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Thiolate-Bridged Binuclear Nickel(II) Complexes with a Mixed-Spin State

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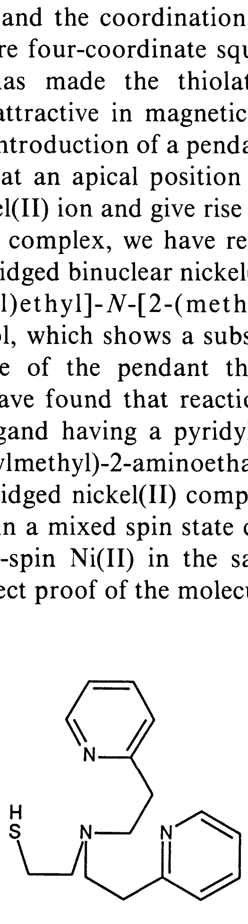
Thiolate-bridged binuclear nickel(II) complexes with *N,N*-bis[2-(2-pyridyl)ethyl]-2-aminoethanethiol (HL), $[Ni_2(L)_2](ClO_4)_2 \cdot 1/2H_2O$ and $[Ni_2(L)_2](PF_6)_2$, have been synthesized and characterized by elemental analyses, infrared and electronic spectra, and magnetic susceptibilities (80—300 K). The crystal structure of the perchlorate has been determined by the single-crystal X-ray diffraction method. The $[Ni_2(L)_2]^{2+}$ cation has a novel binuclear structure where one of the nickel ions is coordinated by a square-planar N_2S_2 donor set and the other has a distorted square-pyramidal configuration (N_3S_2 donor set) with the pendant pyridyl nitrogen at the apex. From the above results, it was concluded that the present complexes are novel mixed-spin state containing a low-spin Ni(II) and a high-spin Ni(II) in the molecule.

Nickel complexes with thiolic ligands have attracted much attention in the last decade because the biological significance of nickel–sulfur complexes has been recognized.[1)] So far, a variety of thiolate-bridged nickel(II) complexes containing two,[2–11)] three,[9,12–21)] four,[17,22,23)] six,[19,24–27)] and eight[28)] nickel atoms have been isolated from reactions of many thiolic ligands with nickel ions. Interestingly, all these complexes are essentially diamagnetic (low-spin) and the coordination environments of nickel(II) ions are four-coordinate square-plane. This diamagnetism has made the thiolate-bridged nickel complexes less attractive in magnetic properties. We may expect 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 paramagnetism. As such a complex, we have recently reported a novel thiolate-bridged binuclear nickel(II) complex with *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(methylthio)ethyl]-2-aminoethanethiol, which shows a substantial paramagnetism by virtue of the pendant thioether donor.[29)] Moreover, we have found that reaction of nickel salts with a thiolic ligand having a pyridyl pendant group, *N,N*-bis(2-pyridylmethyl)-2-aminoethanethiol, gives a novel thiolate-bridged nickel(II) complex which can be presumed to be in a mixed spin state containing a low-spin and a high-spin Ni(II) in the same molecules.[30)] However, no direct proof of the molecular structure has been given yet, because of difficulty in growing the crystals suitable for single-crystal X-ray diffraction studies. Therefore, in this study, we have aimed at establishing the basic structure of this type of thiolate-bridged nickel(II) complexes and prepared *N,N*-bis[2-(2-pyridyl)ethyl]-2-aminoethanethiol (HL) in the hope of obtaining good crystals of the analogous complexes. Here we report the synthesis and X-ray crystal structure, and spectral and magnetic properties of thiolate-bridged binuclear nickel(II) complexes with the ligand, HL.



HL

Experimental

Ligand Synthesis. Ethylene sulfide was obtained from Aldrich Chemical Co., Inc. and was purified by distillation. Bis[2-(2-pyridyl)ethyl]amine was prepared according to the previously reported procedure.[31)] *N,N*-Bis[2-(2-pyridyl)-ethyl]-2-aminoethanethiol, HL, was prepared by the application of the method of Marabella et al.[32)] Bis[2-(2-pyridyl)-ethyl]amine, ethylene sulfide, and toluene were heated in a sealed tube at 110 °C for 30 h. Purification of HL was effected by washing four times with water, filtration, removing the solvent, and finally pumping for 1 h (80 °C).

