

Linking Magnetic Clusters: Ferrimagnetic Interactions in a Nonanuclear Nickel(II) Cluster

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A nonanuclear nickel(II) cluster, $[\text{Ni}_9(\text{H}_4\text{L})_2(\text{OMe})_6(\text{OAc})_{10}(\text{H}_2\text{O})_4] \cdot 14\text{H}_2\text{O}$ (**1**·14H₂O), was synthesized by the reaction of an amide ligand H₅L (= 2-hydroxy-4,6-dimethyl-N1,N3-bis(2-hydroxyethyl)-1,3-benzeneddicarboxamide) with nickel acetate in the presence of triethylamine. The cluster molecule consists of two cubane units and a mononuclear central moiety, connected by acetate bridges. In the cubane cores, ferromagnetic interactions between nickel ions were operative, and the total spin ground state was $S = 7$ due to ferrimagnetic interactions between the two ferromagnetic cubane cores and the mononuclear nickel spacer.

Polynuclear metal complexes have been afforded much interest due to their structure-specific physical properties, such as single molecule magnetism,¹ multiredox behavior,² and catalytic functionality.³ Cubane-type clusters are a well-known class of magnetic molecules, in which the metal ions are connected by alkoxo or phenoxy bridges and tend to exhibit ferromagnetic interactions.⁴⁻¹⁰ The [Cu₄] complex, [Cu₄(eia)₄] (H₂eia: 7-hydroxy-4-methyl-5-azahept-4-en-2-one), is a typical example of such a ferromagnetic cluster, possessing an $S = 2$ spin ground state through the alignment of its four $S_{\text{Cu}} = 1/2$ spins.^{5a} Many [M₄] cubane-type clusters have been reported, and their magnetic properties have been investigated intensively.⁶⁻¹⁰ In cubane cores, the metal ions are usually connected at angles close to 90° by oxygen donor atoms, resulting in the accidental orthogonality of magnetic orbitals. For the purpose of constructing new magnetic cluster molecules with high-spin ground states, using ferromagnetic cubane cores as building units may be a good strategy. One of our approaches to the assembly of metal ions is through alkoxo-bridging multidentate Schiff-base-type ligands, such as 2,6-bis[N-(2-hydroxyethyl)iminomethyl]-4-methylphenol (H₃bemp).¹¹ Homo- and heterometal polynuclear complexes have been obtained, and most have shown antiferromagnetic or ferrimagnetic interactions. The next key challenge in this research is to develop a system by which ferromagnetic units can be extended, while preserving or enhancing their large ground spin states by the addition of further magnetic ions. In this work, a nonanuclear nickel(II) complex, $[\text{Ni}_9(\text{H}_4\text{L})_2(\text{OMe})_6(\text{OAc})_{10}(\text{H}_2\text{O})_4] \cdot 14\text{H}_2\text{O}$ (**1**·14H₂O), was obtained by the reaction of H₅L with Ni(OAc)₂·4H₂O in the presence of triethylamine.¹⁴ Single-crystal X-ray analysis revealed that complex **1**·14H₂O·

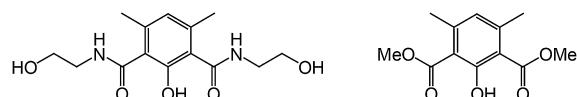


Chart 1.

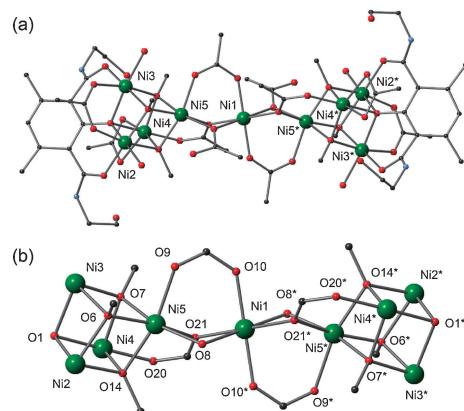


Figure 1. (a) Molecular structure of **1**. C, gray; N, light blue; O, red; Ni(II), light green. Hydrogen atoms and solvent molecules are excluded for clarity. (b) Core structure of **1**. Symmetry operation: * $-1/3 - x, 1/3 - y, 1/3 - z$.

