N1	79.5(3)
)				O5-Ni2-O12	105.4(3)
		·				O5-Ni2-O9	93.3(3)
						O5-Ni2-O6	93.7(3)
						O5-Ni2-N2	87.4(3)
	V					012-Ni2-O9	94.3(3)
						O12-Ni2-O13A	63.1(3)
						O12-Ni2-O6	91.1(3)
						O9-Ni2-O13A	90.2(3)
						O9-Ni2-N2	93.4(3)
						O6-Ni2-O13A	84.4(3)
						O6-Ni2-N2	79.4(3)

 Table 2. Selected bond lengths [Å] and angles [°] for complexes 1, 2, 3 and 4

N2-Ni2-O13A 103.6(3)

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Complex	$E_{pa}\left(V ight)$	$E_{pc}\left(V ight)$	$E_{1/2}(V)$	$\Delta E(V)^{c}$	I_{pa}/I_{pc}
1 ^a	1.34	1.26	1.30	0.08	6.85
2 ^b	-	-0.92	-	-	- 0
4 ^a	1.15	1.00	1.08	0.15	8.06x10 ⁻²

^aPeak potential (V) and half wave potential are recorded in H₂O at 25 °C with glassy carbon electrode, 0.1 M KCl as supporting electrolyte. ^bComplex was insoluble in water, hence data was collected in DMF and 0.1 M (Bu)₄NPF₆ as supporting electrolyte. ^cThe peak potential separation .e u values for the systems. All potentials are referenced to NHE using either methyl viologen or

The Synthesis and Characterization of New Nickel Complexes with Unusual Coordination Modes

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Two mononickel complexes, K₂[Ni(Hccdp)](CH₃OH)[•]8H₂O(1), and

 $[Ni(H_2O)_6][Ni(H_2ccdp)(H_2O)_2]_2$ · 12H₂O(**2**); a dinickel complex,

 $K_2[Ni_2(ccdp)(acac)(H_2O)_2]$ ^{•7} H_2O (**3**); and a tetranickel complex, $Cs_6[Ni_4(ccdp)_2(\mu-\eta^2-\eta^2-CO_3)_2]$ ^{•2} $3H_2O$ (**4**) 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.



CRIF

Keywords

Nickel(II) complexes Carboxylate rich ligand Redox properties Unusual coordination

Highlights

- 1. Four new mono- and polynuclear nickel complexes were synthesized.
- 2. Redox activity of the complexes were studied

3. A novel bis(μ - η^2 - η^2 -CO₃) tetranickel complex, **2**, was produced