Preparation of Complexes. All operations were performed under N_2.

$[Ni_2(L)_2](ClO_4)_2 \cdot 1/2H_2O$ (1). To a solution of nickel(II) perchlorate hexahydrate (366 mg, 1 mmol) in methanol (10 ml) was added a methanol solution (5 ml) of the ligand, HL (287 mg, 1 mmol), and the mixture was stirred for a while to give a black precipitate. It was collected by filtration and recrystallized from methanol as black needles. Found: C, 42.03; H, 4.68; N, 9.16%. Calcd for $C_{32}H_{41}Cl_2N_6Ni_2O_{8.5}S_2$: C, 42.79; H, 4.60; N, 9.36%.

$[Ni_2(L)_2](PF_6)_2$ (2). To a methanol solution (5 ml) of nickel(II) acetate tetrahydrate (249 mg, 1 mmol) was added a solution of HL (287 mg, 1 mmol) in methanol (5 ml) to form a black solution. A methanol solution (36 ml) of ammonium hexafluorophosphate (360 mg, 2.2 mmol) was added to give a black precipitate, which was collected by filtration, washed with methanol, and dried in vacuo over P_2O_5. Found: C, 39.35; H, 4.38; N, 8.24%. Calcd for $C_{32}H_{40}F_{12}N_6Ni_2P_2S_2$: C, 39.21; H, 4.11; N, 8.57%.

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 IR 700 in the region 4000—400 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR recording spectrophotometer Model UV-3100. NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. Magnetic susceptibilities were measured by the Faraday method over the temperature range 80—300 K. The apparatus was calibrated by the use of [Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_3$]S$_2$O$_3$.[33] The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[34] Effective magnetic moments were calculated from the equation, $\mu_{\mathrm{eff}}=2.828\sqrt{\chi_{\mathrm{A}}T}$, where χ_{A} is the atomic magnetic susceptibility.

