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The “Building-Block” Assembly of a [$Ni_{12}Mn_6$] Aggregate

Gang Wu,[a,d] Rodolphe Clérac,[b] Wolfgang Wernsdorfer,[c] Shilun Qiu,*[d]
Christopher E. Anson,[a] Ian J. Hewitt,[a] and Annie K. Powell*[a]

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Reaction of $Mn^{II}(bdoa)(H_2O)_3$ with $Ni(CH_3COO)_2 \cdot 3H_2O$ in methanol gives a heterometallic cluster, $[Ni_{12}Mn_6(bdoa)_6(O_2CMe)_{12}(\mu_3\text{-}OMe)_{12}(MeOH)_{12}] \cdot 21MeOH$, which was structurally characterised by single-crystal X-ray diffraction and possesses three self-assembled tetranuclear nickel cubes connected by a $Mn^{II}_6(bdoa)_6(CH_3COO)_3$ subunit. The magnetic properties were studied in detail and indicate that the compound possesses a high density of spin states with small energy gaps between them.

One of the principal synthetic challenges in the area of polynuclear metal complexes is control of molecular topology. In recent years, this has become of particular importance in the field of Single-Molecule Magnets, in which a combination of high-spin ground states and uniaxial anisotropy leads to an energy barrier to the reversal of the magnetization.[1] Heterometallic aggregates are also of particular interest in the understanding of magnetic interactions between different spin carriers.[2] For the construction of such aggregates, the “metal complex as ligand” approach has often proved to be fruitful in the designed synthesis of compounds,[3] amongst the most successful examples of which are the pre-designed metal-cyanide complexes. By careful selection of such building blocks, the fine control of target compounds with desirable architectures and magnetic properties therefore becomes a reality.[3c,3d,3f] Such a strategy has also been successfully employed in the synthesis of framework compounds constructed from secondary building units (SBUs) in which coordination-compound units are connected through rigid ligands such as 1,3,5-benzenetricarcoxylate or 4,4′-bipyridyl.[4] Using such ideas we thought it should be possible to construct a discrete molecule by choosing the correct combination of SBUs or SBU precursors. For example, a suitable metal-complex building block is one that possesses coordinated functional groups, such as carboxylate groups, which can form magnetically active bridges to other paramagnetic metal ions, and/or has exchangeable terminal ligands (e.g. H_2O, MeOH) that can be replaced by bridging units from other metal complexes. On the other hand, synthetic conditions can be chosen to favour known self-assembly motifs such as metal-cubane structures. Ideally, the components should be soluble in common solvents, and the desired structural motifs should be conserved during the reaction leading to a predictable final structure. Here we present the realisation of such a strategy with the synthesis, structure and magnetic properties of the large heterometallic aggregate $[Ni_{12}Mn_6(bdoa)_6(O_2CMe)_{12}(\mu_3\text{-}OMe)_{12}(MeOH)_{12}] \cdot 21MeOH$ (**2**·21MeOH) ($bdoa^{2-}$ = benzene-1,2-dioxyacetate), which can be described in terms of a trigonal prismatic framework that corresponds to a central $\{Mn^{II}_6(bdoa)_6(\mu\text{-}O_2CMe)_3\}$ core decorated by three self-assembled $\{Ni_4(\mu_3\text{-}OMe)_4\}$ cubane units.

The complex $[Mn^{II}(bdoa)(H_2O)_3]$ (**1**) was selected as the mononuclear, metal-complex building block since, as the X-ray crystal structure[5] shows, the compound is monomeric and has a seven-coordinate metal centre, the tetradentate ligand and three aqua ligands forming a pentagonal-bipyramidal geometry (Figure 1 top). In this way, the two non-coordinated oxygen atoms of the carboxylate groups can be used to form bridges to other metal centres and the three *mer*-distributed aqua ligands can either be replaced by other bridging units, as we indeed observe in the final product, or be deprotonated to form single- or double-hydroxo bridges to other metal centres.

