1104 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 1104—1110 (1993) [Vol. 66, No. 4

Synthesis and Characterization of Thiolate-Bridged Dinuclear Nickel(II) Complexes with Thioether Pendant Arms

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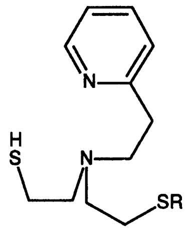
(Received October 15, 1992)

Thiolate-bridged dinuclear nickel(II) complexes with *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(methylthio)ethyl]-2-aminoethanethiol (HL_a) or *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(ethylthio)ethyl]-2-aminoethanethiol (HL_b), $[Ni_2(L_a)_2](ClO_4)_2$ (**1**) and $[Ni_2(L_b)_2](ClO_4)_2$ (**2**), have been synthesized and characterized by elemental analyses, infrared and electronic spectra, magnetic susceptibilities (80—300 K), and XANES. The crystal structures of **1** and **2** were determined by the single-crystal X-ray diffraction method at 118 and 293 K, respectively. The cation molecule has a thiolate-bridged dinuclear structure, in which each nickel ion is essentially coordinated by a square-planar N_2S_2 donor set with a weak apical coordination of the pendant thioether group. The magnetic and spectral properties are discussed based on the crystal structures.

The chemistry of nickel complexes with thiolate ligands has attracted much attention since the discovery of the nickel-sulfur interaction in hydrogenases from *Methanobacterium thermoautotrophicum* and *Desulfovibrio gigas* as well as in the CO dehydrogenase from *Clostridium thermoaceticum*.[1)] While attempts to model the active site of the nickel-enzymes are directed toward the synthesis of mononuclear nickel complexes, interest in the nickel thiolate has resulted in thiolate-bridged dinuclear,[2—11)] trinuclear,[9,12—21)] tetranuclear,[17,22,23)] hexanuclear,[19,24—27)] and octanuclear[28)] nickel(II) complexes. All of these complexes are essentially diamagnetic (low-spin) and the coordination environments of nickel(II) ions have a four-coordinate square-plane geometry owing to the strong covalent character of the Ni–S bonds. This diamagnetism has made the thiolate-bridged nickel(II) complexes less attractive concerning their magnetic properties. We have recently introduced a pendant arm which has an ability of apical coordination in thiolate-bridged nickel(II) complexes in order to change the spin state of the nickel(II) ion and produce a paramagnetism. We found that reactions of nickel salts with a thiolic ligand having a pyridyl pendant arm, *N*,*N*-bis(2-pyridylmethyl)-2-aminoethanethiol or *N*,*N*-bis[2-(2-pyridyl)ethyl]2-aminoethanethiol, give novel thiolate-bridged dinuclear nickel(II) complexes which are in a mixed spin state containing a low-spin and a high-spin Ni(II) in the same molecule.[29,30)] As part of our project concerning on new types of thiolate-bridged nickel complexes, we examined an apical coordination effect of the thioether pendant group by using *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(methylthio)ethyl]-2-aminoethanethiol (HL_a) or *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(ethylthio)ethyl]-2-aminoethanethiol (HL_b), and recently communicated one of the structural features (Chart 1).[31)] It is known that the apical coordination of thioether plays an important role in biological systems.[32)] We therefore expected that interesting thiolate-bridged nickel complexes are formed by introducing a thiolic ligand having a thioether pendant arm. Here, we report on the synthesis, spectral and magnetic properties, XANES, and X-ray crystal structures of thiolate-bridged dinuclear nickel(II) complexes with HL_a or HL_b ligands, $[Ni_2(L_a)_2](ClO_4)_2$ (**1**) and $[Ni_2(L_b)_2](ClO_4)_2$ (**2**).



HL_a (R=CH_3)
HL_b (R=C_2H_5)

Chart 1.

Experimental

Ligand Synthesis. 2-(Methylthio)ethylamine and 2-(ethylthio)ethylamine were prepared by applying a method described in the literature.[33)] [2-(2-Pyridyl)ethyl][2-(alkylthio)ethyl]amine was prepared by a reaction of 2-vinylpyridine with 2-(alkylthio)ethylamine according to a previously reported procedure.[34)] Ethylene sulfide was obtained from Aldrich Chemical Co., Inc. and was purified by distillation. *N*-[2-(2-Pyridyl)ethyl]-*N*-[2-(methylthio)ethyl]-2-aminoethanethiol (HL_a) and *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(ethylthio)ethyl]-2-aminoethanethiol (HL_b) were prepared by the reaction of [2-(2-pyridyl)ethyl][2-(alkylthio)ethyl]amine with ethylene sulfide according to a method of Marabella et al.[30,35)]

Preparation of Complexes. All operations were performed under N_2.

