

One-Dimensional Nickel(II) Complex Based upon Bridging Molybdate Ligand

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Polynuclear metal complexes with bridging ligands have been increasing interest due to their diverse structures and magnetic properties.¹⁻³ The tetraoxo anions such as chromate, molybdate, and tungstate have been known to act as bridging ligands which connected paramagnetic metal centers. For example, one-dimensional nickel(II) complex *catena-(μ-CrO₄-O,O')*[Ni^{II}(cyclam)] · 2H₂O (cyclam = 1,4,8,11-tetraazacyclotetradecane) revealed an octahedral geometry around each nickel(II) ion and showed weak intrachain ferromagnetic interaction, which is explained by means of the accidental degeneracy of the σ-type frontier orbitals.⁴ In dinuclear copper(II) complexes [*μ*-(acpa)]₂(μ-MO₄) (M = Cr, Mo) (acpa = N-(1-acetyl-2-propylidene)(2-pyridylmethyl)amine), two square planar coordination planes of the copper(II) ions are bridged by the [MO₄]²⁻ anion and exhibited ferromagnetic and antiferromagnetic interactions.⁵ Recently, an oxometalate bridged one-dimensional coordination polymers was provided by Zubieta *et al.* who used molybdate to form one- and two-dimensional organic-inorganic composite solids linked through [M(bipy)]²⁺ fragments (M = Co, Ni, and Cu) by hydrothermal synthesis.⁶⁻⁸ Here we report the structure and magnetic properties of an antiferromagnetic chain system *catena-(μ-MoO₄-O,O')*[Ni^{II}(L)] · 3H₂O (**1**) (L = 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane).

Experimental Section

Materials and Physical Measurements. All commercially available products were used without further purification. The complex [Ni(L)(H₂O)₂]Cl₂ was prepared by the literature method.⁹ IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using KBr pellets. Solid-state electronic spectra were measured by the diffuse reflectance method on a Cary 300 UV/vis spectrophotometer. Solution spectra were obtained on a Jasco Uvidec 610 spectrophotometer. Magnetic measurements on powder samples were carried out under 0.5 T using a Quantum Design MPMS-7 SQUID magnetometer. The diamagnetic corrections of **1** were estimated from Pascal's constants. Elemental analyses were carried out by the Korea Basic Science Institute.

Synthesis of *catena-(μ-MoO₄-O,O')*[Ni^{II}(L)] · 3H₂O (1**).**

A methanol solution (10 mL) of [Ni(L)(H₂O)₂]Cl₂ (422 mg, 1 mmol) was added to a solution of triethylamine (101 mg, 1 mmol) and K₂MoO₄ (238 mg, 1 mmol) in water (5 mL). The solution was filtered to remove insoluble material. After the solution was left to stand at room temperature over a period of several days, a quantity of pink crystals precipitated. These were filtered out and one of them was subjected to the X-ray analysis. Anal. Calcd for C₂₈H₇₆N₈Ni₂Mo₂O₁₄: C, 31.78; H, 7.24; N, 10.59. Found: C, 31.85; H, 7.16; N, 10.53. IR (KBr): 3400 (s), 3178 (s), 2965 (s), 2923 (s), 1654 (m), 1633 (m), 1445 (m), 1427 (m), 1375 (m), 1337 (w), 1306 (w), 1250 (w), 1155 (w), 1114 (s), 1067 (m), 1024 (m), 985 (m), 943 (m), 824 (s), 585 (w), 549 (w) cm⁻¹. UV/vis in water [λ_{max}, nm (ε, M⁻¹ cm⁻¹): 458 (72); in diffuse reflectance (λ_{max}, nm): 516.

