Synthesis and Characterization of Dinuclear and Tetranuclear Mixed-Spin Nickel(II) Complexes with 2,6-Bis(salicylideneaminomethyl)-4-methylphenol

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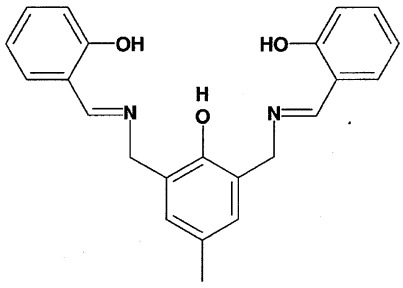
Dinuclear and tetranuclear nickel(II) complexes with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), $[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**) and $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**) (Hpz = pyrazole), have been synthesized and characterized by infrared and electronic spectra, and by temperature dependence of magnetic susceptibilities (80—300 K). The molecular structures of **1** and **2** were determined by single-crystal X-ray structure analysis. Complex **1** is a mixed-spin state complex in which one metal center is square planar and the other octahedral. Complex **2** has a zigzag tetranuclear structure, in which two dinuclear units with mixed spin-states are associated by two phenoxo-bridges and one methanol bridge.

Relatively few studies have been made of dinuclear nickel(II) complexes, although a vast number of dinuclear copper(II) complexes have been reported. One particular aspect of the chemistry of nickel(II) compounds that has received considerable attention is the stereochemical changes involving low-spin four-coordinated species and high-spin five- or six-coordinated species.[1] So far many low-spin or high-spin dinuclear nickel(II) complexes have appeared.[2] Most of them are symmetrical molecules and the coordination environments of the two nickel atoms are identical. In a dinuclear system, we may expect possible formation of unsymmetrical species with mixed-spin states which contain low-spin and high-spin states within the molecule. However, such examples are still rare.[3—12] As part of a continuing project on dinuclear nickel(II) complexes,[6—9,13—19] we recently reported on the structural characterization of dinuclear nickel(II) complexes with pentadentate Schiff-base ligands: 1,3-bis(salicylideneamino)-2-propanol (H_3L_a), 1,4-bis(salicylideneamino)-2-butanol (H_3L_b), and 1,5-bis(salicylideneamino)-3-pentanol (H_3L_c).[19] These dinucleating ligands afford low-spin dinuclear complexes with an alkoxo-bridge and a pyrazolate-bridge, $[Ni_2(L')(pz)]$, ($H_3L' = H_3L_a$, H_3L_b, and H_3L_c; Hpz = pyrazole).[19,20] Concerning these complexes, we have also tried to isolate μ-phenoxo-bridged nickel(II) complexes with a related pentadentate Schiff-base ligand, 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), which is expected to hold two nickel atoms in close proximity (Scheme 1). This dinucleating ligand has a phenoxo-oxygen atom as a bridging group in addition to two terminal phenoxo-oxygen atoms. Therefore we can observe the effect of the bridging donor atom on the structure of the isolated complex. In this study we have successfully isolated a dinuclear nickel(II) complex by using this pentadentate ligand; this is not a low-spin complex, but an interesting mixed-spin state complex. Moreover we have also isolated a novel tetranuclear nickel(II) complex with mixed-spin state in a slightly different reaction condition. Here, we present complete details concerning the synthesis and characterization of these complexes. Preliminary results were reported elsewhere.[9]



H_3L

Scheme 1.

Experimental

Synthesis of the Complexes. 2,6-Bis(salicylideneaminomethyl)-4-methylphenol was synthesized according to a method reported by Mazurek et al.[21]

$[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (1): To a methanol solution (6 ml) of 2,6-bis(salicylideneaminomethyl)-4-methylphenol (36 mg, 0.10 mmol), nickel(II) perchlorate hexahydrate (108 mg, 0.30 mmol), pyrazole (42 mg, 0.61 mmol), and triethylamine (50 mg, 0.50 mmol) were successively added with stirring. The resulting solution was filtered and the filtrate was left to stand for several days. Red crystals were deposited; they were collected by filtration, washed with methanol, and dried in vacuo over P_2O_5 (yield 32 mg, 46%). Anal. Calcd for $C_{31}H_{34}N_6Ni_2O_5$: C, 54.11; H, 4.98; N, 12.21%. Found: C, 53.97; H, 4.81; N, 12.14%. IR (KBr) ν/cm^{-1} ν(OH) 3372; ν(C=N) 1613; ν(Hpz, pz) 1536, 1452, 1390, 1044, 1036.[22]