$[Ni_2(L_a)_2](ClO_4)_2 \cdot H_2O$ ($1 \cdot H_2O$): To a solution of nickel(II) perchlorate hexahydrate (366 mg, 1 mmol) in methanol (20 ml) was added a methanol solution (10 ml) of the ligand, HL_a (255 mg, 1 mmol); the mixture was allowed to stand for a few days to give black crystals. They were collected by filtration, washed with methanol, and dried in vacuo over P_2O_5. Found: C, 34.16; H, 4.71; N, 6.61%. Calcd for $C_{24}H_{40}Cl_2N_4Ni_2O_9S_4$: C, 34.11; H, 4.77; N, 6.63%. IR (Nujol mull, cm^{-1}) ν (H_2O) 3594, 3514, δ (H_2O) 1630, ν (ClO_4) 1099.

$[Ni_2(L_b)_2](ClO_4)_2$ (2): To an ethanol solution (15 ml) of nickel(II) perchlorate hexahydrate (366 mg, 1 mmol) was added a solution of HL_b (270 mg, 1 mmol) in ethanol (10 ml) to form a black precipitate. It was collected by filtration and recrystallized from methanol as black needles. They were collected by filtration, washed with methanol, and dried in vacuo over P_2O_5. Found: C, 36.49; H, 5.02; N, 6.53%. Calcd for $C_{26}H_{42}Cl_2N_4Ni_2O_8S_4$: C, 36.52; H, 4.95; N, 6.55%. IR (Nujol mull, cm^{-1}) ν (ClO_4) 1090.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the region 4000—400 cm^{-1} on a Nujol mull. The electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Sepctrophotometer Model UV-3100. The magnetic susceptibilities were measured by the Faraday method over the 80—300 K temperature range. The apparatus was calibrated using $[Ni(H_2NCH_2CH_2NH_2)_3]S_2O_3$.[36)] The susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's constants.[37)] The effective magnetic moments were calculated from the equation $\mu_{\mathrm{eff}} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility. The nickel K-edge X-ray absorptions for **1** were measured on EXAFS facilities at the BL-10B beamline of the Photon Factory in the National Laboratory of High Energy Physics (KEK-PF). Synchrotron radiation from the electron storage ring (2.5 GeV, 180—300 mA) was monochromated with a silicon (311) channel-cut monochromator.

X-Ray Crystal Structure Analysis. $[Ni_2(L_a)_2](ClO_4)_2$ (1): A black plate with dimensions of $0.13 \times 0.19 \times 0.59$ mm^3 was used for the X-ray structure analysis. The intensity data were measured on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 118 K. The low-temperature measurement was carried out with an attached Rigaku variable-temperature apparatus based on a cold nitrogen stream method.[38)] The data were corrected for Lorentz-polarization, but not for absorption.

Crystal Data: $C_{24}H_{38}Cl_2N_4Ni_2O_8S_4$, F.W.=827.1, orthorhombic, $Pna2_1$ (No.33); $a=15.275(3)$, $b=25.367(6)$, $c=8.635(2)$ Å, $V=3346.0(12)$ Å^3 at 118 K; $a=15.212(2)$, $b=25.652(6)$, $c=8.788(1)$ Å, $V=3429.5(10)$ Å^3 at 292 K; $D_m=1.59$, $D_c=1.60$ $g\,cm^{-3}$, $Z=4$, μ (Mo $K\alpha$)=15.18 cm^{-1}.

A total of 4412 reflections with $2\theta < 56°$ were collected, of which 3128 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure analysis. The structure was solved by direct methods. A refinement was carried out by a block-diagonal least-squares method. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were inserted at their calculated positions and fixed. A weighting scheme, $w=1/[\sigma^2_{\mathrm{count}}+(0.015|F_o|)^2]$, was employed. The final discrepancy factors are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.059$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.061$.

All of the calculations were carried out on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using UNICS-III programs.[39)]

$[Ni_2(L_b)_2](ClO_4)_2$ (2): A black needle with dimensions of $0.08 \times 0.14 \times 0.20$ mm^3 was used for the X-ray work. The data were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) at 293 K. They were corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: $C_{26}H_{42}Cl_2N_4Ni_2O_8S_4$, F.W.=855.2, orthorhombic, $P2_12_12_1$ (No.19); $a=21.166(6)$, $b=16.698(4)$, $c=10.028(2)$ Å, $V=3535.8(15)$ Å^3, $D_m=1.61$, $D_c=1.61$ $g\,cm^{-3}$, $Z=4$, μ (Mo $K\alpha$)=15.02 cm^{-1}.

