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Molecules Composed of Two Weakly Magnetically Coupled [Mn^{III}_4] Clusters

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With the help of a bis(β-diketonate) ligand, a family of robust molecules is formed, all consisting of two [Mn^{III}_4] subunits that interact slightly magnetically with each other, through two bridging pyrazine ligands.

The discovery of single-molecule magnets (SMMs) more than a decade ago[1] raised expectations of using individual molecules as the smallest possible unit for magnetic information storage. More recently, SMMs have been proposed as candidates for either one- or two-qubit gates for the implementation of quantum-information processing.[2,3] A recently reported model for the second category consists of a pair of [Mn_4] SMMs, which are weakly coupled antiferromagnetically[4] because of the presence of intermolecular Cl···H−N interactions between them. This coupling causes not only a bias of the magnetic field at which quantum tunneling of the magnetization occurs but also the quantum mechanic mixing of the magnetic wave functions of both components of the dimer,[5] necessary for quantum computing. Another interesting system proposed as a potential model of the two-qubit quantum gate consists of pairs of heterometallic wheel-like [Cr_7Ni] clusters, linked via hydrogen bonds to alkylammonium groups of two-headed spacers.[6] This link, however, has not yet proved to lead to sizable magnetic interaction.

Both of the above models rely on hydrogen bonds to establish the link between the two spin clusters. In this context, a very attractive prospect would be that of combining in one sole molecule both elements of the two-qubit gate, while keeping the molecules from interacting with the environment to prevent decoherence through this mechanism. We here report a family of Mn^{III} aggregates that represent a promising approach toward fulfilling these requirements. Each of these compounds contains two tetranuclear spin clusters that are held separated but within the same molecule by bis(β-diketonate) ligands, while the weak exchange between them is ensured by bridging pyrazine ligands.

For some years, we have synthesized novel multidentate ligands containing rows of O donors aimed at facilitating the assembly of transition-metal clusters into linear topologies.[7−9] The disposition of donors in these ligands is achieved by combining various β-diketone and phenol groups in the same molecule. A recently prepared new such ligand [H_4L, 1,3-bis[3-oxo-3-(2-hydroxyphenyl)propionyl]-2-methoxybenzene] is given in Figure 1.[10] H_4L has its two β-diketones in the enolic form both in the solid state[11] (Figure 1, top) and in a chloroform solution, as evidenced by X-ray crystallography and ^1H NMR spectroscopy, respectively.

In order to check the potential of H_4L to link clusters into a molecular species, its reactions with preformed polymetallic species were studied. We herein report the results obtained using the manganese basic carboxylates [$Mn_3O(RCO_2)_6(py)_3$](ClO_4) (R = Me, Ph, *p*-MePh).[12] Reactions in $CHCl_3$ produced a family of compounds with formula [$Mn_4O_2(RCO_2)_6(pz)(H_2L)$]$_2$ (R = Me, **1**; Ph, **2**; *p*-MePh, **3**)[13] that can be easily crystallized by slow diffusion of hexanes into the filtered reaction mixture, producing single crystals suitable for X-ray diffraction. The molecular structures of **1**,[11] **2**, and **3** were determined and showed the three compounds to be analogous, differing only in the nature of the R group of the carboxylate. In this Communication, only the properties of compound **1** will be discussed in detail.

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(1) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141−143.

(2) Leuenberger, M. N.; Loss, D. *Nature* **2001**, *410*, 789−793.

(3) Meier, F.; Levy, J.; Loss, D. *Phys. Rev. Lett.* **2003**, 90.

(4) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406−409.

(5) Hill, S.; Edwards, R. S.; Aliaga-Alcalde, N.; Christou, G. *Science* **2003**, *302*, 1015−1018.

(6) Affronte, M.; Casson, I.; Evangelisti, M.; Candini, A.; Carretta, S.; Muryn, C.; Teat, S. J.; Timco, G. A.; Wernsdorfer, W.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6496−6500.

(7) Aromí, G.; Berzal, P. C.; Gamez, P.; Roubeau, O.; Kooijman, H.; Spek, A. L.; Driessen, W. L.; Reedijk, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3444−3446.