$[Ni_4(L)_2(pz)_2(CH_3OH)]$ (2): After 2,6-bis(salicylideneaminomethyl)-4-methylphenol (36 mg, 0.10 mmol) had been dissolved in 6.0 ml of methanol, nickel(II) perchlorate hexahydrate (108 mg, 0.30 mmol), pyrazole (21 mg, 0.31 mmol), and triethylamine (50 mg, 0.50 mmol) were added. The solution was filtered and the filtrate was left to stand for several days. Black crystals were deposited; they were collected by filtration, washed with methanol, and dried in vacuo over P_2O_5 (yield 29 mg, 26%). Anal. Calcd for $C_{53}H_{48}N_8Ni_4O_7$: C, 55.65; H, 4.23; N, 9.80%. Found: C, 55.51; H, 4.30; N, 9.74%. IR (KBr) ν/cm^{-1} ν(C=N) 1616; ν(pz) 1535, 1449, 1394, 1043.[22]

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the 4000—400 cm^{-1} region on a KBr disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. The magnetic susceptibilities were measured by the Faraday method over the 80—300 K temperature range. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[23] The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analyses. The unit-cell parameters and intensities were measured on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \leq 2\theta \leq 30°$. The intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data. **$[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (1):** $C_{31}H_{34}N_6Ni_2O_5$, F.W. = 688.07, monoclinic, $P2_1/n$, a = 13.673(4), b = 12.898(2), c = 18.489(5) Å, β = 170.03(1)°, V = 3117.8(13) Å^3, D_m = 1.48, D_c = 1.47 g cm^{-3}, Z = 4, μ(Mo $K\alpha$) = 12.60 cm^{-1}. Specimen: red crystal, 0.41×0.21×0.09 mm. A total of 5312 reflections were measured in the range $1 \leq 2\theta \leq 48°$; 2192 with $I > 3\sigma(I)$ were assumed as observed. R = 0.052, R_W = 0.059.

$[Ni_4(L)_2(pz)_2(CH_3OH)]$ (2): $C_{53}H_{48}N_8Ni_4O_7$, F.W. = 1143.86, triclinic, $P\bar{1}$, a = 13.017(3), b = 13.018(4), c = 17.782(5) Å, α = 96.00(2), β = 107.26(2), γ = 116.82(2)°, V = 2465.5(14) Å^3, D_m = 1.52, D_c = 1.54 g cm^{-3}, Z = 2, μ(Mo $K\alpha$) = 15.72 cm^{-1}. black crystal, 0.24×0.22×0.20 mm. A total of 6855 reflections were measured in the range $1 \leq 2\theta \leq 46°$; 3576 with $I > 3\sigma(I)$ were assumed as observed. R = 0.087, R_W = 0.091.

The structures were solved by the direct methods and refined by the full-matrix least-squares method. All the non-hydrogen atoms of **1** and the Ni, O, and N atoms of **2** were refined with anisotropic thermal parameters. For **1**, the hydrogen atoms of the dinucleating ligand, pyrazolate ion, and pyrazole were inserted at their calculated positions and fixed at these positions. For **2**, the hydrogen atoms were not included in the calculations. The weighting scheme: $w = 1/[\sigma^2(|F_o|) + (0.02|F_o|)^2 + 1.0]$ was employed.

All of the calculations were carried out on a Micro-VAXII computer using an Enraf–Nonius SDP program package.[24] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the $F_o - F_c$ tables were deposited as Document No. 69005 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

In the present study, we have isolated two kinds of nickel(II) complexes by using the dinucleating ligand 2,6-bis(salicylideneaminomethyl)-4-methylphenol. When the dinucleating ligand, nickel(II) perchlorate, pyrazole, and triethylamine were mixed in a ratio of 1:3:3:5 in methanol, a tetranuclear complex $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**) was obtained.[25] However, a similar reaction with a greater excess of pyarazole afforded a dinuclear complex $[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**). The addition of pyrazole in excess may promote a further coordination of pyrazole (Hpz) in **1**, which hinders the association of two dinuclear units. These results show that the amount of pyrazole is an important factor governing the formation of the tetranuclear complex.

The X-ray crystal structure of **1** has been determined. A perspective drawing of the molecular structure of **1** is given in Fig. 1. Bond distances and angles are listed in

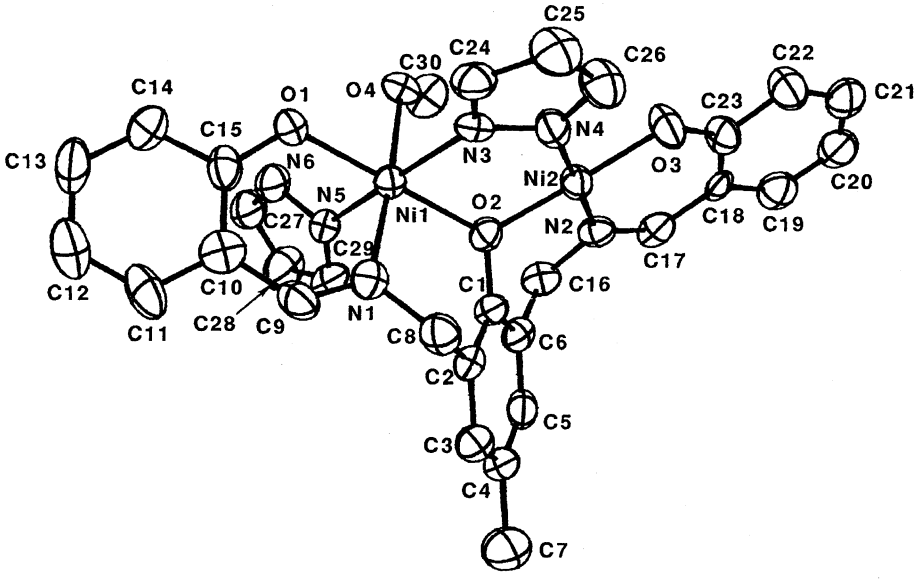


Fig. 1. ORTEP view of the structure of $[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**). Solvent molecule is not shown.