Of the 3575 reflections ($2\theta < 40°$) measured, 1077 unique reflections with $I > 3\sigma(I)$ were considered as observed. The structure was solved by direct methods and refined by a full-matrix least-squares method. Because of the paucity of the data, all of the non-hydrogen atoms were refined with isotropic temperature factors; the hydrogen atoms were not included in the calculations. A weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. The final discrepancy factors are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.106$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.126$. All of the calculations were carried out on a Micro VAXII computer using a SDP program package.[40)]

The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms and the F_o-F_c tables have been deposited as Document No.66008 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The diffuse reflectance spectra of $1 \cdot H_2O$ and **2** are shown in Fig. 1, together with that of the corresponding thiolate-bridged nickel(II) complex without any pendant arms, bis{μ[*N*-[2-(2-pyridyl)ethyl]-2-aminoethanethiolato]-*N*,*N'*,μ-*S*}dinickel(II) perchlorate, $Ni_2(L')_2(ClO_4)_2$ (**3**).[5)] The spectra of $1 \cdot H_2O$ and **2** are characterized by three or four absorptions in the visible region ($1 \cdot H_2O$: 581, 834, 1350 nm; **2**: 500sh, 634, 900, 1270 nm), which can be associated with d-d transitions and intense absorptions in the range 250—400 nm; these are charge-transfer transitions in origin. On the other hand, the spectrum of **3** shows two absorption bands at 521 and 700 nm which can be assigned to d-d transitions ($^1A_{1g} \rightarrow {}^1A_{2g}$, $^1B_{2g}$) that are characteristic of low-spin nickel(II) complexes.[41)] The complicated visible spectra of $1 \cdot H_2O$ and **2** are consistent with the presence of a high-spin nickel(II) ion in the complexes, suggesting that the thioether pendant arm has considerable influence on the electronic state of the nickel(II) ion.

Table 1. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å$^{2\mathrm{a)}}$
$[Ni_2(L_a)_2](ClO_4)_2$ (**1**)				
Ni1	0.3075(1)	0.3240(1)	0.2164(2)	1.2
Ni2	0.2341(1)	0.4172(1)	0.0857(2)	1.2
Cl1	0.6260(2)	0.3861(1)	0.0347(3)	1.9
Cl2	−0.0207(2)	0.3504(2)	−0.3996(4)	6.7
S1	0.2234(1)	0.3343(1)	0.0138(3)	1.2
S2	0.3983(2)	0.2355(1)	0.1215(3)	2.3
S3	0.3708(1)	0.3910(1)	0.0978(3)	1.4
S4	0.2458(2)	0.4782(1)	−0.1823(3)	2.2
O1	0.5725(5)	0.4245(3)	−0.0430(9)	2.5
O2	0.7164(5)	0.3950(4)	0.0037(13)	5.0
O3	0.6122(6)	0.3905(3)	0.2008(9)	4.0
O4	0.5997(6)	0.3343(3)	−0.0088(10)	4.3
O5	0.0245(6)	0.3303(5)	−0.2733(16)	6.8
O6	−0.1058(7)	0.3601(5)	−0.3718(11)	7.1
O7	0.0489(11)	0.3756(7)	−0.4617(24)	4.1
O7′	−0.0203(14)	0.4209(8)	−0.3961(23)	5.8
O8	−0.0282(11)	0.2927(7)	−0.4802(21)	3.9
O8′	−0.0108(11)	0.3474(8)	−0.5623(19)	4.1