Reaction of complex **1** with $Ni(O_2CMe)_2 \cdot 3H_2O$ in methanol in a 1:2 molar ratio gave pale-green plate-like crystals of **2**·21MeOH in good yield after one week. The structure of **2**, viewed down the molecular threefold axis, is shown in Figure 1. The structure can be described as being built up

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[a] Institute für Anorganische Chemie, Universität Karlsruhe,
Engesserstr. Geb 30,45, 76128 Karlsruhe, Germany
Fax: +49-721-608-8142
E-mail: powell@chemie.uni-karlsruhe.de
[b] Centre de Recherche Paul Pascal, CNRS UPR-8641,
115 Av. Albert Schweitzer, 33600 Pessac, France
[c] Laboratoire Louis Néel, CNRS,
B. P. 166, 25 Av. des Martyrs, 38042 Grenoble, France
[d] State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University,
2699 Qianjin Street, Changchun 130012, P. R. China
Fax: +86-431-5166279
E-mail: sqiu@mail.jlu.edu.cn

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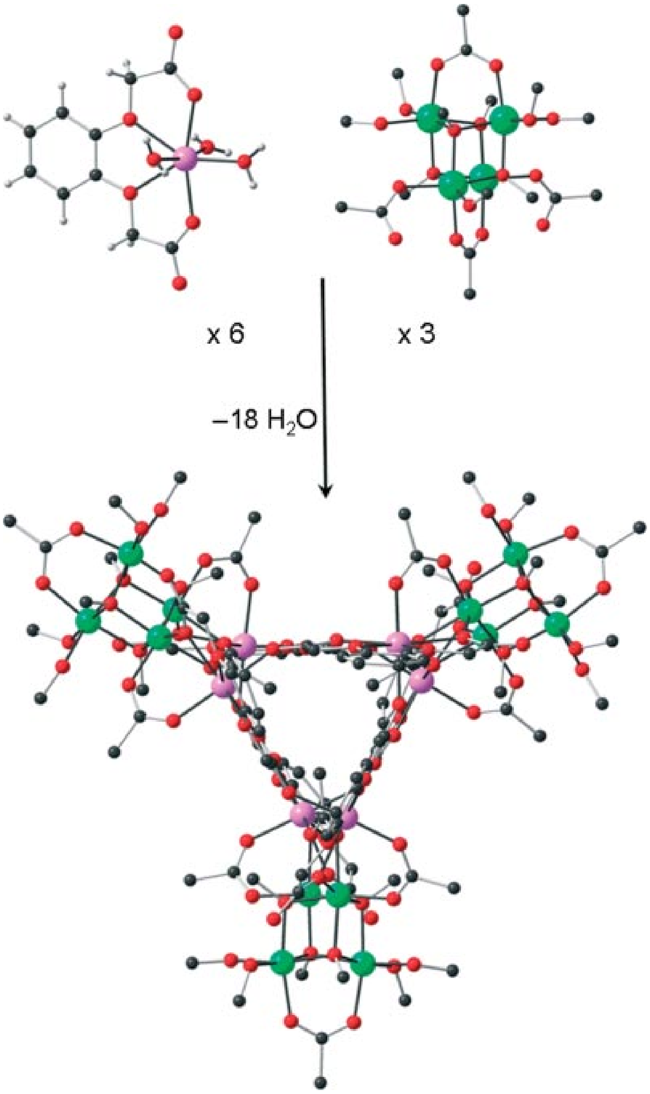

Figure 1. The self-assembly of six Mn^{II}(bdoa)(H$_2$O)$_3$ building blocks and three [Ni$_4$(O$_2$CMe)$_4$(OMe)$_4$(MeOH)$_4$] cubanes to form the [Ni$_{12}$Mn$_6$] cluster. The bottom picture shows the structure of **2**, viewed down the molecular threefold axis.