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} a)	Atom	x	y	z	B_{eq}/Å^{2} a)
$[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**)					N3	0.852(1)	−0.166(1)	0.6257(7)	6.1(4)
Ni1	0.5120(1)	0.3511(1)	0.40582(7)	2.78(3)	N4	0.798(1)	−0.098(1)	0.6343(8)	5.7(4)
Ni2	0.5224(1)	0.4718(1)	0.24556(7)	2.85(3)	N5	0.6889(9)	−0.0714(9)	0.9275(6)	4.0(3)
O1	0.5330(5)	0.3488(6)	0.5191(4)	3.7(2)	N6	0.356(1)	0.071(1)	0.7903(7)	6.9(3)
O2	0.4910(5)	0.3525(6)	0.2905(3)	3.1(2)	N7	0.766(1)	0.164(1)	0.8653(8)	5.6(4)
O3	0.5644(6)	0.5909(6)	0.2086(4)	4.3(2)	N8	0.707(1)	0.226(1)	0.8739(7)	6.5(4)
O4	0.4150(5)	0.4847(5)	0.3992(4)	3.3(2)	C1	0.569(1)	−0.410(1)	0.6439(8)	3.5(3)*
O5	0.739(1)	0.445(1)	0.1595(9)	20.2(6)	C2	0.568(1)	−0.492(1)	0.6906(9)	4.5(3)*
N1	0.5974(6)	0.2186(7)	0.4161(4)	3.2(2)	C3	0.459(1)	−0.595(1)	0.675(1)	5.6(4)*
N2	0.4204(6)	0.4411(7)	0.1541(4)	3.1(2)	C4	0.351(1)	−0.622(1)	0.615(1)	5.8(4)*
N3	0.6270(6)	0.4500(6)	0.4044(4)	3.0(2)	C5	0.346(1)	−0.547(1)	0.5642(9)	4.1(3)*
N4	0.6271(6)	0.4989(7)	0.3379(4)	3.5(2)	C6	0.459(1)	−0.441(1)	0.5794(8)	3.6(3)*
N5	0.3739(6)	0.2674(7)	0.3908(4)	3.4(2)	C7	0.228(2)	−0.733(2)	0.600(1)	7.7(5)*
N6	0.3219(7)	0.2906(8)	0.4384(5)	4.1(2)	C8	0.692(1)	−0.457(1)	0.753(1)	5.8(4)*
C1	0.4891(7)	0.2641(8)	0.2511(5)	3.1(2)	C9	0.826(2)	−0.510(2)	0.710(1)	8.1(6)*
C2	0.5578(8)	0.1837(8)	0.2795(5)	3.1(2)	C10	0.920(2)	−0.485(2)	0.670(1)	8.4(6)*
C3	0.5497(8)	0.0928(9)	0.2368(6)	3.7(3)	C11	0.937(3)	−0.600(3)	0.677(2)	14(1)*
C4	0.4768(9)	0.0829(9)	0.1669(6)	3.8(2)	C12	1.032(3)	−0.569(3)	0.642(2)	14(1)*
C5	0.4118(8)	0.1644(9)	0.1395(5)	3.7(3)	C13	1.083(2)	−0.490(2)	0.612(2)	11.4(8)*
C6	0.4177(7)	0.2556(8)	0.1806(5)	3.0(2)	C14	1.067(2)	−0.379(2)	0.602(2)	13(1)*
C7	0.471(1)	−0.018(1)	0.1215(7)	6.5(4)	C15	0.965(2)	−0.403(2)	0.640(1)	8.0(6)*
C8	0.6400(8)	0.1964(9)	0.3538(6)	3.6(3)	C16	0.466(1)	−0.358(1)	0.5244(8)	3.7(3)*
C9	0.6101(8)	0.1538(9)	0.4704(6)	3.7(3)	C17	0.429(1)	−0.196(1)	0.5459(9)	4.7(3)*
C10	0.5769(7)	0.1652(9)	0.5381(6)	3.6(3)	C18	0.452(1)	−0.078(1)	0.5824(9)	4.7(4)*
C11	0.5868(9)	0.0782(9)	0.5849(6)	4.8(3)	C19	0.362(1)	−0.051(1)	0.534(1)	6.3(4)*
C12	0.565(1)	0.084(1)	0.6519(7)	6.0(4)	C20	0.384(2)	0.067(2)	0.560(1)	7.1(5)*
C13	0.529(1)	0.176(1)	0.6732(6)	5.5(3)	C21	0.491(2)	0.151(2)	0.624(1)	7.5(5)*
C14	0.519(1)	0.262(1)	0.6286(6)	4.7(3)	C22	0.578(1)	0.125(1)	0.673(1)	5.6(4)*
C15	0.5420(8)	0.2618(9)	0.5586(6)	3.5(3)	C23	0.554(1)	0.005(1)	0.6513(9)	4.7(4)*
