

# Symmetry-breaking substitutions of $[\text{Re}(\text{CN})_8]^{3-}$ into the centered, face-capped octahedral clusters $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{M}'_6(\text{CN})_{48}$ ( $\text{M} = \text{Mn}, \text{Co}; \text{M}' = \text{Mo}, \text{W}$ )<sup>†</sup>

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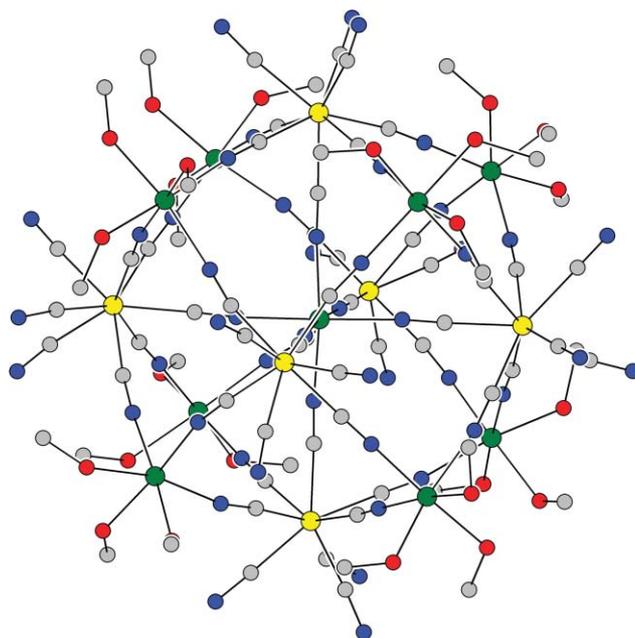
The diamagnetic complex  $[\text{Re}(\text{CN})_8]^{3-}$  is shown to react with  $\text{Mn}^{2+}$  ions in methanol to generate the centered, face-capped octahedral cluster  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Re}_6(\text{CN})_{48}$ , which is structurally analogous to  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$ . Related reactions involving stoichiometric mixtures of octacyanometalate complexes generate the substituted species  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_5\text{Re}(\text{CN})_{48}$ ,  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{Mo}_5\text{Re}(\text{CN})_{48}$ ,  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_3\text{Re}_3(\text{CN})_{48}$ ,  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{W}_5\text{Re}(\text{CN})_{48}$  and  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_5\text{Re}(\text{CN})_{48}$ , in which the  $O_h$  symmetry of the cluster core is broken. Reassessment of the magnetic properties of the  $\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  cluster confirm that it possesses a ground state spin of  $S = 39/2$ , but does not exhibit single-molecule-magnet behavior. Lowering the symmetry of the molecule by substitutions of  $\text{Re}^{\text{V}}$  at one or three of the  $\text{Mo}^{\text{V}}$  sites does not lead to an overall increase in the magnetic anisotropy, as probed by ac magnetic susceptibility measurements. A similar result occurs for the other substituted species, with the important exception of the new single-molecule magnet  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_5\text{Re}(\text{CN})_{48}$ , for which the spin reversal barrier is significantly reduced relative to that observed previously in  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_6(\text{CN})_{48}$ .

## Introduction

Molecular clusters displaying magnetic bistability have generated considerable recent interest, owing to their potential applications in information storage and quantum computing.<sup>1</sup> Such species, referred to as single-molecule magnets, possess a large ground state spin  $S$  and a negative axial zero-field splitting  $D$ , which combine to produce a spin reversal barrier of  $U = S^2|D|$  for integer spins or  $U = (S^2 - 1/4)|D|$  for half-integer spins. For more than a decade now, researchers have synthesized new single-molecule magnets attempting to increase  $U$ , and yet the largest barrier is still found in a variation<sup>2</sup> of the first single-molecule magnet identified:  $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]^{3-}$ .<sup>3</sup> This cluster has a ground state spin of  $S = 10$  and an axial magnetic anisotropy of  $D = -0.5 \text{ cm}^{-1}$ , resulting in a barrier of  $U = 50 \text{ cm}^{-1}$ . Much early research focused on oxo-bridged clusters incorporating transition metal ions possessing a large single-ion anisotropy.<sup>1,4</sup> Recently, however, a number of high-spin metal–cyanide coordination clusters have been synthesized, and these are more amenable to the substitution of one metal for another, enabling the modification of ground state magnetic properties.<sup>5,6</sup>