X-ray Crystallography. The crystal of *catena-(μ-MoO₄-O,O')*[Ni^{II}(L)] · 3H₂O (**1**) (dimensions 0.46 × 0.15 × 0.12 mm³) was mounted on an Enraf-Nonius CAD4 diffractometer and intensity measurements were carried out at room temperature using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 reflections. An asymmetric unit of intensity data were collected in the ω-2θ scan mode. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ϕ-scan was applied (T_{min} = 0.599, T_{max} = 0.804). A total of 6779 reflections were measured in the 2.19° < θ < 24.98°, and 3572 reflections were assumed to be observed applying the condition I > 2σ(I). The structure was solved by direct methods and refined using weighted full-matrix least-squares on F².^{10,11} All hydrogen atoms were included in calculated positions and refined using a riding model. All non-hydrogen atoms were refined anisotropically. The crystallographic data of **1** are listed in Table 1 and the selected bond distances and angles in Table 2.

Results and Discussion

An ORTEP view of **1** with the atomic numbering scheme is presented in Figure 1. There are two crystallographically independent *catena-(μ-MoO₄-O,O')*[Ni^{II}(L)] · 3H₂O (**1**) complexes. The crystal structure of **1** consists of a [MoO₄]²⁻ anion, water molecules and two kinds of crystallographically independent [Ni(L)]²⁺ cations located on the center of inversion. These cationic units are bridged by molybdate anions to give a chain structure in the lattice. In the chain structure,

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Table 1. Crystallographic data for **1**

Formula	C ₂₈ H ₇₆ N ₈ Ni ₂ Mo ₂ O ₁₄
Formula weight	1058.24
Crystal color/habit	Pink/rod
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> , Å	10.156(1)
<i>b</i> , Å	13.665(6)
<i>c</i> , Å	18.888(3)
α , deg	73.40(2)
β , deg	74.44(1)
γ , deg	68.40(2)
<i>V</i> , Å ³	2296.1(10)
<i>Z</i>	2
<i>D</i> _{calcd.} , g/cm ³	1.530
μ , mm ⁻¹	1.394
<i>F</i> (000)	1088
2 θ _{max} , deg	49.96
Index ranges	-11 ≤ <i>h</i> ≤ 12, -15 ≤ <i>k</i> ≤ 16, 0 ≤ <i>l</i> ≤ 22
No. of unique reflns	6779
No. of reflns with [<i>I</i> > 2 σ (<i>I</i>)]	3572
No. of params	487
<i>R</i> ₁ ^a	0.051
<i>wR</i> ₂ ^b	0.107
Goodness of fit on <i>F</i> ²	0.987

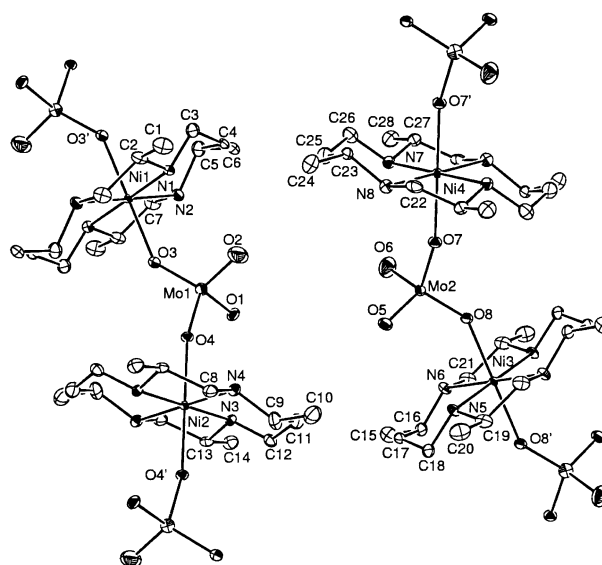
$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2]]^{1/2}}{[\sum w(F_o^2)]^{1/2}}$$