7MeOH·5Et₂O was a nonanuclear cluster with two tetranuclear cubane cores and mononuclear linkage unit (Figure 1).¹⁴

The asymmetric unit is a half of $[\text{Ni}_9(\text{H}_4\text{L})_2(\text{OMe})_6(\text{OAc})_{10}(\text{H}_2\text{O})_4]$, with an inversion center at the Ni1 site. Four nickel ions (Ni2–Ni5) assembled to form a cubane structure via MeO⁻ bridges. The average Ni–O–Ni bond angle is 96.22° in the cubane core, which will mediate ferromagnetic interactions due to the accidental orthogonality of magnetic orbitals. Three acetate ions bridge between the cubane core and the central nickel ion in different coordination manners. One acetate anion (with O9 and O10 donor atoms) bridges between Ni1 and Ni5 in the common *syn-syn* carboxylate configuration, while the O20 and O21 donating acetate ion connects three nickel ions (Ni1, Ni5, and Ni4) in the (1 κ O:2 κ O') manner. The remaining acetate anion (with O8 and O18) acts as a μ_2 -bridging unit between the Ni1 and Ni5 ions via the O8 donor atom. All Ni ions have octahedral geometry with six oxygen donor atoms. H₅L behaves as a multidentate ligand via three oxygen donor atoms and binds two nickel ions through its phenoxy oxygen. The pendant ethyl alcohol moieties are not involved in coordination bonds. The remaining coordination sites of the cubane nickel ions are occupied by bidentate acetate ions and water molecules.

The temperature dependence of magnetic susceptibility for **1** is shown in Figure 2. The $\chi_m T$ value of 11.372 emu mol⁻¹ K at 300 K increased as the temperature was lowered, reaching a maximum value of 21.701 emu mol⁻¹ K at 1.8 K. The spin only

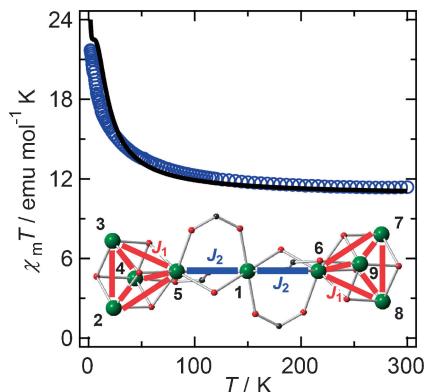


Figure 2. Plots of $\chi_m T$ vs. T for **1**. Solid line corresponding to the data fitted using the parameters described in the text. Inset: fitting model.

value of nine magnetically uncorrelated Ni(II) ions is $9.00 \text{ emu mol}^{-1} \text{ K}$ with $g = 2.00$. The maximum value at 1.8 K is smaller than the expected value of $45.00 \text{ emu mol}^{-1} \text{ K}$, which is estimated based on the perfect ferromagnetic coupling ($S_T = 9$) of all nine Ni(II) ions, but is close to the spin only value of $28.00 \text{ emu mol}^{-1} \text{ K}$ derived from $S_T = 7$ ferrimagnetic spin ground state. In the low-temperature region, the observed $\chi_m T$ values may show the effects of magnetic anisotropy, reaching a lower magnetic moment than expected. The existence of magnetic anisotropy is suggested by the reduced magnetization measurements; however, the zero-field splitting parameter could not be simulated for the $S_T = 7$ spin state. Further measurements, such as HF-EPR spectra, may help to elucidate the deviation.

The magnetic behavior was simulated using a two J model based on nine spin centers and is depicted in Figure 2 inset.¹⁴ The intracubane magnetic interactions J_1 were estimated to be ferromagnetic $J_1 = +3.3 \text{ K}$, whereas antiferromagnetic interactions of $J_2 = -1.2 \text{ K}$ between the cubane core and mononuclear unit were suggested ($g = 2.18$). Note that the plateau in fitted $\chi_m T$ values (ca. $23 \text{ emu mol}^{-1} \text{ K}$) at around 2 K corresponds to the onset of antiferromagnetic interactions between the two $S = 4$ cubanes and the central $S = 1$ nickel(II) ion. In the previously reported $[\text{Ni}_4]$ cubane complexes, ferromagnetic interactions with exchange constant of around $2\text{--}15 \text{ K}$ were calculated, leading to $S_T = 4$ spin ground states.^{6b} In this cluster, the intracubane coupling constant was of the same order. When considering the magnetic path via the acetate bridges between cubane and mononuclear nickel linker, the $\mu_2\text{-O}^-$ bridge is expected to predominate over the $\mu_2\text{-acetato}$ bridge. Although the $\text{Ni}_1\text{-O-Ni}_5$ angle of the $\mu_2\text{-O}(8 \text{ and } 21)$ bridges is within the expected range for ferromagnetic coupling ($<98^\circ$),¹² the deviation from coplanarity (dihedral angle: 144°) of the two mean equatorial planes, defined by $(\text{Ni}_1\text{O}_8\text{O}_2\text{O}_2^*,\text{O}_2\text{O}_2^*)$ and $(\text{Ni}_5\text{O}_6\text{O}_7\text{O}_8\text{O}_2)$ respectively, weakens the expected ferromagnetic contribution. Thus the effect of the *syn-syn* type carboxylato bridges (O_9O_10), known to propagate antiferromagnetic interactions, is increased.¹³ Complex **1**, therefore, displays overall ferrimagnetic interactions.

