Assembly of Seven Nickel(II) Metals by Chiral, Salen-Type Ligands with μ_3-OH Bridges

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A chiral heptanuclear nickel(II) complex $[Ni^{II}(Ni^{II}_2L)_3(\mu_3\text{-}OH)_2]\cdot3H_2O$ [H_4L = (2*R*,3*R*)-1,4-bis(3,5-di-*tert*-butylsalicylideneamino)-2,3-butanediol], containing two μ_3-OH bridges, has been prepared and structurally characterized; its thermal and magnetic properties were investigated.

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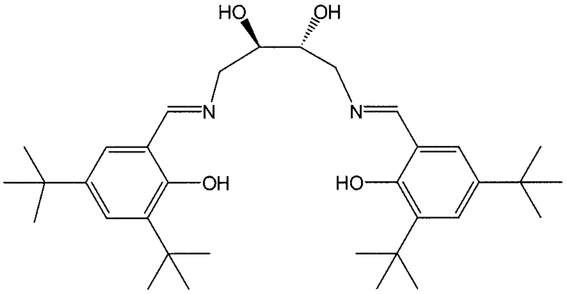
Introduction

Polynuclear complexes have recently attracted much attention in molecular assembly, with one of the major goals being to try to obtain single-molecule magnets by designing discrete polynuclear entities with high-spin ground states that exhibit useful magnetic properties.[1] Among these multinuclear systems, OH^-, RO^-, RCO_2^- and other groups are often used as bridging ligands.[2] In our research of transition metal complexes, some new salen-type ligands with optically active diamino moieties have been prepared to bind metals in the same manner as in Jacobson's catalysts.[3] Considering the flexibility of the ligands and the known bridging ability of hydroxyl groups, we have chosen (2*R*,3*R*)-1,4-diamino-2,3-butanediol to react with salicylaldehyde derivatives to get a number of Schiff bases as chiral ligands. Herein we report the first preparation and crystal structure of an unusual heptanuclear nickel(II) complex, $[Ni^{II}(Ni^{II}_2L)_3(\mu_3\text{-}OH)_2]\cdot3H_2O$, together with its magnetic and thermal behavior.



H_4L

Results and Discussion

Preparation and Characterization

The title complex was synthesized by reaction of H_4L with $NiCl_2\cdot6H_2O$ in methanol in the presence of triethylamine. The ligand was prepared by the Schiff-base condensation of 3,5-di-*tert*-butylsalicylaldehyde with (2*R*,3*R*)-1,4-diamino-2,3-butanediol, which was, in turn, obtained by hydrolization of (4*R*,5*R*)-4,5-bis(aminomethyl)-2-isopropyl-1,3-dioxolane.[4] The tetra-deprotonated ligand was formed in situ in the presence of the metal ions.

The crystal structure of the complex is shown in Figure 1. It is a heptanuclear nickel(II) compound with three water molecules of crystallisation. The structure is composed of three dinuclear $[Ni_2L\cdot1/3(\mu_3\text{-}OH)_2]$ units, with a six-coordinate Ni^{II} moiety in the center (Figure 2). In the structure, there is a threefold symmetry axis containing Ni(3), O(1) and O(4). The three units are obtained by symmetry operations. Thus, the whole system has D_3 symmetry. Each ligand has six ligating groups which are evenly divided into two groups to encapsulate two nickel atoms in two open compartments, where each metal is coordinated by a phenolic oxygen anion, an imine nitrogen atom and an alkyloxy anion of the ligand, as well as a bridging OH^- group. It is noted that there are two hydroxy anions in the molecule and each of them functions as a bridge to connect three metal atoms bound by three ligands. In comparison to quite a number of examples of μ_3-hydroxo bridges in six-coordinate polynuclear nickel(II) complexes,[5] the current example, where three nickel(II) ions in a square-planar geometry are linked by one μ_3-OH^- bridge, is rare. It is also interesting to note that the RO^- anion in the ligand works as a bridging group to connect two metal atoms, whereas the PhO^- anion does not. Consequently, there are three types of "O" donor atoms in this heptanuclear compound.