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

Atom	x	y	z	$B_{\mathrm{eq}}/\mathrm{Å}^{2}$[a]
Ni1	0.21854(6)	0.02845(8)	0.11525(4)	4.29(2)
Ni2	0.24561(6)	−0.07302(8)	0.20623(4)	4.85(3)
Cl1	−0.0002(1)	0.6897(2)	0.4083(1)	6.84(7)
Cl2	0.3607(2)	0.4363(2)	0.6132(1)	7.66(8)
S1	0.1750(1)	0.0445(2)	0.19156(9)	5.18(6)
S2	0.3221(1)	0.0126(2)	0.17600(9)	5.38(6)
OW	0.500	0.337(3)	0.750	20(2)[b]
O1	0.0325(6)	0.7708(7)	0.4063(5)	16.0(4)
O2	0.0327(7)	0.6332(8)	0.3786(4)	16.0(4)
O3	0.0098(7)	0.653(1)	0.4527(4)	17.5(5)
O4	−0.0692(5)	0.699(1)	0.3931(5)	17.3(5)
O5	0.3615(7)	0.3550(7)	0.5904(5)	16.3(4)
O6	0.2933(5)	0.4538(9)	0.6253(4)	13.2(4)
O7	0.4105(5)	0.4348(8)	0.6555(3)	11.9(3)
O8	0.3759(6)	0.5011(7)	0.5802(4)	13.4(3)
N1	0.1134(4)	−0.0065(5)	0.0838(3)	4.6(2)
N2	0.2664(4)	−0.0242(5)	0.0590(3)	4.6(2)
N3	0.2199(4)	0.1563(5)	0.0898(3)	4.6(2)
N4	0.3194(4)	−0.1696(5)	0.2116(3)	5.8(2)
N5	0.1777(4)	−0.1430(6)	0.2370(3)	5.8(2)
N6	0.4386(5)	−0.2217(7)	0.3565(4)	9.5(3)
C1	0.0828(5)	0.0086(7)	0.1713(4)	6.2(3)
C2	0.0767(5)	−0.0463(6)	0.1247(4)	5.4(2)
C3	0.1092(5)	−0.0733(6)	0.0434(4)	5.7(2)
C4	0.1724(5)	−0.1382(6)	0.0479(4)	5.9(3)
C5	0.2401(5)	−0.0957(6)	0.0330(3)	4.8(2)
C6	0.2727(6)	−0.1274(7)	−0.0067(4)	6.5(3)
C7	0.3331(6)	−0.0869(8)	−0.0189(4)	7.2(3)
C8	0.3599(5)	−0.0150(7)	0.0080(4)	6.2(3)
C9	0.3260(5)	0.0148(6)	0.0467(3)	5.4(2)
C10	0.0738(5)	0.0752(6)	0.0659(4)	5.2(2)
C11	0.1127(5)	0.1290(7)	0.0298(4)	5.8(3)
C12	0.1720(5)	0.1896(6)	0.0533(3)	4.6(2)
C13	0.1767(5)	0.2774(6)	0.0373(4)	5.5(2)
C14	0.2318(6)	0.3308(7)	0.0583(4)	6.2(3)
C15	0.2808(5)	0.2975(6)	0.0949(4)	5.7(3)
C16	0.2732(5)	0.2099(6)	0.1094(4)	5.3(2)
C17	0.3883(6)	−0.0689(8)	0.1620(4)	7.2(3)
C18	0.3582(6)	−0.1615(8)	0.1674(4)	7.8(3)
C19	0.2912(7)	−0.2623(7)	0.2103(5)	7.8(3)
C20	0.2124(6)	−0.2681(7)	0.1889(4)	7.4(3)
C21	0.1662(6)	−0.2302(7)	0.2230(4)	6.8(3)
C22	0.1176(7)	−0.2811(9)	0.2456(4)	8.7(3)
C23	0.0831(7)	−0.246(1)	0.2818(5)	10.1(4)
C24	0.0946(6)	−0.158(1)	0.2956(4)	8.3(3)
C25	0.1425(5)	−0.1073(8)	0.2726(4)	7.2(3)
C26	0.3735(7)	−0.1586(9)	0.2575(4)	8.3(3)
C27	0.3379(7)	−0.148(1)	0.3037(4)	10.8(5)
C28	0.3984(6)	−0.1463(9)	0.3479(4)	8.2(3)
C29	0.4108(7)	−0.0715(9)	0.3766(5)	9.0(4)
C30	0.4639(7)	−0.074(1)	0.4156(5)	11.2(4)
C31	0.5040(7)	−0.153(1)	0.4268(5)	11.4(4)
C32	0.4910(6)	−0.2237(9)	0.3961(5)	9.9(4)

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) Atom refined with occupancy factor of 0.25.

X-Ray Crystal Structure Analysis. Single crystals of **1** grew from methanol. A black crystal with dimensions of 0.17×0.22×0.52 mm^3 was used for the X-ray structure analysis. The unit-cell paramaters and intensities were measured on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: C$_{32}$H$_{41}$Cl$_2$N$_6$Ni$_2$O$_{8.5}$S$_2$, F.W.=898.1, monoclinic, $C2/c$ (No.15); a=18.738(7), b=14.942(3), c=27.316(9) Å, β=97.31(2)°, V=7585.8(41) Å^3, D_{m}=1.58, D_{c}=1.57 g cm^{-3}, Z=8, μ(Mo-$K\alpha$)=13.0 cm^{-1}.

Of the 10105 reflections ($1<2\theta<44°$) measured, the unique 3045 reflections with $I>3\sigma(I)$ were considered as observed. The structure was solved by the direct methods and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms (except for those bound to the water oxygen atom) were inserted at their calculated positions and fixed at their positions. The weighting scheme $w=1/[\sigma^2(|F_{\mathrm{o}}|)+(0.02|F_{\mathrm{o}}|)^2+1.0]$ was employed. The final discrepancy factors are $R=\sum||F_{\mathrm{o}}|-|F_{\mathrm{c}}||/\sum|F_{\mathrm{o}}|=0.056$ and $R_{\mathrm{w}}=[\sum w(|F_{\mathrm{o}}|-|F_{\mathrm{c}}|)^2/\sum w|F_{\mathrm{o}}|^2]^{1/2}=0.062$.

