



Nickel(II) complexes with tetradentate N₄ ligands: Synthesis, structure, electrochemistry and thermochromism in solution

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ABSTRACT

Complexes of nickel(II) chloride with homologous tetradentate aminopyridine ligands 1,8-bis(2-pyridyl)-3,6-dimethyl-3,6-diazaoctane (pdao) and 1,6-bis(2-pyridyl)-2,5-dimethyl-2,5-diazaheptane (bpmen) were prepared in the crystalline state and characterized by elemental analysis and X-ray diffraction as [Ni(pdao)(H₂O)₂]Cl₂·H₂O (**1**) and [Ni(bpmen)Cl₂]·H₂O (**2**). In the solid state, both complexes are blue-green and contain octahedral Ni(II) with a *cis-α*-coordinated tetramine. In aqueous solution, both complexes are strong electrolytes as follows from the measurements of electrical conductivity: complex **2** is hydrated and forms purple [Ni(bpmen)(H₂O)₂]²⁺(aq). Complex **1** displays thermochromic behavior in solution (it is blue-green at low temperatures and yellow at high temperatures) due to a temperature sensitive equilibrium [Ni(pdao)(H₂O)₂]²⁺(aq) ⇌ [Ni(pdao)]²⁺(aq) + 2H₂O(l), ΔH° = +30(1) kJ/mol and ΔS° = +80(3) J/mol K in 0.1 M NaClO₄(aq). Complex **1**, but not **2**, can be reversibly reduced to the Ni(I) species (E_{1/2} = −0.9 V versus SHE in aqueous solution and −1.37 V versus Fc⁺/Fc in acetonitrile). The relative stabilization of nickel(I) by ligand pdao can be attributed to an optimal size of the ligand bite and to the presence of the pyridine and tertiary amine N-donors.

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1. Introduction

Complexes of nickel(II) with tetramines have attracted attention as catalysts and electrocatalysts of such interesting reactions as the reduction of CO₂, haloalkanes and thioethers [1,2]. Tetrapyrrole-derived macrocyclic NiF₄₃₀ cofactor uses a Ni(II)/Ni(I) redox couple in the enzyme methyl-CoM reductase to convert a methyl thioether into methane in certain bacteria [3]. We discovered that a non-macrocyclic tetradentate aminopyridine ligand pdao (Scheme 1) can form both a stable Ni(II) and a relatively stable Ni(I) complex in organic solvents (like acetonitrile) and support the electrocatalytic reduction of a haloalkane [4]. In this article, we report the synthesis of a novel NiCl₂-pdao complex, its structural characterization in the solid state and in solution, along with similar studies of Ni(II) complexes of two other non-macrocyclic tetramine ligands – bpmen and 3,2,3-tet (Scheme 1). The ligand bpmen is a lower homolog of pdao with shorter methyl-pyridyl arms, while 3,2,3-tet has the same number of carbon linkers between N-donor atoms as pdao but is less bulky and lacks N-methyl and pyridyl groups. Complexes of nickel(II) with bpmen were reported previously [5,6], but none of them was structurally characterized. In this paper, we report the crystal structure of a

NiCl₂-bpmen complex. Nickel(II) complexes of 3,2,3-tet [7–10] and other similar N₄-ligands [11–15] were subjected to detailed studies by others and served as useful reference points in our present investigation.