round a central, slightly twisted, trigonal-prismatic {Mn$_6$(bdoa)$_6$(μ-O$_2$CMe)$_3$} core, and the triangular faces correspond to two trinuclear units in which each Mn(bdoa) centre is bridged, through an outer, non-chelating bdoa^{2-} carboxylate oxygen atom, to the next manganese atom in a cyclic fashion. The resulting {Mn$_3$(bdoa)$_3$} triangles are linked by three *anti-anti*-bridging acetate ligands to form the prism, which has an idealised D_3 (32) molecular symmetry. The pentagonal-bipyramidal coordination geometry of the Mn^{II} centres in precursor **1** (Figure 1, top) has been preserved during the self-assembly process. As hoped, the three *mer* terminal water ligands have been substituted and replaced by oxygen atoms from two acetate ligands and one carboxylate oxygen atom from another precursor unit. In the structure of **2**, each of the three acetate ligands that link the triangles together is incorporated into and is thus also structurally part of each of the [Ni$_4$(O$_2$CMe)$_4$(OMe)$_4$(MeOH)$_4$] cubane structures. They are oriented such that their methyl groups point towards the centre of the core and bridge the two Ni^{II} centres of one face of the cubane in a *syn,syn* coordination mode. Another acetate ligand bridges across the opposite face of the cubane in the same fashion and the remaining two acetates provide further links between the cubane and the Mn core. The μ$_3$-methoxy ligands bridge three Ni centres rather unsymmetrically, and for each ligand, the three Ni–O–Ni angles fall in the ranges 89.3–91.5°, 96.3–97.5° and 99.6–101.8°; the smallest angle refers to an acetate-bridged Ni···Ni edge. All Ni centres are six coordinate, and the coordination spheres of the outer Ni centres are completed by two further methanol ligands on each centre. Conceptually, compound **2** is the combination of three neutral Ni^{II} cubanes and six neutral Mn^{II} precursors, which results in a neutral molecular framework.

Figure 2 shows the attachment of the cubanes onto the Mn$_6$ core in detail. As well as the links involving ligand oxygen atoms mentioned above, in which each Mn···Ni linkage involves a pair of oxygen bridges with Mn–O–Ni angles in the range 96.5–99.0°, further stabilisation of the overall structure is provided by rather strong hydrogen bonds between the methanol ligands on the cubanes and the carboxylate oxygen atom of the Mn$_6$ core unit. Complex **2** can be likened to a wind-turbine and the three Ni$_4$(OMe)$_4$ cubanes correspond to the blades attached to the Mn$_6$(bdoa)$_6$(μ-O$_2$CMe)$_3$ core that acts as the spindle (Figure 1 bottom).

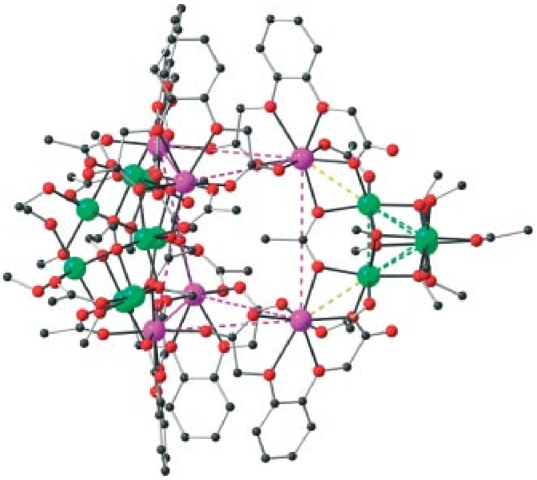

Figure 2. The linkage of the Ni$_4$Mn$_2$ units to the {Mn$_6$(bdoa)$_6$(O$_2$CMe)$_3$} core in **2**; the magnetic interaction pathways are highlighted by dashed lines and the triangular prismatic framework in pink.

Metal-cubane complexes, which have four metal ions and four μ$_3$-bridging atoms alternately aligned at the vertices of the cube, often have high-spin ground states because of the orthogonality of the magnetic orbitals. The Ni–O–Ni angles and Ni–Ni distances of the Ni$_4$(OMe)$_4$ portions in complex **2** are very similar to those in previous examples in which all the Ni^{II} couple ferromagnetically to give an $S_T = 4$ spin ground state.[6] To the best of our knowledge, **2** is the first cluster compound that contains more than one such tetranuclear Ni cubane complex in which the cubane units are well-separated but linked through a magnetically active structure. The magnetic properties of **2** were therefore investigated.

The temperature dependence of the magnetic susceptibility of **2**·21CH_3OH was measured between 1.8 and 300 K at H = 1000 Oe (Figure 3). The χT value at room temperature is 42.3 $cm^3 K mol^{-1}$, which is in very good agreement with the spin-only value of twelve $S = 1$ Ni^{II} and six $S = 5/2$ Mn^{II} metal ions (42.25 $cm^3 K mol^{-1}$ with $g = 2$). Upon decreasing the temperature, the slight increase followed by a decrease in the χT product reveals the presence of competing magnetic interactions. The maximum value of 44.6 $cm^3 K mol^{-1}$ for χT, reached at ca. 12 K, suggests, at a first glance, that **2** has a large-spin ground state. Below 12 K, the χT product significantly decreases rapidly, probably as a result of zero-field splitting of the ground state or antiferromagnetic intra-/intercluster interactions.