All the calculations were carried out on the Micro VAXII computer using an SDP program package.[35] Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms, and the $F_{\mathrm{o}}-F_{\mathrm{c}}$ tables have been deposited as a Document No. 8979 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The infrared spectra of the complexes **1** and **2** show the ν(Cl–O) and ν(P–F) bands at 1090 and 840 cm^{-1}, respectively. Little splitting of these bands suggest no coordination of the perchlorate ion nor hexafluorophosphate ion to the metal ion,[36] which was confirmed by the X-ray structure analysis of **1**.

Diffused reflectance spectra of **1** and **2** are shown in Fig. 1, together with that of the corresponding thiolate-bridged nickel(II) complex without the pendant group, 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 **3** shows two absorption bands at 521 and 700 nm which can be assigned to d–d transitions (^{1}A$_{1g}$→^{1}A$_{2g,}$ ^{1}B$_{2g}$) characteristic of low-spin nickel(II) complexes.[37] On the other hand, the spectra of the present complexes are characterized by four absorptions

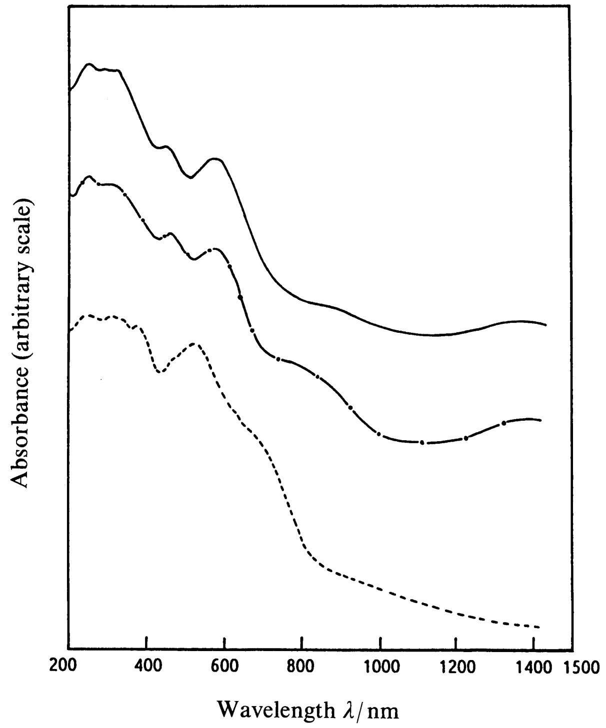


Fig. 1. Diffused reflectance spectra of $Ni_2(L)_2(ClO_4)_2 \cdot 1/2H_2O$ (——), $Ni_2(L)_2(PF_6)_2$ (—·—), and $Ni_2(L')_2(ClO_4)_2$ (----).

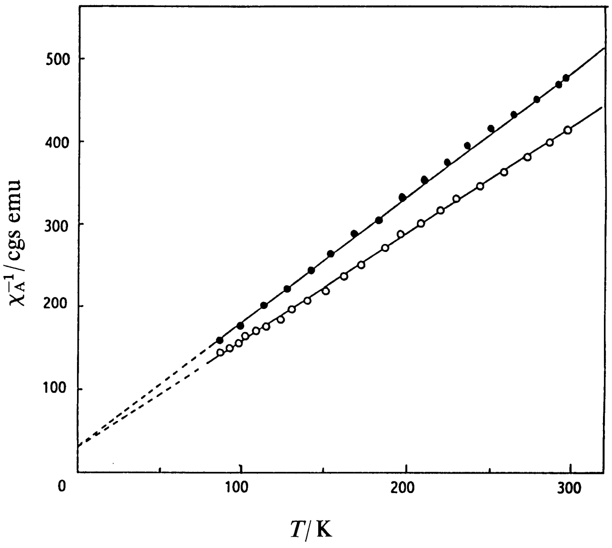


Fig. 2. Temperature dependence of the magnetic susceptibilities of $Ni_2(L)_2(ClO_4)_2 \cdot 1/2H_2O$ (●) and $Ni_2(L)_2(PF_6)_2$ (○).

