Inorg. Chem. **2003**, *42*, 4501–4503

Inorganic Chemistry
Communication

Heterometallic Hexanuclear Cluster with an $S = 8$ Spin Ground State: $Mn^{II}\{Mn^{II}(hfac)_2\}_3\{Ni^{II}(pao)_3\}_2$ (hfac$^-$ = Hexafluoroacetylacetonate, pao$^-$ = Pyridine-2-aldoximate)

Hitoshi Miyasaka,*[†,‡] Tomohiro Nezu,[†] Fumiyasu Iwahori,[†] Sachie Furukawa,[†] Kunihisa Sugimoto,[§] Rodolphe Clérac,*[||] Ken-ichi Sugiura,[†] and Masahiro Yamashita[†]

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan, "Structural Ordering and Physical Properties," PRESTO, Japan Science and Technology Corporation, Japan, X-ray Research Laboratory, Rigaku Co., Ltd., 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan, and Centre de Recherche Paul Pascal, CNRS UPR 8641, 115 Avenue du Dr. A. Schweitzer, 33600 Pessac, France

Received March 20, 2003

The heterometallic $Mn^{II}_4Ni^{II}_2$ title compound has been synthesized and characterized by X-ray crystallography. The compound consists of a Ni–Mn–Ni linear moiety, $[\{Ni–(\mu\text{-}NO)_3\}_2–Mn]$, linked by oximate bridges and three Mn(II) hfac terminal units attached by oximate oxygens in a di-μ-oxo fashion, forming a novel heterometallic cluster: $Mn\{Mn(hfac)_2\}_3\{Ni(pao)_3\}_2$ (**1**). Magnetic measurements reveal the antiferromagnetic nature of the oximate pathway between Mn(II) and Ni(II) metal ions, which imposes an unusual high-spin ground state ($S = 8$) for **1**.

In recent years, high-spin clusters have been attracting much attention in the fields of molecule-based magnetism and solid-state physics. One of the reasons is the emergence of single-molecule magnets (SMMs) in the beginning of the 1990s. The first example of an SMM is the mixed-valent dodecanuclear Mn cluster, $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$, which possesses an $S = 10$ spin ground state and a large uniaxial anisotropy.[1] To date, a number of SMMs with peculiar magnetic properties such as metastable magnetization,[2] quantum spin tunneling,[3] and quantum phase interference have been reported.[4] A major part of the research aimed at the development of new SMMs and giant-spin paramagnetic clusters is devoted to the fine control of magnetic interactions between magnetic centers.[5] Knowledge of the magneto-structural correlations between homometallic ions with different oxidation states or heterometallic centers is considered to be the key to the design of such new high-spin complexes. Nevertheless, examples of heterometallic clusters are usually limited to those with low nuclearity, and those exhibiting a large high-spin ground state are still extremely rare.[5] In this regard, we focused on the assembly of heterometallic ions by oximate linkages, which is known to act as a good magnetic pathway. Among the available ways of introducing oximate bridges, we selected the pyridine-2-aldoximate ligand.[6−9] Here we report the synthesis, structural determination, and magnetic properties of a novel

---

* To whom correspondence should be addressed. E-mail: miyasaka@comp.metro-u.ac.jp (H.M.); clerac@crpp.u.bordeaux.fr (R.C.). Fax: +81-426-77-2525 (H.M.); +33-556-84 5600 (R.C.).

[†] Tokyo Metropolitan University.

[‡] PRESTO, JST.

[§] Rigaku Co. Ltd.

[||] Centre de Recherche Paul Pascal.

(1) Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* **1991**, *113*, 5873.

(2) (a) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (b) Eppley, H. J.; Tsai, H.-L.; de Vries, N.; Folting, K.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 301. (c) Aubin, S. M. J.; Sun, Z.; Pardi, L.; Krzystek, J.; Folting, K.; Brunel, L.-C.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1999**, *38*, 5329.

(3) (a) Friedman, J. R.; Sarachik, M. P.; Tejada, J.; Ziolo, R. *Phys. Rev. Lett.* **1996**, *76*, 3830. (b) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145.

(4) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133.

(5) (a) Schake, A. R.; Tsai, H.-L.; Webb, R. J.; Folting, K.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1994**, *33*, 6020. (b) Larionova, J.; Gross, M.; Pilkington, M.; Andres, H.; Stoeckli-Evans, H.; Güdel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605. (c) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, H. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (d) Berseth, P. A.; Sokol, J. J.; Shores, M. P.; Heinrich, J. L.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 9655.