C16	0.3524(8)	0.3491(9)	0.1532(6)	3.6(2)	C24	0.952(2)	−0.105(2)	0.606(1)	8.4(6)*
C17	0.4076(8)	0.4875(9)	0.0907(5)	3.5(2)	C25	0.959(2)	0.000(2)	0.604(1)	8.7(6)*
C18	0.4639(7)	0.5786(8)	0.0795(5)	3.1(2)	C26	0.865(2)	0.013(2)	0.623(1)	7.5(5)*
C19	0.4403(9)	0.6210(9)	0.0057(6)	4.4(3)	C27	0.445(1)	−0.075(1)	0.8560(8)	3.5(3)*
C20	0.488(1)	0.708(1)	−0.0082(6)	4.8(3)	C28	0.481(1)	−0.120(1)	0.9211(8)	3.5(3)*
C21	0.5606(8)	0.7542(9)	0.0506(6)	4.6(3)	C29	0.390(1)	−0.215(1)	0.9349(9)	4.3(3)*
C22	0.5843(9)	0.716(1)	0.1238(7)	4.8(3)	C30	0.264(1)	−0.263(1)	0.886(1)	5.8(4)*
C23	0.5378(8)	0.6263(8)	0.1390(6)	3.5(3)	C31	0.229(1)	−0.217(1)	0.824(1)	5.4(4)*
C24	0.7087(8)	0.4846(9)	0.4571(6)	3.6(3)	C32	0.316(1)	−0.123(1)	0.8092(9)	4.5(3)*
C25	0.7631(8)	0.553(1)	0.4266(6)	4.5(3)	C33	0.165(2)	−0.372(2)	0.899(1)	7.8(5)*
C26	0.7076(8)	0.562(1)	0.3519(6)	4.4(3)	C34	0.617(1)	−0.060(1)	0.9757(8)	3.7(3)*
C27	0.3122(9)	0.2075(9)	0.3383(6)	4.5(3)	C35	0.759(1)	−0.116(1)	0.9548(9)	4.7(3)*
C28	0.2219(9)	0.193(1)	0.3524(7)	6.0(3)	C36	0.839(1)	−0.131(1)	0.9185(9)	4.6(3)*
C29	0.2274(9)	0.247(1)	0.4162(7)	5.1(3)	C37	0.915(1)	−0.172(1)	0.966(1)	6.5(5)*
C30	0.3246(8)	0.509(1)	0.3378(6)	4.5(3)	C38	1.008(2)	−0.174(2)	0.941(1)	7.6(5)*
C31	0.743(1)	0.357(1)	0.191(1)	12.2(7)	C39	1.027(2)	−0.133(2)	0.876(1)	7.3(5)*
					C40	0.953(1)	−0.095(1)	0.828(1)	5.5(4)*
$[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**)					C41	0.853(1)	−0.097(1)	0.8478(9)	4.6(3)*
Ni1	0.8121(2)	−0.3081(2)	0.6594(1)	5.78(6)	C42	0.289(1)	−0.062(1)	0.746(1)	6.2(4)*
Ni2	0.6614(2)	−0.1547(2)	0.6755(1)	3.68(5)	C43	0.280(2)	0.115(2)	0.789(1)	7.7(5)*
Ni3	0.6698(2)	−0.0141(2)	0.8246(1)	3.66(5)	C44	0.344(2)	0.247(2)	0.830(1)	8.0(6)*
Ni4	0.5324(2)	0.1529(2)	0.8406(1)	5.84(6)	C45	0.223(3)	0.259(3)	0.822(2)	14(1)*
O1	0.942(1)	−0.309(1)	0.6374(9)	9.7(4)	C46	0.288(3)	0.391(3)	0.857(2)	14(1)*
O2	0.6738(7)	−0.3046(7)	0.6649(6)	4.2(3)	C47	0.399(2)	0.470(2)	0.888(2)	11.8(8)*
O3	0.6353(8)	−0.0178(8)	0.7000(5)	4.4(3)	C48	0.521(2)	0.465(2)	0.899(2)	13.0(9)*
O4	0.7819(8)	−0.0645(8)	0.7998(5)	4.4(3)	C49	0.453(2)	0.323(2)	0.860(1)	7.5(5)*
O5	0.5303(8)	0.0077(7)	0.8346(5)	4.3(2)	C50	0.890(2)	0.243(2)	0.877(1)	8.0(6)*
O6	0.553(1)	0.305(1)	0.8633(8)	9.5(4)	C51	0.895(2)	0.354(2)	0.897(1)	8.1(6)*
O7	0.5265(9)	−0.2234(9)	0.7498(6)	5.4(3)	C52	0.789(2)	0.345(2)	0.894(1)	8.3(6)*
N1	0.780(1)	−0.435(1)	0.7102(8)	7.0(4)	C53	0.429(3)	−0.316(3)	0.748(2)	14(1)*
N2	0.5011(9)	−0.2386(9)	0.5724(7)	4.0(3)					