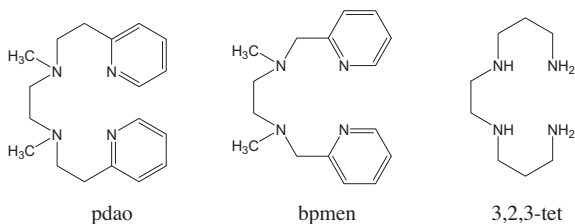
2. Experimental

2.1. Materials and instrumentation

Ligands pdao and bpmen were synthesized according to published procedures [16,17]. Complex [Ni(3,2,3-tet)(H₂O)₂]Cl₂·3H₂O (**3**) was prepared by a published procedure [7]. All other chemicals and solvents were obtained from Sigma-Aldrich and used as received. Elemental analysis was performed by Desert Analytics (Tucson, Arizona, USA). IR spectra (in nujol mulls) were recorded using a Mattson 1000 FTIR Spectrometer. Conductivity measurements were performed with a Thermo Orion 4 Star pH/Conductivity Benchtop instrument. Electronic spectra in solution were recorded using a dip-probe device from Ocean Optics, a Cary 100 Bio UV-Vis spectrophotometer, and a Jasco V-570 UV-Vis-NIR spectrophotometer. Electronic spectra of solids were taken in nujol mulls using a Hitachi U-2000 spectrophotometer. Electrochemical experiments in 1.0 M KCl(aq) were done under an inert gas atmosphere with a CHI 830 Electrochemical Analyzer using a three electrode setup with a pyrolytic graphite working electrode, platinum

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Scheme 1. Tetradentate ligands used in this work.

Table 1

Crystallographic parameters and details of structure determination for [Ni(pdao)(H₂O)₂Cl₂·H₂O (**1**)] and [Ni(bpmn)Cl₂·H₂O (**2**)]. *T* = 292 K.

Complex	1	2
Formula	C ₁₈ H ₃₂ Cl ₂ N ₄ NiO ₃	C ₁₆ H ₂₄ Cl ₂ N ₄ NiO
Formula weight	482.07	417.98
Crystal system	monoclinic	orthorhombic
Space group	<i>P2₁/c</i>	<i>Pnc2</i>
<i>a</i> (Å)	9.8771(10)	7.6818(5)
<i>b</i> (Å)	13.7582(15)	14.4670(11)
<i>c</i> (Å)	18.2661(15)	8.1697(6)
β (°)	117.411(4)	90
<i>V</i> (Å ³)	2203.5(4)	907.92(11)
<i>Z</i>	4	2
<i>D</i> _{calcd} (g cm ⁻³)	1.453	1.529
μ (mm ⁻¹)	1.149	1.374
Reflections (measured, unique, <i>I</i> > 2 σ)	8732, 4133, 3540	4882, 1693, 1481
Parameters	274	114
<i>R</i> , <i>wR</i> ² , <i>S</i>	0.044, 0.124, 1.06	0.039, 0.096, 1.13

wire counter-electrode, and an Ag/AgCl (1 M KCl) reference electrode. The electrochemical experiments in acetonitrile were performed with a similar setup using a silver wire as a pseudo-reference electrode and ferrocene as an internal redox standard [18] and 0.10 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte; acetonitrile was cleansed shortly before use in an Innovative Technologies PureSolv 400 solvent purifier.

2.2. Synthesis of [Ni(pdao)(H₂O)₂Cl₂·H₂O (**1**)]

NiCl₂·6H₂O (0.238 g, 1 mmol) was dissolved in water (1 mL), filtered, diluted with ethanol (2 mL), heated to 70 °C and mixed with a solution of pdao (0.298 g, 1 mmol) in ethanol (1 mL). A clear dark green solution obtained was left to slowly evaporate in ambient air protected from dust. The gradual evaporation first led to the formation of a viscous concentrate, which spontaneously crystallized in a few months. Yield: 0.480 g (100%). *Anal. Calc.* for C₁₈H₃₂Cl₂N₄NiO₃: C, 44.99; H, 6.72; N, 11.67; Ni, 12.06. Found: C, 44.79; H, 6.52; N, 11.65; Ni, 11.95%. IR (cm⁻¹): 3300 br sh, 3140 br, 1635, 1600, 1565, 1460, 1450, 1375, 1325, 1290, 1260, 1205, 1155, 1140, 1105, 1070, 1060, 1040, 1010, 970, 955, 890, 880, 790, 775, 620 br, 545, 485, 440. UV–Vis–NIR (nm): 376, 643, 785, 1080.

