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Research paper

Mononuclear Cu(II) and Ni(II) complexes of bis(naphthalen-2-ol) Schiff base ligands

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ABSTRACT

With this work, we describe the synthesis and characterization of two new coordination complexes, a mononuclear **Cu(II)L** and a mononuclear **Ni(II)L** where the free base ligand is **H_2L** = 1,1′-(((2-hydroxypropane-1,3-diyl)bis(azanylylidene)) bis(methanylylidene))bis(naphthalen-2-ol). In both metal complexes, the coordination environments are observed to be 4-coordinate square planar with two phenolic oxygens and two imine nitrogens coordinating the metal while the central pendant hydroxyl group was not observed to participate in coordination. In contrast to previously reported dinuclear complexes with similar ligand systems, the alkaline conditions presented in this work resulted in only the mononuclear coordination environments observed.

1. Introduction

Coordination compounds have been of interest in a wide array of applications in the field of bioinorganic chemistry. Examples of metal complexes that can act as biomimics, as therapeutic agents in biological settings, as ion sensors, and – of note recently – in optical materials have been described in the literature [1–5]. Many metalloenzymes and metalloproteins found in nature are stable over only a modest temperature and pH range and coordinate transition metals, such as copper and nickel, through oxygen and nitrogen donor amino acids [6,7]. Many biological examples of metalloenzyme/metalloproteins feature nitrogen and oxygen as the core Lewis base atom with additional open coordination sites for labile waters [8]. The need for new metal-ligand complexes to observe unique or unusual coordination environments and better characterize their activity is still a growing area of interest [9,10].

Examples of multi-dentate ligand metal complexes with oxygen and nitrogen donors have been found to exhibit antimicrobial behavior comparatively showing inhibition concentrations for lower than that of standard antibacterial and antifungal medications such as Ampicillin and Nystatin [1,11]. For these purposes, electronically dense functional groups, such as phenol and imine groups, are of interest for their versatility and relative pH stability, as compared to metalloenzymes with similar coordination geometries [7]. Salen ligands, containing two phenol and two imine donor atoms, have been investigated for their use as antimicrobial compounds and have shown some promise in this area. Imine containing compounds, Schiff base ligands, have been used in this chemistry due its stability over a wide pH range, versatility in coordination environments, flexibility of geometry, and relative simplicity of synthesis and purification [12].

We have designed and synthesized a Schiff-base ligand from a flexible 2-hydroxy-1,3-diaminopropanol back-bone and the highly conjugated 2-hydroxynaphthaldehyde moiety to form a tetra-dentate Schiff base with an aliphatic hydroxyl oxygen, two phenol oxygen donors and two imine nitrogen donors (Scheme 1). The Schiff-base ligand **H_2L** [1,1′-(((2-hydroxypropane-1,3-diyl)bis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol)] investigated here is a Schiff base ligand that was observed to coordinate metals in a traditional “salen-like” tetradentate O-N-N-O donor set, with the additional pendant hydroxyl group that was not observed to participate in coordination of the metal ions. This ligand has similar coordination environments to some copper and nickel metalloenzymes [10,13,14], as well as with complexes demonstrated to have cytotoxicity and antimicrobial activity [1,7].

The synthesis of **H_2L** has been reported previously, but most examples of **M_xL** complexes characterized in the solid-state by X-ray diffraction were observed to be dinuclear complexes [15–18]. This study is the first report of a crystal structure of **H_2L**, the mononuclear **Cu(II)L** complex, and mononuclear **Ni(II)L** complex. The two unusual crystal structures of these mononuclear complexes each feature a square planar

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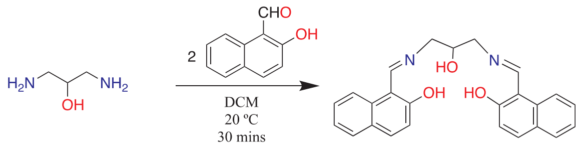

Scheme 1. Synthesis of $\mathbf{H_2L}$.

geometry about the coordinated metal while the pendent hydroxyl group was not observed to coordinate the metal. These complexes have been characterized using single crystal X-ray diffraction, UV–Vis, IR, and HRMS.