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter 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.

Table 2. The two nickel atoms, Ni1 and Ni2, are bridged by a phenoxo-oxygen atom, O2, and two pyrazolate nitrogen atoms, N3 and N4. The Ni1–Ni2 separation is 3.387(2) Å and the Ni1–O2–Ni2 angle is 119.2(3)°. The coordination environments of the two nickel atoms are different. The Ni1 atom is coordinated by an imine nitrogen N1, a pyrazolate nitrogen N3, a pyrazole nitrogen N5, a briging phenoxo oxygen O2, a terminal phenoxo oxygen O1, and a meth-

Table 2. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

$[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**)			
Ni1–Ni2	3.387(2)	Ni1–O1	2.029(7)
Ni1–O2	2.066(6)	Ni1–O4	2.156(7)
Ni1–N1	2.047(9)	Ni1–N3	2.030(9)
Ni1–N5	2.121(9)	Ni2–O2	1.858(7)
Ni2–O3	1.841(8)	Ni2–N2	1.892(7)
Ni2–N4	1.912(7)		
O1–Ni1–O2	179.6(3)	O1–Ni1–O4	88.3(3)
O1–Ni1–N1	89.3(4)	O1–Ni1–N3	98.4(3)
O1–Ni1–N5	88.8(4)	O2–Ni1–O4	92.1(2)
O2–Ni1–N1	90.4(4)	O2–Ni1–N3	81.7(3)
O2–Ni1–N5	91.1(3)	O4–Ni1–N1	175.8(4)
O4–Ni1–N3	87.9(4)	O4–Ni1–N5	83.7(3)
N1–Ni1–N3	95.9(3)	N1–Ni1–N5	92.8(3)
N3–Ni1–N5	168.7(3)	O2–Ni2–O3	174.7(2)
O2–Ni2–N2	91.1(3)	O2–Ni2–N4	87.9(3)
O3–Ni2–N2	94.1(4)	O3–Ni2–N4	86.9(4)
N2–Ni2–N4	178.3(4)	Ni1–O2–Ni2	119.2(3)
Ni1–N3–N4	120.1(5)	Ni2–N4–N3	121.0(6)
$[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**)			
Ni1–Ni2	3.416(4)	Ni2–Ni3	3.002(3)
Ni3–Ni4	3.418(4)	Ni1–O1	1.850(16)
Ni1–O2	1.853(11)	Ni1–N1	1.911(14)
Ni1–N3	1.893(17)	Ni2–O2	2.023(11)
Ni2–O3	1.988(12)	Ni2–O4	2.112(8)
Ni2–O7	2.415(12)	Ni2–N2	2.039(9)
Ni2–N4	1.987(15)	Ni3–O3	2.117(10)
Ni3–O4	1.984(12)	Ni3–O5	2.014(12)
Ni3–O7	2.419(9)	Ni3–N5	2.038(12)
Ni3–N7	1.987(12)	Ni4–O5	1.869(11)
Ni4–O6	1.853(14)	Ni4–N6	1.894(11)
Ni4–N8	1.886(16)		
Ni1–Ni2–Ni3	130.35(8)	Ni2–Ni3–Ni4	130.30(7)
O1–Ni1–O2	171.0(5)	O1–Ni1–N1	95.6(7)
O1–Ni1–N3	88.1(7)	O2–Ni1–N1	91.0(6)
O2–Ni1–N3	86.4(6)	N1–Ni1–N3	170.9(6)
O2–Ni2–O3	169.8(4)	O2–Ni2–O4	99.4(4)
O2–Ni2–N2	90.7(4)	O2–Ni2–N4	83.0(5)
O3–Ni2–O4	76.3(4)	O3–Ni2–N2	90.6(4)
O3–Ni2–N4	106.5(6)	O4–Ni2–N2	159.2(6)
O4–Ni2–N4	94.5(4)	N2–Ni2–N4	104.8(5)
O3–Ni3–O4	76.3(4)	O3–Ni3–O5	99.1(5)
O3–Ni3–N5	159.3(4)	O3–Ni3–N7	94.3(5)
O4–Ni3–O5	169.3(3)	O4–Ni3–N5	90.8(6)
O4–Ni3–N7	107.0(6)	O5–Ni3–N5	90.7(5)
O5–Ni3–N7	82.8(5)	N5–Ni3–N7	105.1(5)
O5–Ni4–O6	171.0(5)	O5–Ni4–N6	91.3(5)
O5–Ni4–N8	86.1(5)	O6–Ni4–N6	95.2(6)
O6–Ni4–N8	88.5(6)	N6–Ni4–N8	170.8(6)
Ni1–O2–Ni2	123.5(4)	Ni2–O3–Ni3	94.0(4)
Ni2–O4–Ni3	94.2(4)	Ni3–O5–Ni4	123.3(4)