Five years ago, two closely-related cyano-bridged clusters were reported as possessing the highest spin ground states known at the time. The molecule  $(\text{CH}_3\text{CH}_2\text{OH})_{24}\text{Mn}_9\text{W}_6(\text{CN})_{48}$  was shown to have an  $S = 39/2$  ground state, arising from antiferromagnetic coupling between the high-spin  $\text{Mn}^{\text{II}}$  centers and the  $\text{W}^{\text{V}}$  centers.<sup>7</sup> In contrast,  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  was reported as having an  $S = 51/2$  ground state, consistent with ferromagnetic coupling between the  $\text{Mn}^{\text{II}}$  and  $\text{Mo}^{\text{V}}$  centers.<sup>8</sup> Both molecules display the

same structure type (see Fig. 1), consisting of an octahedron of six  $[\text{M}'(\text{CN})_8]^{3-}$  ( $\text{M}' = \text{Mo}, \text{W}$ ) complexes, with a single  $\text{Mn}^{\text{II}}$  ion situated at the center of the octahedron and a cube of eight methanol-capped  $\text{Mn}^{\text{II}}$  ions capping the faces of the octahedron. While a theoretical argument explaining the difference in the nature of the magnetic exchange coupling for the two clusters



**Fig. 1** Structure of the centered, face-capped octahedral cluster  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Re}_6(\text{CN})_{48}$  in **1**. Yellow, dark green, red, blue and grey spheres represent Re, Mn, O, N and C atoms, respectively; H atoms are omitted for clarity. This structure is isotopic with that of  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$ .<sup>8</sup>

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has been postulated,<sup>9</sup> recently the ground state spin of the molybdenum-containing species was reexamined with electronic structure calculations, as well as polarized neutron diffraction experiments.<sup>10</sup> Interpretation of these latest results led to the conclusion that the exchange coupling is in fact antiferromagnetic, leading to a ground state of  $S = 39/2$ , rather than  $51/2$ .

Although the  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{M}'_6(\text{CN})_{48}$  clusters display an exceptionally high ground state spin, neither exhibits single-molecule magnet behavior. This can in part be accounted for by recognition that the constituent high-spin  $\text{Mn}^{\text{II}}$  centers do not deliver the single-ion anisotropy necessary for generating a spin reversal barrier. Indeed, substitution of  $\text{Co}^{\text{II}}$  at all of the  $\text{Mn}^{\text{II}}$  centers has been demonstrated to give rise to a spin reversal barrier.<sup>11</sup> The overall anisotropy for these molecules is still very small, however, with ac susceptibility measurements indicating an effective barrier of just  $19 \text{ cm}^{-1}$  for  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_6(\text{CN})_{48}$ . A key factor that might lead to low spin reversal barriers despite the presence of a high-spin ground state is cancellation of individual ion anisotropy contributions owing to the cubic symmetry of the cluster cores.

Recent work in our laboratory led to the synthesis of a new cyanometalate complex,  $[\text{Re}(\text{CN})_8]^{3-}$ .<sup>12</sup> This diamagnetic complex has a structure analogous to those of  $[\text{M}'(\text{CN})_8]^{3-}$  ( $\text{M}' = \text{Mo}, \text{W}$ ), making it an excellent candidate as a replacement unit within the foregoing high-spin clusters. Here, we show that  $[\text{Re}(\text{CN})_8]^{3-}$  can indeed be incorporated into the body-centered, face-capped octahedral structure type, and that symmetry-breaking substitutions of  $\text{Re}^{\text{V}}$  for  $\text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$  in such species do not necessarily lead to enhanced spin reversal barriers.

## Experimental

### Syntheses

The compounds  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$ ,<sup>12</sup>  $(\text{Bu}_4\text{N})_3[\text{W}(\text{CN})_8]$ ,<sup>13</sup>  $(\text{Bu}_4\text{N})_3[\text{Mo}(\text{CN})_8]$ ,<sup>13</sup>  $(\text{CH}_3\text{OH})_{24}\text{M}_9\text{M}_6(\text{CN})_{48}$  ( $\text{M} = \text{Mn}, \text{Co}$ ),<sup>13</sup> and  $(\text{CH}_3\text{OH})_{24}\text{M}_9\text{W}_6(\text{CN})_{48}$  ( $\text{M} = \text{Mn}, \text{Co}$ )<sup>13</sup> were synthesized as previously reported. All reactions were performed in the absence of light due to the extreme photosensitivity of the products. Crystalline products were stored under methanol to prevent desolvation. IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with a horizontal attenuated total reflectance accessory. Metal contents for samples were determined using inductively-coupled plasma atomic absorption (ICP-AA) analyses. Methanol and water solvate molecule content in the product formulae were taken from crystal structure determinations when available, but are not wholly reliable owing to crystallographic disorder. Unfortunately, confirmation of these results by other means was not possible owing to rapid desolvation of the crystals upon removal from the mother liquor.

