This article is published as part of the Dalton Transactions themed issue entitled:

Molecular Magnets

Guest Editor Euan Brechin University of Edinburgh, UK

Published in issue 20, 2010 of Dalton Transactions



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Use of a rhenium cyanide nanomagnet as a building block for new clusters and extended networks[†]

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Received 23rd December 2009, Accepted 14th April 2010 First published as an Advance Article on the web 27th April 2010 DOI: 10.1039/b927242a

Derivatives of the single molecule magnet (SMM) {[Re(triphos)(CN)₃]₄[MnCl]₄} (Re₄Mn₄) {[Re(triphos)(CN)₃]₄[Mn(CH₃CN)]₄}(ClO₄)₄ (**2**) and {[Re(triphos)(CN)₃]₄[Mn(ClO₄)]₃[Mn(CH₃OH)-(CH₃O)]} (**3**), were prepared by reacting [Et₄N][Re(triphos)(CN)₃] (**1**) with Mn(ClO₄)₂.6H₂O. Reaction of sodium dicyanamide, NaN(CN)₂, with compound **2** in CH₂Cl₂ results in the product {[Re(triphos)-(CN)₃]₄[Mn(N(CN)₂)]₄} (**4**), in which each Mn(II) site is terminated by a dicyanamide ligand. A similar reaction of compound **3** in CH₂Cl₂–MeOH solution with LiTCNQ (TCNQ = 7,7,8,8-tetracyanoquino-dimethane) leads to the formation of {[Re(triphos)(CN)₃]₄[Mn(TCNQ-TCNQ)₃(Mn(HTCNQ)-(CH₃O))]] (**5**) whose structure is best described as a chain of dimers of Re₄Mn₄ cubes bridged by σ -bonded (TCNQ₂)²⁻ linkers with one capping HTCNQ ligand.

Introduction

The discovery in 1993 that the molecule $[Mn_{12}O_{12}(O_2CMe)_{16}$ - $(H_2O)_4]$ (Mn_{12} -acetate) exhibits a barrier to reversing its magnetization introduced a new concept, *viz.*, single-molecule magnetism, to the field of molecular magnetism.¹⁻⁴ Single molecule magnets (SMMs) have received much attention due to their potential applications in quantum computing and data information storage owing to the fact that they exhibit slow paramagnetic relaxation and hysteresis characteristic of bistable magnetic behavior.⁵ The studies performed on the Mn_{12} -acetate compound indicated that the origin of the bistability is the combination of a large ground state spin value (S) and a negative uniaxial magnetic anisotropy (–D). The numerous subsequent examples of SMMs prepared by incorporating paramagnetic metal ions into clusters with suitable bridging ligands are valuable for gaining deeper insight into this intriguing phenomenon.^{3,6-20}

Of particular relevance to the present topic are the cyanidebased SMMs that have appeared in the literature over the last decade.⁴ This class of SMMs is much smaller than those based on oxide type ligands, but they cover a wider range of metal ions including those of the second and third row transition elements. From these examples one can learn a great deal about the effects of spin–orbit coupling on the magnetic properties, especially quantum tunneling. One of these SMM cyanide compounds reported by this group several years ago is ${[Re(triphos)(CN)_3]_4[MnCl]_4}$ (Re_4Mn_4) whose structure is that of a distorted molecular cube with four octahedral Re(II) ions and four tetrahedral Mn(II) sites bridged by cyanide ligands.^{10,21} This cluster was the first example of a SMM with a 5d metal ion. The compound exhibits hysteretic behavior at low temperatures, with strong temperature and sweeprate dependent coercivity. The magnetic measurements also show a significant step at zero field, which is the result of fast tunneling relaxation of the magnetization.^{21,22}

The surprising finding that a mixed-metal cube molecule exhibits slow relaxation of the magnetization, a phenomenon thought to be possible only with molecules with an easy axis of magnetization, prompted the development of a theoretical model that takes into account the unquenched orbital angular momentum of the Re(II) ion in a trigonal crystal field and the distortion of the cluster due to a compression along one of the C₃ axes.²² The successful application of this model notwithstanding, clearly we need more examples of SMM molecules with strong spin orbit coupling in order to gain a general understanding of the role of the crystal field and the identities and anisotropy of the metal ions. Recently, Long and co-workers, reported a new cyanide based SMM, [(PY₅Me₂)₄Mn₄Re(CN)₇](PF₆)₅.6H₂O, with a record effective barrier of 33 cm⁻¹ for cyanide-bridged SMMs where the heptacyanorhenate(IV) ion is coordinated to four Mn(II) ions resulting in a complex with an S = 21/2 ground state. Further analysis of this system is required to determine the conditions that lead to the observed ferromagnetic coupling between the Re(IV) and Mn(II) metal ions in this complex.23