N1	0.2195(5)	0.2737(3)	0.3017(9)	1.5
N2	0.3802(5)	0.3264(3)	0.3994(9)	1.5
N3	0.2679(5)	0.4834(3)	0.1950(10)	1.6
N4	0.1088(4)	0.4297(3)	0.0920(10)	1.4
C1	0.1236(6)	0.3018(4)	0.0811(13)	1.8
C2	0.1306(6)	0.2938(4)	0.2560(12)	1.8
C3	0.2188(7)	0.2708(4)	0.4792(11)	2.1
C4	0.2447(7)	0.3236(4)	0.5508(10)	1.9
C5	0.3445(7)	0.3297(4)	0.5458(10)	1.7
C6	0.3952(8)	0.3368(4)	0.6733(11)	2.2
C7	0.4843(7)	0.3385(5)	0.6602(13)	2.6
C8	0.5226(7)	0.3349(4)	0.5140(14)	2.3
C9	0.4684(7)	0.3286(4)	0.3867(12)	1.9
C10	0.2320(6)	0.2185(4)	0.2445(11)	1.7
C11	0.3248(7)	0.1997(5)	0.2487(12)	2.5
C12	0.3544(8)	0.2177(5)	−0.0661(13)	3.0
C13	0.4130(6)	0.4408(4)	0.2311(14)	2.0
C14	0.3389(7)	0.4682(4)	0.3102(12)	2.0
C15	0.1937(7)	0.5066(4)	0.2906(12)	2.1
C16	0.1341(7)	0.4619(4)	0.3521(11)	1.8
C17	0.0723(6)	0.4464(3)	0.2277(13)	1.7
C18	−0.0183(6)	0.4486(4)	0.2457(13)	2.2
C19	−0.0722(6)	0.4334(4)	0.1203(15)	2.3
C20	−0.0332(6)	0.4188(4)	−0.0150(13)	1.8
C21	0.0563(6)	0.4181(4)	−0.0268(11)	1.6
C22	0.3018(6)	0.5260(4)	0.0956(14)	2.0
C23	0.2477(7)	0.5345(4)	−0.0546(14)	2.1
C24	0.3602(7)	0.4754(4)	−0.2426(12)	2.4
$[Ni_2(L_b)_2](ClO_4)_2$ (**2**)				
Ni1	0.5228(4)	0.8514(4)	0.5623(7)	3.4(1)*
Ni2	0.4001(3)	0.8297(5)	0.6229(7)	3.4(1)*
Cl1	0.6346(8)	0.559(1)	0.450(2)	5.9(4)*
Cl2	0.326(1)	0.471(1)	0.402(2)	10.0(7)*
S1	0.4742(9)	0.8862(9)	0.759(2)	4.0(4)*
S2	0.6328(8)	0.820(1)	0.606(2)	6.1(5)*
S3	0.4719(8)	0.7336(9)	0.631(2)	3.7(3)*
S4	0.3102(8)	0.794(1)	0.799(2)	4.4(4)*
O1	0.638(2)	0.481(3)	0.474(4)	6(1)*
O2	0.614(3)	0.615(4)	0.549(7)	16(2)*
O3	0.695(3)	0.587(4)	0.424(7)	14(2)*
O4	0.579(4)	0.564(5)	0.420(9)	22(3)*
O5	0.380(3)	0.485(4)	0.460(7)	15(2)*
O6	0.272(5)	0.461(6)	0.45(1)	25(4)*
O7	0.335(4)	0.405(5)	0.332(7)	17(3)*
O8	0.315(3)	0.542(3)	0.331(5)	9(2)*
N1	0.552(2)	0.978(3)	0.552(5)	5(1)*
N2	0.538(2)	0.824(2)	0.361(4)	4(1)*
N3	0.350(2)	0.752(3)	0.495(5)	6(1)*
N4	0.352(2)	0.923(3)	0.583(4)	4(1)*
C1	0.493(3)	0.993(4)	0.748(6)	6(2)*
C2	0.502(3)	0.025(4)	0.621(7)	7(2)*
C3	0.552(3)	1.000(4)	0.399(7)	6(2)*
C4	0.501(3)	0.965(3)	0.313(6)	5(2)*
C5	0.515(3)	0.882(3)	0.277(5)	5(2)*
C6	0.509(3)	0.858(4)	0.135(6)	6(2)*
C7	0.475(3)	0.290(3)	0.396(6)	7(2)*
C8	0.551(3)	0.736(4)	0.179(6)	6(2)*
C9	0.564(3)	0.754(4)	0.329(6)	5(2)*
C10	0.611(2)	0.989(3)	0.601(5)	3(1)*
C11	0.660(3)	0.919(4)	0.580(6)	5(2)*
C12	0.629(3)	0.805(4)	0.818(7)	8(2)*
C13	0.693(4)	0.793(5)	0.841(8)	9(3)*
C14	0.442(2)	0.670(3)	0.506(4)	3(1)*
C15	0.394(3)	0.709(3)	0.422(5)	4(1)*
C16	0.306(3)	0.804(3)	0.403(6)	5(2)*
C17	0.336(2)	0.874(3)	0.357(5)	4(1)*
C18	0.331(3)	0.951(3)	0.464(5)	4(1)*
C19	0.306(3)	0.029(3)	0.440(6)	5(2)*
C20	0.295(3)	0.076(4)	0.541(6)	6(2)*
C21	0.313(3)	0.060(3)	0.669(5)	3(1)*
C22	0.339(3)	0.979(3)	0.677(5)	4(2)*
C23	0.305(2)	0.702(3)	0.566(6)	4(1)*
C24	0.263(3)	0.744(3)	0.666(5)	4(1)*
C25	0.338(3)	0.704(4)	0.886(8)	8(2)*
C26	0.365(4)	0.734(5)	1.015(7)	8(2)*

