

Coordination Mode of 2-Dimethylaminomethyl-3-hydroxypyridine with Nickel(II) Halides: Structural and Electrochemical Properties

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Study the structures and properties of dimeric transition metal complexes are important due to their possible chemical and physical properties and their aiding in understanding the role of multinuclear enzymes.¹ Dimeric nickel(II) complexes based on pyridine ligands have attracted much attention because of their rich physico-chemical properties and potentially useful biological activity.² Halide anions exhibit a strong ability to bridge two or more nickel atoms to form complexes (NiX)_n (X = Cl, Br and I) with various structural skeletons.³ Dimeric nickel complexes have been investigated extensively,⁴ however, the understanding between structure and reactivity of chloride bridged dimeric nickel complexes is still interesting,⁵ since the small changes in structure play important roles in determining the kinetics and thermodynamics of redox reactions. Recently, we reported⁶ the halide-bridged copper(II) complexes, [Cu(dmamhp)X₂]₂ (where dmamhp = 2-dimethylaminomethyl-3-hydroxypyridine), which revealed that both the chloride and bromide complexes form dimeric structures, as well as other interesting intermolecular and intramolecular interactions. In order to investigate the structure of the nickel(II) complexes, as they compare to the copper(II) complexes, we herein report the synthesis and characterization of dimeric nickel(II) complexes based on pyridine coordination units constructed from the dmamhp ligand. The electrochemical properties of the complexes are discussed along with crystal structure.

Experimental Section

Materials and synthesis of complexes. All reagents and solvents for syntheses and analyses were purchased from the Aldrich Chemical Company and used as received.

The chloro complex, [Ni(dmamhp)Cl₂(CH₃OH)]₂·2CH₃OH (**1**), was prepared by mixing equimolar amounts of the dmamhp ligand (1.0 g, 6.5 mmol) and NiCl₂·6H₂O (1.54 g, 6.5 mmol) in 40.0 mL of methanol. The solution changed to green color immediately without any precipitate and was stirred overnight. Green needle crystals suitable for X-ray analysis were obtained by slow evaporation from this solution. Elemental analyses were performed at the Korean Basic Science Center: Anal. (%) Calcd. for C₂₀H₄₀N₄Cl₂O₆Ni₂: C, 34.83; H, 5.55; N, 8.12. Found: C, 34.70; H, 5.00; N, 8.03. The bromo-complex (**2**) was obtained by an analogous

method using NiBr₂. Anal. (%) Calcd. for C₂₀H₄₀N₄Br₂O₆Ni₂: C, 27.62; H, 4.63; N, 6.44. Found: C, 28.30; H, 4.64; N, 6.25.

Physical measurements. UV-visible spectra were recorded on a Jasco V-570 UV-vis spectrophotometer. Electrochemical measurements were performed under nitrogen atmosphere with a Bioanalytical Systems CV-50 W electrochemical analyzer using 3 electrode cell assemblies. The electrochemical cell consists of a glassy carbon working electrode, platinum wire counter electrode, and an Ag/AgCl reference electrode. Each oxidation potential was calibrated with ferrocene as a reference. X-ray intensity data was collected on a Bruker SMART APEX-II CCD diffractometer equipped with graphite monochromated Mo K α radiation. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed by SAINTPLUS.⁷ An empirical absorption correction based on the multiple measurements of equivalent reflections was applied using the SADABS program.⁸ Structures were obtained by a combination of the direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F², using SHELXTL.⁹

Results and Discussion

The direct reaction of equimolar amount of dmamhp with NiCl₂ in methanol medium gave [Ni(dmamhp)Cl₂(CH₃OH)]₂·2CH₃OH. Green crystals were grown from the methanol solution and characterized using X-ray crystallography.¹⁰ The geometry around the nickel(II) metal ions is a distorted octahedral structure (Fig. 1a), whereby a methanol molecule coordinates with the nickel(II) ion. It is unlike the [Cu(dmamhp)Cl₂]₂ complex which has a trigonal bipyramidal structure.⁶ Interestingly, [Ni(dmamhp)Cl₂(CH₃OH)]₂·2CH₃OH has a dimeric structure with the 2 Ni atoms, sharing 2 bridging chlorides (Cl2, Cl2'), and the bridging Ni₂Cl₂ units are planar with a crystallographic inversion center located in the center of the 2 nickel(II) atoms. Niⁱ (symmetry code: (i) -x+1, -y+1, -z+1). The N1 and N9 of the dmamhp ligand, along with the Cl2 and Cl2' atoms make a square plane with the C11 atom and O12 atom of methanol, that lies at an axial position. The selected bond lengths and bond angles are in Table 1. In addition, there are non-ligated