**$(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Re}_6(\text{CN})_{48} \cdot \text{CH}_3\text{OH} \cdot 7.8\text{H}_2\text{O}$  (1).** A solution of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.027 g, 0.075 mmol) in 1.5 mL of methanol was added to a solution of  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (0.055 g, 0.049 mmol) in 1.5 mL of methanol. Diffusion of diethyl ether vapor into the resulting pale orange solution produced pale orange, parallelepiped-shaped crystals suitable for X-ray analysis. The mother liquor was decanted and the crystals were quickly washed with successive

aliquots of methanol ( $3 \times 1.5 \text{ mL}$ ) to give 0.015 g (49%) of product. IR:  $\nu_{\text{CN}}$  2186 (s), 2115 (s)  $\text{cm}^{-1}$ .

**$(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_5\text{Re}(\text{CN})_{48} \cdot 4.5\text{CH}_3\text{OH} \cdot 5.5\text{H}_2\text{O}$  (2).** A solution of  $(\text{Bu}_4\text{N})_3[\text{Mo}(\text{CN})_8]$  (0.050 g, 0.048 mmol) and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (0.011 g, 0.0098 mmol) in 10 mL of methanol was added to a solution of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.031 g, 0.086 mmol) in 6 mL of methanol. Diffusion of diethyl ether vapor into the resulting red solution produced red, parallelepiped-shaped crystals suitable for single-crystal X-ray analysis. Molar metal ratios *via* ICP-AA analysis: Mn : Mo : Re = 8.31 : 5.04 : 0.94.

**$(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{Mo}_5\text{Re}(\text{CN})_{48} \cdot 3\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}$  (3).** A solution of  $(\text{Bu}_4\text{N})_3[\text{Mo}(\text{CN})_8]$  (0.050 g, 0.048 mmol) and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (0.010 g, 0.0089 mmol) in 10 mL of methanol was added to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.020 g, 0.086 mmol) in 6 mL of methanol. Diffusion of diethyl ether vapor into the resulting red solution produced red, parallelepiped-shaped crystals suitable for single-crystal X-ray analysis. Molar metal ratios *via* ICP-AA analysis: Co : Mo : Re = 9.38 : 5.10 : 0.89

**$(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_3\text{Re}_3(\text{CN})_{48} \cdot 0.5\text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$  (4).** A solution of  $(\text{Bu}_4\text{N})_3[\text{Mo}(\text{CN})_8]$  (0.030 g, 0.029 mmol) and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (0.032 g, 0.029 mmol) in 10 mL of methanol was added to a solution of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.031 g, 0.086 mmol) in 6 mL of methanol. Diffusion of diethyl ether vapor into the resulting red solution produced red, parallelepiped-shaped crystals suitable for single-crystal X-ray analysis. Molar metal ratios *via* ICP-AA analysis: Mn : Mo : Re = 8.90 : 2.80 : 3.19.

**$(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{W}_5\text{Re}(\text{CN})_{48} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$  (5).** A solution of  $(\text{Bu}_4\text{N})_3[\text{W}(\text{CN})_8]$  (0.050 g, 0.044 mmol) and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (0.010 g, 0.0088 mmol) in 10 mL of methanol was added to a solution of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.029 g, 0.079 mmol) in 6 mL of methanol. Diffusion of diethyl ether vapor into the resulting red solution produced red, parallelepiped-shaped crystals. Molar metal ratios *via* ICP-AA analysis: Mn : W : Re = 9.04 : 4.86 : 1.14.

**$(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_5\text{Re}(\text{CN})_{48} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$  (6).** A solution of  $(\text{Bu}_4\text{N})_3[\text{W}(\text{CN})_8]$  (0.050 g, 0.044 mmol) and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  (0.010 g, 0.0088 mmol) in 10 mL of methanol was added to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.019 g, 0.079 mmol) in 6 mL of methanol. Diffusion of diethyl ether vapor into the resulting red solution produced red, parallelepiped-shaped crystals. Molar metal ratios *via* ICP-AA analysis: Co : W : Re = 9.01 : 4.87 : 1.13.

### X-Ray structure determinations

X-Ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on Kapton loops. Each crystal was frozen under a stream of  $\text{N}_2$  while data were collected on a Bruker APEX diffractometer. An initial matrix scan using at least 20 centered reflections was used to determine lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed and background using SAINT 4.05. Absorption corrections, including odd and even oriented spherical harmonics were performed using SADABS. Space group assignments were based upon systematic absences,  $E$  statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 5.0

