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Microwave-Assisted Synthesis of a Hexanuclear Mn^{III} Single-Molecule Magnet

**Constantinos J. Milios,[†] Alina Vinslava,[‡] A. Gavin Whittaker,[†] Simon Parsons,[†]
Wolfgang Wernsdorfer,[§] George Christou,*[‡] Spyros P. Perlepes,*[||] and Euan K. Brechin*[†]**

*School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.,
Laboratoire Louis Néel, CNRS, 38042 Grenoble Cedex 9, France, Department of Chemistry,
University of Florida, Gainesville, Florida 32611-7200, and Department of Chemistry,
University of Patras, 26504 Patras, Greece*

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The use of microwave heating has improved the reaction rate, enhanced the yield of an inorganic cluster complex, and allowed for the high-temperature/high-pressure synthesis of a Mn^{III} single-molecule magnet.

Microwave heating is an increasingly common tool in chemical synthesis, and the advantages and convenience of microwave dielectric heating are now well documented.[1,2] As a preparative method, it may provide an efficient and rapid approach to a wide range of syntheses. Reports involving liquid reaction media are particularly interesting in view of the reported improvements in yields and reaction rates and nowhere less so than in homogeneous organic reactions,[3,4] where superheating effects are primarily believed to be responsible.[5,6] Microwaves are now used routinely in analytical chemistry,[7] liquid-phase organic syntheses,[2] solid-state reactions,[8] organic dry-media reactions,[9] intercalation reactions,[10] and a wide range of other synthetic schemes. Despite the range of applications and advantages of this heating method, reactions involving liquid-phase inorganic syntheses have not yet received great attention. In the area of polymetallic cluster compounds, this is hugely surprising because the major problems are often associated with yield and reproducibility. This tends to be especially true as the nuclearity of the product increases and is clearly a stumbling block if detailed physical characterization is to follow.

Here we show, for the first time, that microwave-assisted reactions can be used to (1) dramatically improve the reaction rate and yield of an inorganic cluster complex and (2) produce an all-Mn^{III} single-molecule magnet (SMM) despite the use of high temperatures/pressures and a reducing solvent.

$Mn(ClO_4)_2 \cdot 4H_2O$ (362 mg, 1.0 mmol), $saoH_2$ (salicylaldoxime; 137 mg, 1 mmol), NaOMe (108 mg, 2.0 mmol), and MeOH (8 mL) were placed in a sealed glass tube, which was then inserted into the cavity of a microwave reactor. The reaction mixture was maintained at $T = 110$ °C, power $= 200$ W, and pressure $= 110$ psi for a total of 5 min. After cooling (ca. 1 min), the solution was filtered and allowed to stand. Green-black crystals of $[Mn^{III}_6O_2(sao)_6(O_2CH)_2(CH_3OH)_4] \cdot 2MeOH$ (**1**·2MeOH) started to form immediately, and after 24 h, the yield was ~80%.

Complex **1** can also be made without microwave irradiation under ambient conditions, but crystalline material does not appear immediately; indeed, the maximum yield of ~30% is only achieved after a 60 min reaction and a 5 day crystallization period. The complex crystallizes in the triclinic space group $P\bar{1}$, with the molecule lying on an inversion center.[11] The core of the complex (Figure 1) contains a nonplanar $[Mn^{III}_6(\mu_3\text{-}O^{2-})_2(\mu_3\text{-}OR)_2]^{12+}$ unit of two off-set, stacked $[Mn^{III}_3(\mu_3\text{-}O^{2-})]^{7+}$ triangular subunits linked by

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* To whom correspondence should be addressed. E-mail: christou@chem.ufl.edu (G.C.), perlepes@patreas.upatras.gr (S.P.P.), ebrechin@staffmail.ed.ac.uk (E.K.B.).

[†] University of Edinburgh.

[‡] University of Florida.

[§] CNRS.

[||] University of Patras.