In addition to seeking new SMMs, research groups are also using existing SMMs as building blocks for the synthesis of higher nuclearity clusters or networks.²⁴⁻³⁴ In this vein, trinuclear clusters with the [M₃(µ₃–O)] core (M = Mn(III), Fe(II), Fe(II), Co(II), Ni(II), Cu(II), V(II), or Cr(III)) have been used to prepare frustrated lattices, single-chain magnets and 2D magnetic networks.^{35–41} In one such example, Sato *et al.*, reported the preparation of a singlechain magnet from the reaction of the Mn^{III}₃O(Meppz)₃(EtOH)₅Cl (Meppz = 3-(5-methyl-2-phenolate)pyrazolate) with sodium acetate. The product consists of [Mn₃O] units connected through bridging acetate units.⁴¹ In another case, double-cuboidal [Mn₄] SMMs were reacted with cyanometallates as well as the dicyanamide (dca⁻) ligand, the results of which are the formation of extended networks consisting of SMM building blocks.⁴²⁻⁴⁴

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[†] Electronic supplementary information (ESI) available: Fig. S1–S4, magnetization data and Fig. S5–S6 additional AC susceptibility studies. CCDC reference numbers 764601–764604 . For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927242a

This "bottom-up" approach is a convenient strategy for constructing 1-, 2-, and 3-D architectures based on SMM units, an attractive idea prompted by the discovery that weak antiferromagnetic interactions in a dimer of single molecular magnets lead to a tuning of the quantum properties of the original SMM unit.⁴⁵ In another exciting finding Christou *et al.*, reported that a supramolecular dimer of SMMs ([Fe₉]₂) exist in the *OFF* and *ON* exchange-coupled states mediated solely by a hydrogen bond.⁴⁶ These breakthroughs have opened up new perspectives for the eventual implementation of SMMs in devices.

Given the aforementioned issues in the field of SMMs, and the current interest in cyanide compounds of heavier transition metals in particular, we undertook the present study with the aim of preparing derivatives of the Re_4Mn_4 cube equipped with different co-ligands. The goal is to use ligands that will be more easily substituted than the chloride atom or will act as a potential bridge between the individual Re_4Mn_4 cube units. Herein we report our findings with the use of acetonitrile, methanol, dicyanamide and TCNQ (TCNQ = 7,7,8,8-tetracyano-quinodimethane) to prepare new derivatives including a chain compound.

Experimental

Syntheses

Unless otherwise stated, all experiments were performed using standard anaerobic Schlenk-line techniques. The starting materials $Mn(ClO_4)_2 \cdot 6H_2O$ and $Na(C_2N_3)$ were purchased from Aldrich and used as received. All solvents were dried by standard methods.

[Et₄N][Re(triphos)(CN)₃] (1). Compound 1 was prepared by a slightly modified procedure of the previously reported method.⁴⁷ Samples of [(triphos)Re(µ−Cl)₃Re(triphos)]Cl⁴⁸ (0.656 g, 0.301 mmol) and [Et₄N]CN (0.283 g, 1.81 mmol) were stirred in 25 mL of CH₃CN. The solution was then reacted with a solution of TlPF₆ in 25 mL of CH₃CN (0.421 g, 1.2 mmol) to give a dark-green solution along with a white precipitate. The white solid was removed by filtration and the dark green filtrate was concentrated to 10 mL. At this stage, a bright yellow-green solid was collected by filtration and washed with 5 mL of acetonitrile and 20 mL of acetone followed by 15 mL of a 2/1 mixture of THF−CH₃CN and finally 15 mL of diethyl ether. Yield: 0.203 g (0.199 mmol, 33%). Anal. Calcd for 1, C₅₂H₅₉N₄P₃Re: C, 61.22; H, 6.41; N, 5.59. Found: C, 61.10; H, 6.63; N, 5.76. IR(Nujol): ν (C≡N) = 2060, 2070 cm⁻¹.

{**[Re(triphos)(CN)₃]₄**[**Mn(CH₃CN)]₄**}(**CIO**₄)₄ (**2).** A colorless solution of Mn(ClO₄)₂.6H₂O (0.070 g, 0.195 mmol) in 10 mL of acetonitrile was slowly added to a dark green-yellow solution of [Et₄N][Re(triphos)(CN)₃] (0.200 g, 0.196 mmol) in 25 mL of acetonitrile. The mixture was left to stand undisturbed for 2 days under nitrogen. The solution was then concentrated to approximately 10 mL and the red powder isolated was washed with copious amounts of diethyl ether. Yield = 0.050 g (0.012 mmol, 24%). Elemental analysis calcd. for **2**, C₁₈₄H₁₆₈N₁₆P₁₂Cl₄O₁₆Re₄Mn₄: C 50.92, H 3.90, N 5.17, O 5.90, Cl 3.23; found: C 50.62, H 3.69, N 4.98, O 5.52, Cl 3.02. IR(Nujol), *v*(C=N), cm⁻¹: 2296(s), 2089(s), and 2070(w). Single crystals of compound **2** were grown over a one week period in a 3 mm diameter sealed thin tube by slow diffusion of a CH₂Cl₂ solution of the compound into diethyl ether.