**Table 1** Crystallographic data<sup>a</sup> for (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Re<sub>6</sub>(CN)<sub>48</sub>·CH<sub>3</sub>OH·7.8H<sub>2</sub>O (**1**), (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>3</sub>Re(CN)<sub>48</sub>·4.5CH<sub>3</sub>OH·5.5H<sub>2</sub>O (**2**), (CH<sub>3</sub>OH)<sub>24</sub>-Co<sub>9</sub>Mo<sub>3</sub>Re(CN)<sub>48</sub>·3CH<sub>3</sub>OH·8H<sub>2</sub>O (**3**) and (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>3</sub>Re<sub>3</sub>(CN)<sub>48</sub>·0.5CH<sub>3</sub>OH·6H<sub>2</sub>O (**4**)

	1	2	3	4
Formula	C <sub>73</sub> H <sub>115.6</sub> Mn <sub>9</sub> N <sub>48</sub> O <sub>32.8</sub> Re <sub>6</sub>	C <sub>76.5</sub> H <sub>125</sub> Mn <sub>9</sub> Mo <sub>3.17</sub> N <sub>48</sub> O <sub>34</sub> Re <sub>0.83</sub>	C <sub>75</sub> H <sub>124</sub> Co <sub>9</sub> Mo <sub>4.74</sub> N <sub>48</sub> O <sub>35</sub> Re <sub>1.26</sub>	C <sub>72.5</sub> H <sub>110</sub> Mn <sub>9</sub> Mo <sub>3.12</sub> N <sub>48</sub> O <sub>30</sub> Re <sub>2.88</sub>
<i>M<sub>r</sub></i>	3800.6	3404.02	3476.98	3471.28
<i>T</i> /K	135	178	147	179
Space group	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>
<i>Z</i>	4	4	4	4
<i>a</i> /Å	29.235(5)	29.366(3)	28.963(3)	29.385(4)
<i>b</i> /Å	18.748(3)	19.029(2)	18.810(2)	18.742(3)
<i>c</i> /Å	32.554(6)	32.886(4)	32.276(3)	32.641(5)
<i>β</i> /°	114.856(2)	114.532(2)	114.586(2)	114.837(3)
<i>V</i> /Å <sup>3</sup>	16190(8)	16718(5)	15990(4)	16314(7)
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.512	1.688	1.393	1.369
<i>R</i> <sub>1</sub> ( <i>wR</i> <sub>2</sub> ) <sup>b</sup> (%)	7.87 (21.43)	9.04 (21.66)	9.32 (23.61)	10.31 (26.47)

<sup>a</sup> Obtained with graphite-monochromated Mo-Kα ( $\lambda = 0.71073$  Å) radiation. <sup>b</sup>  $R_1 = \sum \|F_o| - |F_c|\| / \sum |F_o|$ ,  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

software package. Rhenium site occupancies were determined through the use of a floating variable in the structures of **2–4**. In **1** three of the C–O distances were restrained to 1.40(1) Å and another two were restrained to 1.40(3) Å. In **2** four of the C–O distances were restrained to 1.40(1) Å. In **3**, the C–N distances were restrained at 1.17(1) Å, the Mo–C distances on the terminal cyanides were restrained to 2.14(1) Å, two of the Mo–N distances were constrained to 3.33(1) Å, and four of the C–O distances were restrained to 1.40(1) Å. In **4**, the C–N distances were restrained at 1.17(1) Å, the Mo–C distances on the terminal cyanides were constrained to 2.13(2) Å the Mo–N distances were restrained to 3.33(3) Å, five C–O distances were restrained to 1.40(3) Å, two C–O distances were restrained to 1.40(1) Å, and two Mn–C distances, where C is part of a terminal methanol, were restrained to 3.20(3) Å. All atoms with *Z* > 8 were refined using anisotropic thermal parameters. Final crystallographic refinement parameters are listed in Table 1.

CCDC reference numbers 292902–292905.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517707c

### Magnetic susceptibility measurements

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Dc susceptibility data were collected at temperatures ranging from 5 to 300 K, and at fields of 50, 100, 500, 1000, 5000, 10000 and 50000 G. Magnetization data were collected at 2, 5 and 8 K for compounds **2–6** and at 2, 5 and 10 K for (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>6</sub>(CN)<sub>48</sub>, with applied fields ranging from 0 to 5 T. Ac susceptibility measurements were performed in zero applied field using a switch field of 4 G at temperatures from 1.8 to 7 K. All data were corrected for diamagnetic contributions employing both a background subtraction of the sample holder with solvent and Pascal's constants. Single crystals of samples were frozen in methanol and sealed in a borosilicate tube under vacuum. In order to determine the mass of the samples, the sealed tubes were broken into a flask, then were dissolved in concentrated hydrochloric acid, and diluted with distilled water. Sample masses were then determined through ICP-AA metal analyses.