(8) Aromí, G.; Gamez, P.; Roubeau, O.; Kooijman, H.; Spek, A. L.; Driessen, W. L.; Reedijk, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1168−1170.

(9) Aromí, G.; Gamez, P.; Boldron, C.; Kooijman, H.; Spek, A. L.; Reedijk, J. *Eur. J. Inorg. Chem.* **2006**, 1940−1944.

(10) Aromí, G.; Gamez, P.; Krzystek, J.; Kooijman, H.; Spek, A. L.; MacLean, E. J.; Teat, S. J.; Nowell, H. *Inorg. Chem.* **2007**, *46*, 2519−2529.

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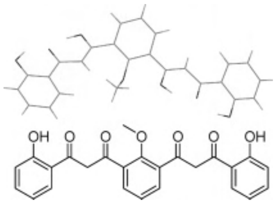

Figure 1. (top) Stick representation of the true solid-state molecular structure of H_4L as determined by single-crystal X-ray diffraction, emphasizing the fact that it is found in the ketoenolic form. (bottom) Scheme of H_4L in the 1,3-diketone tautomeric form.

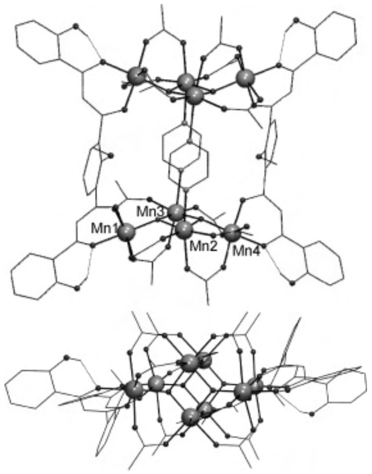

Figure 2. PovRay representations showing two views of $[Mn_4O_2(MeCO_2)_6(pz)(H_2L)]_2$ (**1**), indicating (top) the labeling of the unique Mn ions. The structures of compounds **2** and **3** are equivalent to this, except for the nature of the carboxylate. The dashed lines indicate hydrogen bonds. Code: large, Mn; medium dark, O; medium light, N; all of the rest, C.

Complex **1** crystallizes in the monoclinic space group *C*2/*c*. The structure (Figure 2) consists of two tetranuclear Mn^{III} clusters assembled into a centrosymmetric molecule by two H_2L^{2-} and two pyrazine ligands. The oxidation state of the metals was established unambiguously to be 3+ from bond-valence-sum calculations and because they show Jahn−Teller axial elongated octahedral coordination. The diketonate ligand should then possess a 2− charge to ensure electroneutrality, as suggested from the crystal structure, which indicates hydrogen bonds between the phenol O atoms (O21 and O15) and those from adjacent diketonate groups (O20 and O16). Each tetranuclear fragment features a $[Mn_4O_2]$ structure, commonly called a "butterfly", consisting of four Mn^{III} ions with distorted octahedral coordination bridged by two μ_3-oxides. Each pair of Mn atoms is also bridged by either one (Mn1−Mn3 and Mn2−Mn4) or two (Mn1−Mn2 and Mn2−Mn4) *syn,syn*-μ-AcO^- groups. The terminal or "wing" Mn ions (Mn1 and Mn4) complete their coordination with a chelating group, as is usual in "butterfly"-type clusters;[14,15] in this case, the chelating ligand is a diketonate group from the H_2L^{2-} ligands, which thus subtend the clusters opposite to each other. Two pyrazine ligands bind the two central Mn atoms or the "body" Mn ions (Mn2 and Mn3) of each "butterfly", thereby further linking the two $[Mn^{III}]_4$ units and leading to the shortest intercluster Mn⋯Mn distance of 7.443 Å. The pyrazine groups are important to ensure the magnetic interaction between the clusters (see below). The H_2L^{2-} ligand, in turn, links the $[Mn_4O_2]$ clusters into dimers for this interaction to occur within a robust molecular structure. Indeed, two dimers of independent $[Mn_4]$ "butterfly" clusters have been reported before, bridged by long bipyridineethene (bpe) or ethene-linked 2,2′-bipyridine ligands that keep both metal aggregates too far apart for a magnetic interaction to occur.[16,17] A remarkable feature of complexes **1**−**3** is that they are stable molecules, even in solution. They are indeed soluble in CH_2Cl_2 while maintaining the solid-state molecular structure as revealed by paramagnetic ^1H NMR (see Figure S1 in the Supporting Information; full details shall be reported in due course).

