Volume 35

Number 13

June 19, 1996

Inorganic Chemistry

Communications

Structure and Magnetic Properties of a Heptanuclear Nickel(II) Compound: $[Ni_7(\mu\text{-}NO_2)_8(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(OHpn)_2(Opn)_2]_2 \cdot 7H_2O$

M. Salah El Fallah, Eva Rentschler, Andrea Caneschi, Roberta Sessoli, and Dante Gatteschi*

Dipartimento di Chimica, Università degli Studi di Firenze, Via Maragliano, 75/77, 50144 Firenze, Italy

Received January 5, 1996

Magnetic molecular clusters have attracted much interest in the last few years,[1−4] for their relevance both to biological systems, ranging from the active site of photosystem II[5,6] to ferritin,[7,8] and to the understanding of the mechanism of the transition from ferromagnetic to bulk magnet behavior.[9] In particular, we reported that Mn_{12}[10] and Fe_8[11] clusters show evidence of superparamagnetic behavior. One of the key features for the observation of such behavior is the presence of a large magnetic anisotropy in the cluster. Since nickel(II) is known to have a large single-ion zero-field splitting and often gives rise to ferromagnetic coupling, we decided to systematically investigate these properties of nickel(II) clusters with the aim of isolating new superparamagnetic clusters. We have not been successful so far, but we wish to report here the crystal and the magnetic properties of $[Ni_7(\mu\text{-}NO_2)_8(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(OHpn)_2(Opn)_2]_2 \cdot 7H_2O$ (**1**), in which OHpn is 1,3-diamino-2-propanol.

The structure of the **1** was determined by X-ray crystallography.[12] The asymmetric unit contains two independent clusters and seven water molecules. The structures of the two clusters are very similar; therefore only one cluster will be discussed further.

As shown in Figure 1, the arrangement of the Ni atoms may be described as a distorted hexagon (Ni1−Ni6), with the seventh Ni atom in the center. Although the deviations from planarity for the six Ni atoms are large, ranging from −0.026(2) to 0.999(2) Å, the position of Ni7 can be well distinguished, as it is found 1.842(2) Å above the plane. In the cluster, the nearest-neighbor Ni−Ni distances vary between 3.085(2) and 3.493(2) Å, the average of which is larger than that found in other pentameric Ni(II) complexes with nitrite and μ_3-hydroxo bridges.[13] On the other hand, the shortest distance between Ni atoms belonging to different clusters is 5.39(2) Å. The nickel atoms are found in distorted and variable octahedral environments. The Ni1 and Ni4 atoms are coordinated by two nitrites in a *trans* configuration, two μ_2-alkoxide oxygens of two different amine ligands, and two N atoms of two different amines. Ni2 and Ni5 are coordinated by two N atoms and one oxygen atom of three different nitrite groups, one μ_3-hydroxide oxygen atom, and one N atom of an amine. Ni3 and Ni6 coordinate two different nitrite groups, one μ_2-alkoxide oxygen of an amine ligand, and two different hydroxide oxygen atoms (μ_2 and μ_3). The coordination of Ni3 and Ni6 is completed by one N atom of an amine ligand. Finally the Ni7 atom is coordinated by six oxygen atoms (two nitrite groups and four hydroxide oxygen atoms in two different modes, μ_2 and μ_3).

The Ni−O distances range from 1.988(6) to 2.164(6) Å, whereas the Ni−N bond lengths are larger, varying between 2.117(7) and 2.181(7) Å. All these distances should be considerated as normal, except that of Ni1−N4, which is 2.250(7) Å. In the cluster, there are four different sets of Ni−O−Ni angles which vary in the ranges 112.6(3)−115.2(3), 92.5(2)−94.1(2), 98.8(2)−100.1(1), and 110.3(3)−111.2(3)° correspond-

---

[1] Miller, J. S., Dougherty, D. A., Eds. *Mol. Cryst. Liq.Cryst.* **1989**, *176*.

[2] Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds. *Nato ASI Ser. E* **1991**, *198*.

[3] Heath, S. L.; Powell, A. K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 191.

[4] Taft, K. L.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 191.

[5] Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153

[6] Wemple, M. W.; Tsai, H. L.; Folting, K. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1993**, *32*, 2025 and references therein.

[7] Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

[8] Taft, K. L.; Papaefthymiou, G. C.; Lippard, S. J. *Inorg. Chem.* **1994**, *33*, 1510.

[9] Gatteschi, D.; Pardi, L.; Barra, A.-L.; Müller, A.; Döring, J. *Nature* **1991**, *354*, 463.

[10] Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.

[11] Delfs, C.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Wieghardt, K.; Hanke, D. *Inorg. Chem.* **1993**, *32*, 3099.