## Results and discussion

### Syntheses and crystal structures

Initial reactions tested whether [Re(CN)<sub>6</sub>]<sup>3-</sup> could be employed in the formation of centered, face-capped octahedral clusters. Indeed, under conditions analogous to those known to generate (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>6</sub>(CN)<sub>48</sub>,<sup>8,13</sup> diffusion of ether vapor into a methanol solution containing two equivalents of (Bu<sub>4</sub>N)<sub>3</sub>[Re(CN)<sub>6</sub>] and three equivalents of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was found to produce (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Re<sub>6</sub>(CN)<sub>48</sub>·CH<sub>3</sub>OH·7.8H<sub>2</sub>O (**1**). X-Ray analysis of a single crystal revealed the expected structure type (see Fig. 1), wherein an octahedron of six Re<sup>v</sup> centers are linked through cyanide bridges to one central and eight face-capping Mn<sup>ii</sup> ions. The cluster core is capped by three terminal cyanide ligands at each rhenium site and three methanol ligands at each of the eight outer manganese sites. Thus, the manganese atoms all exhibit an octahedral coordination geometry, while the coordination about rhenium is best described as a distorted triangular dodecahedron.<sup>10,14</sup> The interatomic distances and angles (see Table 2) show no significant deviations from those found in (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>6</sub>(CN)<sub>48</sub>,<sup>8</sup> indicating that little strain should be associated with substituted clusters of the type (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>6-n</sub>Re<sub>n</sub>(CN)<sub>48</sub>.

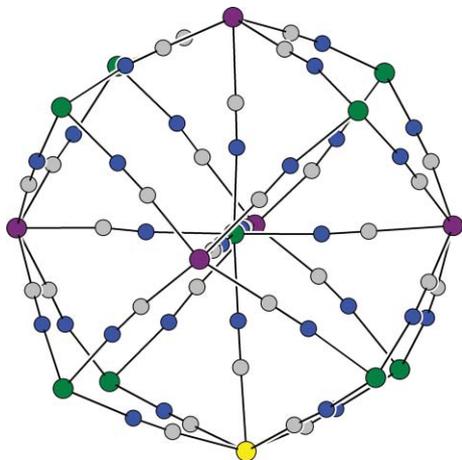
Substitution of rhenium into (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>6</sub>(CN)<sub>48</sub> proceeds with use of a mixture of (Bu<sub>4</sub>N)<sub>3</sub>[Mo(CN)<sub>6</sub>] and (Bu<sub>4</sub>N)<sub>3</sub>[Re(CN)<sub>6</sub>] under similar reaction conditions. Employing, for

**Table 2** Selected mean interatomic distances and angles for the M<sub>9</sub>M'<sub>6</sub>(CN)<sub>48</sub> clusters in (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Re<sub>6</sub>(CN)<sub>48</sub>·CH<sub>3</sub>OH·7.8H<sub>2</sub>O (**1**), (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>3</sub>Re(CN)<sub>48</sub>·4.5CH<sub>3</sub>OH·5.5H<sub>2</sub>O (**2**), (CH<sub>3</sub>OH)<sub>24</sub>-Co<sub>9</sub>Mo<sub>3</sub>Re(CN)<sub>48</sub>·3CH<sub>3</sub>OH·8H<sub>2</sub>O (**3**) and (CH<sub>3</sub>OH)<sub>24</sub>Mn<sub>9</sub>Mo<sub>3</sub>Re<sub>3</sub>(CN)<sub>48</sub>·0.5CH<sub>3</sub>OH·6H<sub>2</sub>O (**4**)

	1	2	3	4
M'–C	2.08(5)	2.13(5)	2.13(5)	2.12(8)
M–N	2.21(4)	2.21(3)	2.08(5)	2.2(1)
C–N	1.18(6)	1.17(5)	1.17(1) <sup>a</sup>	1.17(1) <sup>a</sup>
M'–C–N	173(5)	175(3)	173(5)	169(6)
C–N–M	173(4)	174(4)	174(4)	170(8)

<sup>a</sup> Value fixed.

example, a 5 : 1 molar ratio of these reactants generates a compound of formula  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_5\text{Re}(\text{CN})_{48} \cdot 4.5\text{CH}_3\text{OH} \cdot 5.5\text{H}_2\text{O}$  (**2**), as indicated by ICP-AA analysis. X-Ray analysis of a single crystal of **2** was also consistent with this formulation. Crystallizing in space group  $Cc$ , **2** is isostructural with  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  and **1**, and the 33 electron difference between molybdenum and rhenium enabled estimation of the rhenium content, despite the presence of statistical disorder of the two metals over the six crystallographically independent  $M'$  sites. Refinement of the rhenium occupancy at these sites using a floating variable resulted in a content of 13.8% rhenium, which is close to the 16.7% expected for a 5 : 1 Mo : Re ratio. The final residual factor of  $wR_2 = 0.1902$  compares favorably with the values of 0.1992 and 0.2912 obtained when the structure was refined as containing 100% molybdenum or 100% rhenium, respectively. Note that, while these analyses do not exclude the possibility that the crystals contain a 5 : 1 mixture of  $\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  and  $\text{Mn}_9\text{Re}_6(\text{CN})_{48}$  clusters, the magnetic data discussed below are not generally consistent with such a scenario. Thus, crystals of **2** likely contain primarily  $\text{Mn}_9\text{Mo}_5\text{Re}(\text{CN})_{48}$  clusters with the  $C_{4v}$ -symmetry core structure depicted in Fig. 2.