(6) Birkelbach, F.; Winter, M.; Flörke, U.; Haupt, H.; Butzlaff, C.; Lengen, M.; Bill, E.; Trautwein, A. X.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1994**, *33*, 3990.

(7) (a) Chaudhuri, P.; Winter, M.; Della Védova, B. P. C.; Bill, E.; Trautwein, A.; Gehring, S.; Fleischhauer, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 2148. (b) Chaudhuri, P.; Winter, M.; Della Védova, B. P. C.; Fleischhauer, P.; Haase, W.; Flörke, U.; Haupt, H. *Inorg. Chem.* **1991**, *30*, 4777. (c) Birkelbach, F.; Weyhermüller, T.; Lengen, M.; Gerdan, M.; Trautwein, A. X.; Wieghardt, K.; Chaudhuri, P. *J. Chem. Soc., Dalton Trans.* **1997**, 4529. (d) Burdinski, D.; Birkelbach, F.; Weyhermüller, T.; Flörke, U.; Haupt, H.; Lengen, M.; Trautwein, A. X.; Bill, E.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1998**, *37*, 1009. (e) Birkelbach, F.; Flörke, U.; Haupt, H.; Butzlaff, C.; Trautwein, A. X.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1998**, *37*, 2000.

10.1021/ic034302o CCC: $25.00

heterometallic $Mn^{II}_4Ni^{II}_2$ cluster, Mn{Mn(hfac)$_2$}$_3${Ni(pao)$_3$}$_2$ (**1**) (hfac$^-$, hexafluoroacetylacetonate; pao$^-$, pyridine-2-aldoximate). In **1**, the antiferromagnetic couplings mediated by oximate bridges between Ni(II) and Mn(II) lead to an $S = 8$ spin ground state.

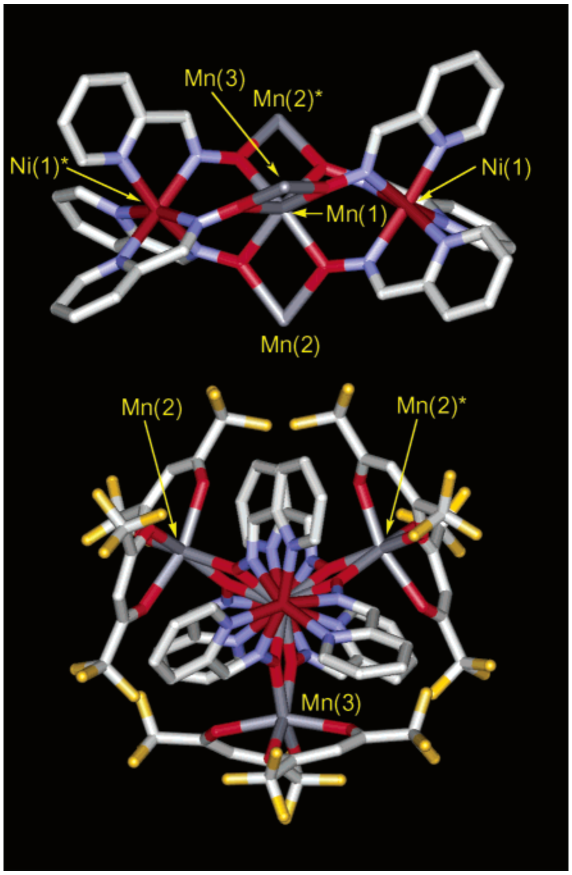
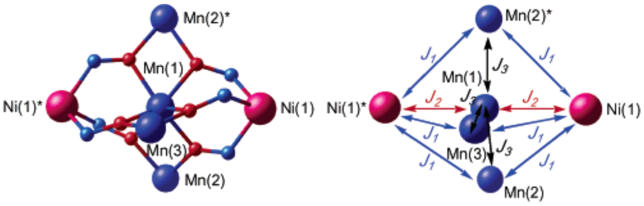


Figure 1. Molecular structure of **1**: side view (top) and a view projected along [Ni(1)−Mn(1)−Ni(1)*] axis (bottom). In the side view (top), the hfac$^-$ ligands on the terminal Mn ions are omitted for clarity.