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. b) Starred atoms were refined isotropically.

In a previous communication we reported on the crystal structure of **1**·H_2O at 292 K.[31] The crystal structure comprises discrete dinuclear cations, $[Ni_2(L_a)_2]^{2+}$, perchlorate ions, and water molecules. In the dinuclear cation, both of the nickel ions adopt an elongated square pyramidal coordination geometry with an amino nitrogen, a pyridyl nitrogen, and two bridging thiolate sulfur atoms in the basal plane and a thioether sulfur atom in the apical position (Fig. 2). The coordination environments of the two nickel ions are similar to each other, but are not the same. One pendant thioether sulfur atom (S2) is weakly coordinated to a nickel ion (Ni1) with a Ni1–S2 distance of 2.563(4) Å; the other thioether pendant arm is apart from the coordination sphere (Ni2–S4 2.797(4) Å). The weak coordination (Ni1–S2)

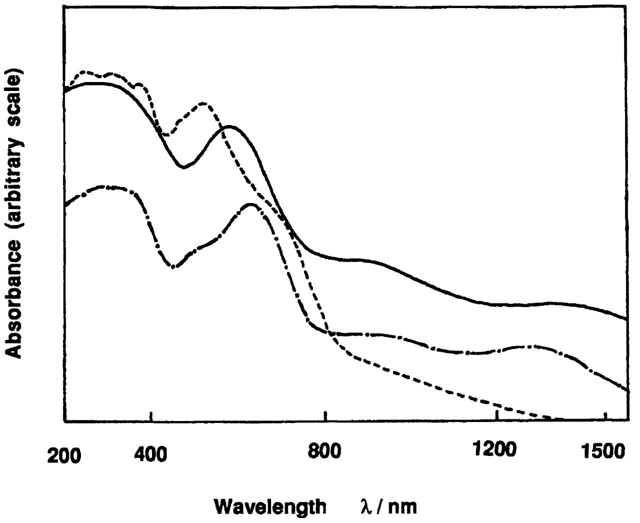


Fig. 1. Diffuse reflectance spectra of $Ni_2(L_a)_2(ClO_4)_2 \cdot H_2O$ ($1 \cdot H_2O$) (—), $Ni_2(L_b)_2(ClO_4)_2$ (**2**) (–••–), and $Ni_2(L')_2(ClO_4)_2$ (**3**) (---).

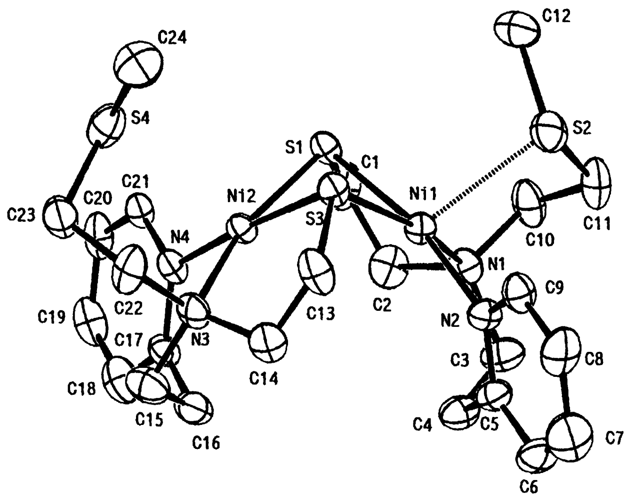


Fig. 2. Perspective view of the $[Ni_2(L_a)_2]^{2+}$ in $\mathbf{1} \cdot H_2O$ (at 292 K).

may affect the electronic state of the nickel(II) ion, because the Ni1–S(thiolate) distances (Ni1–S1 2.244(4) Å, Ni1–S3 2.257(3) Å) are significantly longer than the Ni2–S(thiolate) distances (Ni2–S1 2.208(3) Å, Ni2–S3 2.192(3) Å), which are common for low-spin thiolate-bridged nickel(II) complexes (2.158(2)—2.225(2) Å).[2—11] This weak coordination effect may be responsible for the complicated visible spectrum of $\mathbf{1} \cdot H_2O$. As would be expected from the weak coordination of the thioether sulfur, the magnetic property of $\mathbf{1} \cdot H_2O$ is different from those of the thiolate-bridged nickel(II) complexes without the pendant arms so far reported.[2—11] The magnetic moment per nickel atom is 1.51 B.M. at 298 K, and gradually decreases to 0.45 B.M. at 87 K. These values are considerably lower than the spin-only value for the high-spin nickel(II) ion (2.82 B.M.), thus suggesting the existence of an antiferromagnetic interaction. Variable-temperature magnetic susceptibility data (80—300 K) are shown in Fig. 3.[42] We tried to interpret the temperature dependence of the magnetic susceptibilities in terms of the Van Vleck equation for a two high-spin nickel(II) ions system (S=1—S=1) based on the Heisenberg model. However, the agreement between the experimental and theoretical susceptibilities was rather poor, showing that the magnetic behavior is not simple antiferromagnetism within a dinuclear molecule.[31] Another possible explanation for this magnetic behavior is structural changes in the coordination environments with temperature.[38] In elucidating the origin of the magnetic behavior it is necessary to know the low-temperature crystal structure. We have thus undertaken an X-ray structure analysis of **1** at 118 K. A perspective view of $[Ni_2(L_a)_2]^{2+}$ in the crystal structure at 118 K is shown in Fig. 4. The crystal structure at 118 K is essentially the same as that found at 292 K, except for the existence of water molecules. We could not find any water molecules in the crystal structure of **1** at 118 K, in contrast to the room-temperature structure.[31] This difference may result from some kind of possible polymorphism in $\mathbf{1} \cdot H_2O$, since the unit-cell volume (V=3429.5(10) Å^3) of the present crystal at 292 K is significantly smaller than that of the crystal previously reported (V=3493.6(11) Å^3).[31] The analytical and IR data of the same crop of crystals suggest the existence of water molecules in the bulk of the sample. We therefore seem to have taken the anhydrous crystal **1** for the low-temperature X-ray work, by some chance, from crystals of the sample, most of which are monohydrate complexes $\mathbf{1} \cdot H_2O$. To settle this problem,