[12] X-ray analysis and refinement: brown rectangular crystal, size 0.2 × 0.2 × 0.4 mm, Enraf-Nonius CAD4 diffractometer, Mo Kα radiation, graphite monochromator, corrections applied for Lorentz and polarization effects but not for absorption, $M = 2537.28$, triclinic, $P\bar{1}$, $a = 10.608(2)$ Å, $b = 14.712(4)$ Å, $c = 25.898(6)$ Å, $\alpha = 90.84(2)°$, $\beta = 91.81(2)°$, $\gamma = 90.91(2)°$, $V = 4039.2(2)$ Å^3, $F(000) = 2596$, $Z = 2$, $D_c = 2.086$ g cm^{-3}, $\lambda = 0.7107$ Å, $T = 25$ °C, scan type $\omega - 2\theta$, $5° < 2\theta < 44°$. For 10 449 reflections measured, there were 8890 unique observed reflections with $F_o^2 > 2\sigma(F_o^2)$. $R = 0.054$; $R_w = 0.051$. The crystal structure was solved by direct methods using the SIR 92 program.[24] Refinement was carried out by using the SHELX76 program package.[25] The positions of 40 H atoms were computed and refined with overall isotropic factors, using a riding model. The others were located from a difference Fourier synthesis. All the remaining non-H atoms were treated anisotropically.

[13] Finney, A. J.; Hitchman, M. A.; Raston, C. L.; Rowbottom, G. L.; White, A. H. *Aust. J. Chem.* **1981**, *34*, 2139.

S0020-1669(96)00002-X CCC: $12.00

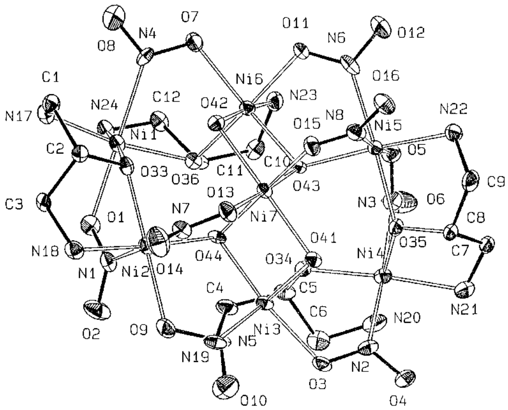

Figure 1. ORTEP view of the heptameric unit of compound **1** with labeled atoms. Selected distances (Å) and angles (deg): Ni1···Ni2 3.484(2), Ni1···Ni6 3.399(2), Ni2···Ni3 3.463(2), Ni2···Ni7 3.308(2), Ni3···Ni4 3.381(2), Ni3···Ni7 3.104(2), Ni4···Ni5 3.486(2), Ni5···Ni6 3.493(2), Ni5···Ni7 3.303(2), Ni6···Ni7 3.085(2), Ni1−O33 2.058(5), Ni1−O36 2.025(6), Ni2−O33 2.067(5), Ni2−O44 1.988(6), Ni3−O34 2.033(6), Ni3−O41 2.192(5), Ni3−O44 2.028(6), Ni4−O34 2.031(6), Ni4−O35 2.093(5), Ni5−O35 2.048(5), Ni5−O43 1.998(5), Ni6−O36 2.050(5), Ni6−O42 2.128(6), Ni6−O43 2.037(5), Ni7−O41 2.105(5), Ni7−O42 2.088(6), Ni7−O43 2.026(5), Ni7−O44 2.021(5); Ni1−O33−Ni2 115.2(3), Ni3−O34−Ni4 112.6(3), Ni4−O35−Ni5 114.7(3), Ni1−O36−Ni6 113.0(3), Ni3−O41−Ni7 92.5(2), Ni6−O42−Ni7 94.1(2), Ni6−O43−Ni7 98.8(2), Ni3−O44−Ni7 100.1(3), Ni5−O43−Ni7 110.3(3), Ni2−O44−Ni7 111.2(3), Ni5−O43−Ni6 119.9(3), Ni2−O44−Ni3 119.1(3).

ing to μ_2-alkoxide, μ_2-hydroxide, and two μ_3-hydroxide oxygen bridges, respectively. The bond angles related with the nitrite ligand vary in the ranges 120.6(5)−124.8(5) and 113.4(5)−117.7(5)° corresponding to Ni−N−O and Ni−O−N angles, respectively. Two of the four OHpn amines are deprotonated, which is in agreement with the total charge of **1**. The same situation was previously seen in analogous Cu(II) and Ni(II) compounds.[14,15]

The variable-temperature magnetic susceptibility data for **1** were recorded between 260 and 2 K.[16] The plot of $\chi_M T$ vs T in Figure 2 shows typical antiferromagnetic behavior, decreasing from 7.971 emu mol^{-1} K at 260 K, which is close to that expected for seven uncoupled $S = 1$ spins, to 1.046 emu mol^{-1} K at 2.2 K. In the cluster, four different superexchange J parameters can be identified, due to the different bridging ligands, whereas the g value is considered isotropic and equal for all Ni(II) ions. The experimental magnetic data have been fitted using the Hamiltonian

$$H = J_1(S_1S_2 + S_1S_6 + S_3S_4 + S_4S_5) + J_2(S_3S_7 + S_6S_7) + J_3(S_2S_7 + S_5S_7) + J_4(S_2S_3 + S_5S_6)$$

where the numbering of the spins follows the numbering of the nickel atoms in Figure 1. The best fit parameters[17] obtained were $J_1 = 8$, $J_2 = -4$, $J_3 = 6$, and $J_4 = 12$ cm^{-1} with $g = 2.18$.