2. Experimental section

2.1. Materials

All solvents not specifically mentioned were ACS grade from EMD and used as received with no further purification. The reagents methanol (MeOH) (HPLC grade, EMD), dichloromethane (DCM) (BDH), tetrahydrofuran (THF) (Macron), dimethylformamide (anhydrous, BDH), 2-hydroxynapthaldehyde (Alpha Aesar), 1,3-diamino-2-propanol (Alpha Aesar), nickel(II) chloride hexahydrate (99.9 + % STREM), nickel (II) nitrate hydrate (99.9 + % STREM), copper(II) sulfate pentahydrate (Acros), copper(II) acetate hydrate (> 98%, MC/B), and triethylamine (99%, Alpha Aesar) were used as received without further purification.

2.2. Instrumentation

2.2.1. NMR spectroscopy

^{1}H NMR spectra were recorded using a Bruker AC400 spectrometer at 400 MHz. ^{13}C NMR spectra were recorded with a Bruker AC400 spectrometer at 100 MHz. NMR spectroscopic data were collected using deuterated chloroform ($CDCl_3$) or deuterated dimethylsulfoxide (d_6-DMSO) obtained from Cambridge Isotope Laboratory as indicated.

2.2.2. Mass spectrometry

High resolution mass data was obtained, with the ligand-metal complexes, dissolved in DMSO, and characterized using a Waters Q-TOF ESI Premier in the positive ion mode.

2.2.3. Absorbance spectroscopy

All electronic spectra were collected using a VARIAN Cary 50 WinUV Spectrometer. Serial titrations were completed by introducing a known amount of the metal salt (either $Ni(NO_3)_2$ or $Cu(C_2H_3O_2)_2$ in H_2O) to a solution of the free base $\mathbf{H_2L}$ in each solvent. Titrations were completed in DMF by adding the metal salt in aqueous solution, adding 10 µL per addition to maintain less than 1% (v/v) water in DMF. The solutions were shaken for 5 s and replaced in the spectrometer and the absorbance spectrum was collected. This was repeated until an excess of metal salt was present. Blank absorption of water addition was also conducted. Absorbance was adjusted for concentration by this serial dilution method by the reporting the data as extinction coefficient.

2.2.4. Infrared spectroscopy

presence of the predicted functional groups was confirmed using a Thermo Scientific Nicolet iS50 Fourier-transform-IR.

2.3. Crystallographic studies

Suitable crystals were selected and mounted on a glass fiber using paratone-n oil and data collection was completed for **Cu(II)L** and **Ni(II)L** on a Bruker APEX diffractometer with a CCD detector and was completed for $\mathbf{H_2L}$ on a Bruker D8 Venture κ-geometry diffractometer with a photon detector. The **Cu(II)L** and **Ni(II)L** crystals were kept at 180(2) K during unit cell and data collection and the $\mathbf{H_2L}$ crystals were kept at 100(2) K during unit cell and data collection. The structures were solved with the ShelXL structure solution program using Direct Methods [19] and refined with the ShelXL refinement package using full-matrix Least Squares minimization [20], using the Olex2 software package [21,22]. Projections were created using the Olex2 software [21,22].