{[Re(triphos)(CN)₃]₄[Mn(ClO₄)]₃[Mn(CH₃OH)(CH₃O)]} (3). A colorless solution of Mn(ClO₄)₂·6H₂O (0.070 g, 0.195 mmol) in 10 mL of methanol was slowly added to a dark green-yellow solution of [Et₄N][Re(triphos)(CN)₃] (0.200 g, 0.196 mmol) in 25 mL of methanol. The mixture was left to stand undisturbed for 2 days under nitrogen. The solution was then concentrated to ~10 mL and the red powder that had formed was collected by filtration and washed with copious amount of diethyl ether. Yield = 0.076 g (0.019 mmol), 38%. Elemental analysis calcd. for 3, C178H163P12N12Cl3O14Re4Mn4: C 51.64, H 3.97, N 4.06, Cl 2.54, O 5.41; found: C 51.07, H 3.64, N 3.92, Cl 2.27, O 5.12. IR(Nujol), $v(C \equiv N)$, cm⁻¹: 2088(s), 2076(w). Single crystals of compound 4 were grown over a period of one week in a 3 mm diameter sealed thin tube by slow diffusion of a CH₂Cl₂ solution of the compound into diethyl ether.

{**[Re(triphos)(CN)₃]₄**[**Mn(N(CN)₂)]₄**} (4). A colorless solution of Na(N(CN)₂) (0.018 g, 0.186 mmol) in 15 mL of ethanol was slowly added to a red solution of compound **2** (0.200 g, 0.046 mmol) in 25 mL of dichloromethane. The mixture was stirred for 3 days under nitrogen. An orange powder was isolated by filtration and washed with copious amount of diethyl ether. Yield = 0.118 g (0.029 mmol), 64%. Elemental analysis calcd. for **4**, C₁₈₄H₁₅₆N₂₄P₁₂Re₄Mn₄: C 54.65, H 3.89, N 8.32; found: C 54.52, H 3.68, N 8.15. IR(Nujol), $v(C\equiv N)$, cm⁻¹: 2262(s), 2206(s), 2156(s), 2095(s), 2077(w). Single crystals of compound **4** were obtained after one week by slow diffusion of a CH₂Cl₂ solution of compound **2** into an ethanol solution of Na(N(CN)₂) in a 3 mm diameter sealed thin tube.

{[Re(triphos)(CN)₃]₄[Mn(TCNQ - TCNQ)₃(Mn(HTCNQ)-(CH₃O))]] (5). A dark blue solution of LiTCNQ (0.051 g, 0.244 mmol) in 15 mL of methanol was slowly added to a red solution of compound **3** (0.250 g, 0.061 mmol) in 25 mL of dichloromethane. The mixture was stirred for 4 days under nitrogen. A red-brown powder removed by filtration in air was washed with copious amount of diethyl ether. Yield = 0.062 g (0.013 mmol), 22%. Elemental analysis calcd. for **5**, C₂₂₅H₁₇₃N₂₈P₁₂O₁Re₄Mn₄: C 58.42, H 3.77, N 8.48; found: C 57.95, H 3.59, N 8.24. IR(Nujol), v(C=N), cm⁻¹: 2195(s), 2171(s), 2130(s), 2113(s), 2087(s), 2074(w). Single crystals of compound **5** grew over the period of one month in a 3 mm diameter sealed thin tube by slow diffusion of a CH₂Cl₂ solution of the compound **3** into a methanol solution of LiTCNQ.

Single crystal X-ray structures

In a typical experiment, a crystal selected for study was suspended in polybutene oil (Aldrich) and mounted on a cryoloop which was placed in an N₂ cold stream. Single crystal X-ray data for all the compounds were collected on a Bruker APEX diffractometer at 110 K. The data sets were recorded as three ω -scans of 606 frames each, at 0.3° stepwidth, and integrated with the Bruker SAINT²⁹ software package. For compounds **2**, **3**, and **4**, the diffraction patterns were each indexed using a monoclinic unit cell and were solved in the space group $P2_1/n$ (No. 14) based on the systematic absences. The diffraction patterns for compound **5** were indexed using a triclinic unit cell and solved in the space group $P\overline{1}$. The absorption correction (SADABS³⁰) was based on fitting a function to the empirical transmission surface as sampled by multiple