Since the bridging geometries of the eight nitrite ligands exhibit very small variations, they are expected to transmit the same coupling among the nickel atoms. In contrast, the interactions through the alkoxide and hydroxide bridges should differ remarkably due to the large differences found in the bond distances and angles; for these bridges it has been shown that the magnetic behavior is related to the Ni−O−Ni angles in [Ni_4O_4] cubane complexes.[18] These complexes show ferromagnetic exchange interactions when the Ni−O−Ni angle is close to 90° [19,20] or antiferromagnetic interactions if this angle is larger than ca. 101°,[21,22] which is in full agreement with the different J values found for compound **1**.

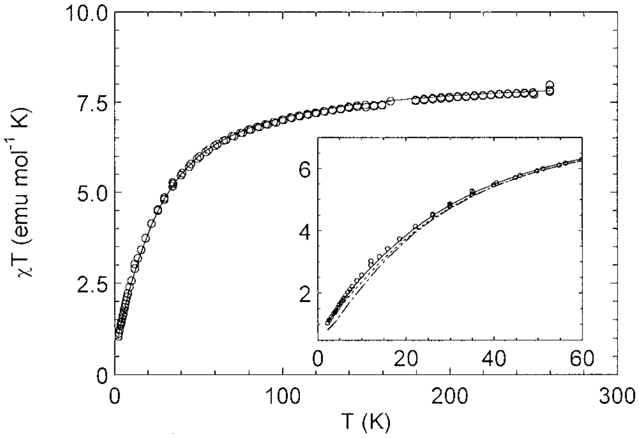

Figure 2. $\chi_M T$ vs T for compound **1**. The solid line corresponds to the best fit (see text), the dotted line corresponds to the best fit with $J_1 = J_3 = J_4 > J_2$, and the dashed line corresponds to the fit with $J_2 < J_1 = J_3 < J_4$.

In our case, the nitrite groups seem to participate very little in the magnetic exchange interactions, while Meyer et al.[23] found remarkable coupling constants of ca. 30 cm^{-1} for a series of nitrite chain compounds; this could be due to the fact that in compound **1** all the nitrite groups bridge two different nickel atoms in a *cis* conformation, while they bridge in a *trans* conformation in the chain compounds.

Supporting Information Available: Tables of complete crystal data, anisotropic thermal parameters, atom coordinates, and bond distances and angles for **1** (16 pages). Ordering information is given on any current masthead page.

IC960002D

---

(14) Bertrand, J. A.; Marabella, C. P.; Vanderveer, D. G. *Inorg. Chim. Acta* **1977**, *25*, L69.

(15) Ribas, J.; Montfort, M.; Costa, R.; Solans, X. *Inorg. Chem.* **1993**, *32*, 695.

(16) The magnetic susceptibility of a powdered sample was measured by using a Métronique MSO3 SQUID magnetometer in the temperature range 260−2 K with applied fields of 1 T from 260 to 30 K and 0.1 T down to 2 K. The contribution of the sample holder was determined separately in the same temperature ranges and fields. Diamagnetic corrections were estimated from Pascal's constants.

(17) In a first approach, we considered the three parameters $J_1 = J_3 = J_4 > J_2$. The best fit parameters obtained were $J_1 = J_2 = J_4 = 8.5$ and $J_2 = -4$ cm^{-1} with $g = 2.18$. Then we kept the J_2 value constant and fitted J_1, J_3, and J_4 with ($J_1 = J_3 < J_4$). The best values obtained were $J_1 = J_3 = 7$ and $J_4 = 12$ cm^{-1}. The same procedure was repeated, but with $J_3 < J_1 < J_4 = 12$, affording values of 6 and 8 cm^{-1} for J_3 and J_1, respectively. The series of calculations were made using the computer program CLUMAG, which uses the irreducible tensor operator formalism (ITO): Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

(18) Halcrow, M. A.; Sun, J. S.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1995**, *34*, 4167.

(19) (a) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1456. (b) Betrand, J. A.; Ginsberg, A. P.; Kaplan, R. I.; Kirkwood, C. E.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1971**, *10*, 240.

(20) El Fallah, M. S.; Rentschler, E.; Caneschi, A.; Gatteschi, D. *Inorg. Chim. Acta*, in press.

(21) Gladfelter, W. L.; Lynch, M. W.; Schaefer, W. P.; Hendrickson, D. N.; Gray, H. B. *Inorg. Chem.* **1981**, *20*, 2390.

(22) Ballester, L.; Coronado, E.; Gutiérrez, A.; Monge, A.; Perpinan, M.-F.; Pinilla, E.; Rico, T. *Inorg. Chem.* **1992**, *31*, 2053.

(23) Meyer, A.; Gleizes, A.; Girerd, J. J.; Verdaguer, M.; Kahn, O. *Inorg. Chem.* **1982**, *21*, 1729.

(24) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1994**, *27*, 1045.

(25) Sheldrick, G. M. SHELX 76: Program for Crystal Structure Determination. University of Cambridge, England, 1976.