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Thiolate-Bridged Binuclear Nickel(II) Complex with Thioether Pendant Groups

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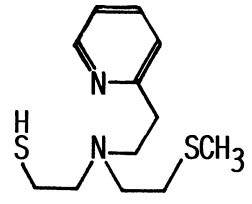
A binuclear nickel(II) complex with N-[2-(2-pyridyl)ethyl]-N-[2-(methylthio)ethyl]-2-aminoethanethiol (HL), $[Ni_2(L)_2](ClO_4)_2 \cdot H_2O$ has been prepared and characterized by electronic spectra and magnetic susceptibilities (87–300 K). X-Ray structure analysis has revealed that the two nickel ions are bridged by two thiolate sulfur atoms, and each of them takes an elongated square-pyramidal configuration with a pendant thioether at the apex.

The chemistry of nickel with thiolic ligands has attracted much attention in the last decade because the biological significance of nickel-sulfur complexes has been recognized.[1] While attempts to model the active site of the nickel-enzymes are directed toward synthesis of mononuclear nickel complexes, interest in the chemistry of nickel thiolates has resulted in a variety of thiolate-bridged multinuclear nickel(II) complexes containing two,[2-5] three,[5-7] four,[7,8] six,[9] and eight[10] nickel atoms. All these complexes are essentially diamagnetic showing the nickel(II) ions are low-spin owing to the strong covalent character of the Ni-S bond. This makes the thiolate-bridged nickel complexes less attractive in magnetic properties. However, we may expect that the introduction of a pendant group capable of coordinating at an apical position changes the spin state of the nickel(II) ion and give rise to a substantial paramagnetism. As such a ligand, we have synthesized N-[2-(2-pyridyl)ethyl]-N-[2-(methylthio)ethyl]-2-aminoethanethiol (HL) in the hope of obtaining a novel thiolate-bridged binuclear nickel(II) complex. In this paper, we report the synthesis, X-ray crystal structure, and spectral and magnetic properties of a thiolate-bridged binuclear nickel(II) complex with this ligand, $[Ni_2(L)_2](ClO_4)_2 \cdot H_2O$ (**1**).

The ligand, HL, was prepared by the reaction of [2-(2-pyridyl)ethyl][2-(methylthio)ethyl]amine[11] with ethylene sulfide. The complex was prepared by the reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol) with HL (1 mmol) in methanol. Anal. $[Ni_2(L)_2](ClO_4)_2 \cdot H_2O$; Found: C, 34.16; H, 4.71; N, 6.61%. Calcd for C_{24}-



HL

$H_{40}Cl_2N_4Ni_2O_9S_4$: C, 34.11; H, 4.77; N, 6.63%.

A black plate with dimensions of 0.14×0.15×0.42 mm^3 was used for the X-ray work. Crystal data are: $[Ni_2(L)_2](ClO_4)_2 \cdot H_2O$, F.W. = 845.1, orthorhombic, $Pna2_1$ (no. 33), a = 15.200(3), b = 25.935(5), c = 8.862(2) Å, V = 3493.6(11) $Å^3$, D_c = 1.607 g cm^{-3}, Z = 4, μ(Mo-Kα) = 15.18 cm^{-1}. Intensity data were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation; they were corrected for the Lorentz-polarization and absorption effects. Independent 2347 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure analysis. The structure was solved by direct methods. Refinement was carried out by the block-diagonal least-squares methods to yield final values R = 0.047 and R_w = 0.060.[12)]

The crystal structure consists of discrete binuclear cations, $[Ni_2(L)_2]^{2+}$, perchlorate ions, and water molecules. A perspective view of $[Ni_2(L)_2]^{2+}$ is illustrated in Fig. 1. The two nickel ions are bridged by two thiolate sulfur atoms. The Ni1-Ni2 distance is 2.839(2) Å and the Ni-S-Ni angles are 79.2(1) and 79.3(1)°. Both nickel ions adopt an elongated square pyramidal coordination geometry with an amino nitrogen, a pyridine nitrogen, and two bridging sulfur atoms in the basal plane and a thioether sulfur atom in the apical position. The two N_2S_2 planes are bent at the S1-S3 edge with a dihedral angle of 99.2°. The most