Scheme 1



Heterometallic cluster **1** is obtained in good yield from the reaction of Mn(hfac)$_2$ with Ni(pao)$_2$(py)$_2$ in chloroform.[10,11] Simultaneous to the assembly process of **1**, a complicated ligand exchange occurs to form a Ni(pao)$_3^-$ building block and free Mn(II) ion, both of which are derived from the partial replacement of the hfac ligands of the Mn(hfac)$_2$ precursor, which is followed by the formation of a cluster moiety of [(pao)$_3$Ni−Mn−Ni(pao)$_3$]. Nevertheless, such byproducts as Ni(hfac)$_2$ or Ni(hfac)$_2$(py)$_2$, which are predicted to be formed from the ligand-exchange reaction, are not cocrystallized from the solution. The structure of neutral cluster **1** is depicted in Figure 1.[12] Compound **1** crystallizes in tetragonal space group $P4_32_12$ ($Z = 4$). The heterometallic cluster lies on the C_2 axis located on Mn(1) and Mn(3) metal ions. On the basis of bond distance and charge balance considerations, the three types of Mn ion are divalent, and **1** is therefore neutral. All metal centers adopt a slightly distorted octahedral geometry. The Ni(II) ion is surrounded by three pao$^-$ ligands in a perpendicular fashion with average Ni−N bond distances of Ni−N$_{oximate}$ = 2.042(4) Å and Ni−N$_{py}$ = 2.109(4) Å. The coordinating oximate groups are gathered on one side; therefore, [Ni(pao)$_3$]$^-$ acts as a tridentate coordination-donor building block. Two [Ni(pao)$_3$]$^-$ units and their six oximate groups cap the centered octahedral Mn(II) ion with an average Mn−O bond distance of 2.171(3) Å to form a bridging motif of [{Ni−(μ-NO$_{pao}$)$_3$}$_2$−Mn]. Each of these oximate oxygens further links to a Mn$_{terminal}$(hfac)$_2$ unit (with Mn$_{terminal}$ as Mn(2), Mn(2)*, or Mn(3)) in the [Mn$_{central}$(1)−(μ-O$_{ox}$)$_2$−Mn$_{terminal}$] mode with an average Mn$_{terminal}$−O$_{ox}$ distance of 2.132(3) Å. The crucial role played by the oximate oxygen in assembling and fortifying the hexanuclear core should be emphasized here. Indeed, as the Mn(II) metal ions are all connected through the −O$_{ox}$N− bridge to Ni(II) sites, the oximate oxygens further cement the cluster through (μ-O$_{ox}$)$_2$ that connects the three terminal Mn(II) species to the central one (Scheme 1). The average intermetal distances within the cluster are Ni−Mn$_{center}$ = 3.65 Å, Ni−Mn$_{terminal}$ = 5.05 Å, Mn$_{center}$−Mn$_{terminal}$ = 3.49 Å, and Mn$_{terminal}$−Mn$_{terminal}$ = 6.05 Å.

The magnetic susceptibility of a polycrystalline sample of **1** is studied from 300 to 1.9 K at 1000 Oe. The χT versus T plot, shown in Figure 2, slightly decreases from 17.8 emu·

---

(8) Chaudhuri, P.; Birkelbach, F.; Winter, M.; Staemmler, V.; Fleischhuer, P.; Hasse, W.; Flörke, U.; Haupt, H. *J. Chem. Soc., Dalton Trans.* **1994**, 2313.

(9) Sreerama, S. G.; Pal, S. *Inorg. Chem.* **2002**, *41*, 4843.

(10) Krause, R. A.; Busch, D. H. *J. Am. Chem. Soc.* **1960**, *82*, 4830.