(**1**: 450, 576, 844sh, 1376 nm; **2**: 459, 573, 800sh, 1388 nm), which can be associated with d–d transitions, and intense absorptions in the range 250—400 nm, which are charge transfer transitions in origin. The complicated spectra suggest the presence of a high-spin nickel(II) ion in the complexes **1** and **2**.

The magnetic moments of **1** and **2** are 2.23 and 2.39 B.M./Ni, respectively, at room temperature. These values are much lower than the spin-only value 2.83 B.M., although the values indicate the presence of a paramagnetic nickel ion. In order to obtain further information, the magnetic susceptibilities were measured over the temperature range 80—300 K, and the results are shown in Fig. 2. The magnetic moments slightly decrease to 2.11 and 2.18 B.M./Ni for **1** and **2**, respectively, at liquid nitrogen temperature. The magnetic data obey the Curie–Weiss low, $\chi_A = C/(T-\theta)$, with small Weiss constants ($\theta = -18$ and -22 K for **1** and **2**, respectively). This indicates that the antiferromagnetic interaction is not so strong as the antiferromagnetic spin-pairing explains the low magnetic moments. Since the magnetic moments per binuclear units are calculated to give 3.15 and 3.38 B.M. at room temperature for **1** and **2**, respectively, which are quite common to a high-spin nickel(II) ion,[38] it is concluded that the complexes **1** and **2** are novel mixed-spin complexes composed of one high-spin (S=1) and one low-spin (S=0) nickel(II) ions and the observed small magnetic interaction may be ascribed to the intermolecular interaction. So far, only a few mixed-spin nickel(II) complexes have been isolated.[30,39—42] Especially, to our knowledge, only two X-ray structures of mixed-spin nickel(II) complexes have been known hitherto.[41,42]

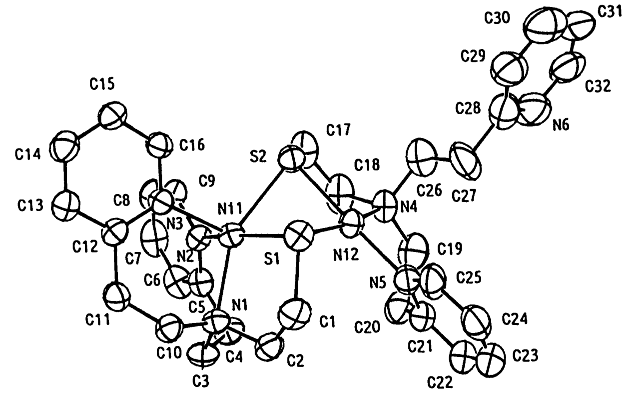


Fig. 3. A perspective view of the $[Ni_2(L)_2]^{2+}$ cation.

In order to elucidate the structure of the novel mixed-spin state, the crystal structure of **1** was determined by X-ray crystallography. The crystal consists of discrete binuclear complex cations, $[Ni_2(L)_2]^{2+}$, uncoordinated perchlorate ions, and crystal water molecules. The water molecules are in the vicinity of the perchlorate ions by hydrogen bonds ($OW\cdots O7(ClO_4^-)$ 3.240(19) Å). A perspective view of $[Ni_2(L)_2]^{2+}$ is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. The two nickel ions are bridged by two thiolate sulfur atoms. The Ni1–Ni2 distance is 2.900(2) Å and the Ni1–S–Ni2 angles are 78.8(1) and 79.2(1)°. It is noteworthy that the coordination environments of the two nickel ions are different. One of the nickel ions, Ni1, adopts a square pyramidal geometry with an amino nitrogen (N1), a pyridyl nitrogen (N2), and two bridging sulfur atoms (S1 and S2) in the basal plane and a