anol oxygen O4, forming a distorted octahedron, while the Ni2 atom takes a square planar arrangement with an imine nitrogen N2, a pyrazolate nitrogen N4, a bridging phenoxo oxygen O2, and a terminal phenoxo oxygen O3. The Ni1–N [2.030(9)—2.121(9) Å] and Ni1–O [2.029(7)—2.156(7) Å] bond lengths are significantly longer than any of the Ni2–N and Ni2–O distances and fall in the range of those for high-spin nickel(II) complexes.[16,17] On the other hand, the Ni2–N [1.892(7), 1.912(7) Å] and Ni2–O [1.858(7), 1.841(8) Å] bond distances are comparable to the corresponding distances found in the dinuclear low-spin nickel(II) complexes with the related pentadentate Schiff-base ligands, $[Ni_2(L')(pz)]$, and typical of those found in low-spin, square-planar nickel(II) complexes.[19] Therefore the Ni1 and Ni2 atoms can be assigned to a high-spin (paramagnetic) nickel(II) ion and a low-spin (diamagnetic) nickel(II) ion, respectively.[6–8] This assignment is supported by the magnetic and spectral data of **1**.

The diffuse reflectance spectrum of **1** is shown in Fig. 2, together with that of **2**. The spectrum of **1** is characterized by five absorptions (410sh, 483, 575sh, 955, and 1380 nm) in the visible and near-infrared regions, which can be associated with d–d transitions and intense absorptions in the range 300—400 nm; these are charge-transfer transitions in origin. The two absorption bands at 483 and 575 nm may be assigned as d–d transitions characteristic of low-spin nickel(II) complexes ($^1A_{1g}\rightarrow{}^1B_{2g}$ and $^1A_{1g}\rightarrow{}^1A_{2g}$).[26] The corresponding two bands are observed at 460—500 and 580—650 nm, respectively, in the related dinuclear nickel(II) complexes with low-spin state, $[Ni_2(L')(pz)]$.[19] The other three bands at 410, 955, and 1380 nm can be attributed in an octahedral model to the transitions $^3A_{2g}\rightarrow{}^3T_{1g}(P)$, $^3A_{2g}\rightarrow{}^3T_{1g}$, and $^3A_{2g}\rightarrow{}^3T_{2g}$, respectively.[26] This fact is compatible with the coexistence of high-spin and low-spin nickel(II) ions within the molecule.

The magnetic moment of **1** is 3.18 B.M. per dinuclear molecule at room temperature, which is quite common for a high-spin nickel(II) ion, showing the existence of one paramagnetic high-spin and one diamagnetic low-spin nickel(II) ions per dinuclear molecule. The magnetic moments are almost constant over the 80—300 K temperature range. As can be seen in Fig. 3, the magnetic data obey the Curie–Weiss law, $\chi_A = C/(T-\theta)$, with a small Weiss constant ($\theta = -3.3$ K). From these results, we conclude that complex **1** is a mixed-spin complex having one high-spin ($S=1$) and one low-spin ($S=0$) nickel(II) ions within the molecule. Such a mixed-spin state has been found in only a few dinuclear nickel(II) complexes.[3–12] The mixed-spin state may be maintained in the solution, since the electronic spectrum of **1** in *N*,*N*-dimethylformamide is similar to that in the solid state [370 ($\varepsilon = 11600$ mol^{-1} dm^3 cm^{-1}), 478 (510), 582 (110), 990 (21) nm]. This means that a packing effect in the crystal is not responsible for the mixed-spin state. In an earlier report, we described the crystal structure of the related dinuclear nickel(II) complex of 1,5-bis(salicylideneamino)-3-pentanol (H_3L_c), $[Ni_2(L_c)(pz)]$ (**3**).[19] The structure consists of two square-planar nickel(II) centers bridged by an alkoxo oxygen and a pyrazolate ion. This compound is low-spin. In **1** and **3**, both the Schiff-base backbones seem to be twisted to accomodate their coordination environments and the conformational difference in the dinucleating ligands may not contribute to the formation of the mixed-spin state. Thus

