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Novel Tetranuclear Nickel(II) Complex with a Mixed-Spin State Generated by Pairing of Dimers

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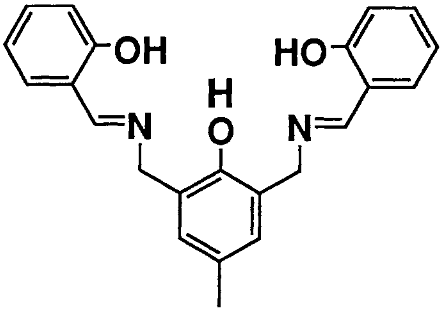
A tetranuclear nickel(II) complex with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (pz=pyrazolate ion) has been synthesized and characterized by electronic spectra and magnetic susceptibilites (80—300 K). The X-ray crystal structure analysis has demonstrated that it consists of tetranuclear (low-spin—high-spin—high-spin—low-spin) molecules with a zigzag structure.

There has been growing interests in the synthesis of new tetranuclear transition metal complexes, since tetranuclear manganese complexes have attracted a remarkable attention as model compounds of the Mn_4 center in the oxygen evolution center of the photosystem II of green plants.1) In order to achieve tetranuclear structures, we are pursuing a "pairing of dimers" method using dinucleating ligands.2) The synthetic studies of dinuclear or tetranuclear nickel(II) complexes have not been extensively developed comparing with those of a large number of dinuclear or tetranuclear copper(II) complexes. Most of the nickel(II) systems that have been studied are high-spin nickel(II) dimers or low-spin nickel(II) dimers. Interestingly these systems afford a mixed-spin state which contains both the high-spin and low-spin nickel(II) ions in the same molecule, although only a few examples of such mixed-spin complexes have been reported.3-5) During the course of the application of our method to these systems, we have found that reaction of dinucleating ligand, 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), with nickel(II) salt affords a novel tetranuclear complex with a mixed-spin state generated by pairing of dimers. Herein we report the synthesis and structural characterization of the tetranuclear nickel(II) complex, $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (pz = pyrazolate ion) (**1**).

The nickel(II) complex **1** was synthesized as follows. To a methanol solution of 2,6-bis(salicylideneaminomethyl)-4-methylphenol (36 mg, 0.10 mmol), nickel(II) perchlorate hexahydrate (108 mg, 0.30 mmol), pyrazole (21 mg, 0.31 mmol), and triethylamine (50 mg, 0.50 mmol) were successively added with stirring. The resulting dark red solution was filtered and left to stand for several days to give black crystals. The crystals were collected by filtration and washed with methanol.6)



H_3L

The molecular structure of **1** was determined by X-ray crystallography.7) A perspective view of **1** is shown in Fig. 1. The structure shows a zigzag tetranuclear unit which is formed by association of