(11) The synthesis of **1** was carried out under dried nitrogen atmosphere. First, a diethyl ether/*n*-heptane solution containing Mn(hfac)$_2$(H$_2$O)$_2$ (0.127 g, 0.25 mmol) was refluxed and then evaporated to remove solvents. This procedure was repeated three times. The orange powder finally obtained was dissolved in a solution of diethyl ether/CHCl$_3$ (3 mL/20 mL). The resultant solution was allowed to diffuse into a CHCl$_3$ solution (20 mL) containing Ni(pao)$_2$(py)$_2$ (0.21 g, 0.25 mmol). Red-orange single crystals of **1** were obtained after one week in 34% yield (48 mg, 0.021 mmol). An alternative route for obtaining **1** was found by simply stirring together Mn(hfac)$_2$ and Ni(pao)$_2$(py)$_2$ precursors. An orange powder was obtained in 62% yield (88 mg, 0.038 mmol). Physical measurements confirmed that this orange powder and the red-orange single crystals are identical. Nevertheless, the crystalline sample was used systematically for elemental analysis, infrared spectroscopy, and all magnetic measurements. Calcd for **1**, $C_{66}H_{36}N_{12}O_{18}F_{36}Ni_2Mn_4$: C, 34.37; H, 1.57; N, 7.29. Found: C, 34.06; H, 1.64; N, 7.41. IR (Nujol) ν(C=N) = 1606.6 cm^{-1}, ν(hfac) = 721.3, 1145.6, 1647.1 cm^{-1}.

(12) Crystal structure data for **1**: $C_{66}H_{36}N_{12}O_{18}F_{36}Mn_4Ni_2$, $M_r = 2306.17$, orange prism, tetragonal space group $P4_32_12$ (No. 96), $a = 16.701(3)$ Å, $c = 30.590(5)$ Å, $V = 8532.5(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.795$ g cm^{-3}, $T = 113$ K, $F(000) = 4560$, μ(Mo Kα) = 1.157 mm^{-1}, $2\theta_{max} = 59.0°$, 38927 reflections collected, 7441 unique ($R_{int} = 0.040$), variable parameters = 642, R1 = 0.0440 using 7105 reflections with $I > 2\sigma(I)$, wR2 = 0.1140 (all data), GOF = 1.066, min./max. residual electron density = −0.73/1.93 e Å^{-3}. The structure was solved by direct methods (SIR97: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined by full-matrix least-squares treatments on F^2. The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were introduced as fixed contributors. Additional crystallographic details are available as Supporting Information or by application to the Cambridge Data Centre (CCDC-202735), 12 Union Road, Cambridge CB21EZ, U.K. (Fax: (+44) 1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

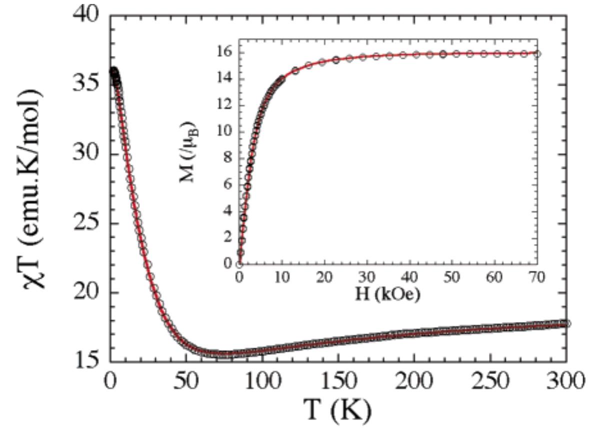


Figure 2. Temperature dependence of χT product measured at 1000 Oe in the temperature range 1.9−300 K. The solid line is the best fit obtained with the magnetic model described in the text (Scheme 1). Inset: field dependence of magnetization measured at 1.9 K, where the solid line is the best fit obtained using a Brillouin function with $S = 8$ ($g = 2$).

K/mol at 300 K to reach a minimum of 15.6 emu·K/mol at 75 K. At even lower temperatures, χT increases to reach a plateau at 36.0 emu·K/mol below 2.5 K. This low-temperature value of χT suggests an $S = 8$ ground state with $g \approx 2$ as the predicted value because the $S = 8$ spin state is 36.0 emu·K/mol assuming $g = 2.00$. At 1.9 K, the field dependence of magnetization saturates at 16 μ_B and is perfectly reproduced using an $S = 8$ Brillouin function with $g = 2.00$ (inset of Figure 2). This result confirms the $S = 8$ ground state of **1**.