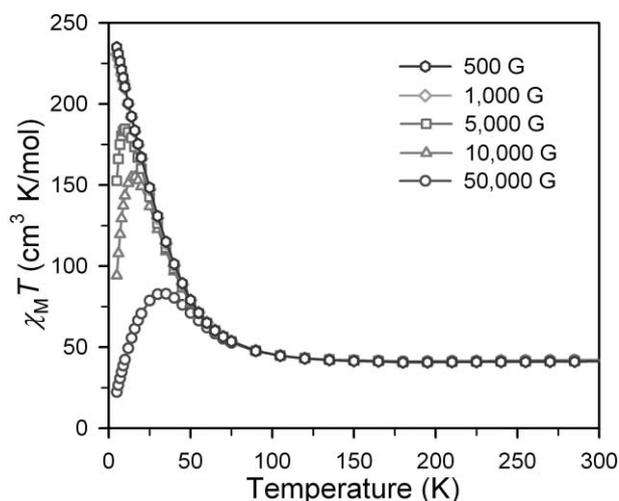
**Fig. 2** Core structure of the centered, face-capped octahedral cluster  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_5\text{Re}(\text{CN})_{48}$  in **2**. Yellow, purple, green, blue and grey spheres represent Re, Mo, Mn, N and C atoms, respectively. In the crystal structure, the Re site occupancy is distributed evenly over all six Mo/Re positions.

The foregoing approach readily extends to other mixed-metal clusters of this type. Preparations involving stoichiometric mixtures of  $(\text{Bu}_4\text{N})_3[\text{Mo}(\text{CN})_8]$  and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  or  $(\text{Bu}_4\text{N})_3[\text{W}(\text{CN})_8]$  and  $(\text{Bu}_4\text{N})_3[\text{Re}(\text{CN})_8]$  afforded the isostructural compounds  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{Mo}_5\text{Re}(\text{CN})_{48} \cdot 3\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}$  (**3**),  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_3\text{Re}_3(\text{CN})_{48} \cdot 5\text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$  (**4**),  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{W}_5\text{Re}(\text{CN})_{48} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$  (**5**) and  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_5\text{Re}(\text{CN})_{48} \cdot x\text{CH}_3\text{OH} \cdot y\text{H}_2\text{O}$  (**6**). For **3** and **4**, X-ray analyses resulted in rhenium occupancy factors of 21% and 48%, respectively, which are reasonably close to the expected values of 16.7 and 50%. In the cases of **5** and **6**, compound formulations were only verified through ICP-AA analyses, since it was deemed unlikely that tungsten and rhenium could be distinguished crystallographically. Selected mean interatomic distances and angles from the structures of **2–4** are listed in Table 2, and reveal no significant differences from those within the structure of **1**. While the monosubstituted

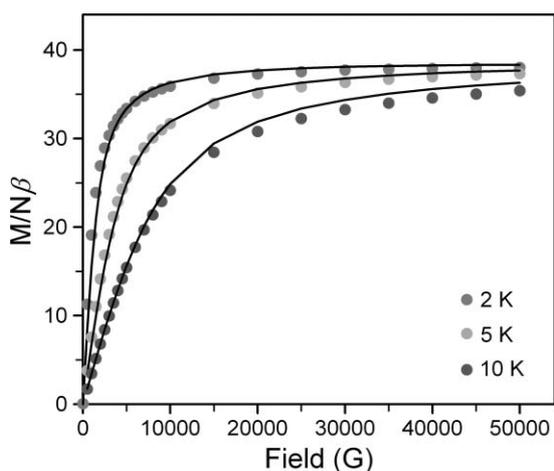
clusters in **3**, **5** and **6** should have a  $C_{4v}$ -symmetry structure analogous to that depicted for **2** in Fig. 2, the trisubstituted cluster cores in **4** most likely occur as a mixture of two isomers: a  $C_{3v}$ -symmetry *fac* isomer and a  $C_{2v}$ -symmetry *mer* isomer.