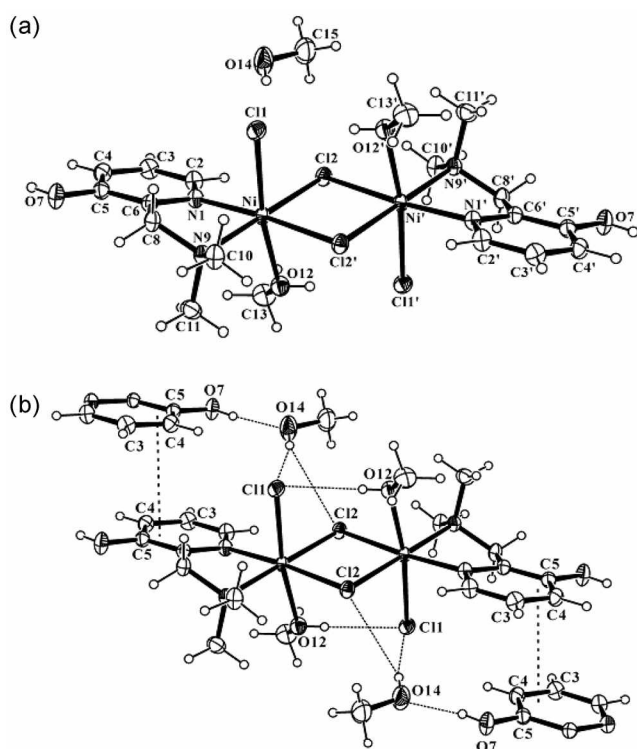


Figure 1. (A) Ortep diagram of $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$. (B) A molecular packing diagram of $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$. Intermolecular hydrogen bonds are shown with short-dashed lines. Intermolecular π - π interactions are shown with long-dashed lines.

Table 1. Selected bond lengths and angles of $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$

Bond distances (Å)	Bond angles (°)
Ni-N1 = 2.0705(16)	N1-Ni-N9 = 80.40(6)
Ni-N9 = 2.1354(17)	N1-Ni-O12 = 95.06(7)
Ni-O12 = 2.1624(16)	N9-Ni-O12 = 93.39(7)
Ni-C11 = 2.4094(7)	N1-Ni-C11 = 91.07(5)
Ni-C12 = 2.4263(9)	N9-Ni-C11 = 94.07(5)
Ni-C12' = 2.4329(7)	O12-Ni-C11 = 171.04(5)
Cl2-Ni' = 2.4329(7)	N1-Ni-C12 = 96.55(5)
	N9-Ni-C12 = 175.86(5)
	O12-Ni-C12 = 84.06(5)
	C11-Ni-C12 = 88.77(3)
	N1-Ni-C12' = 174.81(5)
	N9-Ni-C12' = 94.79(5)
	O12-Ni-C12' = 83.22(5)
	C11-Ni-C12' = 91.21(2)
	Cl2-Ni-C12' = 88.15(2)
	Ni-C12-Ni' = 91.85(2)

methanol molecules used as a solvent for recrystallization. The observed Ni-C11, Ni-C12 and Ni-C12' bond distances are 2.4094(7), 2.4263(9) and 2.4329(7) Å respectively, which are longer than normal Ni-Cl bond distance (2.270 Å).⁵ The terminal chlorides (C11) bonded more strongly to the Ni^{II} ions than the bridging ones. The molecules are held together in a one-dimensional network and stabilized through hydrogen bonds and π - π interactions as shown in Figure 1b. The

Table 2. The bond distances (Å) and bond angle (°) of hydrogen bond for $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
O7-H7-O14 ^m	0.78(3)	1.83(3)	2.602(3)	170(3)
O12-H12-C11'	0.76(3)	2.42(3)	3.1690(19)	173(3)
O14-H14-C11'	0.74(4)	2.59(4)	3.301(2)	162(4)
O14-H14-Cl2'	0.74(4)	2.92(4)	3.380(3)	123(4)

distance of the π - π interaction taking part in the 2 pyridine rings of the complex is 3.39 Å, calculated by the deviation of C3-C4-C5 plane and C4^m (symmetry code: (iii) $-x+2, -y+2, -z+1$). These distances are as short as the π - π interaction distance in graphite. The hydrogen bond distances and bond angles are summarized in Table 2. There are 3 types of hydrogen bonding interactions present in $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$ compound: (i) The bifurcated hydrogen bonding¹¹ is observed between O14 of free methanol molecule and C11, C12 atoms of terminal chloride and bridged chloride moiety; (ii) The O12 of coordinated methanol forms hydrogen bond with terminal C11 atom forming rectangle shape, therefore C11 atom participates in 2 hydrogen bonds; (iii) There is a strong hydrogen bond between the hydroxyl group of dmamhp ligand and O14 of methanol moiety. The bifurcated hydrogen bond distances (O14-H14-Cl2' = 2.92(4) Å & O14-H14-C11' = 2.59(4) Å) are longer than the other hydrogen bond distances (O7-H7-O14^m = 1.83(3) Å & O12-H12-C11' = 2.42(3) Å). The hydrogen bonds contribute to form a stable molecular stack.