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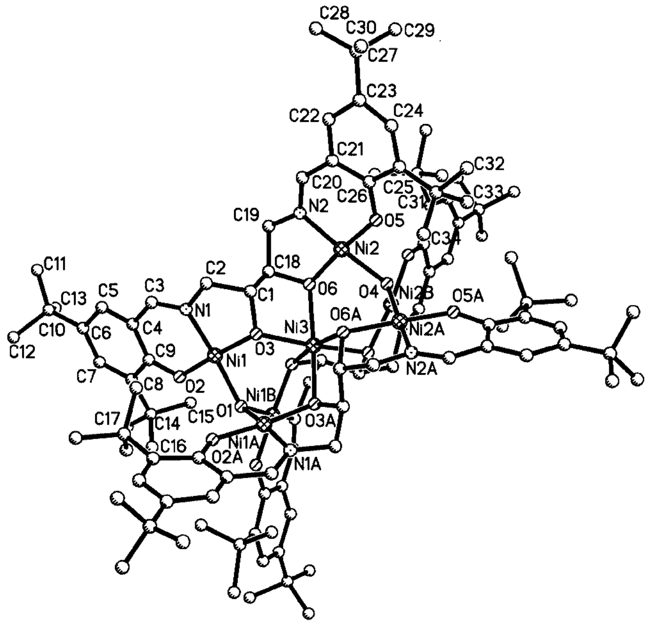

Figure 1. View of the heptanuclear complex, crystalline water molecules are omitted (the labels A and B indicate that these atoms are obtained by symmetry operations)

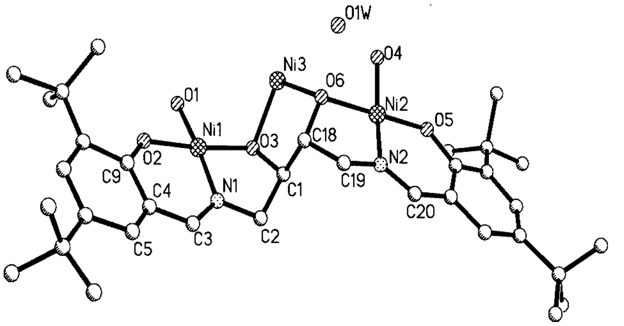

Figure 2. Structure of the dinuclear unit [Ni$_2$L·1/3(μ_3-OH)$_2$]·H$_2$O (50% probability ellipsoids)

More significantly, three dinuclear units share a central nickel atom coordinated by six alkyloxy groups from three ligands, whose 2+ charge is balanced by two μ_3-OH$^-$ anions. The geometry of the central Ni atom is distorted octahedral, and the Ni−O distances are in agreement with normal values.[5] In the [Ni$_2$L] unit, each metal atom is in a configuration of a distorted square plane consisting of N(1)O(1)O(2)O(3) or N(2)O(4)O(5)O(6); the deviation from the appropriate plane is 0.0410 Å for Ni(1) and 0.0279 Å for Ni(2). The average bond lengths for PhO−Ni (1.82 Å) and N−Ni (1.83 Å) are similar to the values reported for mononuclear salen Ni^{II} complexes.[6] For RO−Ni bonds, the mean distance is 1.87 Å, which is shorter than the usual Ni−O distance in six-coordinate Ni^{II} complexes[7] and close to those in a planar Ni^{II} coordination geometry.[8] In addition, the μ_3-HO-Ni distance of 1.90 Å here is also shorter than the reported values in six-coordinate Ni^{II}.[5]

The seven metal atoms adopt the topology of two tetrahedra sharing a common apex at Ni(3). Ni(1), Ni(1A) and Ni(1B) form an equilateral triangle (Ni−Ni distance: 3.209 Å), which is parallel to its counterpart composed of Ni(2), Ni(2A) and Ni(2B) (Ni−Ni distance: 3.216 Å). Ni(3) is located in the center of the two triangular planes, forming a trigonal prismatic structure (Figure 3). The distance between two triangular planes is 5.538 Å, and that of Ni(3) to these two planes are 2.754 Å and 2.784 Å, respectively. Although a few heptanuclear nickel(II) compounds have recently been reported,[9] our complex is the first example of a heptanuclear nickel(II) complex of a chiral ligand.