### Magnetic behavior

The magnetic susceptibility data for  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  were reassessed, owing to the likelihood that prior data had been affected by rapid desolvation of the crystals.<sup>8,10</sup> To prevent desolvation, magnetic measurements were performed on crystalline samples immersed in methanol inside a borosilicate tube. A similar procedure had been employed previously in determining the magnetic properties of  $(\text{CH}_3\text{CH}_2\text{OH})_{24}\text{Mn}_9\text{W}_6(\text{CN})_{48}$ .<sup>7</sup> The resulting data are plotted in Fig. 3 for a variety of applied field strengths. In each case, as the temperature is lowered, the value of  $\chi_M T$  decreases gradually, reaching a shallow minimum of  $41 \text{ cm}^3 \text{ K mol}^{-1}$  at 180 K, before increasing more rapidly. This trend is consistent with the presence of weak antiferromagnetic exchange coupling to give a high-spin ground state. Below 70 K, the data display significant field dependence, reaching a maximum that shifts to higher temperature as the field increases from 5000 to 10000 to 50000 G. In applied fields of 1000 G and below, however, the data does not vary with field. This behavior is also consistent with the presence of a high-spin ground state, for which depopulation of the highest-energy Zeeman levels at high magnetic fields leads to a drop in  $\chi_M T$  at low temperatures. The maximum  $\chi_M T$  value attained is  $235 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K in an applied field of 500 G. The expected values of  $\chi_M T$  for ground states of  $S = 39/2$  and  $51/2$  with  $g = 2.00$  are 200 and  $338 \text{ cm}^3 \text{ K mol}^{-1}$ , respectively. Thus, the magnetic susceptibility data are most consistent with an  $S = 39/2$  ground state, arising from antiferromagnetic exchange coupling between the six  $S = 1/2$   $\text{Mo}^V$  centers and the nine  $S = 5/2$   $\text{Mn}^{II}$  centers. This conclusion is supported by magnetization data collected at low temperatures, which exhibit close agreement with the Brillouin functions calculated for an  $S = 39/2$  ground state with  $g = 1.97$  (see Fig. 4). Moreover, it is in agreement



**Fig. 3** Temperature-dependent magnetic susceptibility data for  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  at 500, 1000, 5000, 10000 and 50000 G. Note that the 500 G data superimposes on the 1000 G data, and that the expected values of  $\chi_M T$  for  $S = 39/2$  and  $51/2$  with  $g = 2.00$  are 200 and  $338 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ , respectively.



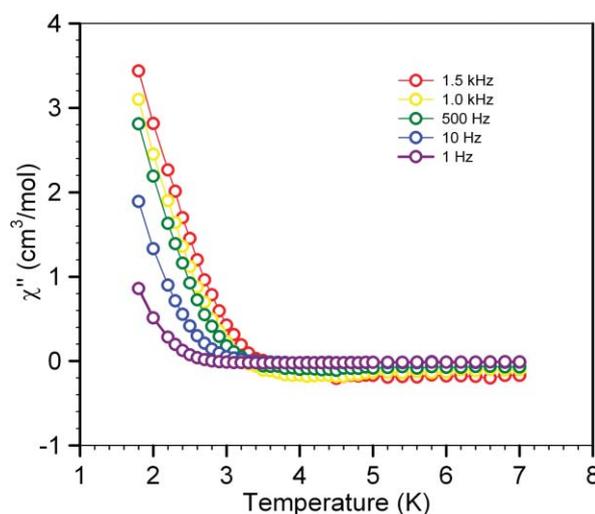
**Fig. 4** Magnetization data for  $(\text{MeOH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  at 2, 5 and 10 K. Solid lines correspond to simulations employing the Brillouin function for  $S = 39/2$  with  $g = 1.97$ .

with the recent results obtained using density functional theory calculations and inelastic neutron scattering spectroscopy.<sup>10</sup> The much stronger field dependence evident in previously published data (wherein  $\chi_M T$  achieves a maximum of  $40000 \text{ cm}^3 \text{ K mol}^{-1}$  in an applied field of 1.5 G) most likely arose as a consequence of cyanide bridge formation between clusters upon loss of capping methanol ligands.