Considering the molecular structure of **1**, the possible exchange pathways are shown in Scheme 1. Due to the geometric similarity of the −NO− bridges between Ni(1) and $\mathrm{Mn}_{\mathrm{terminal}}$ and the necessity to reduce the number of parameters in the model, magnetic interactions are imposed equal the exchange coupling parameter, J_1, even if they are crystallographically not symmetrically related. The same approximation is adopted for exchange interactions between Mn(1) and $\mathrm{Mn}_{\mathrm{terminal}}$ (J_3). Therefore, the magnetic data are analyzed with the following Hamiltonian:

$$H = -2J_1[\sum_{i=2,2^*,3} S_{\mathrm{Ni}(1)}S_{\mathrm{Mn}(i)} + S_{\mathrm{Ni}(1)^*}S_{\mathrm{Mn}(i)}] - 2J_2[\sum_{i=1,1^*} S_{\mathrm{Mn}(1)}S_{\mathrm{Ni}(i)}] - 2J_3[\sum_{i=2,2^*3} S_{\mathrm{Mn}(1)}S_{\mathrm{Ni}(i)}]$$

The complicated topology of the magnetic pathways precludes a simple calculation of the cluster's spin levels by Kambe's method;[13] hence, we use a more general procedure developed by Clemente-Juan and co-workers (MAGPACK program).[14] From a simulation with the Hamiltonian, the best set of parameters is $g = 2.0$, $J_1/k_B = -4.3(2)$ K, $J_2/k_B = -10(1)$ K, and $J_3/k_B = -0.57(5)$ K (red line in Figure 2). Comparison of J_1 and J_2 with previously published values is not possible due to the fact that, as far as we know, **1** presents the first example of Ni(II)−Mn(II) magnetic interactions mediated by oximate linkages. Nevertheless, it should be noted that the obtained J_2 is more than twice the value of J_1. This result is in agreement with the structure of **1** that reveals that J_2 is mediated by three −NO− bridges when only one of these links supports J_1. The obtained value of J_3 is also reasonable considering that Mn(II) compounds with bis(μ-O) bridging are generally weakly coupled either antiferromagnetically[15] or ferromagnetically.[15a,16] A simple picture of the $S = 8$ ground state is given by all the Mn(II) $S = {}^5/_2$ spins aligning in the same direction in opposition to Ni(II) $S = 1$ spins. Indeed, this configuration is obtained because the antiferromagnetic Mn−Ni interactions (J_1 and J_2), which force all Mn spins to be parallel, overcome the weak antiferromagnetic Mn−Mn interaction (J_3) ($|J_1|$ and $|J_2| \gg |J_3|$).

In summary, a new heterometallic $\mathrm{Mn^{II}}_4\mathrm{Ni^{II}}_2$ cluster, $\mathrm{Mn\{Mn(hfac)_2\}_3\{Ni(pao)_3\}_2}$ (**1**), was synthesized and structurally characterized. Although **1** was the result of complicated ligand-exchange reactions, it was selectively obtained in high yield. As expected, the use of the pao ligand led to the formation of oximate bridges between Mn(II) and Ni(II) that mediated the antiferromagnetic interactions, as shown by magnetic susceptibility measurements. The architecture of the $\mathrm{Mn_4Ni_2}$ cluster and the strength of the antiferromagnetic Mn−Ni interaction imposed an overall high-spin ground state: $S = 8$.

Acknowledgment. This work was supported by Japan Science and Technology Corporation (JST) (H.M.) and the CNRS and the Conseil Regional d'Aquitaine (R.C.). The authors are also grateful to J. Modesto Clemente-Juan for explaining and providing the MAGPACK package. The Université de Bordeaux I is also acknowledged for funding the scientific stay of H.M. in November 2002.

Supporting Information Available: X-ray crystallographic file of **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034302O

---

(13) Kambe, K. *J. Phys. Soc. Jpn* **1950**, *5*, 48.

(14) (a) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *Inorg. Chem.* **1999**, *38*, 6081. (b) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *J. Comput. Chem.* **2001**, *22*, 985.

(15) (a) Wada, H.; Motoda, K.; Ohba, M.; Sakiyama, H.; Matsumoto, N.; Okawa, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1105. (b) Pence, L. E.; Caneschi, A.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 3069. (c) Nihei, M.; Hoshino, N.; Ito, T.; Oshio, H. *Chem. Lett.* **2002**, 1016.

(16) (a) Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683. (b) Chang, H.; Larsen, S. K.; Boyd, P. D. W.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4565. (c) Wesolek, M.; Meyer, D.; Osborn, J. A.; Cian, A. D.; Fischer, J.; Derory, A.; Legoll, P.; Drillon, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1592.