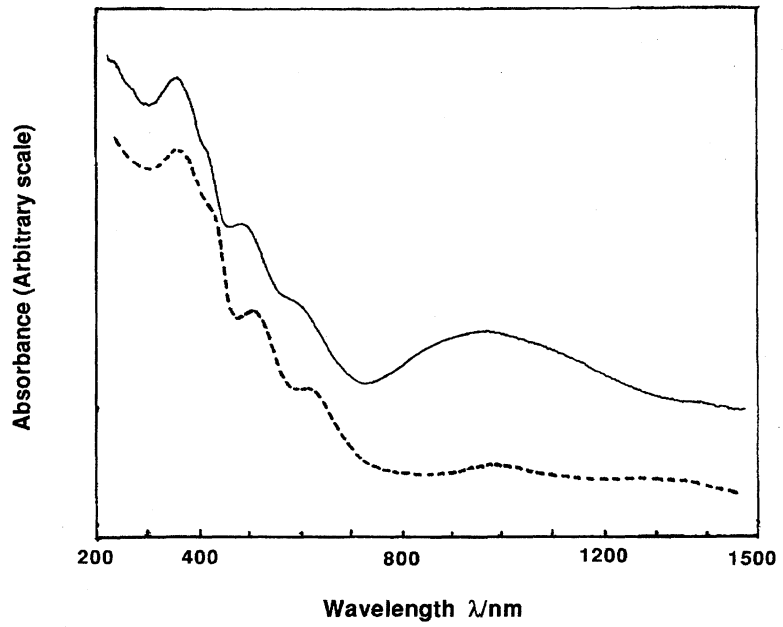


Fig. 2. Diffuse reflectance spectra of $[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**) (—) and $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**) (- - -).

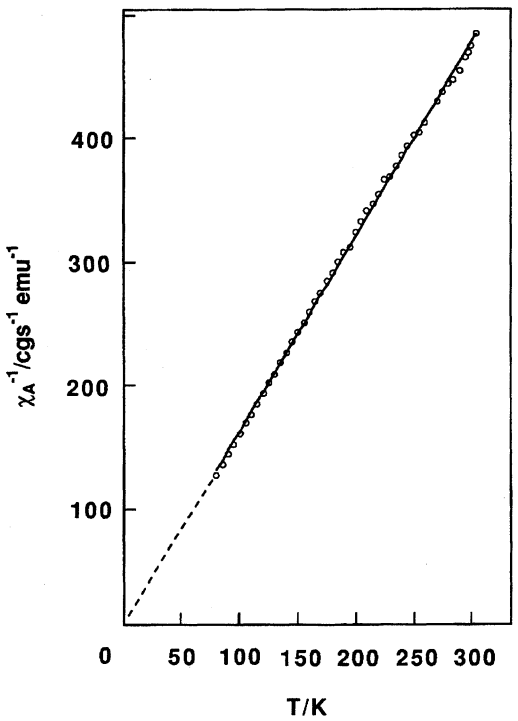


Fig. 3. Plots of inverse of magnetic susceptibility for $[Ni_2(L)(pz)(Hpz)(CH_3OH)]\cdot CH_3OH$ (**1**).

we can conclude that substitution of the phenoxo-oxygen for the alkoxo-oxygen in the dinucleating ligand results in an intermediate field generating the mixed-spin state.

On the other hand, complex **2** has a tetranuclear structure consisting of two dinuclear units (Fig. 4). In one dinuclear half, two nickel atoms (Ni1 and Ni2) are bridged by a central phenoxo-oxygen atom (O2) of L and a pyrazolate ion (N3 and N4). Similarly the Ni3 and Ni4 atoms are bridged by a phenoxo-oxygen atom (O5) and a pyrazolate ion (N7 and N8) in the other dinuclear unit. These two dinuclear halves are associated to a zigzag-shaped tetranuclear molecule by two terminal phenoxo-oxygen atoms (O3 and O4) of L and a methanol oxygen atom (O7). Both the Ni2 and Ni3 atoms consequently take distorted octahedral geometries, forming a face-shared bioctahedron. The Ni1–Ni2–Ni3 and Ni2–Ni3–Ni4 angles are 130.35(8) and 130.30(7)°, respectively. In contrast, the other two nickel atoms, Ni1 and Ni4, assume square planar geometries. A comparison of the Ni–N and Ni–O bond lengths reveals that the bonds involving the distorted octahedral nickel(II) atoms are significantly longer than the bonds to the square-planar nickel(II) atoms, and the bond lengths are consistent with previous observations relating to high- and low-spin nickel(II).[9] Thus we can conclude that the Ni2 and Ni3 atoms are high-spin nickel(II) and the Ni1 and Ni4 atoms are low-spin nickel(II) atoms, respectively. This is a very novel example of a tetranuclear nickel(II) complex with mixed-spin state. A number of tetranuclear nickel(II) complexes are reported in the literature. Four nickel(II) atoms are in a rectangular arrangement for some complexes.[27—34] Most tetranuclear nickel(II) complexes reported to date have a "cubane"-like structure.[35—48] To our knowledge, only one similar linear Ni_4 complex is reported; in this case, however, the four nickel atoms are arranged to form a linear chain-like structure.[49]

The diffuse reflectance spectrum of **2** is similar to that of **1** (Fig. 2). The five absorption bands (420sh, 502, 609, 980, and 1280 nm) in the visible and near-infrared regions may be due to the overlap of the d–d transitions for the low-spin and high-spin nickel(II) ions.[26] The electronic spectrum in *N,N*-dimethylformamide is similar to that in the solid state, although the lowest energy band in the diffused reflectance spectrum could not be observed in the solution spectrum, owing to the low solubility of the complex [370 ($\varepsilon = 22120$ mol^{-1} dm^3 cm^{-1}), 476 (937), 582 (218), 985 (41) nm].