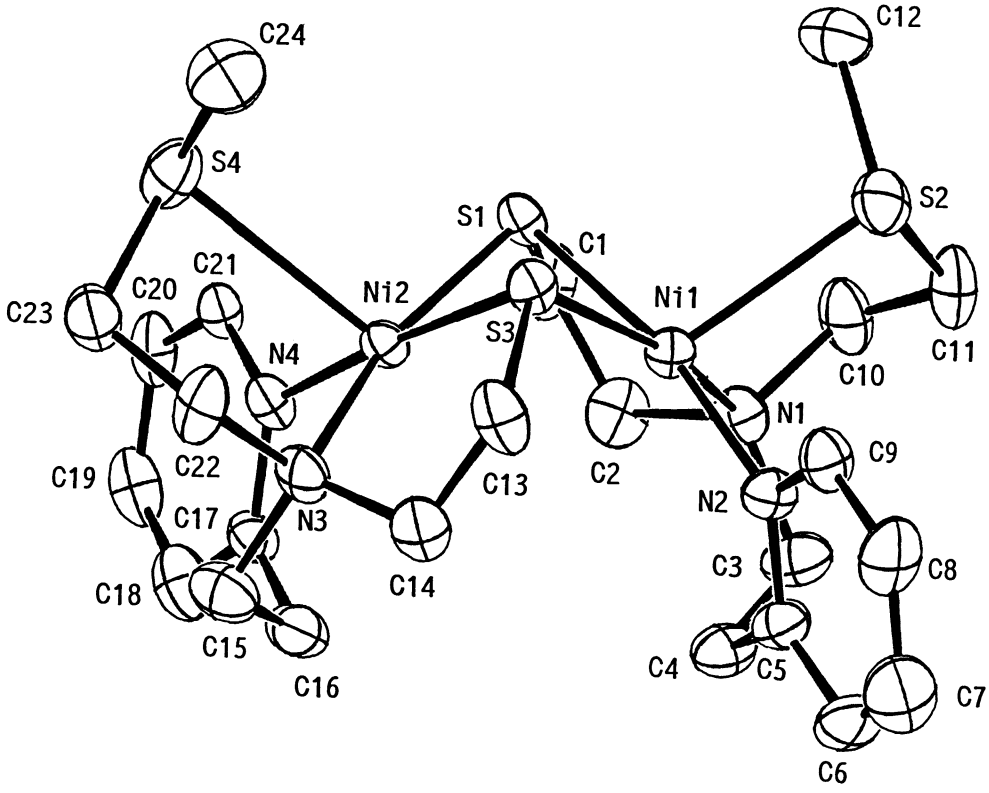


Fig. 1. Perspective view of $[Ni_2(L)_2]^{2+}$. Selected bond distances (l/Å) and (φ/°) are: Ni1-Ni2 2.839(2), Ni1-S1 2.244(4), Ni1-S3 2.257(3), Ni1-S2 2.563(4), Ni1-N1 2.067(9), Ni1-N2 1.989(9), Ni2-S1 2.208(3), Ni2-S3 2.192(3), Ni2-S4 2.797(4), Ni2-N3 2.017(9), Ni2-N4 1.953(8); Ni1-S1-Ni2 79.2(1), Ni1-S3-Ni2 79.3(1).

striking feature of this structure is the thioether coordination. The Ni1-S2 and Ni2-S4 distances are 2.563(4) and 2.797(4) Å, respectively. This axial coordination seems to cause the elongation of the in-plane bonds. All the Ni-S (2.192(3)–2.257(3) Å), Ni-N(amino) (2.017(9), 2.067(9) Å), and Ni-N(pyridine) (1.953(8), 1.989(9) Å) distances are significantly longer than those of the corresponding thiolate-bridged binuclear nickel(II) complex without the pendant group, bis{μ-[N-[2-(2-pyridyl)ethyl]-2-aminoethanethiolato]-N,N',μ-S}dinickel(II) perchlorate (**2**) (Ni-S 2.169(1), 2.186(1) Å; Ni-N(amino) 1.967(4) Å; Ni-N(pyridine) 1.905(4) Å).[2] The axial coordination effect can be further observed in the lifting of the nickel atom from the basal N_2S_2 plane: the deviations of the basal atoms from the mean planes are within ±0.04 Å, and Ni1 and Ni2 are displaced by 0.22 and 0.14 Å, respectively, from the mean plane toward the thioether sulfur.