Table 1	Crystallographic da	ta and structural	refinement parameters	for compounds 2–5
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	(2)	(3)	(4)	(5)
Formula	$Re_4Mn_4C_{184}H_{xx}P_{12}N_{16}Cl_4O_{16}$	$\frac{Re_4Mn_4C_{178}H_{183}P_{12}N_{12}}{Cl_3O_{14}}$	$Re_4Mn_4C_{184}H_{156}P_{12}N_{23}$	$Re_4Mn_4C_{225}H_{173}N_{28}P_{12}O$
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 1̄ (No. 2)
Unit cell	a = 24.5782(8) Å	a = 18.088(2) Å	a = 25.262(8) Å	a = 17.514(3) Å
	b = 25.4175(8) Å	b = 34.418(4) Å	b = 24.985(8) Å	b = 18.087(3) Å
	c = 31.9582(9) Å	c = 33.490(4) Å	c = 32.556(11) Å	$c = 38.106(7)$ Å, $\alpha = 90.764(5)^{\circ}$,
	$\beta = 105.908(2)^{\circ}$	$\beta = 95.824(2)^{\circ}$	$\beta = 108.033(4)^{\circ}$	$\beta = 97.408(5)^{\circ}, \gamma = 102.736(5)^{\circ}$
Unit cell volume, V	19200.2(10) Å ³	20742(4) Å ³	19539(11) Å ³	11605(3) Å ³
Density, $\rho_{\rm c}$	1.304 g cm ⁻³	1.340 g cm ⁻³	1.517 g cm ⁻³	1.365 g cm ⁻³
Abs. coeff., µ	2.913 mm ⁻¹	2.745 mm ⁻¹	3.000 mm^{-1}	2.459 mm ⁻¹
Crystal color and habit	Dark red plate	Dark red plate	Red plate	Red plate
Crystal size	$0.30 \times 0.22 \times 0.08 \text{ mm}$	$0.34 \times 0.32 \times 0.06 \text{ mm}$	$0.19 \times 0.12 \times 0.06 \text{ mm}$	$0.17 \times 0.11 \times 0.06 \text{ mm}$
Temperature	110(2) K	110(2) K	110(2) K	110(2) K
Radiation, λ	Μο-Κα, 0.71073 Α	Μο-Κα, 0.71073 Α	Μο-Κα, 0.71073 Α	Μο-Κα, 0.71073 Α
Min. and max. θ	0.93 to 27.05°	1.28 to 26.45°	1.47 to 26.95°	1.20 to 23.59°
Reflections collected	$221692 [R_{int} = 0.2514]^a$	$218950 [R_{int} = 0.0860]$	$[198.684 [R_{int} = 0.2308]]$	$[133941 [R_{int} = 0.0945]]$
Independent reflections	11213	42507	40874 (1024 (0	32306
Data/parameters/restraints $D[E = 4\pi(E)]$	11213/982/0 D 0078h	425077120470 P 0.1104	408/4/1034/0	32300/1230/0 D 0.115(
$K[\Gamma_0 > 40(\Gamma_0)]$	$K_1 = 0.0976^2$	$K_1 = 0.1104$	$K_1 = 0.104\delta$	$K_1 = 0.1130$
	$w R_2 = 0.2020^2$	$w_{\Lambda_2} = 0.5555$	$w_{\Lambda_2} = 0.4342$	$w \Lambda_2 = 0.5545$

 ${}^{a} R_{int} = \sum |F_{o}^{2} - F_{o}^{2}(\text{mean})| / \sum [F_{o}^{2}], {}^{b} R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, {}^{c} w R_{2} = \{ \sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}, w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP], P = [F_{o}^{2} + 2F_{c}^{2}] / 3.$ For **2**, *a* = 0.1566, *b* = 1064.5675; for **3**, *a* = 0.1840, *b* = 811.8245; for **4**, *a* = 0.2, *b* = 0; for **5**, *a* = 0.1724, *b* = 561.6464.

equivalent measurements. Solution and refinement of the crystal structures was carried out using the SHELX³¹ suite of programs and X-SEED,³² a graphical interface. Structure solution by direct methods resolved positions of all metal atoms and most of the lighter atoms. The remaining non-hydrogen atoms were located by alternating cycles of least squares refinements and difference Fourier maps. The option SQUEEZE in PLATON³³ was used to eliminate the contribution of the electron density in the solvent region from the intensity data for compound 4. Hydrogen atoms were placed at calculated positions and refined with displacement parameters 1.2 or 1.5 times that of the heavy atoms to which they are bonded. A summary of pertinent information relating to unit cell parameters, data collection, and refinement is provided in Table 1. Selected metal-ligand bond distances for a representative cube, compound 3, and the chain of cubes, compound 5, are listed in Tables 2 and 3. It is necessary to point out that crystals of compounds 2-5 invariably are poorly diffracting due to rapid solvent loss and inherent disorder, leading to lower quality data and refinement issues that could not be fully resolved. Nevertheless, the models shown in Fig. 2-5 are chemically sensible and correlate well with magnetic and spectroscopic properties and, as such, are still quite useful.

Results and discussion

Syntheses

The building block approach has proven to be an effective method for systematic preparation of families of magnetic molecular complexes. Prior to this work, a family of cyanide-bridged molecular cubes was prepared by reacting 3d metal chloride salts with the mononuclear cyanide precursor, TEA[Re(triphos)-(CN)₃].⁴⁷ Of particular interest is the {[Re(triphos)(CN)₃]₄-[MnCl₂]₄} molecule which is a SMM. Our early attempts to use this cluster as a starting material by substituting the chloride ligands with other groups such as CN⁻ and dicyanamide (dca⁻)

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Table 2Selected bond distances (Å) and angles (°) for compound 3