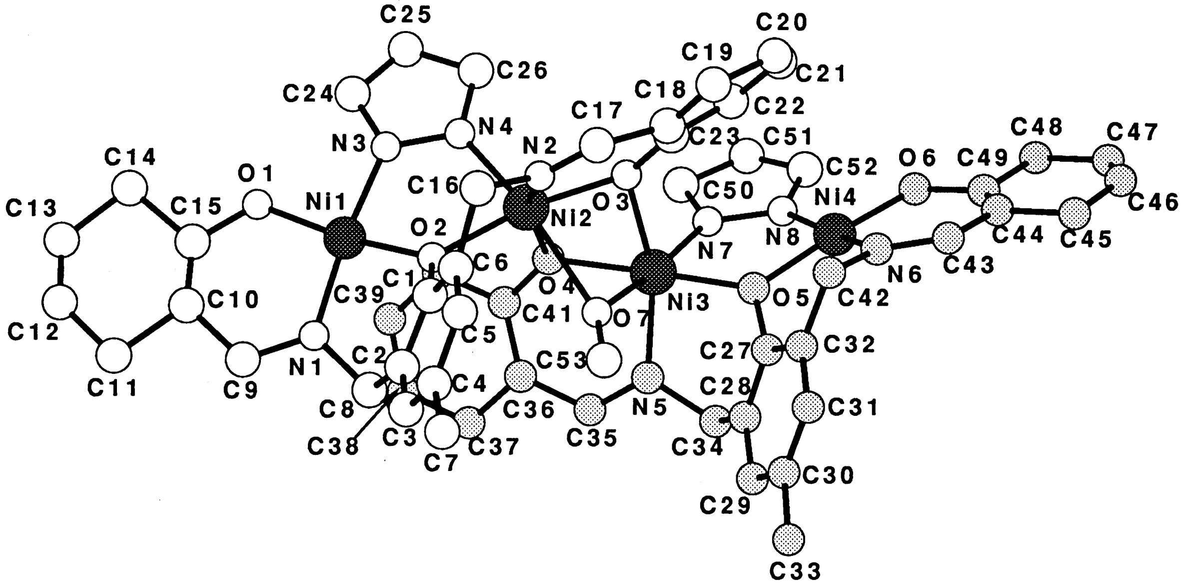
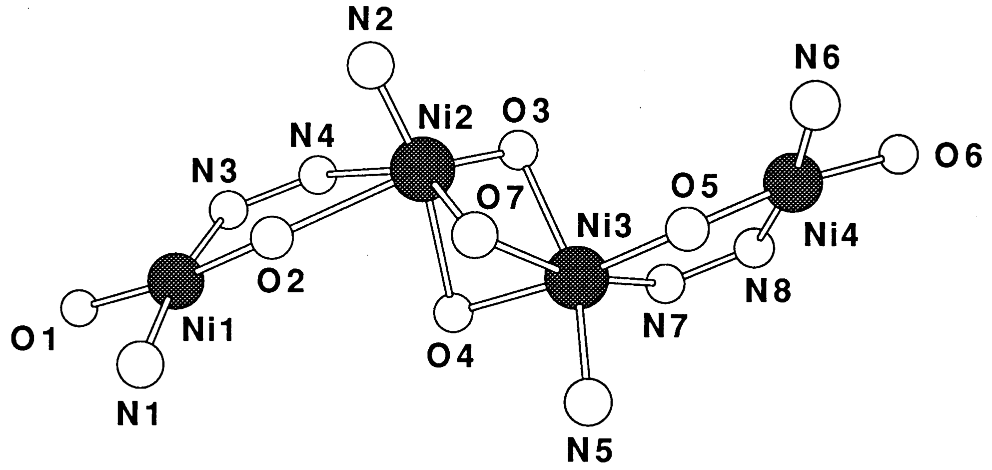


Fig. 1. Perspective view of [$Ni_4(L)_2(pz)_2(CH_3OH)$] (**1**).



		Ni1-Ni2	3.416(4)Å		Ni2-O3-Ni3	94.0(4)°	
		Ni2-Ni3	3.002(3)		Ni2-O4-Ni3	94.2(4)	
		Ni3-Ni4	3.418(4)		Ni2-O7-Ni3	76.8(3)	
Ni1-O1	1.849(16)Å	Ni2-O2	2.023(11)Å	Ni3-O3	2.117(10)Å	Ni4-O5	1.870(11)Å
Ni1-O2	1.853(11)	Ni2-O3	1.988(12)	Ni3-O4	1.984(12)	Ni4-O6	1.853(14)
Ni1-N1	1.911(14)	Ni2-O4	2.112(8)	Ni3-O5	2.014(12)	Ni4-N6	1.894(11)
Ni1-N3	1.893(17)	Ni2-N2	2.039(9)	Ni3-N5	2.038(12)	Ni4-N8	1.886(16)
		Ni2-N4	1.987(15)	Ni3-N7	1.987(12)		
		Ni2-O7	2.415(12)	Ni3-O7	2.419(9)		

Fig. 2. Coordination spheres of [$Ni_4(L)_2(pz)_2(CH_3OH)$] (**1**).

the two dinuclear molecules by virtue of phenoxo-bridges and methanol bridge. In the dinuclear unit, the Ni1 and Ni2 atoms are bridged by a phenoxo-oxygen atom (O2) and two nitrogen atoms of the pyrazolate ion (N3 and N4). Similarly the Ni3 and Ni4 atoms are bridged by a phenoxo-oxygen atom (O5) and two pyrazolate-nitrogen atoms (N7 and N8). These dinuclear units are connected by phenoxo-oxygen atoms (O3 and O4) and methanol oxygen atom (O7) forming a face-shared bioctahedron. The Ni-Ni separations are 3.416(4), 3.002(3), and 3.418(4) Å, for Ni1-Ni2, Ni2-Ni3, and Ni3-Ni4, respectively. The coordination geometries of the Ni2 and Ni3 atoms are distorted octahedra (Fig. 2). Except for the Ni2-O7 (2.415(12) Å) and Ni3-O7 (2.419(9) Å) bonds, the Ni-O and Ni-N bond distances are 1.984(12)—2.117(10) Å and 1.987(12)—2.039(9) Å, respectively, and fall in the range of those for high-spin nickel(II) complexes.[8,9] On the other hand, the environments of the Ni1 and Ni4 atoms are close to a square plane. The Ni-O (1.849(16)—1.870(11) Å) and Ni-N (1.886(16)—1.911(14) Å) distances are significantly shorter than the corresponding distances for the Ni2 and Ni3 atoms and comparable to those found in diamagnetic low-spin nickel(II) complexes.[10] These structural features are consistent with the assignment that theNi2 and Ni3 atoms are high-spin (paramagnetic) Ni(II), and the Ni1 and Ni4 atoms are low-spin (diamagnetic) Ni(II) atoms. This is the first example of structurally characterized tetranuclear nickel(II) complex with a novel mixed-spin state.

