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A Thiolate-Bridged Binuclear Nickel(II) Complex with a Tripod-like N_3S-ligand. Formation of a Novel Disulfide-Bridged Binuclear Nickel(II) Complex

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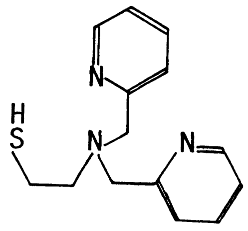
Reaction of nickel salts with N,N-bis(2-pyridylmethyl)-2-aminoethanethiol (HL) gives a thiolate-bridged binuclear nickel(II) complex, $[Ni_2(L)_2](ClO_4)_2$, and a novel disulfide-bridged binuclear nickel(II) complex, $[Ni_2(LL)(CH_3COO)_2](PF_6)_2 \cdot C_2H_5OH$ (LL is the disulfide formed upon oxidation of the ligand, HL). X-Ray structure analysis of the latter complex has revealed that the two nickel ions are bridged by the disulfide group and two acetate ions.

Nickel complexes of thiolic ligands have attracted much attention in the last decade because the biological significance of nickel-sulfur complexes has been recognized.[1)] Recently we have reported the synthesis and characterization of a thiolate-bridged binuclear nickel(II) complex having thioether pendant arms, $[Ni_2(L')_2](ClO_4)_2 \cdot H_2O$ (HL' = N-[2-(2-pyridyl)ethyl]-N-[2-(methylthio)ethyl]-2-aminoethanethiol).[2)] Contrary to the known thiolate-bridged nickel(II) complexes without the pendant arms,[3)] the complex shows a substantial paramagnetism. This could be attributed to the apical coordination effect of the thioether group. In order to investigate this effect further we have prepared a new thiolate-bridged nickel(II) complex with pyridyl pendant groups. The thiolate-bridged binuclear nickel(II) complex, $[Ni_2(L)_2](ClO_4)_2$ (**1**), which is paramagnetic, is formed on reaction of nickel(II) perchlorate with N,N-bis(2-pyridylmethyl)-2-aminoethanethiol (HL). During the course of this study, we have found that reaction of nickel(II) acetate with the thiolic ligand, HL, in ethanol leads to formation of a novel disulfide-bridged binuclear nickel(II) complex, $[Ni_2(LL)(CH_3COO)_2](PF_6)_2 \cdot C_2H_5OH$ (**2**) (LL = bis{2-[N,N-bis(2-pyridylmethyl)]aminoethyl} disulfide). Here we report the synthesis, X-ray crystal structure and magnetic properties of **2**.



HL

The thiolate-bridged binuclear nickel(II) complex **1** was obtained as greenish powder from the reaction mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mmol) and HL(1 mmol)[4)] in ethanol. Anal. Found: C, 40.23; H, 4.13; N, 10.03%. Calcd for $C_{14}H_{16}ClN_3NiO_4S$ ($[Ni_2(L)_2](ClO_4)_2$): C, 40.37; H, 3.87; N, 10.09%. The magnetic moment per nickel atom of **1** is 2.40 and 2.18 B.M. at 286 and 93 K, respectively. This fact suggests that the two nickel ions are in a mixed spin state containing a low-spin Ni(II) and a high-spin Ni(II).[5)]

The disulfide-bridged binuclear nickel(II) complex **2** was prepared as follows. Nickel(II) acetate tetrahydrate (1 mmol) and HL (1 mmol) were dissolved in ethanol and the mixture was stirred. To the resulted dark green solution was added an aqueous solution of KPF_6 to form a small amount of greenish precipitate. The greenish precipitate[6)] was removed by filtration. Upon standing the filtrate in air overnight blue crystals were deposited. They were collected by filtration and washed with methanol. Anal. Found: C, 37.63; H, 4.14; N, 7.80%. Calcd for $C_{34}H_{44}F_{12}N_6Ni_2O_5P_2S_2$ ($[Ni_2(LL)(CH_3COO)_2](PF_6)_2 \cdot C_2H_5OH$): C, 37.53; H, 4.08; N, 7.72%.