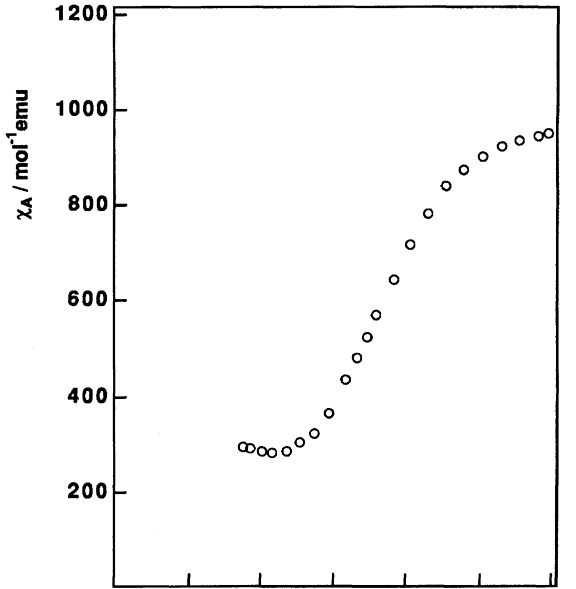


Fig. 3. Temperature dependence of the magnetic susceptibility of $\mathbf{1} \cdot H_2O$.

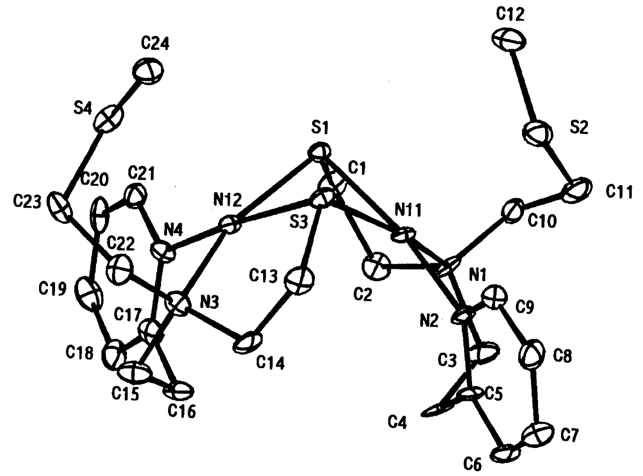


Fig. 4. Perspective view of the $[Ni_2(L_a)_2]^{2+}$ in **1** (at 118 K).

Table 2. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°)

	$[Ni_2(L_a)_2](ClO_4)_2$ (**1**) 118 K	$[Ni_2(L_a)_2](ClO_4)_2$ (**1**) 292 K[a]	$[Ni_2(L_b)_2](ClO_4)_2$ (**2**) 293 K
Ni1–Ni2	2.848(2)	2.839(2)	2.69(1)
Ni1–S1	2.186(3)	2.244(4)	2.30(2)
Ni1–S3	2.206(3)	2.257(3)	2.35(2)
Ni1–N1	1.994(8)	2.067(9)	2.20(5)
Ni1–N2	1.932(8)	1.989(9)	2.10(4)
Ni1–S2	2.764(3)	2.563(4)	2.42(2)
Ni2–S1	2.198(3)	2.208(3)	2.28(2)
Ni2–S3	2.193(2)	2.192(3)	2.21(2)
Ni2–N3	1.995(8)	2.017(9)	2.11(5)
Ni2–N4	1.941(7)	1.953(8)	1.91(4)
Ni2–S4	2.789(3)	2.797(4)	2.66(2)
Ni1–S1–Ni2	81.04(9)	79.2(1)	71.9(6)
Ni1–S3–Ni2	80.70(9)	79.3(1)	72.3(5)
S1–Ni1–S3	78.1(1)	77.5(1)	75.8(5)
S1–Ni1–N1	88.6(2)	88.7(3)	85(1)
S1–Ni1–N2	171.3(3)	168.2(3)	162(1)
N1–Ni1–N2	96.0(3)	94.5(4)	97(2)
N1–Ni1–S3	163.6(2)	162.3(3)	161(1)
N2–Ni1–S3	96.0(3)	97.0(3)	100(1)
S2–Ni1–S1	98.9(1)	102.5(1)	109.1(6)
S2–Ni1–S3	105.6(1)	106.5(1)	102.0(7)
S2–Ni1–N1	85.9(2)	87.2(3)	87(1)
S2–Ni1–N2	88.8(2)	89.0(3)	89(1)
S1–Ni2–S3	78.16(9)	79.6(1)	78.9(7)
S1–Ni2–N4	95.3(2)	95.5(3)	99(1)
S1–Ni2–N3	163.4(2)	165.1(3)	164(2)
S3–Ni2–N3	89.2(2)	88.6(3)	86(2)
S3–Ni2–N4	170.8(2)	172.7(3)	166(1)
N3–Ni2–N4	95.9(3)	95.3(4)	96(2)
S4–Ni2–S1	107.5(1)	105.8(1)	100.8(6)
S4–Ni2–S3	98.4(1)	98.9(1)	107.6(6)
S4–Ni2–N3	84.8(2)	84.8(3)	85(1)
S4–Ni2–N4	89.7(3)	87.6(3)	87(1)

a) Ref. 31.