Despite having a very high spin ground state,  $(\text{CH}_3\text{OH})_{24}\text{Mn}_9\text{Mo}_6(\text{CN})_{48}$  does not exhibit single-molecule magnet behavior at temperatures of 1.7 K and above. Potentially, this could arise from cancellation of anisotropy terms due to the  $O_h$  symmetry of the cluster core. The substituted  $\text{Mn}_9\text{Mo}_3\text{Re}(\text{CN})_{48}$  clusters in **2** provide a means of testing whether lowering the symmetry to  $C_{4v}$  might generate a single-molecule magnet. Low-temperature magnetization data collected for **2** showed slightly elevated values compared to those shown in Fig. 4, consistent with the expected increase of the spin ground state to  $S = 20$  upon replacement of an  $S = 1/2$   $\text{Mo}^{\text{V}}$  center by an  $S = 0$   $\text{Re}^{\text{V}}$  center. Ac magnetic susceptibility measurements, however, revealed no out-of-phase component,  $\chi''$ , at temperatures down to 1.7 K and switching frequencies as high as 1500 Hz. Thus, the lower-symmetry species  $\text{Mn}_9\text{Mo}_3\text{Re}(\text{CN})_{48}$  does not exhibit slow magnetic relaxation and is not a single-molecule magnet. Similar ac susceptibility experiments performed on the trisubstituted  $\text{Mn}_9\text{Mo}_3\text{Re}_3(\text{CN})_{48}$  clusters of **4** and the tungsten-based  $\text{Mn}_9\text{W}_3\text{Re}(\text{CN})_{48}$  clusters of **5** also revealed no significant spin reversal barrier.

The absence of a spin reversal barrier associated with the high-spin ground states of these molecules could be due to a positive zero-field splitting parameter  $D$ , or simply to insufficient single-ion anisotropy associated with the high-spin  $\text{Mn}^{\text{II}}$  and  $\text{Mo}^{\text{V}}/\text{W}^{\text{V}}$  centers within the clusters. Indeed, replacement of  $\text{Mn}^{\text{II}}$  centers with high-anisotropy  $\text{Co}^{\text{II}}$  ions has been shown to generate the single-molecule magnets  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{Mo}_6(\text{CN})_{48}$  and  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_6(\text{CN})_{48}$ . The latter species exhibits an effective spin reversal barrier of  $U_{\text{eff}} = 19 \text{ cm}^{-1}$ , despite having  $O_h$  core symmetry and a ground state spin of just  $S = 21/2$ .<sup>11</sup> Ac magnetic susceptibility measurements were performed on the  $\text{Co}_9\text{Mo}_3\text{Re}(\text{CN})_{48}$  and  $\text{Co}_9\text{W}_3\text{Re}(\text{CN})_{48}$  clusters of **3** and **6**, in order to test whether lowering the core symmetry to  $C_{4v}$  might

enhance the spin reversal barriers. Data obtained for the former compound, revealed a  $\chi''$  signal at low temperatures that did not reach a maximum, but increased in intensity as the switching frequency increased. Overall, the data was very similar to that previously reported for  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{Mo}_6(\text{CN})_{48}$ ,<sup>11</sup> suggesting that  $\text{Co}_9\text{Mo}_3\text{Re}(\text{CN})_{48}$  also behaves as a single-molecule magnet with approximately the same  $U_{\text{eff}}$  value. In contrast, the ac susceptibility data for compound **6** (see Fig. 5) is markedly different from that reported for  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_6(\text{CN})_{48}$ .<sup>11,15</sup> A rising  $\chi''$  signal occurs at low temperatures; however, the values are much lower, such that no maxima are observed, even at a switching frequency of 1500 Hz. This indicates a significantly reduced spin reversal barrier for the sample. Thus, lowering the symmetry of the cluster core from  $O_h$  to  $C_{4v}$  by metal ion substitution has indeed altered the barrier height, but has had the unexpected effect of lowering rather than raising it.



**Fig. 5** Out-of-phase portion of the ac susceptibility data for  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_3\text{Re}(\text{CN})_{48}$  (**6**) at 1, 10, 500, 1000 and 1500 Hz.

## Outlook

The foregoing results demonstrate for the first time that the magnitude of the spin reversal barrier of a single-molecule magnet can be manipulated by a symmetry-breaking substitution at a metal ion site. Although in this case the resultant barrier was lowered, it is anticipated that substitutions of this type may also serve to enhance the barrier height. Future efforts will attempt to apply this technique by a means that instead breaks the symmetry of the highest anisotropy ion components of cyano-bridged clusters. In particular, attention will focus on replacing a single ion in the outer cube of  $\text{Co}^{\text{II}}$  centers within the centered, face-capped octahedral cluster  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_6(\text{CN})_{48}$ ,<sup>11</sup> and in the cube of  $\text{Fe}^{\text{III}}$  centers within the face-centered cubic cluster  $[(\text{Tp})_8(\text{H}_2\text{O})_6\text{Cu}_6\text{Fe}_8(\text{CN})_{24}]^{4-}$  ( $\text{Tp}^- = \text{hydrotris}(\text{pyrazolyl})\text{borate}$ ).<sup>6g</sup>

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- 15 To confirm the apparent difference, an unsubstituted sample of  $(\text{CH}_3\text{OH})_{24}\text{Co}_9\text{W}_6(\text{CN})_{48}$  was synthesized and measured, leading to ac susceptibility data in excellent agreement with the previously published results.<sup>11</sup>