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

Ni1–S1	2.345(3)	Ni2–S1	2.204(3)
Ni1–S2	2.399(3)	Ni2–S2	2.162(3)
Ni1–N1	2.112(6)	Ni2–N4	1.991(8)
Ni1–N2	2.034(7)	Ni2–N5	1.922(8)
Ni1–N3	2.034(7)		
Ni1–S1–Ni2	79.15(9)	Ni1–S2–Ni2	78.80(9)
S1–Ni1–S2	74.77(9)	S1–Ni2–S2	82.6(1)
S1–Ni1–N1	88.6(2)	S1–Ni2–N5	95.6(2)
S1–Ni1–N2	161.4(2)	S1–Ni2–N4	170.3(3)
N1–Ni1–N2	94.3(3)	S2–Ni2–N4	88.2(2)
N1–Ni1–S2	152.6(2)	S2–Ni2–N5	175.8(3)
N2–Ni1–S2	95.1(2)	N4–Ni2–N5	93.8(3)
N3–Ni1–S1	103.2(2)		
N3–Ni1–S2	106.6(2)		
N3–Ni1–N1	98.3(3)		
N3–Ni1–N2	94.5(3)		

pendant pyridyl nitrogen (N3) in the apical position, while the other nickel ion, Ni 2, takes a square planar arrangement allowing the other pyridyl pendant group to be apart from the coordination sphere. The Ni2–S (2.204(3), 2.162(3) Å), Ni2–N4 (amino) (1.991(8) Å) and Ni2–N5 (pyridyl) (1.922(8) Å) distances are typical of those found in low-spin thiolate-bridged binuclear nickel(II) complexes without the pendant groups.[2–11] On the other hand, all the in-plane bond lengths of the Ni1 ion (Ni1–S1 2.345(3), Ni1–S2 2.399(3), Ni1–N1 2.112(6), Ni1–N 2 2.034(7) Å) are significantly longer than the corresponding bond distances of the Ni 2 ion. These elongation may be caused by the strong axial coordination of the pendant pyridyl nitrogen N3 (Ni1–N3 2.034(7) Å). The axial coordination effect can be also observed in the lifting of the nickel ion (0.40 Å) from the basal N_2S_2 plane toward the axial pyridyl nitrogen. Therefore the Ni 1 and Ni 2 ions can be assigned to a high-spin (paramagnetic) Ni(II) and a low-spin (diamagnetic) Ni(II) ions, respectively. This is the first example of structurally characterized thiolate-bridged binuclear nickel(II) complex with a novel mixed-spin state. Is the mixed-spin state realized incidentally by a packing effect in the crystals? In order to examine this effect we measured ^{1}H NMR and electronic absorption spectra of **1** and **2** in acetonitrile. The NMR spectra do not reveal any significant peaks probably due to the presence of the high-spin paramagnetic nickel(II) ions. The electronic spectra in acetonitrile (**1**: 445 (ε=514 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$), 584 (229), 841sh(17), 1406(14) nm; **2**: 447 (ε=702 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$), 588(358), 792sh(62), 1392(21) nm) are essentially the same as the spectra in the solid state. These results show that the mixed-spin state is maintained in the solution and the packing effect is not responsible for the different coordinating behavior of the pendant groups.

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References

1) J. R. Lancaster, Jr., "The Bioinorganic Chemistry of Nickel," VCH, New York (1988).

2) G. A. Barclay, E. M McPartlin, and N. C. Stephenson, *Inorg. Nucl. Chem. Lett.*, **3**, 397 (1967); *Acta Crystallogr., Sect. B*, **25**, 1262 (1969).

3) D. J. Baker, D. C. Goodall, and D. S. Moss, *J. Chem. Soc., Chem. Commun.*, **1969**, 325.

4) A. C. Villa, A. G. Manfredotti, M. Nardelli, and C. Pelizzi, *J. Chem. Soc., Chem. Commun.*, **1970**, 1322.

5) T. B. Vance, L. G. Warner, and K. Seff, *Inorg. Chem.*, **16**, 2106 (1977).

6) A. D. Watson, C. P. Rao, J. R. Dorfman, and R. H. Holm, *Inorg. Chem.*, **24**, 2820 (1985).

7) B. S. Snyder, C. P. Rao, and R. H. Holm, *Aust. J. Chem.*, **39**, 963 (1986).

8) M. Mikuriya, S. Kida, and I. Murase, *Bull. Chem. Soc. Jpn.*, **60**, 1180 (1987).