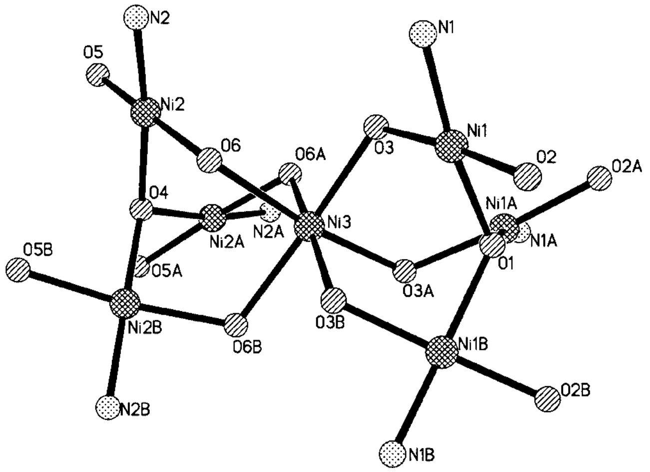

Figure 3. A view of the coordination environments around the nickel atoms; pertinent bond lengths (Å) and angles (°): Ni(1)−O(2) 1.806(3), Ni(1)−N(1) 1.831(4), Ni(1)−O(3) 1.860(3), Ni(1)−O(1) 1.895(13), Ni(2)−N(2) 1.826(4), Ni(2)−O(5) 1.838(3), Ni(2)−O(6) 1.884(3), Ni(2)−O(4) 1.9025(13), Ni(3)−O(3) 2.066(3), Ni(3)−O(6) 2.124(3), N(1)−Ni(1)−O(1) 170.19(16), O(2)−Ni(1)−O(3) 174.55(15), N(2)−Ni(2)−O(4) 171.21(16), O(5)−Ni(2)−O(6) 172.87(15), O(3)−Ni(3)−O(6)B 171.68(12), O(3)−Ni(3)−O(6) 81.54(11), Ni(1)−O(3)−Ni(3) 115.38(15), Ni(2)−O(6)−Ni(3) 113.10(15) (the labels A and B mean these atoms are obtained by symmetry operations)

The variable magnetic susceptibilities of the title complex in the range 77 to 300 K have been measured, and the related $\chi_m T$ vs. T curve is shown in Figure 4. As the temperature decreases, the $\chi_m T$ value is essentially constant (Curie-like behavior). The room temperature magnetic moment of the complex is 3.15 BM (300 K), compatible with that of a free single nickel(II) ion. This result indicates that the magnetic behavior of the compound is characterized as one paramagnetic nickel(II) ion. This is consistent with the six-coordinate Ni^{II} atom being in an octahedral configuration in the structure; the other six Ni^{II} atoms in a square-planar configuration make no contribution to the system.

A TGA analysis of the compound showed that it loses 3.29% of its weight between 15 °C and 67 °C, which can be accounted for by the loss of three waters of crystallisation together with another water molecule probably resulting from the conversion of the Ni(OH)$_2$ part of the compound to NiO and H$_2$O. The compound then decomposes gradually in the range from 67 °C to 310 °C, followed by a rapid weight loss in the range 310−580 °C, indicating the decomposition of the organic ligand. The residue (ca. 24% of