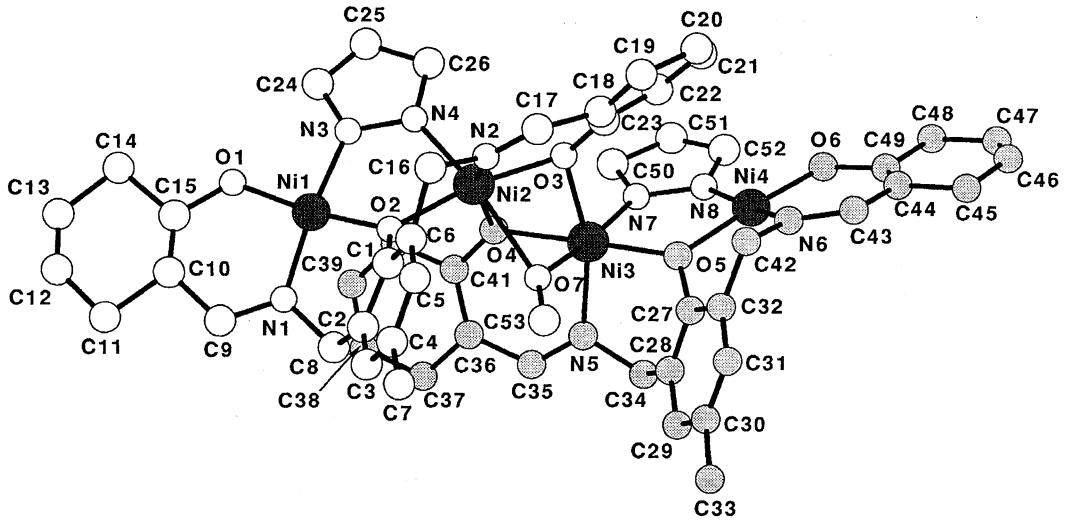


Fig. 4. A view of the structure of $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**).

The effective magnetic moment of **2** is 2.25 B.M./Ni at room temperature, which is lower than the spin-only value (2.83 B.M.) for high-spin nickel(II). The temperature dependence of the magnetic susceptibilities of **2** was measured in the temperature range 80—300 K (Fig. 5). For the analysis of the magnetic susceptibility data, we employed the $(S_{Ni1}=0)-(S_{Ni2}=1)-(S_{Ni3}=1)-(S_{Ni4}=0)$ system based on the Heisenberg model. The resulting spin Hamiltonian is $\mathcal{H}=-2JS_{Ni2}\cdot S_{Ni3}$ and thus the magnetic susceptibility expression is given by

$$\chi_M=\frac{2Ng^2\beta^2}{kT}\left[\frac{5+\exp(-4J/kT)}{5+3\exp(-4J/kT)+\exp(-6J/kT)}\right]. \quad (1)$$

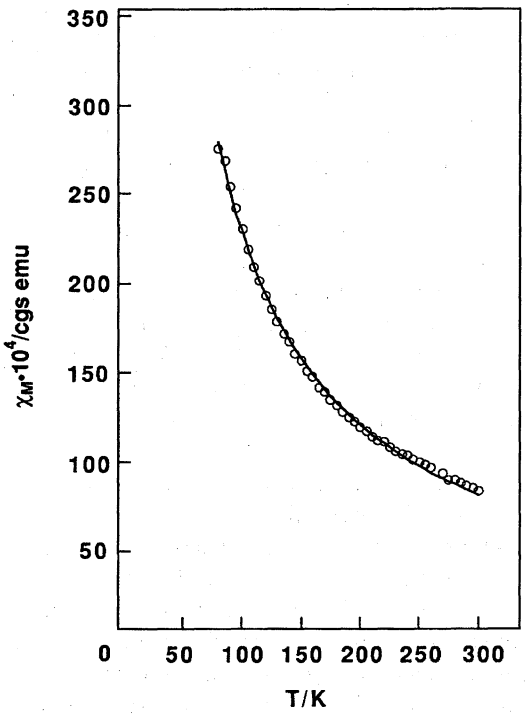


Fig. 5. Plots of magnetic susceptibility for $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (**2**).

The symbols N, β, k, and g have their usual meanings.[50] The best fitting parameters are $g=2.25$ and $J=-4.71$ cm^{-1}; the solid curve in Fig. 5 was calculated using these parameters. This result shows that there is an antiferromagnetic interaction between the two central nickel(II) ions.

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