it is desirable to examine the room-temperature structure of **1** and the low-temperature structure of **1**·H_2O. However, we presently believe that water molecules can be neglected in discussing the spectral and magnetic properties of **1**·H_2O, since the crystal structure at 292 K shows that the water molecules are not coordinated to the metal ions, but are included as lattice water. A structural comparison can be made concerning the bond lengths and angles given in Table 2. It is noted that both of the thioether pendant arms are apart from the coordination spheres at 118 K, the Ni1–S2 and Ni2–S4 distances being 2.764(3) and 2.789(3) Å, respectively. Moreover, the Ni–S(thiolate) distances (Ni1–S1 2.186(3), Ni1–S3 2.206(3), Ni2–S1 2.198(3), Ni2–S3 2.193(2) Å) are typical of those found in low-spin thiolate-bridged dinuclear nickel(II) complexes (2.158(2)—2.225(2) Å).[2—11] These facts suggest that the electronic states of the two nickel(II) ions have a low-spin character at low temperature. The magnetic moment is 0.52 B.M./Ni at 118 K, indicating that the magnetic property is almost diamagnetic. At 292 K, the Ni1–S2 distance becomes shorter (2.563(4) Å), although the Ni2–S4 distance does not change much. The shortening of the axial coordination seems to cause some degree of paramagnetic character for the nickel(II) ion at room temperature (1.48 B.M./Ni at 291 K). In addition to these results, the X-ray absorption near-edge structure (XANES) of **1**·H_2O has also been examined, since the XANES features are useful indicators of the geometry of nickel complexes.[1] Figure 5 compares the edge features of **1** with the temperature variation. The XANES pattern at 300 K gradually changes to that at 50 K upon lowering the temperature (300, 230, 170, 100, and 50 K), though the differences are very small. In the case of Ni(II) complexes, two features have been assigned to specific electronic transitions.[1] A small shoulder near to 8332 eV and a discernable shoulder at 8338 eV may be assigned to a 1s→3d transition and a 1s→$4p_z$ transition, respectively. Since these absorptions are both observed in tetragonal complexes lacking one or more axial ligands, it is not easy to distinguish between four-coordinate planar and five-coordinate pyramidal geometries from the XANES data.[43]

The magnetic moment of **2** is 2.11 B.M./Ni at 296 K. This value is also lower than the spin-only value, 2.83 B.M. However, the magnetic moments are almost constant over the 80—300 K temperature range (say 2.08 B.M./Ni at 82 K). As can be seen in Fig. 6, the magnetic data obey the Curie–Weiss low, $\chi_A = C/(T-\theta)$, with a small Weiss constant ($\theta = -6$ K for **2**). This means that the antiferromagnetic interaction is weak. Since the magnetic moments per dinuclear units are calculated to give 2.99 B.M. at room temperature, which is quite common for a high-spin nickel(II) ion,[44] it is concluded that complex **2** is a mixed-spin complex having one high-spin (S=1) and one low-spin (S=0) nickel(II) ion within the molecule; the observed weak magnetic interaction may be ascribed to the intermolecular inter-

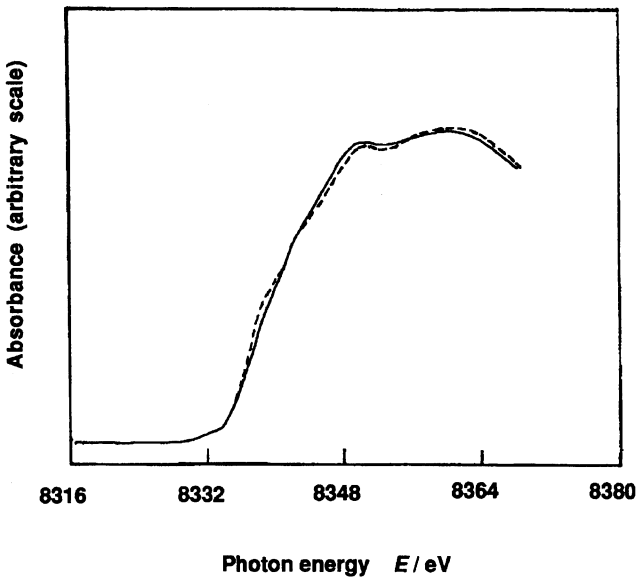


Fig. 5. XANES spectra of **1**·H_2O at 300 (—) and 50 (---) K.