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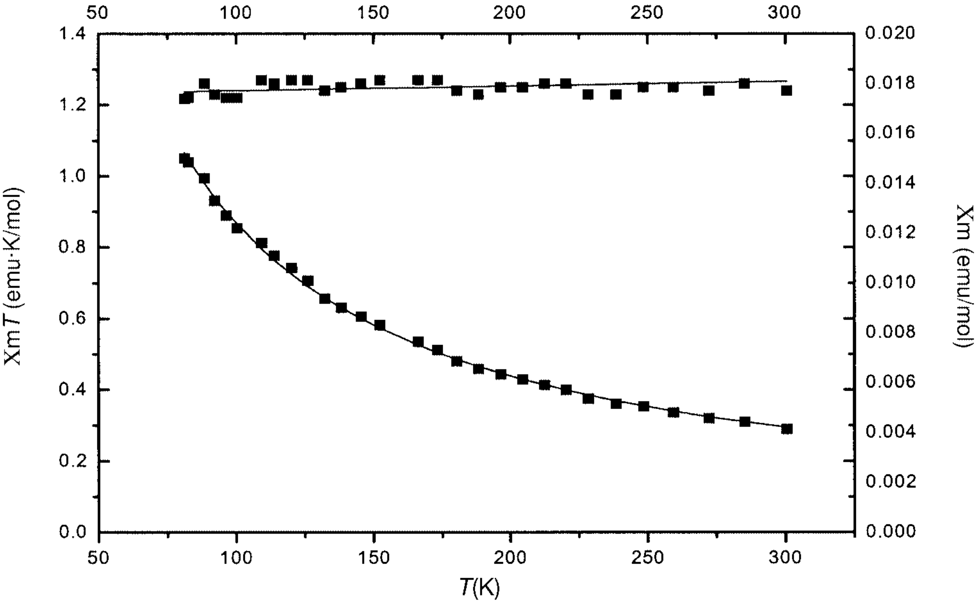

Figure 4. $\chi_m T$ product and χ_m vs. T for the complex; solid lines represent the best fit to the result in agreement with Curie law.

the original weight) is due to the formation of NiO, compatible with the theoretical value of 23.5%.

Experimental Section

Materials and General Methods: All solvents and chemicals were of analytical grade and used without further purification. Elemental analyses were measured with a Perkin−Elmer 1400C analyzer. Infrared spectra (4000−400 cm^{-1}) were recorded on a Nicolet FT-IR 170X spectrophotometer. Electrospray ionization (ES) mass spectra were performed in CH_3CN/CH_3OH on a Finnigan MAT SSQ 710 mass spectrometer in the scan range 300−1200 amu.

$[Ni^{II}(Ni^{II}_2L)_3(\mu_3\text{-}OH)_2]\cdot 3H_2O$ (1): The ligand **L** was prepared by a Schiff-base condensation. The title complex was obtained by the following method. $NiCl_2\cdot 6H_2O$ (0.120 g, 0.5 mmol) and the ligand (0.140 g, 0.25 mmol, 1 equiv.) were dissolved in methanol (20 mL). After stirring the resultant solution for thirty minutes, Et_3N (2 equiv.) was added. The mixture was kept refluxing for an hour, then cooled down to room temperature. The brown precipitate was filtered off and dried (Yield: 15%). Single crystals for crystal determination were obtained by slow evaporation of the solvent at room temperature. $C_{102}H_{152}N_6Ni_7O_{17}$ (2145.3): calcd. C 57.02, H 7.26, N 3.85; found C 57.23, H 7.16, N 3.93. IR (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (O−H), 1619 (C=N), 1439 (phenyl),1172(C−O). ESI-MS: *m/z* (%) = 553.5 (100) $[H_5L]^+$, 609.5 (26)$[NiH_3L]^+$. $[\alpha]_D^{15} = -98.7$ (*c* = 0.1, $CHCl_3$).

X-ray Crystallography Study: $C_{102}H_{152}N_6Ni_7O_{17}$, M = 2145.27, trigonal, space group $P321$, a = 17.9182(12), b = 17.9182(12), c = 22.363(3) Å, V = 6218.0(10) Å^3, Dc = 1.146 g cm^{-3}, Z = 2, μ = 1.091 mm^{-1}, S = 1.016, $F(000)$ = 2276, T = 293(2) K, $2\theta_{max}$ = 49.98°, 7343 unique data, final $R1$ = 0.0543, $wR2$ = 0.1141 for 5789 observed reflections $[I > 2\sigma(I)]$ with 403 variables. A single crystal was mounted on a glass fiber for measurement. Data were collected on a SMART 4 K CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected data were reduced with the program SAINT, and empirical absorption corrections were done with the SADABS program. The structure was solved by direct methods and refined by least-squares method on F^2_{obs} with the SHELXTL-PC97 software package. CCDC-198224 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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