Diffuse reflectance spectrum of **1** shows a broad band at 17.4×10^3 cm^{-1} and a band at 25.6×10^3 cm^{-1}. The positions of both bands are shifted to lower frequencies compared with the spectrum of **2** (19.0×10^3 cm^{-1}, 27×10^3 cm^{-1}) and the low frequency band is broader than that of **2**. This fact may be due to the five-coordinate structures of the nickel ions.

As would be expected from the thioether coordination, the magnetic property of **1** is different from those of the thiolate-bridged binuclear nickel(II) complexes so far reported.[2-5] The magnetic susceptibility was measured over the temperature range 87–300 K and the result is shown in Fig. 2. The magnetic moment per nickel atom is 1.66 BM at 298 K and decreases to 0.51 BM at 87 K. These values are considerably lower than the magnetic moments for high-spin nickel(II) ion (2.8–3.4 BM) and suggest the existence of an antiferromagnetic spin-exchange interaction within the molecule. It was attempted to interpret the magnetic data in terms of the Van-Vleck equation for the (S=1)-(S=1) system based on the Heisenberg model,

$$\chi_A = \frac{Ng^2\beta^2}{kT} \cdot \frac{5 + \exp(-4J/kT)}{5+3\exp(-4J/kT)+\exp(-6J/kT)} + N\alpha \qquad (1)$$

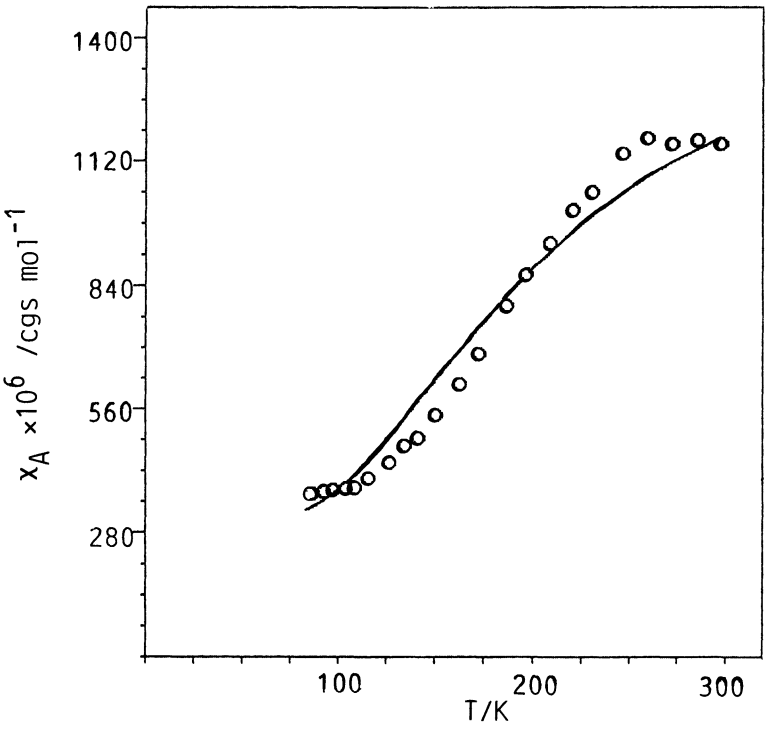


Fig. 2. Temperature dependence of magnetic susceptibility of $[Ni_2(L)_2](ClO_4)_2\cdot H_2O$. The solid curve was calculated from the equation (1) with g = 2.5, J = -200 cm^{-1}, and $N\alpha = 300\times10^{-6}$ cm^3mol^{-1}.

where χ_A is the susceptibility per nickel ion and other symbols have their usual meanings. No good agreement between the experimental and theoretical χ_A–T curves could be obtained with reasonable magnetic parameters (cf. Fig. 2). This fact means that the magnetic behavior is not simple. As one of possible explanations for this magnetism, we may invoke a spin-crossover phenomenon between the high- and low-spin states of the nickel ions. The X-ray structure determination at low temperature is in progress in order to elucidate the origin of the unusual magnetic behavior of **1** .

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11) The amine was prepared by the reaction of 2-vinylpyridine with 2-(methylthio)-ethylamine.
12) All the calculations were carried out with the UNICS-III programs on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science.

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