Table 2. Selected bond distances (Å) and angles (°) for **1**^a

Ni(1)-N(1)	2.076(7)	Ni(3)-N(5)	2.086(7)
Ni(1)-N(2)	2.090(8)	Ni(3)-N(6)	2.069(7)
Ni(1)-O(3)	2.109(6)	Ni(3)-O(8)	2.088(6)
Ni(2)-N(3)	2.054(8)	Ni(4)-N(7)	2.087(8)
Ni(2)-N(4)	2.071(7)	Ni(4)-N(8)	2.088(7)
Ni(2)-O(4)	2.076(5)	Ni(4)-O(7)	2.076(6)
Ni(1)-Ni(2)	6.850(3)	Ni(3)-Ni(4)	6.832(3)
Ni(1)-Ni(4)	9.447(2)	Ni(3)-Mo(2)	3.638(2)
Ni(2)-Ni(3)	9.444(1)	Ni(4)-Mo(2)	3.738(2)
Ni(1)-Mo(1)	3.642(2)	Mo(1)-Mo(2)	6.425(2)
Ni(2)-Mo(1)	3.750(2)		
N(1)-Ni(1)-N(2)	93.4(3)	N(5)-Ni(3)-N(6)	93.9(3)
N(1)-Ni(1)-N(2) ⁱ	86.6(3)	N(5)-Ni(3)-N(6) ⁱⁱⁱ	86.1(3)
N(1)-Ni(1)-O(3)	88.1(3)	N(5)-Ni(3)-O(8)	89.5(3)
N(2)-Ni(1)-O(3)	87.7(3)	N(6)-Ni(3)-O(8)	88.6(3)
N(3)-Ni(2)-N(4)	95.3(3)	N(7)-Ni(4)-N(8)	93.2(3)
N(3)-Ni(2)-N(4) ⁱⁱ	84.7(3)	N(7)-Ni(4)-N(8) ^{iv}	86.8(3)
N(3)-Ni(2)-O(4)	89.7(3)	N(7)-Ni(4)-O(7)	87.6(3)
N(4)-Ni(2)-O(4)	86.8(3)	N(8)-Ni(4)-O(7)	88.1(3)
Ni(1)-O(3)-Mo(1)	142.9(3)	Ni(3)-O(8)-Mo(2)	144.2(3)
Ni(2)-O(4)-Mo(1)	159.7(3)	Ni(4)-O(7)-Mo(2)	158.9(4)

^aSymmetry transformations used to generate equivalent atoms: (i) *x*, *y*+2, *z*+1; (ii) *x*+1, *y*+1, *z*+1; (iii) *x*+1, *y*+1, *z*; (iv) *x*+1, *y*+2, *z*.

each nickel(II) ion exists in distorted octahedral environment with the four secondary amines of the macrocycle in which two *trans* molybdate ions have assembled around each metal center. The nickel atom and the four nitrogen atoms of the macrocycle are exactly in a plane. The bond distances from the nickel(II) ions to the oxygen atoms of the molybdate

**Figure 1.** An ORTEP view of **1** with the atomic numbering scheme. The water molecules are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

ligands are Ni(1)-O(3) 2.109(6), Ni(2)-O(4) 2.076(5), Ni(3)-O(8) 2.088(6) and Ni(4)-O(7) 2.076(6) Å. The four bond angles related to the molybdate ligands are Ni(1)-O(3)-Mo(1) 142.9(3), Ni(2)-O(4)-Mo(1) 159.7(3), Ni(3)-O(8)-Mo(2) 144.2(3) and Ni(4)-O(7)-Mo(2) 158.9(2)°; the larger angles corresponding to the shorter bond distances. Furthermore, the dihedral angles between two neighboring NiN₄ planes are 36.1(3) and 32.9(3)°, respectively. The Ni(1)⋯Ni(2) and Ni(3)⋯Ni(4) distances in the chain structures are 6.850(3) and 6.832(3) Å, respectively, whereas the closest Ni(1)⋯Ni(4) and Ni(2)⋯Ni(3) distances between neighboring complexes are 9.447(2) and 9.444(1) Å, respectively. The coordination geometries around the Mo atoms are pseudotetrahedral, where Mo-O bond distances are in the range of 1.625(1)-1.835(9) Å with the O-Mo-O bond angles of 100.8(3)-114.8(2)°. [MoO₄]²⁻ anions bridge the nickel(II) ions and form a one-dimensional chain with Ni-Mo separations from 3.638(2) to 3.750(2) Å. The average Ni-N (secondary amines) bond distance of 2.078(3) Å is similar to that observed for the octahedral nickel(II) complexes with 14-membered tetraaza macrocycles.^{9,12,13} The N-Ni-N angles of the six-membered chelate rings are larger than those of the five-membered chelate rings. Also, the axial Ni-O bonds are not perpendicular to the NiN₄ planes as the O_{axial}-Ni-N_{basal} angles range from 86.8(3) to 89.7(3)°.