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(11) Anal. Calcd (found) for dried **1** (solvent free): C, 41.28 (41.46); H, 3.88 (3.91); N, 5.78 (5.85). Crystal data for **1**·$2CH_3OH$: $C_{52}H_{64}Mn_6N_6O_{26}$, fw $= 1518.67$ g, $T = 150$ K, triclinic $P\bar{1}$, $a = 9.3612(3)$ Å, $b = 12.8616(4)$ Å, $c = 13.8655(5)$ Å, $\alpha = 107.441(2)°$, $\beta = 96.022(2)°$, $\gamma = 95.548(2)°$, $V = 1569.36(9)$ Å^3, $d_{calc} = 1.607$ mg/m^3, independent reflections 8856 [R(int) $= 0.031$], data 8856, parameters 406, conventional R [$F > 4\sigma(F)$], R1 $= 0.0363$ (6576 data).

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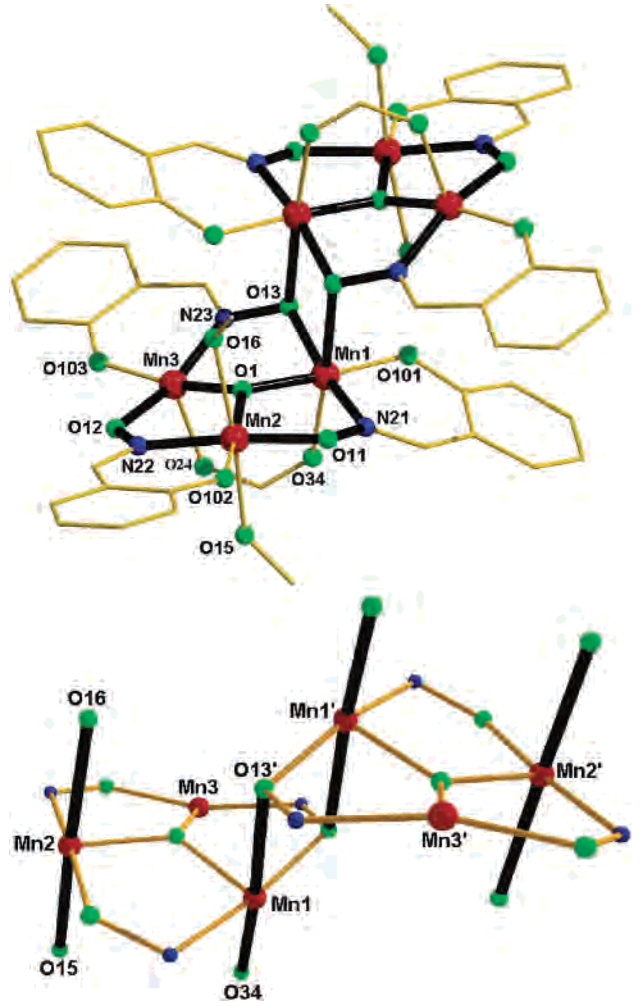

Figure 1. Molecular structure of **1** (top) and the core highlighting the Jahn−Teller axes of the four six-coordinate Mn^{III} ions (bottom). Color code: Mn = red; O = green; N = blue; C = yellow.

Table 1. BVS Calculations for Complex **1**

atom	Mn^{II}	Mn^{III}	Mn^{IV}	assignment
Mn1	3.38	3.12	3.06	Mn^{III}
Mn2	3.42	3.16	3.10	Mn^{III}
Mn3	3.39	3.13	3.07	Mn^{III}

two central oximato O atoms. The remaining sao^{2-} ligands bridge in a η^1:η^1:η^1:μ fashion along the edges of the $[\mathrm{Mn^{III}}_3(\mu_3\text{-O}^{2-})]^{7+}$ triangles, with the coordination geometry of the metal ions completed by a combination of terminal methanol and μ-formate groups, the latter derived from the (high-temperature/pressure-assisted) oxidation of the solvent. All six Mn ions are in the 3+ oxidation state, as confirmed by a combination of bond length and charge balance considerations and bond valence sum (BVS) calculations (Table 1).[12] Four Mn atoms (Mn1, Mn2, and symmetry-equivalent partners) are six-coordinate and in distorted octahedral geometries displaying the expected Jahn−Teller elongations (Figure 1), while the remaining two (Mn3 and Mn3′) are five-coordinate and square-pyramidal. The four Jahn−Teller axes and the apical bonds of the five-coordinate