9) J. R. Nicholson, G. Christou, J. C. Huffman, and K. Folting, *Polyhedron*, **6**, 863 (1987).

10) M. Handa, M. Mikuriya, Z. J. Zhong, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **61**, 3883 (1988).

11) G. J. Colpas, M. Kumar, R. O. Day, and M. J. Maroney, *Inorg. Chem.*, **29**, 4779 (1990).

12) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

13) M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, **1975**, 2594.

14) W. Tremel, B. Krebs, and G. Henkel, *Inorg. Chim. Acta*, **80**, L31 (1983).

15) H. Barrera, J. Suades, M. C. Perucaud, J. L. Brainso, *Polyhedron*, **3**, 839 (1984).

16) W. Tremel, B. Krebs, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, **23**, 634 (1984).

17) W. Tremel, B. Krebs, and G. Henkel, *J. Chem. Soc., Chem. Commun.*, **1986**, 1527.

18) S. G. Rosenfield, M. L. Y. Wong, D. W. Stephan, and P. K. Mascharak, *Inorg. Chem.*, **26**, 4119 (1987).

19) W. Tremel, M. Kriege, B. Krebs, and G. Henkel, *Inorg. Chem.*, **27**, 3886 (1988).

20) N. Baidya, M. M. Olmstead, and P. K. Mascharak, *Inorg. Chem.*, **28**, 3426 (1989).

21) M. A. Turner, W. L. Driessen, and J. Reedijk, *Inorg. Chem.*, **29**, 3331 (1990).

22) W. Gaete, J. Ros, X. Solans, M. Font-Altaba, and J. H. Brianso, *Inorg. Chem.*, **23**, 39 (1984).

23) W. Tremel and G. Henkel, *Inorg. Chem.*, **27**, 3896 (1988).

24) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Am. Chem. Soc.*, **87**, 5251 (1965).

25) R. O. Gould and M. M. Harding, *J. Chem. Soc. A*, **1970**, 875.

26) M. Capdevila, P. G.-Duarte, J. Sola, C. F.-Foces, F. H. Cano, and M. M.-Ripoll, *Polyhedron*, **8**, 1253 (1989).

27) T. Yamamura, *Bull. Chem. Soc. Jpn.*, **61**, 1975 (1988); H. Miyamae and T. Yamamura, *Acta Crystallogr., Sect. C*, **44**, 606 (1988).

28) I. G. Dance, M. L. Scudder, and R. Secomb, *Inorg. Chem.*, **24**, 1201 (1985).

29) M. Handa, M. Mikuriya, H. Ōkawa, and S. Kida, *Chem. Lett.*, **1988**, 1555.

30) M. Handa, M. Mikuriya, and H. Ōkawa, *Chem. Lett.*, **1989**, 1663.

31) J. K. Romary, R. D. Zachariasen, J. D. Barger, and H. Schiesser, *J. Chem. Soc. C,* **1968**, 2884.

32) C. P. Marabella, J. H. Enemark, K. F. Miller, A. E. Bruce, N. Pariyadath, J. L. Corbin, and E. I. Stiefel, *Inorg. Chem.,* **22**, 3456 (1983).

33) N. F. Curtis, *J. Chem. Soc.,* **1961**, 3147.

34) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp. 78, 91.

35) B. A. Frenz, "The SDP-User's Guide," Enraf-Nonius: Delft, The Netherlands (1985).

36) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Wiley, New York (1978), pp. 242—243.

37) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam (1968), p. 343.

38) F. A. Cotton, "Advanced Inorganic Chemistry," 5th ed, Wiley, New York (1988), pp. 744—746.

39) H. Ōkawa, T. Tokii, Y. Muto, and S. Kida, *Bull Chem. Soc. Jpn.,* **46**, 2464 (1973).

40) M. Tanaka, M. Kitaoka, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.,* **49**, 2469 (1976).

41) M. D. Glick, R. L. Lintvedt, T. J. Anderson, and J. L. Mack, *Inorg. Chem.,* **15**, 2258 (1976).

42) M. Mikuriya, S. Kida, and I. Murase, *J. Chem. Soc., Dalton Trans.,* **1987**, 1261.