The electronic spectrum of $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$, recorded in methanol at 298 K, showed a band at ~1040 ($\epsilon \sim 45$) and 661 nm ($\epsilon \sim 30$), assigned to the ν_1 (${}^3T_{2g} \leftarrow {}^3A_{2g}$) and ν_2 (${}^3T_{1g}(\text{F}) \leftarrow {}^3A_{2g}$) transitions of d⁸-octahedral geometries around the Ni(II) ions. Similarly, the analogous bromide complex showed bands at ~1035 ($\epsilon \sim 20$) and ~637 nm ($\epsilon \sim 28$). The ν_2/ν_1 ratio of 1.57 & 1.62 for chloride and bromide complexes is in the usual range of ~1.50-1.75 for octahedral nickel(II) complexes.¹² These complexes exhibited a band in a range of 390-393 nm ($\epsilon \sim 70$), which may have charge transfer character and bands in the region 320 ($\epsilon \sim 1450$) and 290 nm ($\epsilon \sim 2890$) attributable to the n- π^* and π - π^* transitions, respectively. Based on the electronic properties and the elemental analyses, the bromide complex has an octahedral symmetry around the nickel metal ion, indicating that the bromide complex should be either a monomer with 6-coordination by 2 nitrogen atoms of the dmamhp ligand, 2 oxygen atoms of the methanol molecules, and 2 Br atoms, or a dimer with the formula of $[\text{Ni}(\text{dmamhp})\text{Cl}_2(\text{CH}_3\text{OH})]_2 \cdot 2\text{CH}_3\text{OH}$ and a similar structure of a μ -chloride nickel(II) complex. Evidence for this suggestion may be obtained from structural determination by X-ray crystallography, but we have yet to obtain this quality from our experiments.

The cyclic voltammograms (Fig. 2) of both the chloride (1) and bromide complexes (2) display 1 quasi/irreversible Ni(II)/Ni(I) redox couple and 1 quasi/irreversible Ni(II)/Ni(III) redox couple. A greater anodic reduction potential

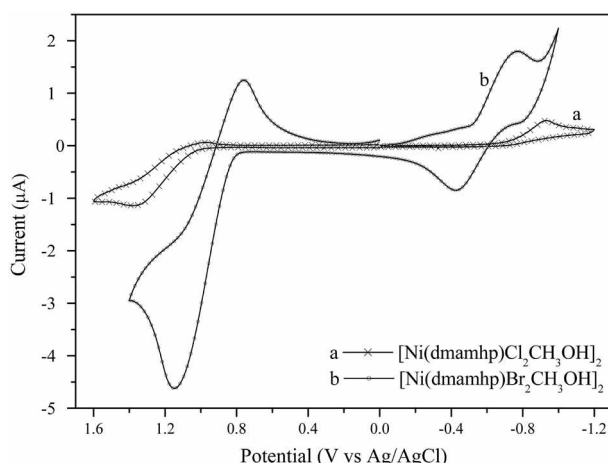


Figure 2. Cyclic voltammogram patterns of nickel(II) complexes **1** and **2** in 0.1 M *n*-tetrabutylammonium perchlorate in CH₃OH medium, scan rate 50 mVs⁻¹.

was observed for complex (**2**) (−0.77 V), compared with that of complex (**1**) (−0.96 V), and may be related more to the reduced electron density at the metal center of the bromide complex than the chloride-bridged complex. The reversibility also increases for bromide complexes when compared to the chloride-bridged complex. Complexes (**1**) and (**2**) oxidize at $E_{pa} = 1.35$ and 1.15 V and are consistent previously reported results.^{2c,13}

In conclusion, [Ni(dmamhp)Cl₂(CH₃OH)]₂·2CH₃OH has been synthesized and characterized, having a distorted octahedral geometry with a nearly symmetric chloride-bridged dimeric form. The molecules are held together in a one-dimensional network and stabilized through hydrogen bonds and π - π interactions. We are currently involved in further development of the halide-bridged dimer complexes and are investigating their applicability to catalytic processes.

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- Crystal data for 1 C₂₀H₃₀N₄Cl₄O₈Ni₂: Triclinic P-1, $a = 9.1514(18)$, $b = 9.3854(19)$, $c = 9.3854(19)$ Å. $\alpha = 112.299(18)$, $\beta = 104.685(13)$, $\gamma = 98.100(8)^\circ$, $V = 738.0(3)$ Å³, $Z = 1$, $d_{calc} = 1.557$ Mg/m³. θ Range = 2.53–27.70°. Data/Restraints/parameters = 3248/0/178. Goodness-of-fit on $F^2 = 1.031$. Reflection collected/unique = 9563/3248 [R(int) = 0.0220]. Final R indices [$I > 2\sigma(I)$] $R1 = 0.0265$, $wR2 = 0.0587$, $\Delta\rho_{max}$ and $\Delta\rho_{min} = 0.303$ and -0.259 eÅ⁻³. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-671926). That data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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