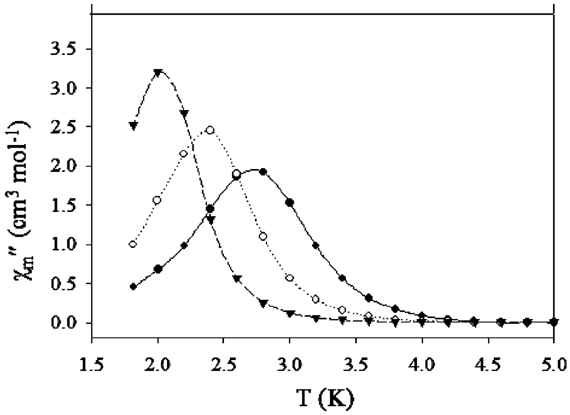

Figure 2. Out-of-phase (χ_M'') ac susceptibility measurements for complex **1** in the temperature range of 1.8−5 K and frequencies 50 (▼), 250 (○), 1000 (◆) Hz.

Mn ions are approximately coparallel, all perpendicular to the [Mn$_3$] planes.

Variable-temperature magnetic susceptibility data were collected on **1** in the temperature range of 5.0−300 K in an applied field of 1.0 kG. The room temperature $\chi_M T$ value of approximately 16.7 cm^3 K mol^{-1} decreases with decreasing temperature to 7.3 cm^3 K mol^{-1} at 20 K before increasing to a value of approximately 11.1 cm^3 K mol^{-1} at 5.0 K. Because the spin-only ($g = 2$) value for six noninteracting Mn^{III} ions is 18 cm^3 K mol^{-1}, this behavior is indicative of dominant antiferromagnetic exchange interactions between the metal centers, with the low-temperature maximum in $\chi_M T$ indicative of an $S = 4$ ground state. To determine the spin ground state for complex **1**, magnetization data were collected in the ranges 1−70 kG and 1.8−6.0 K. The data were fit by a matrix diagonalization method to a model that assumes that only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^{\,2}$) and the Zeeman interaction, and carries out a full powder average.[13] The corresponding Hamiltonian is given by eq 1, where D is the axial anisotropy,

$$\mathscr{H} = D\hat{S}_z^{\,2} + g\mu_B\mu_0\hat{S}\cdot H \tag{1}$$

μ_B is the Bohr magneton, μ_0 is the vacuum permeability, S_z is the easy-axis spin operator, and H is the applied field. The best fit gave $S = 4$, $g = 1.99(3)$, and $D = -1.39$ cm^{-1}. The ground state can be rationalized by assuming an antiferromagnetic interaction within each [Mn$^{III}_3$] subunit and a ferromagnetic interaction between [Mn$^{III}_3$] subunits. The $|D|$ value is the largest yet seen for any polynuclear Mn SMM and is likely the consequence of the parallel alignment of the single-ion anisotropy axes of the six Mn^{III} ions within the molecule.[14]

Ac magnetization measurements were performed in the 1.8−16 K range in a 3.5 G ac field oscillating at 50−1000 Hz. The in-phase (χ_M') signal shows a frequency-dependent decrease at $T \approx 4$ K indicative of the onset of slow magnetic relaxation. The magnitude of the in-phase $\chi_M'T$ vs T signal at low temperature supports a ground-state spin of $S = 4$.