The magnetic properties of complex **1** were investigated by means of bulk, variable-temperature magnetization measurements, under a constant magnetic field of 3 kG. The $\chi_M T$ vs T plot per 1 mol of the $[Mn_4]$ fragment (Figure 3) shows a value of 7.27 $cm^3\ K\ mol^{-1}$ at 300 K (considerably smaller than that, 11.88 $cm^3\ K\ mol^{-1}$, predicted for four noncoupled Mn^{III} ions with $g = 1.99$) and then decreases almost linearly with cooling until near 25 K. Below this temperature, the $\chi_M T$ product decreases sharply to a value of 1.88 $cm^3\ K\ mol^{-1}$ at 2 K. These results indicate that antiferromagnetic interactions clearly dominate the coupling within this cluster. Fitting these data is a complex task because of the presence

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(11) Crystal data for **1**: $C_{82}H_{80}Mn_8N_4O_{42}\cdot 3.4CHCl_3$, data collected on a red plate crystal (0.08 × 0.06 × 0.01 mm), monoclinic, space group *C*2/*c* (No. 15) with $a = 30.935(6)$ Å, $b = 14.330(3)$ Å, $c = 25.247(5)$ Å, $\beta = 97.716(2)°$, $V = 11091(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.581$ g cm^{-3}, $\mu = 1.717$ mm^{-1}. A total of 25 241 reflections were measured, 5821 of which were independent ($R_{int} = 0.0812$; $R = 0.0659$), on station 16.2 smx of the Daresbury synchrotron facility ($T = 150$ K, $3.62 < \theta < 23.21°$, and $\lambda = 0.7848$ Å). Data were cut at 1 Å as above $\langle I/\sigma \rangle < 2$. The structure was solved by direct methods (*SHELXS97*) and refined on F^2 (*SHELXL-97*). H atoms were included on calculated positions, riding on their carrier atoms. Refinement of 692 parameters converged at final wR2 = 0.1714, R1 = 0.0645, and $S = 1.031$ [for 5821 reflections with $I > 2\sigma(I)$], $-0.679 < \Delta\rho < 1.237$ e Å^{-3}. Crystal data for H_4L: $C_{25}H_{20}O_7$; data collected on a pale-yellow lath crystal (0.45 × 0.11 × 0.03 mm), triclinic, space group $P\bar{1}$ (No. 15) with $a = 7.2156(6)$ Å, $b = 15.7051(14)$ Å, $c = 18.6098(16)$ Å, $\alpha = 71.677(2)°$, $\beta = 85.469(2)°$, $\gamma = 85.651(2)°$, $V = 1992.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.441$ g cm^{-3}, $\mu = 0.128$ mm^{-1}. A total of 32 765 reflections were measured, 5821 of which were independent ($R_{int} = 0.0812$; $R = 0.0659$), on station 11.3.1 of the Advanced Light Source synchrotron facility ($T = 193$ K, $1.26 < \theta < 33.63°$, and $\lambda = 0.774$ Å). The structure was solved by direct methods (*SHELXS97*) and refined on F^2 (*SHELXL-97*). H atoms were included on calculated positions, riding on their carrier atoms, except the hydroxyl H atoms, which were found in the difference map and allowed to refine freely. Refinement of 692 parameters converged at final wR2 = 0.1649, R1 = 0.0575, and $S = 1.033$ [for 11 750 reflections with $I > 2\sigma(I)$], $-0.265 < \Delta\rho < 0.516$ e Å^{-3}.

(12) Vincent, J. B.; Chang, H. R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703−5711.