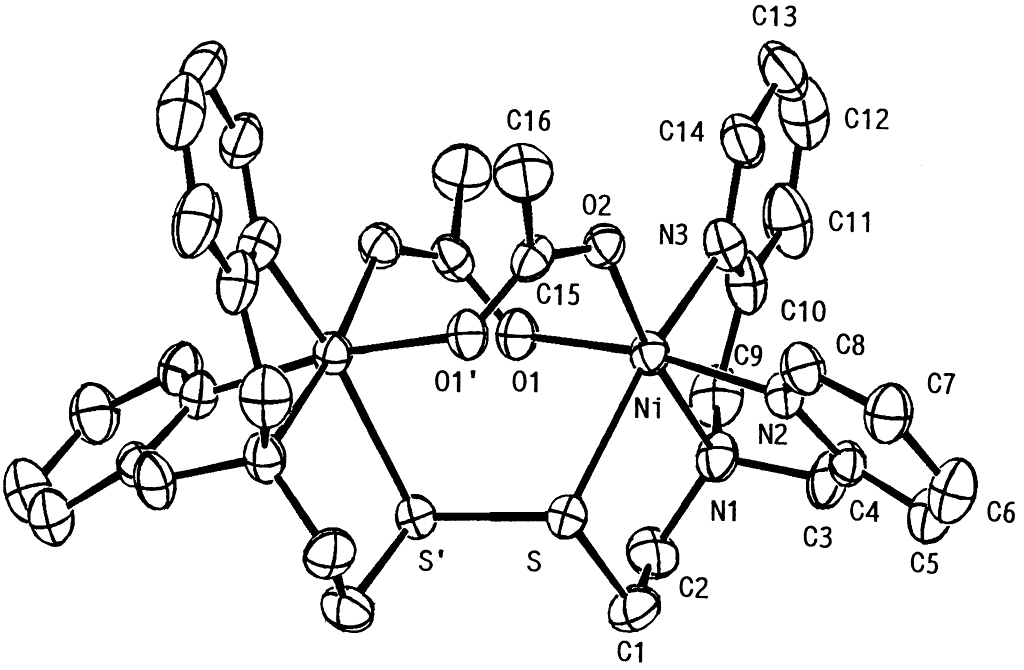


Fig. 1. Perspective view of $[Ni_2(LL)(CH_3COO)_2]^{2+}$. The left and right halves are related by the two-fold axis through the midpoint of the S-S bond. Primes refer to atoms related by this operation. Selected bond lengths (l/Å) and angles (φ/°): Ni-Ni' 4.134(2), Ni-S 2.503(3), Ni-O1 2.079(5), Ni-O2 2.006(6), Ni-N1 2.120(8), Ni-N2 2.065(6), Ni-N3 2.044(8), S-S' 2.056(3); S-Ni-O1 88.0(2), S-Ni-O2 100.5(2), S-Ni-N1 84.5(2), S-Ni-N2 86.2(2), S-Ni-N3 164.2(2), O1-Ni-O2 94.6(2), O1-Ni-N1 90.5(2), O1-Ni-N2 170.8(3), O1-Ni-N3 87.9(2), O2-Ni-N1 173.0(3), O2-Ni-N2 93.4(2), O2-Ni-N3 95.1(3), N1-Ni-N2 81.9(3), N1-Ni-N3 80.3(3), N2-Ni-N3 95.8(3).

The structure of **2** was determined by X-ray crystallography. A blue crystal with dimensions of 0.18×0.21×0.35 mm^3 was used for the X-ray work. Crystal data are: $[Ni_2(LL)(CH_3COO)_2](PF_6)_2\cdot C_2H_5OH$, F.W. = 1088.2, monoclinic, C2/c (No. 15), a = 26.264(3), b = 13.562(2), c = 13.871(2) Å, β = 113.35(1)°, V = 4535.9(10) Å^3. D_m = 1.60, D_c = 1.59 gcm^{-3}, Z = 4, μ(Mo-Kα) = 10.84 cm^{-1}. Intensity data were collected on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation. A total of 4670 reflections (1.5°<2θ<58°) were collected, of which independent 2471 reflections ($|F_o|>3\sigma(|F_o|)$) were considered as observed. The structure was solved by the direct methods and refined by the block-diagonal least-squares method.7) The final residual values were R = 0.067 and R_w = 0.090.8)