Atoms	Distance (Å)	Atoms	Angle (°)
Re1–C1	2.074(5)	N1–Mn1–N7	106.3(2)
Re1–C2	2.089(5)	N1-Mn1-N4	106.68(2)
Re1–C3	2.042(5)	N7-Mn1-N4	99.3(2)
Re2–C4	2.077(5)	N2-Mn2-N5	108.1(2)
Re2–C5	2.083(4)	N2-Mn2-N10	112.1(2)
Re2–C6	2.056(4)	N5-Mn2-N10	106.5(2)
Re3–C7	2.089(5)	N3-Mn3-N8	109.4(2)
Re3–C8	2.075(4)	N3-Mn3-N11	114.2(2)
Re3–C9	2.076(4)	N8-Mn3-N11	120.7(2)
Re4-C10	2.057(5)	N9-Mn4-N6	101.6(2)
Re4-C11	2.062(5)	N9-Mn4-N12	110.9(2)
Re4-C12	2.089(5)	N6-Mn4-N12	107.1(2)
Mn1–N1	2.139(5)	C1-N1-Mn1	168.7(4)
Mn1–N4	2.108(5)	C4-N4-Mn1	170.5(4)
Mn1–N7	2.097(4)	C7-N7-Mn1	169.0(4)
Mn1–O3	2.13(2)	C2-N2-Mn2	162.9(4)
Mn2–N2	2.051(4)	C5-N5-Mn2	166.6(4)
Mn2–N5	2.035(4)	C10-N10-Mn2	168.1(4)
Mn2-N10	2.067(4)	C3–N3–Mn3	167.3(4)
Mn2–O4	2.097(4)	C8-N8-Mn3	163.7(4)
Mn3–N3	2.053(5)	C11-N11-Mn3	157.4(4)
Mn3–N8	2.011(4)	C6-N6-Mn4	168.6(4)
Mn3-N11	2.049(5)	C9-N9-Mn4	167.0(4)
Mn3–O7	2.331(13)	C12-N12-Mn4	169.1(4)
Mn4–N6	2.054(4)		
Mn4–N9	2.037(4)		
Mn4–N12	2.059(4)		
Mn4-011	2.168(7)		

anions in the presence of TIPF₆ as a chloride sequestering agent met with failure. We suspect that the inert nature of the compound is due to steric effects caused by the bulky triphos. As an alternative route, we sought to prepare partially solvated molecular cubes by reacting TEA[Re(triphos) (CN)₃] (1), with Mn(ClO₄)₂·6H₂O in acetonitrile (Fig. 1). The results were disappointing in that the products were inevitably contaminated with small quantities of chloride,

Table 3 Selected bond distances (Å) and angles (°) for compound 5

Atoms	Distance (Å)	Atoms	Angle (°)
Re1–C1	2.095(19)	N1-Mn1-N7	104.6(7)
Re1–C2	2.111(17)	N1-Mn1-N4	100.4(7)
Re1–C3	2.084(19)	N7-Mn1-N4	107.9(7)
Re2–C4	2.127(17)	N2-Mn2-N5	108.1(6)
Re2–C5	2.094(18)	N2-Mn2-N10	107.6(7)
Re2–C6	2.064(17)	N5-Mn2-N10	107.3(7)
Re3–C7	2.10(2)	N3-Mn3-N8	108.1(7)
Re3–C8	2.07(2)	N3-Mn3-N11	107.6(7)
Re3–C9	2.13(2)	N8-Mn3-N11	106.8(7)
Re4-C10	2.077(17)	N9-Mn4-N6	121.5(7)
Re4-C11	2.102(18)	N9-Mn4-N12	118.5(8)
Re4-C12	2.097(18)	N6-Mn4-N12	111.6(7)
Mn1–N1	2.057(18)	C1-N1-Mn1	167.8(17)
Mn1–N4	2.052(17)	C4-N4-Mn1	165.9(16)
Mn1–N7	2.063(19)	C7-N7-Mn1	169.7(18)
Mn1–N13	2.190(16)	C2-N2-Mn2	164.6(15)
Mn2–N2	2.062(17)	C5-N5-Mn2	165.7(17)
Mn2–N5	2.081(17)	C10-N10-Mn2	167.1(16)
Mn2-N10	2.068(17)	C3–N3–Mn3	167.4(17)
Mn2-N17	2.124(19)	C8-N8-Mn3	164.4(18)
Mn3–N3	2.021(18)	C11-N11-Mn3	168.3(17)
Mn3–N8	2.066(19)	C6-N6-Mn4	160.3(16)
Mn3-N11	2.057(19)	C9-N9-Mn4	154.6(19)
Mn3-N21	2.094(18)	C12-N12-Mn4	153.1(17)
Mn4–N6	2.055(19)		
Mn4–N9	2.08(2)		
Mn4–N12	2.066(18)		
Mn4–N25	2.16(2)		



Fig. 1 Structure of compound 1.47 Thermal ellipsoids are projected at the 50% probability level.

e.g., $\{[Re(triphos)(CN)_3]_4[Mn(CH_3CN)]_3[MnCl]_1\}(ClO_4)_3$ (with a 25% chloride contamination) and {[Re(triphos)(CN)₃]₄[Mn-(CH₃CN)]₂[MnCl]₂}(ClO₄)₂ (with a 50% chloride contamination) as confirmed by elemental analysis and X-ray single crystal studies. The only possible source of Cl⁻ in these cases is contamination from the TEA[Re(triphos)(CN)₃] starting material which is prepared from [(triphos)Re(µ-Cl)₃Re(triphos)]Cl. To circumvent this problem, TEA[Re(triphos)(CN)₃] was treated with TlPF₆ which led to the precipitation of TlCl.