(13) Complex $[Mn_3O(MeCO_2)_6(py)_3](ClO_4)$ (0.250 g, 0.3 mmol) was dissolved in $CHCl_3$ (9 mL). Solid H_2L (0.123 g, 0.3 mmol) and pyrazine (0.050 g, 0.6 mmol) were added, and the mixture was refluxed for 2 h. After cooling to room temperature, a light-brown precipitate was filtered and discarded. The dark-brown solution obtained was then layered with an equal volume of hexanes. Crystals of complex **1** grew in 3−4 days and were isolated in 29% yield by filtration. Anal. Calcd (found) for **1**·$CHCl_3$: C, 39.44 (39.74); H, 3.23 (2.95); N, 2.16 (2.14). The solid was dried in vacuo.

(14) Aromí, G.; Bhaduri, S.; Artús, P.; Folting, K.; Christou, G. *Inorg. Chem.* **2002**, *41*, 805−817.

(15) Cañada-Vilalta, C.; Huffman, J. C.; Christou, G. *Polyhedron* **2001**, *20*, 1785−1793.

(16) Wang, S.; Tsai, H. L.; Folting, K.; Martin, J. D.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1994**, 671−673.

(17) Grillo, V. A.; Knapp, M. J.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed.* **1996**, *35*, 1818−1820.

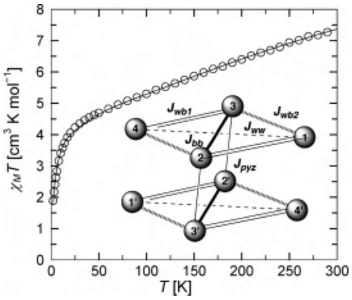

Figure 3. Plot of $\chi_M T$ vs T of **1** per 1 mol of the [Mn_4] fragment. The solid line represents the best fit of the experimental data. The inset contains the description of the five exchange coupling constants employed in the calculations and in the fit for the [Mn_4]$_2$ complex.

Table 1. Calculated and Fitted Exchange Coupling Constants (See the Inset in Figure 4)[a] for the Five Exchange Pathways in Complex **1**, Together with the Number and Type of Bridges

	bridging ligands	expt A[b]	B3LYP[d]	expt B[f]
J_{bb}	two μ_3-O	−50.6 (0.2)	−62.4 (0.2)	−47.0
J_{wb1}	μ_3-O, μ-O_2CMe	−22.0 (0.2)[c]	−12.2 (0.2)	−24.1
J_{wb2}	μ_3-O, two μ-O_2CMe	−22.0 (0.2)[c]	−8.4 (0.2)	−16.3
J_{ww}	two (μ_3-O)−Mn−(μ_3-O)	+7.6 (0.2)	+5.3 (0.2)	+7.9
J_{pyz}	μ-$N_2C_4H_4$		−0.04 (0.2)	−1.4
θ[e]	two μ-$N_2C_4H_4$	−1.2 (0.1)		

[a] In cm^{-1}. [b] Fit using the van Vleck equation. [c] In this model, $J_{wb1} = J_{wb2}$. [d] DFT parameters. Standard deviations are in parentheses. [e] Interaction between [Mn_4] clusters modeled with a Curie−Weiss constant. [f] Fit by full diagonalization.