The crystal structure consists of discrete binuclear cations, $[Ni_2(LL)(CH_3COO)_2]^{2+}$, hexafluorophosphate ions, and ethanol molecules. A perspective view of $[Ni_2(LL)(CH_3COO)_2]^{2+}$ is illustrated in Fig. 1. The two nickel ions are bridged by disulfide group of the ligand, LL, and two acetate ions in unique manner. The Ni-Ni' distance is 4.134(2) Å. The complex cation has the crystallographic two-fold axis passing through the midpoint of the disulfide group. The formation of the disulfide ligand presumably results from the reaction of the original thiol, HL, with molecular oxygen present in the solution during crystal growth. The ligand, LL, functions as an octadentate ligand to coodinate to each nickel ion with two pyridyl nitrogens, one amino nitrogen and one disulfide sulfur, and the two acetate ions act as bridging groups of "syn-anti" configuration9) forming a distorted octahedron for each nickel ion. The Ni-N bond lengths (2.044(8)–2.120(8) Å) fall within the range (2.00–2.16 Å) that has been reported for octahedral nickel(II)-nitrogen distances.10) The Ni-O bond lengths (2.006(6) and 2.079(5) Å) are comparable with the values found in $Ni(CH_3COO)_2\cdot 4H_2O$ (2.12 Å)11) and $[Ni_2((CH_3)_3CCOO)_4Q_2]$ (Q = quinaldine) (2.041(1) Å).12) The Ni-S distance of 2.503(3) Å is slightly longer than those of other nickel(II) complexes of disulfide ligands, $[Ni(pms)X](ClO_4)$ (pms = bis{2-[N-(2-pyridylmethyl)]-aminoethyl} disulfide; X = Cl, Br),10) $[Ni(dtpp)Cl](ClO_4)$ (dtpp = α,α'-[dithiobis(o-phenylenenitrilo)]di-2-picoline)13) (2.456(2)–2.472(5) Å). This structural feature is compatible with high-spin state of the nickel(II) ions.14)

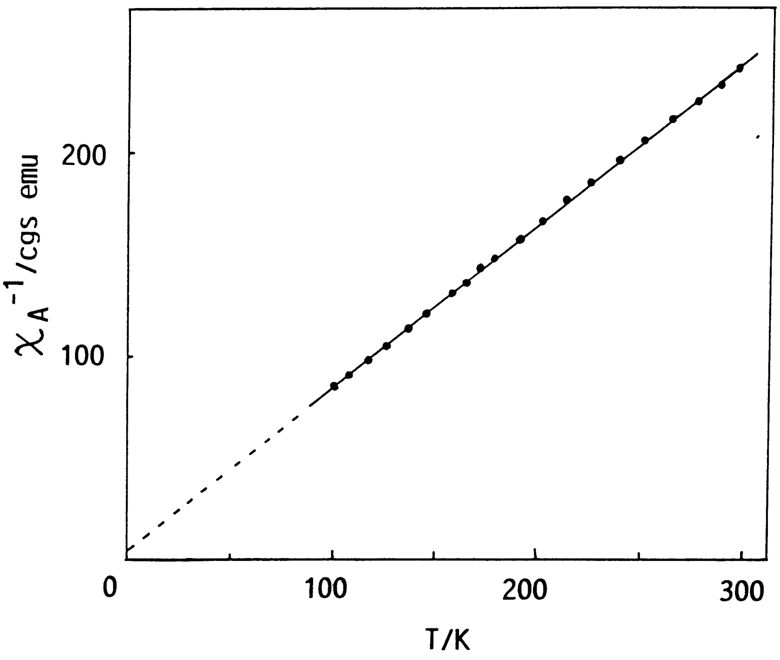


Fig. 2. Temperature dependence of the magnetic susceptibility of $[Ni_2(LL)(CH_3COO)_2](PF_6)_2\cdot C_2H_5OH$.

The magnetic moment per nickel ion (3.14 B.M. at 298

K) falls in the range of those for high-spin nickel(II) complexes (2.8–3.4 B.M.). The magnetic susceptibilities were measured over the temperature range 100–300 K. The magnetic datum obeys the Curie-Weiss law, $\chi_A = C/(T - \theta)$ with $\theta = -4$ K, indicating that the magnetic interaction is very weak (Fig. 2).

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6) Anal. Found: C, 36.14; H, 3.79; N, 7.93%. Calcd for $C_{30}H_{42}F_{12}N_6Ni_2O_3P_2S_2$ ($[Ni_2(L)_2](PF_6)_2 \cdot C_2H_5OH \cdot 2H_2O$): C, 35.81; H, 4.21; N, 8.35%.
7) The weighting scheme $w = [\sigma^2_{count} + (0.015|F_o|)^2]^{-1}$ was employed. Hydrogen atoms are not included in the calculation. The ethanol molecules are located in the vicinity of the crystallographic two-fold axis with occupancy factors of 0.5.
8) 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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14) Diffuse reflectance spectrum of **2** shows four bands in the visible region (27.3 sh, 17.3, 12.4sh, 11.2×10^3 cm^{-1}).

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