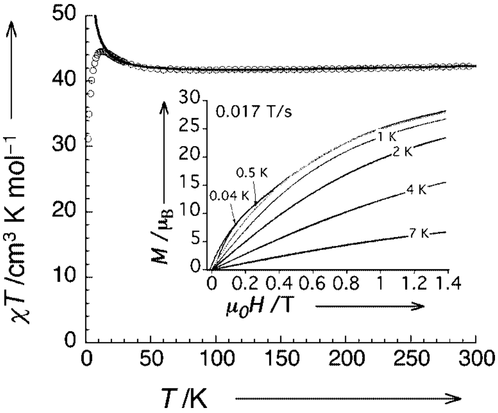

Figure 3. Plot of χT vs. T for **2** measured at 1000 Oe. The solid line is the best fit using the model described in the text. Inset: M vs. H data for **2** between 0.04 and 7 K at a sweep field rate of 0.017 T/s.

Unfortunately, the large number of magnetic centres and the presence of multiple magnetic exchange pathways preclude a determination of the individual exchange parameters in **2**. Nevertheless, by considering previously reported magneto–structural analyses of different bridging modes in the literature, two qualitative approaches can be carried out in order to analyse the magnetic properties. The strongest magnetic couplings are most likely located in a Ni_4Mn_2 unit (Figure 2) that contains two types of magnetic interactions: Ni^{II}–Ni^{II} (J_{Ni-Ni}) and Ni^{II}–Mn^{II} (J_{Ni-Mn}). Since all of the previously reported Ni_4O_4 cubane complexes were found to possess an $S_T = 4$ spin ground state with intracubane ferromagnetic Ni–Ni interactions,[6] we can predict that in the Ni_4Mn_2 units, J_{Ni-Ni} couplings are also likely to be ferromagnetic. We are not aware of any previous case of J_{Ni-Mn} mediated by a double alkoxo- and a *syn-syn* carboxylate bridge, although there are two reports on weakly ferromagnetic Ni^{II}–Mn^{III} interactions through two alkoxo bridges.[7] In **2**, three such Ni_4Mn_2 units are linked in a triangular arrangement through *anti-anti* carboxylate bridges between Mn^{II} ions (J_{Mn-Mn}) that are known to be very weakly antiferromagnetic.[8]

On the basis of this analysis, two possibilities can be considered, depending on the magnitude of these interactions. Firstly, these interactions could be strong enough to stabilise a well-defined ground state at 12 K, which corresponds to a χT value of 44.6 $cm^3 K mol^{-1}$. In this case, the resulting overall ground state (S_T) of **2** is obtained by considering an antiferromagnetically coupled triangle of Ni_4Mn_2 units. In other words, S_T corresponds to the spin ground state of one Ni_4Mn_2 unit. In order to reproduce the experimental χT value at low temperature, the only possibility is to have ferromagnetic J_{Ni-Mn} couplings, which leads to an $S_T = 9$ Ni_4Mn_2 unit and thus $S_T = 9$ for the cluster **2** as a whole, giving a theoretical χT value of 45 $cm^3 K mol^{-1}$ (with $g = 2$). Nevertheless, a second hypothesis can be proposed. From the increase in the χT product, it is clear that the ferromagnetic interactions are dominant, but the other exchanges could be very weak and only experimentally observable below 12 K with the decrease in the χT product. In this case, the magnetic behaviour of **2** should be described at a first approximation by the magnetism of three isolated Ni_4 cubanes in addition to the Curie contributions from the six Mn metal ions. By using an isotropic Heisenberg model and the same J_{Ni-Ni} value between the Ni spins,[9] the magnetic susceptibility was perfectly reproduced down to 15 K[10] and leads to J_{Ni-Ni}/k_B = +0.99(1) K and $g = 2.19(1)$ (solid line Figure 3). Hence, both hypotheses might be relevant even if the usually weak antiferromagnetic J_{Mn-Mn} interactions are in favour of the second one. M vs. H measurements were performed on powdered crystalline samples in fields of up to 7 T at 1.8 K. Even at 7 T, the magnetization is not completely saturated, and reaches 42 μ_B. This value is much larger than expected for a well-defined $S_T = 9$ spin ground state. On the other hand, this result is not surprising as a high-nuclearity complex such as **2**, particularly one in which many of the magnetic interactions are likely to be weak, as would be the case for our second hypothesis, vide supra, is likely to possess a high density of spin states with small energy gaps. So low-lying excited states, including those of greater S value (for example, an $S = 27$ spin state where the spins of the three Ni_4Mn_2 units are aligned parallel), can be populated under an applied field.[11]