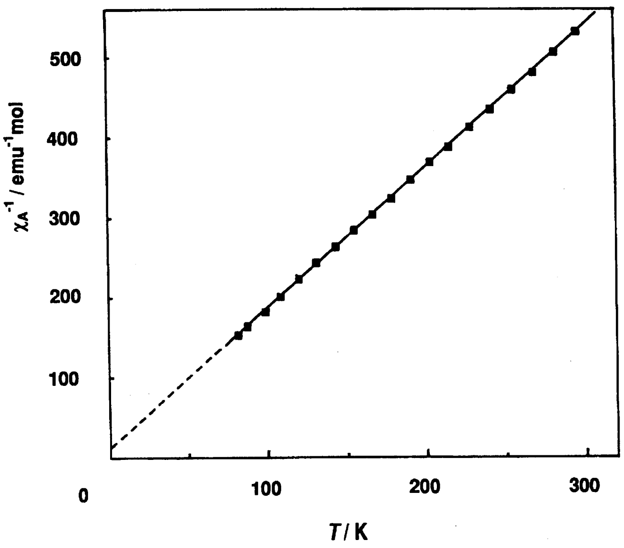


Fig. 6. Temperature dependence of the reciprocal-magnetic susceptibility of **2**.

action. So far, the mixed-spin state has been found in only a few dinuclear nickel(II) systems.[45—48] We have recently found that pyridyl pendant arms give rise to a mixed-spin state in thiolate-bridged dinuclear nickel(II) complexes.[29,30] The X-ray structure of the thiolate-bridged nickel(II) complex with *N*,*N*-bis[2-(2-pyridyl)ethyl]-2-aminoethanethiol shows that one of the two nickel ions is coordinated by a square-planar N_2S_2 donor set, and that the other has a distorted square-pyramidal N_3S_2 donor set with a pendant pyridyl nitrogen at the apex.

In order to elucidate the structure of the novel mixed-spin state, the crystal structure of **2** was determined by X-ray crystallography. The crystal consists of discrete dinuclear complex cations, $[\mathrm{Ni_2(L_b)_2}]^{2+}$ and uncoordinated perchlorate ions. A perspective view of $[\mathrm{Ni_2(L_b)_2}]^{2+}$ is shown in Fig. 7. Selected bond distances and angles are listed in Table 2. These values should be considered with some care because of the low accuracy of this structure determination. The two nickel ions are bridged by two thiolate sulfur atoms. Both of the nickel ions (Ni1 and Ni2) adopt a similar elongated square pyramidal geometry with an amino nitrogen, a pyridyl nitrogen, and two bridging sulfur atoms in the basal plane and a pendant thioether sulfur atom in the apical position. However, the coordination modes of the pendant thioether arms are different: One pendant thioether sulfur atom (S2) approaches the nickel ion, Ni1 (Ni1–S2 2.42(2) Å), whereas the other thioether sulfur atom (S4) is apart from the nickel ion, Ni2 (Ni2–S4 2.66(2) Å). The Ni1–S2 distance is shorter than any other axial Ni–S(thioether) distances found in the present complexes. The Ni1–S(thiolate) distances (Ni1–S1 2.30(2), Ni1–S3 2.35(2) Å) are significantly longer than the corresponding bond distances of the Ni2 ion (Ni2–S1 2.28(2), Ni2–S3 2.21(2) Å) which can be considered as being low-spin Ni–S(thiolate) bonds.[2—11] These elongations may be caused by an axial coordination of the pendant thioether sulfur (S2). Therefore, the Ni1 and Ni2 ions can be assigned to high-spin (paramagnetic) Ni(II) and low-spin (diamagnetic) Ni(II) ions, respectively. This structure is consistent with the electronic spectrum and magnetic property of **2**. This is another novel example of a structurally characterized thiolate-bridged dinuclear nickel(II) complex with a mixed-spin state.

The authors acknowledge Professor Yukio Noda of Chiba University for his kind discussion and his help in performing the XANES experiments. The present work was partially supported by a Grant-in-Aid for Scientific

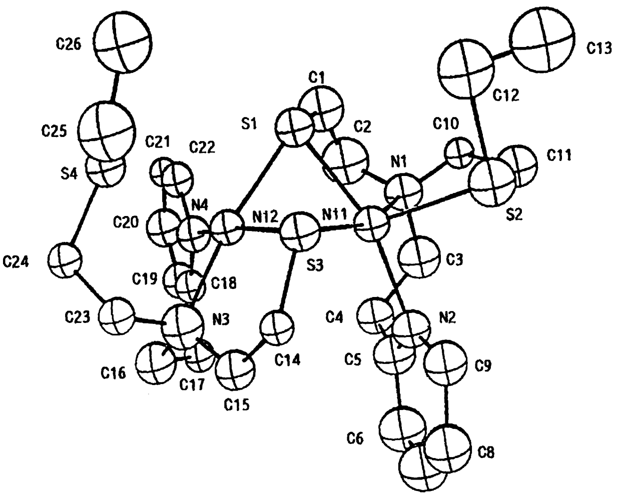


Fig. 7. Perspective view of the $[\mathrm{Ni_2(L_b)_2}]^{2+}$ in **2** (at 293 K).

Research No. 02640489 from the Ministry of Education, Science and Culture.

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