of many exchange interactions. A $\chi_M = f(T)$ equation was obtained as described elsewhere,[18] from the van Vleck equaion for two "butterfly" complexes, each described with the Heisenberg−spin Hamiltonian $H = -J_{wb}(S_1S_2 + S_1S_3 + S_2S_4 + S_3S_4) - J_{bb}S_2S_3 - J_{ww}S_1S_4$ (using the atomic numbering shown in Figures 2 and 3). In this fit, both "wing−body" interactions were considered equivalent, the g value was fixed at 1.99, and the effect of zero-field splitting was not included. The latter is, however, expected to be negligible because the Jahn−Teller axes of the "body" Mn ions are approximately perpendicular to these of the terminal metals (Figure S2 in the Supporting Information). In order to take into account the possible interaction between the [Mn_4] units through the pyrazine ligands, a Curie−Weiss parameter, θ, was introduced to the $\chi_M = f(T)$ expression. Pyrazine bridges are known to mediate weak magnetic exchange between Mn ions,[19,20] and the presence of such an interaction is a crucial point for this family of clusters to be considered possible models of two-qubit gates. By using the above model, the experimental data could be simulated satisfactorily with the following parameters: $J_{bb} = -50.6$ (0.14) cm^{-1}, $J_{wb} = -22.0$ (0.06) cm^{-1}, $J_{ww} = +7.6$ (0.13) cm^{-1}, $\theta = -1.2$ (0.03) K (Table 1), and an agreement factor F [$F = \sum(\chi_{i(\mathrm{exp})} - \chi_{i(\mathrm{calc})})^2/\sum(\chi_{i(\mathrm{calc})})^2$] of 5×10^{-5}. This fit predicts an $S = 2$ ground state for the individual [Mn_4] clusters and that both tetranuclear units within the molecule exhibit weak antiferromagnetic interaction. For comparison, a fit was also performed by setting θ to zero. The results were significantly different [$J_{bb} = -58.8$ (0.80) cm^{-1}, $J_{wb} = -16.2$ (0.15) cm^{-1}, and $J_{ww} = +7.6$ (0.06) cm^{-1}], and the fit was of much lower quality ($F = 5 \times 10^{-2}$; see Figure S6 in the Supporting Information).

Corroboration of the above was sought by means of density functional theory (DFT) calculations,[21−23] as performed with the B3LYP functional[24] and the all-electron triple-ζ basis set[25] using the NWChem program (see the Supporting Information for details). Two different J values for the "wing−body" interactions, as well as the interaction through the pyrazine ligands, were now included in the model. The results (Table 1) are in good agreement with the above fit of the experimental data. This new collection of parameters were used as the starting point of a second fit of the experimental data, now through a full-matrix diagonalization method using the program CLUMAG,[26] with the following Hamiltonian; $H = -J_{wb1}(S_1S_2 + S_3S_4 + S_{1'}S_{2'} + S_{3'}S_{4'}) - J_{wb2}(S_1S_3 + S_2S_4 + S_{1'}S_{3'} + S_{2'}S_{4'}) - J_{bb}(S_2S_3 + S_{2'}S_{3'}) - J_{ww}(S_1S_4 + S_{1'}S_{4'}) - J_{pyz}(S_2S_{3'} + S_3S_{2'})$. The results (Table 1) are in very good agreement with the previous fit and provide an excellent simulation of the experimental curve (Figure 3) leading again to $S = 2$ ground states of the [Mn_4] subunits and a total $S_T = 0$ for the [Mn_8] cluster. If the "butterfly" clusters were independent, these would exhibit a well isolated ground state in any case (about 10 cm^{-1} below the first excited-state using the J's from the second fit, Figure S3). The coupling between both tetramers causes a splitting of the magnetic states and the consequent congestion in the energy domain.

In conclusion, the application of established principles of cluster chemistry combined with the use of designed polynucleating ligands has provided access to a family of molecular species that show promising features in relation to their possible use as models for molecular-based magnetic qubits. We are currently investigating this new entry into molecular "cluster-pairs" and pursuing to control the type and intensity of the interaction by playing with the chemical nature of the spacer that acts as magnetic gate between them.

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Supporting Information Available: X-ray crystallographic data in CIF format, crystallographic and computational details, ^{1}H NMR spectra, a Platon and ORTEP representations, energies of spin states, a plot of $\chi_M T$ vs T, and a list of references. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Aromí, G.; Bhaduri, S.; Artús, P.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2002**, *21*, 1779−1786.
(19) Hong, D. M.; Wei, H. H.; Chang, K. H.; Lee, G. H.; Wang, Y. *Polyhedron* **1998**, *17*, 3565−3573.
(20) Manson, J. L.; Arif, A. M.; Miller, J. S. *Chem. Commun.* **1999**, 1479−1480.
(21) Ruiz, E. *Struct. Bonding* **2004**, *113*, 71.
(22) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297.
(23) Ruiz, E.; Rodríguez-Fortea, A.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **2003**, *24*, 982.
(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(25) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
(26) Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.