Subsequent reactions of purified samples of 1 with $Mn^{II}(ClO_4)_2 \cdot 6H_2O$ in CH₃CN and CH₃OH produced the compounds {[Re(triphos)(CN)₃]₄[Mn(CH₃CN)]₄}(ClO₄)₄ (2) and $\{[Re(triphos)(CN)_3]_4[Mn(ClO_4)]_3[Mn(CH_3OH)(CH_3O)]\}, (3) re$ spectively. Compounds 2 and 3 were further reacted with dcaand TCNQ⁻ ligands. When sodium dicyanamide was added to a red solution of compound 2 in CH_2Cl_2 the rapid formation of

Fig. 2 The molecular structure of $\{[Re(triphos)(CN)_3]_4[Mn(CH_3CN)]_4\}$ - $(ClO_4)_4$ (2). Thermal ellipsoids are projected at the 50% probability level (only the thermal ellipsoids of the atoms that make up the cubic core are shown for the sake of clarity).

One of the best examples in the series is represented by the molecular structure of 3. In the cluster, the perchlorate anions are used to complete the coordination sphere of three Mn(II) sites whereas a methanol ligand is bound to the remaining Mn(II) center, a situation that results in drastic differences in the coordination geometry of this Mn(II) site, a situation that is not found for the other three cubes (Fig. 3). The atom labeled as Mn(1) is compressed towards the center of the cube as evidenced by the fact that the Mn(1)-N=C angles are significantly reduced from linearity as a result of one dangling methanol ligand attached to

pale-brown precipitate was observed. The result is the compound $\{[\text{Re}(\text{triphos})(\text{CN})_3]_4[\text{Mn}(\text{N}(\text{CN})_2)]_4\}$ (4), in which each Mn(II) site is connected to one dicyanamide ligand. A substitution reaction between the dangling acetonitrile ligands connected to the Mn sites of the cube with the dca- ligand is favored most likely due to the formation of a neutral compound which is easily removed from the reaction medium by precipitation. A similar reaction of compound 3 with LiTCNQ in CH₂Cl₂-MeOH solution led to the formation of {[Re(triphos)(CN)₃]₄[Mn(TCNQ- $TCNQ_{3}(Mn(HTCNQ)-(CH_{3}O))]$ (5).

Single crystal X-ray diffraction studies

Single crystal X-ray diffraction experiments performed on 2-4 revealed that the products consist of a distorted molecular cube with four alternating Re(II) and Mn(II) ions. The edges of the neutral clusters are spanned by twelve bridging cyanide ligands that link the metal ions (Fig. 2-5). The Re(II) sites retain their distorted octahedral geometry with the triphos ligand acting as a facially capping ligand and the carbon end of three cyanide ligands completing the coordination sphere of each Re(II) site.





Fig. 3 The molecular structure of the compound $\{[Re(triphos)(CN)_3]_4-[Mn(ClO_4)]_3[Mn(CH_3OH)(CH_3O)]\}$ (3). Thermal ellipsoids are projected at the 50% probability level (only the thermal ellipsoids of the atoms that make up the cubic core are shown for the sake of clarity).

the manganese site in addition to a methoxy ligand coordinated to the same center which points inside the internal cavity of the cube. Such an occupancy inside the internal void of the cube had been previously noted for the Re₄Mn₄ cube in which a methanol ligand is present inside the cavity and for a derivative of the Re₄Fe₄Cl₄ cube, ${[Re(triphos)(CN)_3]_4[FeCl]_{3.5}[Fe(OCH_3)(THF)]_{0.5}}^{21}$ which has a methoxy ligand inside the cavity. The extra methoxy group leads to a flattening of one of the corners of the cube in 3 and also serves to compensate for the loss of one negative charge from the molecule resulting in a neutral cluster. The Mn-N distances for Mn(2), Mn(3), and Mn(4) are similar to the ones observed for 2 and 4, and range from 2.04 Å to 2.14 Å (Table 2). Although the Mn(1) atom adopts a 5-coordinate distorted trigonal bipyramidal geometry, the Mn(1)-N distances are similar to those of the other Mn atoms. The distorted cube molecule in 4 and 2 exhibits a similar molecular structure to that of 3. The Re-C distances adopt values in the range from 2.01 to 2.14 Å, distances that are in reasonable accord with those observed for 3. The Mn-N distances are also comparable to those for 3 and range from 2.00 to 2.09 Å. Fig. 2 and 4 depict the molecular structure of compounds 2 and 4 respectively.

The molecular structure of **5** reveals that the compound consists of chains of cubes connected by σ -[TCNQ₂]²⁻ ligands. The asymmetric unit of **5** consists of one cubic molecule with each manganese site being connected to one TCNQ moiety. Each TCNQ ligand is composed of two C-(CN)₂ units, one of which is sp² and therefore planar with the phenyl ring and is used to connect to the manganese site and a second one that is sp³ due

to the formation of a σ -bonded TCNQ dimer. Once the contents of the unit cell are expanded, it can be seen that only three of the TCNQ ligands participate in the formation of σ -bonded TCNQ dimers (Fig. 5). The fourth TCNQ ligand, however is apparently H–TCNQ, a conclusion that is supported by the observations that (i) the dangling C(23)–(CN)2 unit is twisted with respect to the phenyl ring of the TCNQ ligand suggesting the presence of an atom bonded to C(23) and (ii) this particular TCNQ ligand should not bear a charge since each neutral cube already consists of one methoxy anion and three TCNQ⁻ ligands (half of a σ -[TCNQ₂]²⁻ ligand).