In summary, a ferrimagnetic nonanuclear nickel cluster composed of two ferromagnetic cubane cores and mononuclear unit was prepared using a multidentate amide ligand. This work

is being extended to use multidentate ligands to stabilize further extended magnetic clusters.

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References and Notes

- 1 D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford Press, New York, **2006**. doi:10.1093/acprof:oso/9780198567530.001.0001.
- 2 a) V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759. b) T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, J. Washington, C. P. Kubiak, *Science* **1997**, *277*, 660.
- 3 a) K. A. Gardner, J. M. Mayer, *Science* **1995**, *269*, 1849. b) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, M. Micheloni, *Coord. Chem. Rev.* **2008**, *252*, 1121. c) G. Christou, *Acc. Chem. Res.* **1989**, *22*, 328.
- 4 K. Isobe, A. Yagasaki, *Acc. Chem. Res.* **1993**, *26*, 524.
- 5 a) J. A. Bertrand, J. A. Kelley, *Inorg. Chim. Acta* **1970**, *4*, 203. b) R. Mergehenn, L. Merz, W. Haase, R. Allmann, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 505. c) D. Maity, A. D. Jana, M. Debnath, N. G. R. Hearn, M.-H. Sie, H. M. Lee, R. Clérac, M. Ali, *Eur. J. Inorg. Chem.* **2010**, *3484*. d) C. Aronica, G. Chastanet, G. Pilet, B. L. Guennic, V. Robert, W. Wernsdorfer, D. Luneau, *Inorg. Chem.* **2007**, *46*, 6108.
- 6 a) B. F. Abrahams, T. A. Hudson, R. Robson, *Chem.—Eur. J.* **2006**, *12*, 7095. b) A. Sieber, C. Boskovic, R. Bircher, O. Waldmann, S. T. Ochsenbein, G. Chaboussant, H. U. Güdel, N. Kirchner, J. van Slageren, W. Wernsdorfer, A. Neels, H. Stoeckli-Evans, S. Janssen, F. Juranyi, H. Mutka, *Inorg. Chem.* **2005**, *44*, 4315. c) A. Ferguson, M. Schmidtmann, E. K. Brechin, M. Murrie, *Dalton Trans.* **2011**, *40*, 334.
- 7 a) E.-C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, M. Ledezma-Gairaud, G. Christou, *J. Appl. Phys.* **2002**, *91*, 7382. b) K. W. Galloway, A. M. Whyte, W. Wernsdorfer, J. Sanchez-Benitez, K. V. Kamenev, A. Parkin, R. D. Peacock, M. Murrie, *Inorg. Chem.* **2008**, *47*, 7438. c) A. Scheurer, A. M. Ako, R. W. Saalfrank, F. W. Heinemann, F. Hampel, K. Petukhov, K. Gieb, M. Stocker, P. Müller, *Chem.—Eur. J.* **2010**, *16*, 4784.
- 8 a) H. Oshio, N. Hoshino, T. Ito, M. Nakano, *J. Am. Chem. Soc.* **2004**, *126*, 8805. b) C. R. Sharp, J. S. Duncan, S. C. Lee, *Inorg. Chem.* **2010**, *49*, 6697. c) F. Piga, F. Moro, I. Krivokapic, A. J. Blake, R. Edge, E. J. L. McInnes, D. J. Evans, J. McMaster, J. van Slageren, *Chem. Commun.* **2012**, *48*, 2430.
- 9 W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, G. Christou, *Nature* **2002**, *416*, 406.
- 10 a) M.-C. Suen, J.-C. Wang, *Inorg. Chem. Commun.* **2006**, *9*, 478. b) B.-Q. Ma, D.-S. Zhang, S. Gao, T.-Z. Jin, C.-H. Yan, G.-X. Xu, *Angew. Chem., Int. Ed.* **2000**, *39*, 3644.
- 11 a) G. N. Newton, S. Yamashita, K. Hasumi, J. Matsuno, N. Yoshida, M. Nihei, T. Shiga, M. Nakano, H. Nojiri, W. Wernsdorfer, H. Oshio, *Angew. Chem., Int. Ed.* **2011**, *50*, 5716. b) T. Shiga, T. Onuki, T. Matsumoto, H. Nojiri, G. N. Newton, N. Hoshino, H. Oshio, *Chem. Commun.* **2009**, 3568.
- 12 O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, **1993**.
- 13 a) A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, *Chem.—Eur. J.* **2001**, *7*, 627. b) P. Mukherjee, M. G. B. Drew, C. J. Gómez-García, A. Ghosh, *Inorg. Chem.* **2009**, *48*, 5848.
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