2.3. Synthesis of [Ni(bpmn)Cl₂·H₂O (**2**)]

NiCl₂·6H₂O (0.238 g, 1 mmol) and the ligand bpmn (0.270 g, 1 mmol) were combined in the same manner as used in the preparation of **1**. The resulting dark blue solution was cooled to room temperature and placed in a jar with diethyl ether. Blue-green crystals of **2** formed upon slow diffusion of the ether vapor. Yield: 0.391 g (94%). *Anal. Calc.* for C₁₆H₂₄Cl₂N₄NiO: C, 46.15; H, 5.81; N, 13.46; Ni, 13.92. Found: C, 46.28; H, 5.52; N, 13.32; Ni, 13.90%. IR (cm⁻¹): 3470, 3410, 1620, 1605, 1570, 1560, 1460, 1300, 1265,

1190, 1160, 1145, 1080, 1055, 1025, 1010, 980, 955, 925, 840, 825, 785, 730, 650, 605, 530, 465, 435. UV–Vis–NIR (nm): 400 sh, 628, 835, 1050.

2.4. X-ray crystallography

Suitable crystals of **1** and **2** were mounted on a glass fiber. Data were collected using a Bruker SMART CCD based diffractometer and processed using SAINT [19] (correcting for Lorentz and polarization effects) and SADABS [20] (applying absorption corrections). The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were refined as a riding model. A summary of the data collection and refinement is given in Table 1.

3. Results and discussion

3.1. Synthesis

The synthesis of [Ni(pdao)(H₂O)₂Cl₂·H₂O (**1**)] and [Ni(bpmn)Cl₂·H₂O (**2**)] was performed by combining NiCl₂ with the corresponding ligand in the ethanol–water solvent. It was found that **1** is difficult to crystallize – it took several months for the spontaneous formation of crystalline material. Attempts to speed up the crystallization of **1** by diethyl ether vapor diffusion led to the formation of oily material. The crystallization of **2** was much faster and could be accomplished in a few days by the diethyl ether vapor diffusion method. A different hydrate of complex **2**, formulated as Ni(bpmn)Cl₂·3H₂O, was recently obtained from aqueous methanol by Pandiyan and co-workers [6], but its crystal structure is unknown.

3.2. Crystal structures of **1** and **2**

The coordination of Ni(II) in both **1** and **2** is distorted octahedral (Figs. 1 and 2). The bond angles about the central ion in **1** range from 83.58° to 97.69° with an average deviation of 4.76° from the ideal value of 90°. Similarly, the range of bond angles about Ni(II) in **2** was from 78.50° to 97.38° with an average deviation of 4.98° from the ideal value of 90°. The bond lengths Ni–N (2.094–2.183 Å), Ni–O (2.083–2.134 Å) and Ni–Cl (2.443 Å) in **1** and **2** are typical for six-coordinate high-spin nickel(II) complexes [1,7,11,14,15].

The ligand bpmn has four N donor atoms connected by linkers with two carbon atoms each (Scheme 1), and therefore is classified as a 2,2,2-tetramine, while pdao and 3,2,3-tet have linkers with three, two, and three such carbon atoms and thus are classified as 3,2,3-tetramines [9]. In octahedral complexes, tetradentate ligands with a linear topology of donor atoms may adopt three coordination modes: *trans*, *cis- α* , and *cis- β* (Scheme 2); 2,2,2-tetramines have been found to adopt a *cis*-configuration in most known complexes, with the *trans*-configuration being sterically strained and uncommon; 3,2,3-tetramines are more flexible and may adopt any of the three configurations [9,15,12,21].

The ligand pdao in complex **1** adopts the *cis- α* -coordination (Fig. 1). The same ligand adopts the *trans* configuration in a diamagnetic complex [Ni(pdao)](ClO₄)₂ [4], which differs from **1** only in the nature of the counter-ions (chloride versus perchlorate) and the absence of coordinated water molecules. Such flexibility of the coordination mode of pdao is due to the longer carbon linkers present between the nitrogen donor atoms (Scheme 1). No other complexes of this ligand are listed in the Cambridge Crystallographic Database (CCD). A five-membered chelate ring in **1** has a twisted

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