Further inspection of the σ -bond present in the $[TCNQ_2]^{2-}$ unit by X-ray single crystal studies confirms that two of the σ -[TCNQ₂]²⁻ ligands are identical. Both of these [TCNQ₂]²⁻ bridges are used to connect two cubes to each other, the overall result of which is a dimer of cubes linked through two sets of σ -[TCNQ₂]²⁻ ligands (Fig. 5). The third σ -[TCNQ₂]²⁻ ligand connects these dimers of cubes to form a single chain of cubes (Fig. 6-7). The σ -bond present in the former σ -[TCNQ₂]²⁻ ligand (C(47)-C(59) is 1.55 Å) is shorter than the one in the latter unit (C(35)-C(35')) is 1.605 Å) (Table 3). Both values are in reasonable accord with the distances reported for $[Cu(DMP)_2]_2(TCNQ)_2$ (1.63 Å) prepared by Hatfield *et al.*, which consists of σ -[TCNQ₂]²⁻ stacks.⁴⁹ Moreover, the Mn(TCNQ)₂(MeOH)₂ polymer prepared by Dunbar et al., is composed of a 2D network of six-coordinate Mn(II) ions equatorially bound to four outer nitrile groups of the σ -[TCNQ₂]²⁻ ligands which exhibit a σ-bond of 1.635 Å between the TCNQ⁻ anions.⁵⁰



Fig. 4 The molecular structure of $\{[Re(triphos)(CN)_3]_4[Mn(N(CN)_2)]_4\}$ (4). Thermal ellipsoids are projected at the 50% probability level (only the thermal ellipsoids of the atoms that make up the cubic core are shown for the sake of clarity).

N14

Mn2

N15

Mn3

N2

C8 N4C

C

N10 C10

N11 C11

C5

C12

116



Fig. 5 Structure of a segment of the chain in 5 emphasizing the σ -[TCNQ₂]²⁻ units that are linking the Re₄Mn₄-cubes.



Fig. 6 Structure of a chain of the linked cubes in 5.



Fig. 7 Packing diagram of compound 5 depicted along the c axis.

Infrared spectroscopy

An infrared (IR) spectrum of compound **2** contains three absorptions in the $v_{C=N}$ region. The assignment of these modes was carried out by a comparison to the stretching frequencies of the Re₄Mn₄ cube (2100, 2085 cm⁻¹) as well as the complex [Mn(MeCN)₄](BF₄)₂ (2282, 2307 cm⁻¹) reported by Hathaway *et al.*,⁵¹ which is helpful because **2** contains Mn(II) ions coordinated to acetonitrile. With the help of these data, the two energy modes at 2089 and 2070 cm⁻¹ observed for **2** were assigned to the bridging cyanides that make up the cube core, and the higher energy mode at 2296 cm⁻¹ is attributed to the dangling acetonitrile ligands. The shift of the $v_{C=N}$ stretches of the bridging cyanide ligands to lower frequencies

as compared to the parent Re_4Mn_4 cube is attributed to weaker Mn–N bonds.

Infrared (IR) spectral measurements performed on polycrystalline samples of **3** revealed the presence of two intense $v_{C=N}$ stretches located at 2088 and 2076 cm⁻¹ which are assigned to the bridging cyanides according to the same analysis as employed for compound **2**.

The infrared spectra in the $v_{C=N}$ region of **4** reveal three stretches at 2262, 2206, and 2156 cm⁻¹ which are assigned to the dangling dicyanamide ligands in addition to the modes at 2077 and 2095 cm⁻¹ which correspond to the bridging cyanide ligands. The three former absorptions are indicative of terminal monodentate dicyanamide ligands, which is also consistent with

the X-ray crystal structure of 4. An IR spectrum of Na[N(CN)₂], in which the dicyanamide anions are not coordinated exhibits three $V_{C=N}$ stretches. The stretch located at 2179 cm⁻¹ is assigned to the symmetric $v_{C=N}$ mode, the one at 2232 cm⁻¹ to the asymmetric $V_{C=N}$ mode and the one at 2286 cm⁻¹ to a combination of asymmetric and symmetric $v_{C=N}$ modes. Coordination of the dicyanamide anion to a metal center results in a shift of these bands to higher frequencies similar to what occurs with $v_{C=N}$ stretches of bridging cyanide ligands. For example, $V_{C=N}$ stretches at 2194, 2261, and 2293 cm⁻¹ are observed for the 3D framework compound, Mn(dca)₂ which consists of dicyanamide ligands in which both cyano groups are involved in binding.52 The stretches observed for 4 are in good agreement with other clusters that contain monodentate dicyanamide ligands attached to Mn(II) centers such as $[Mn_4(hmp)_6(NO_3)_2(dca)_2] \cdot 2MeCN$ (hmp = 2hydroxymethylpyridine), which exhibit $v_{C=N}$ stretches at 2264, 2210, and 2154 cm⁻¹.42