2.4. Synthetic details

2.4.1. H_2L

The reagents 2-hydroxynaphthaldehyde (1.8×10^3 mg, 10.0 mmol) and 1,3-diamino-2-propanol (490 mg, 5.4 mmol) were each added to 30 mL of dichloromethane in a 100 mL round bottom flask containing a stir bar. The reaction mixture was allowed to stir at room temperature for 30 min. The reaction was monitored by TLC and judged complete when no starting material was observed. The yellow precipitate formed was isolated via vacuum filtration and dried overnight in a vacuum oven at 60 °C (1.9×10^3 mg, 4.9 mmol, 95%). Crystals suitable for X-ray diffraction were grown from slow diffusion of methanol into a saturated solution of THF (CCDC: 1827295). HRMS (ESI) *m/z* ($M^+ + 1$) Calc'd 399.1630, Found 339.1660. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63–3.68 (m, 2H), 3.81–3.84 (m, 2H), 4.02–4.03 (m, H), 5.68 (s, OH), 5.70 (s, OH), 6.71 (s, 1H), 6.74 (s, 1H), 7.16–7.20 (m, 2H), 7.38–7.43 (m, 2H), 7.62–7.64 (m, 2H), 7.72–7.74 (m, 2H), 8.04–8.06 (m, 2H), 9.07 (s, 1H), 9.10 (s, 1H), 14.06–14.09 (m, 2OH).

2.4.2. Cu(II)L

The ligand $\mathbf{H_2L}$ (210 mg, 0.53 mmol) was added to 30 mL of THF and stirred with gentle heating until dissolved. Triethylamine (0.2 mL), methanol (10 mL), and copper sulfate pentahydrate (130 mg, 0.54 mmol) were then added to the reaction vessel. The solution was allowed to stir at reflux for one hour. Half of the solvent was removed via a rotary evaporator and the greenish black solid was filtered using vacuum filtration and dried in a vacuum oven overnight at 60 °C (59 mg, 0.10 mmol, 24%). Crystals suitable for X-ray diffraction were grown from slow diffusion of methanol into a saturated solution of THF (CCDC: 1571690). IR: 3189.3 (w, br); 1612.0 (m); 1540.3 (m); 1505.7 (w); 1457.2 (m); 1437.3 (w); 1412.7 (w); 1390.7 (m); 1361.0 (m); 1340.5 (m); 1301.6 (w); 1254.7 (w); 1239.1 (w); 1216.4 (w); 1184.4 (m); 1165.7 (m); 1143.7 (m); 1094.1 (w); 1078.1 (w); 1032.3 (w); 998.7 (w); 959.2 (w); 939.6 (w); 857.3 (w); 824.0 (s); 771.5 (w); 737.5 (s); 653.6 (w); 638.9 (w); 599.0 (w); 577.6 (w); 549.9 (w); 522.3 (m); HRMS (ESI) *m/z* ($M^+ + 1$) Calc'd 460.0770, Found 460.0833.

2.4.3. Ni(II)L

The ligand $\mathbf{H_2L}$ (220 mg, 0.55 mmol) was added to 30 mL of THF and stirred with gentle heating until dissolved. Triethylamine (0.20 mL), methanol (10 mL) and nickel(II) chloride hexahydrate (130 mg, 0.54 mmol) were then added to the reaction vessel. The solution was allowed to stir at reflux for one hour. Half of the solution was removed via a rotary evaporator and the greenish black solid was filtered using vacuum filtration and dried in a vacuum oven overnight at 60 °C (49.0 mg, 0.109 mmol, 20%). Crystals suitable for X-ray diffraction were grown from slow diffusion of methanol into a saturated solution of THF (CCDC: 1827294). IR: 3189.3 (w, br); 1612.0 (m); 1540.3 (m); 1505.7 (w); 1457.2 (m); 1437.3 (m); 1412.7 (w); 1390.7 (m); 1361.0 (m); 1340.5 (m); 1301.6 (w); 1254.7 (w); 1239.1 (w); 1216.4 (w); 1184.4 (m); 1165.7 (w); 1143.7 (w); 1094.1 (w); 1078.1 (w); 1032.3 (w); 998.7 (w); 959.2 (w); 939.6 (w); 857.3 (w); 824.0 (s); 771.5 (w); 737.5 (s); 653.6 (w); 638.9 (w); 599.0 (w); 549.9 (w); 577.6 (w); 522.3 (m); HRMS (ESI) *m/z* ($M^+ + 1$) Calc'd 455.0827, Found