The diffuse reflectance absorption spectrum of **1** shows maximum absorption at 516 nm, which is the characteristic spectrum expected for a high-spin d⁸ nickel(II) ion in an octahedral environment.^{14,15} However, it dissolves in water and decomposes into the building block, which was identified by the UV/vis spectrum showing the characteristic chromophore (λ_{max} =458 nm) of the square-planar nickel(II) macrocyclic complexes.^{16,17}

The magnetic susceptibilities (χ_m) were measured in the temperature range 2.0-300 K. The χ_m and μ_{eff} vs *T* plots for **1**

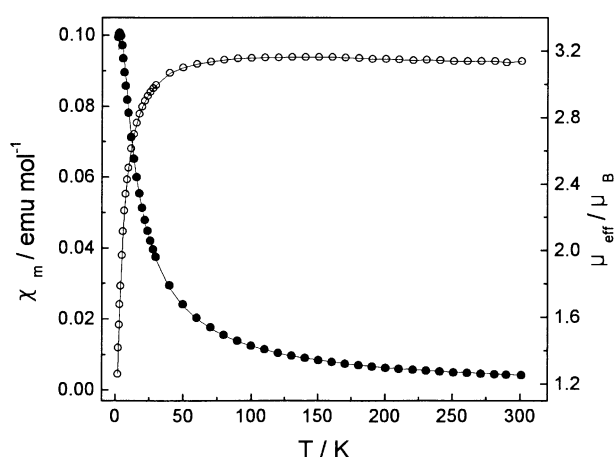


Figure 2. Plots of χ_m vs T (●) and μ_{eff} vs T (○) for **1**. The solid line represents the best fit of the experimental data to eq 1.

are shown in Figure 2. When the temperature is lowered, the χ_m value reaches a sharp maximum at around 3 K. The magnetic moment (μ_{eff}) of **1** (per one Ni) is $3.19 \mu_B$ at 300 K. However, the magnetic moments gradually decrease with decreasing temperature, suggesting the presence of an antiferromagnetic interaction between the nickel(II) ions. The Ni...Ni separations within the intrachain are 6.832(3) and 6.850(3) Å. The magnetic susceptibility data are interpreted with Fisher's model^{4,18} for the classical-spin chain system ($S=1$ and $H_{\text{chain}} = -J\sum S_i \cdot S_{i+1}$). The χ_m data can be expressed as

$$\chi_m = \{N^2 \beta^2 g^2 S(S+1) / 3kT\} \{(1+u)/(1-u)\} \quad (1)$$

with

$$u = \coth[JS(S+1)/kT] - [kT/JS(S+1)]$$

The best-fit parameters are obtained using a nonlinear regression analysis with $g = 2.29(1)$, $J = -2.70(2) \text{ cm}^{-1}$ and $R = 4.8 \times 10^{-3}$ ($R = [\sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum \chi_{\text{obs}}^2]^{1/2}$). In contrast to ferromagnetic chain complex *catena*-(μ -CrO₄-O,O')[Ni^{II}-(cyclam)] · 2H₂O ($g = 2.13(1)$, $J = +0.6(1) \text{ cm}^{-1}$)⁴, complex **1** exhibits only a weak antiferromagnetic interaction. This indicates that the completely weak antiferromagnetic interaction observed in **1** does not occur through the [MoO₄]²⁻ unit but results from the magnetic dipole-dipole interac-

tion.^{5,14}

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Supplementary Material. Atomic coordinates, bond lengths and angles and thermal parameters are available from author K.-Y. Choi on request.

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