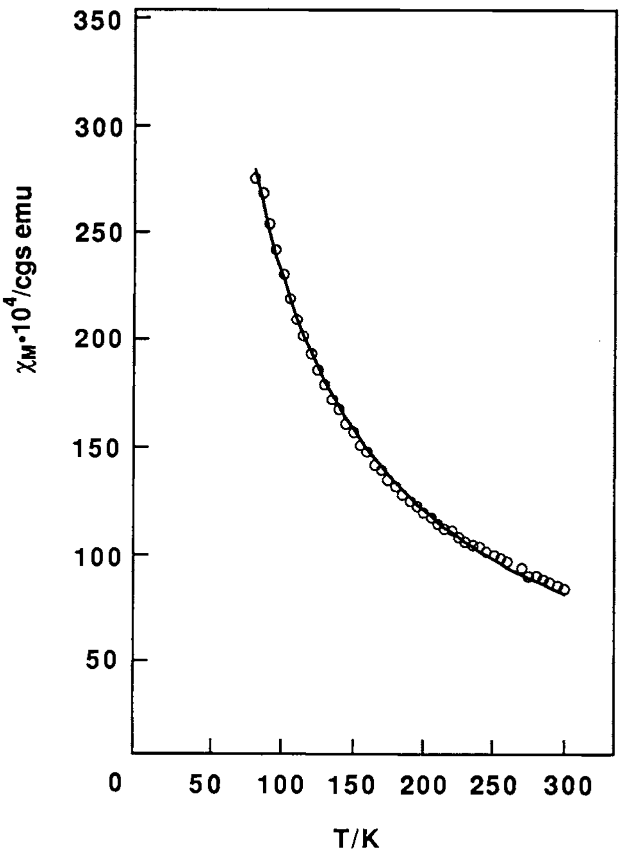
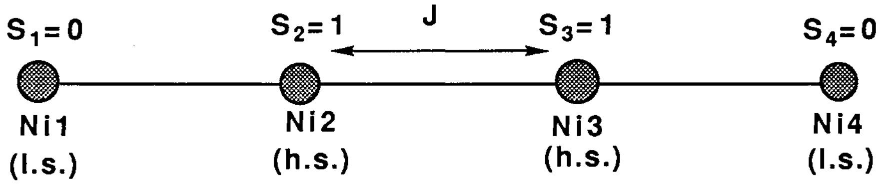


Fig. 3. Temperature dependence of the magnetic susceptibility of **1**.

The effective magnetic moment of **1** is 2.24 B.M./Ni at 300 K, which is smaller than the spin-only value (2.83 B.M.) for high-spin nickel(II). Variable-temperature magnetic susceptibility data were collected over the temperature range 80—300 K (Fig. 3). For the analysis of the magnetic susceptibility data, we employed the following spin coupling model. The resulting spin Hamiltonian is $H=-2JS_2 \cdot S_3$. The fitting parameters are $J=-4.71$ cm^{-1} and $g=2.25$ as given in Fig. 3, where the solid curve is the calculated one.



Diffuse reflectance spectrum of **1** shows five absorption bands (420, 502, 609, 980, and 1370 nm) in the visible region which may be due to the overlap of the d-d transitions for the low-spin and high-spin nickel(II) ions.[4,5]

Finally, we note that the present dinucleating ligand allows us the isolation of the tetranuclear manganese species formed by pairing of dimers. Detailed characterization on these species is in progress.

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6) A satisfactory analysis (C, H, N) has been obtained.

7) Crystal data for **1**: $Ni_4O_7N_8C_{53}H_{48}$, F.W.=1143.86, triclinic, space group $P\bar{1}$, 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, Z=2, D_m=1.52, D_c=1.54 g cm^{-3}, μ(Mo-Kα)=15.72 cm^{-1}. A total of 6855 reflections ($2 \le 2\theta \le 46°$) were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation; 3576 with $I \ge 3\sigma(I)$ were assumed observed. The structure was solved by the direct method and refined by the full-matrix least-squares method. The refinement converged at R=0.087, R_w=0.091. All the calculations were performed on a Micro-VAX II computer with the SDP program package.

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