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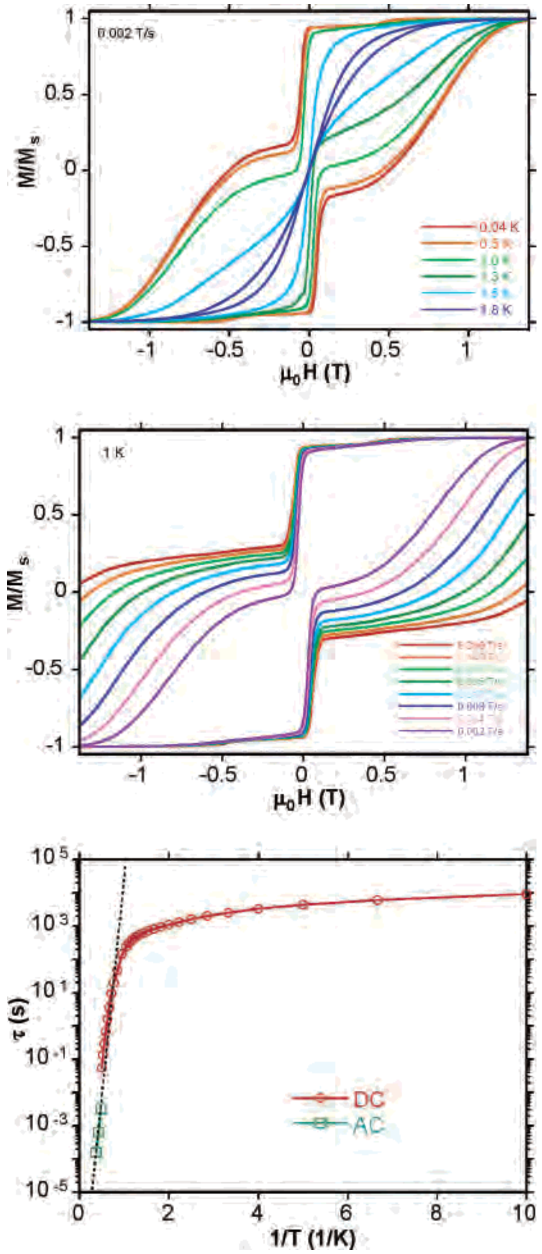

Figure 3. *M* vs *H* hysteresis loops for a single crystal of **1**. The loops are shown at different temperatures (top) and field sweep rates (middle). *M* is normalized to its saturation value. (bottom) Arrhenius plot using ac and dc data. The dashed line is the fit of the thermally activated region to eq 2.

The out-of-phase (χ_M'') signal (Figure 2) shows a peak at ca. 2.7 K at a 1000 Hz ac frequency. The presence of an out-of-phase signal is suggestive of single-molecule magnetism behavior and is caused by the inability of **1** to relax quickly enough, at these temperatures, to keep up with the oscillating field.

To probe the possible SMM behavior further, single-crystal hysteresis loop and relaxation measurements were performed using a micro-SQUID setup.[15] Figure 3 presents typical magnetization (*M*) vs applied dc field (*H*) measurements. Hysteresis loops were observed whose coercivity was strongly temperature- and sweep-rate-dependent, increasing with decreasing temperature and increasing field sweep rate, as is expected for the superparamagnetic-like behavior of a SMM. Relaxation data determined from a combination of single-crystal dc relaxation decay measurements and ac measurements on a powdered sample allow the construction of a τ vs $1/T$ plot based on the Arrhenius relationship of eq 2, where U_{eff} is the effective relaxation barrier, τ is the

$$\tau = \tau_0 \exp(U_{\mathrm{eff}}/kT) \tag{2}$$

relaxation time, and k is the Boltzmann constant. The slope of the thermally activated region yielded an effective energy barrier for the reorientation of the magnetization of $U_{\mathrm{eff}} \approx 28$ K and $\tau_0 = 2 \times 10^{-8}$ s. Below 0.8 K, the relaxation rate becomes almost temperature-independent, suggesting relaxation only via ground-state quantum tunneling.

In conclusion, we have demonstrated that the use of microwaves has (a) improved the reaction rate and enhanced the yield of an inorganic cluster complex and (b) allowed for the high-temperature/high-pressure synthesis of a $\mathrm{Mn^{III}}$ SMM despite reducing (methanolic) reaction conditions. Furthermore, the observed $|D|$ value is the largest yet seen for any polynuclear Mn SMM. The use of microwave heating is a new, appealing approach for the synthesis of large polymetallic transition-metal cluster compounds and thus clearly has enormous potential.

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Supporting Information Available: Crystallographic details in CIF format and magnetism data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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