Since some Ni_4 cubane complexes have either been found to be or suspected to be SMMs,[6c,6d] magnetization measurements were made on **2** at low temperatures by using a microSQUID. Measurements performed at different angles of the applied field with respect to the molecule showed no significant differences. A typical measurement at several temperatures is presented in the inset of Figure 3. Only very small hysteresis effects were observed below 0.3 K in the rather featureless magnetization curves. However, for a cluster with $S_T = 9$ as the ground state, a sharp step in the magnetization at $H = 0$ should be observed at very low temperature (0.04 K). The absence of such a step thus confirms the second hypothesis given above and suggests that, at 0.04 K, **2** possesses a small spin ground state. Moreover, the absence of significant anisotropy in the M vs. H data is indicative of rather low anisotropy within the cluster.

In summary, a new building block, $Mn^{II}(bdoa)(H_2O)_3$, has been successfully incorporated into the framework of a new heterometallic cluster, [$Ni_{12}Mn_6(bdoa)_6(O_2CMe)_{12}(\mu_3$-

OMe)$_{12}$(MeOH)$_{12}$]·21MeOH, which suggests that Mn^{II}-(bdoa)(H$_2$O)$_3$ is a useful precursor for the construction of heterometallic assembles in a rational manner and thus is a potential candidate for the synthesis of new SMMs. A further attractive feature of this strategy is that it should be possible to decorate the M$_6$(bdoa)$_6$(O$_2$CMe)$_3$ frame with different metal cube units, allowing us to probe the effect on magnetic interactions between metal cubes with high-spin ground states and different transition-metal ions. Attempts to synthesize new heterometallic compounds with this precursor are underway.

Experimental Section

Reaction of **1** (prepared following a reported method[5a]) (0.2 mmol) and Ni(OAc)$_2$·3H$_2$O (0.4 mmol) in wet methanol (15 mL) gave a light-green solution, which was filtered and layered with diethyl ether (10 mL). Green plates of **2** were collected in high yield (100 mg, 70%) by filtration after 1 week. C$_{128}$H$_{248}$Mn$_6$Ni$_{12}$O$_{104}$ (4486.44): calcd. C 34.25, H 5.53; found: C 33.89, H 5.21.

Crystal Structural Data for 2: C$_{129}$H$_{252}$Mn$_6$Ni$_{12}$O$_{105}$, F_W = 4517.47 g mol^{-1}; monoclinic, $P2_1/c$, a = 20.4004(11), b = 20.0722(9), c = 48.307(3) Å, β = 94.067(5)°, U = 19730.9(18) Å^3, Z = 4, T = 150 K, $\rho_{\text{calcd.}}$ = 1.521 Mg m^{-3}, ρ(Mo-K_α) = 1.582 mm^{-1}, F(000) = 9408; pale-green plate 0.21 × 0.17 × 0.03 mm, Stoe IPDS-II area detector diffractometer with graphite-monochromated Mo-K_α radiation; 98171 data measured and corrected for absorption, 33821 unique. R_{int} = 0.1378, $2\theta_{\max}$ = 50°, wR_2 = 0.2248, S = 0.966 (all data), R_1 = 0.0942 [13949 reflections with $I \geq 2\sigma(I)$], 2166 parameters, residual electron density +0.72/–0.61 e Å^{-3}; structure solution (direct methods) and full-matrix least-squares refinement with SHELXTL;[12] anisotropic refinement for all non-H atoms in the cluster and one lattice methanol, C and O of remaining methanol groups isotropic, hydrogen atoms in calculated position except for OH of coordinated methanol groups. Most of the lattice methanol groups were disordered; solvent-accessible voids remained in the structure, and the data were corrected using the *squeeze* option in PLATON,[13] which indicated the presence of an additional lattice methanol per cluster.

CCDC-295080 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): MicroSQUID data is available.

Acknowledgments

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[10] With the following spin Hamiltonian for the Ni$_4$ unit: $H = 2J\{S_1 \cdot S_2 + S_3 \cdot S_4 + S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4\}$.

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