Clearly the shift of $v_{C=N}$ modes with respect to reference data is useful for assigning the coordination mode of cyano groups since coordination of the N-atom to a metal center usually leads to a shift to higher frequencies due to σ -donation from the cvanide ligand to the metal ion, but there are complications with this argument for the TCNQ molecule. The $V_{C=N}$ stretching modes of the TCNQ molecule can shift to higher energies if TCNQ acts primarily as a σ -donor or to lower energies if there is significant metal to TCNQ π -back-bonding. As an illustration, we note that three distinct absorptions ranging from 2168 to 2226 cm⁻¹ were observed in the infrared spectra of a series of materials of general formula M(TCNQ)₂(H₂O)₂ (M=Mn, Fe, Co, and Ni).⁵³ Fortunately the δ (C–H) bend of TCNQ is very informative for detecting the presence of the σ -dimer [TCNQ-TCNQ]²⁻ unit. The $Mn(TCNQ)_2(H_2O)_2$ material (which is more appropriately written as $[Mn(TCNQ-TCNQ)(MeOH)_4]_{\infty})$ exhibits a $\delta(C-H)$ mode at ~825 cm⁻¹ indicative of [TCNQ]-* as well as a bending mode at 806 cm⁻¹ which is assigned to the presence of σ -[TCNQ–TCNQ]²⁻. Compound 5 exhibits IR features at 804 and 812 cm⁻¹, which support the findings from the X-ray crystal structure and show the presence of σ-[TCNQ-TCNQ]²⁻ and [H-TCNQ] units. Additional

features in the $v_{C=N}$ region (2050–2300 cm⁻¹) at 2113, 2130, 2171, and 2195 cm⁻¹ are assigned to cyanide stretches of the TCNQ moieties and those at 2079 and 2092 cm⁻¹ are assigned to bridging cyanide ligands in **5**.

Magnetic properties

The magnetic properties of compounds 2-5 are similar to those of the Re₄Mn₄ cube. The behavior in the temperature range of 2-300 K reveals the existence of antiferromagnetic coupling between the metal ions. The χT values at 300 K are 17.57, 16.77, 16.27, and 16.73 emu mol-1 K for compounds 2-5, respectively, which correspond to four non-interacting Re(II) centers (based on the reference value from the starting material of 0.63 emu mol⁻¹ K per metal ion) and four high-spin S =5/2 Mn(II) ions with 4.11 emu mol⁻¹ K per Mn center (Fig. 8). The χT vs. T curve decreases over the low temperature range until it reaches a minimum at ~50 K after which temperature it begins to increase until it reaches a low temperature maximum of 23.05 emu mol⁻¹ K at ~3.8 K for 2, 16.64 emu mol⁻¹ K at ~6.60 K for **3**, 16.81 emu mol⁻¹ K at ~6.5 K for **4**, and 18.70 emu mol⁻¹ K at ~ 6 K for 5. These values are lower than the expected spin only value for an S = 8 ground state (36 emu mol⁻¹ K) resulting from the antiferromagnetic coupling between the S = 1/2 Re(II) and S = 5/2 Mn(II) ions. The type of coupling between the Re(II) and Mn(II) metal ions can be rationalized using the idealized geometries of the metal ions. Considering the Re(II) ions in an idealized octahedral geometry, the d electrons for this ion would adopt a t_{2g}^{5} electronic configuration, while the unpaired spins in the idealized tetrahedral Mn(II) ion are in an $e^2t_2^3$ electronic configuration. By applying the Goodenough-Kanamori rules both ferromagnetic and antiferromagnetic interactions are present between the Re(II) and Mn(II) ions through the cyanide bridge, however, the antiferromagnetic exchange overwhelms the competing ferromagnetic interactions, as expected for superexchange through cyanide between Re(II) (t_{2g}^{5}) and high-spin tetrahedral Mn(II) (e²t₂³) centers.⁵⁴ The difference between the expected spinonly value and the experimental values are a consequence of



Fig. 8 Temperature-dependent magnetic susceptibility data for 2–5 recorded in the range of 1.8–300 K at 1000 Oe.

Downloaded by University of Sussex on 04 January 2013 Published on 27 April 2010 on http://pubs.rsc.org | doi:10.1039/B927242A the anisotropic behavior of the Re(II) ions (Figure S1–4†), which results in g values lower than the isotropic value of 2.0 for these clusters.^{22,55}

AC susceptibility experiments were performed in order to probe whether the clusters exhibit slow paramagnetic relaxation. Measurements performed at 1.8 K using four frequencies from 1–1000 Hz (MPMS SQUID) exhibit signals with both an inphase (χ') and out-of phase (χ'') component which support the conclusion that **2–5** exhibit slow paramagnetic relaxation (Fig. 9). The effective heights of the energy barrier for magnetization reversal are quite low for these compounds, as evidenced by the lack of a maximum in the χ'' vs. T data in this temperature range at these frequencies.



Fig. 9 AC susceptibility studies of 5 from 1.8–5 K with $H_{DC} = 0$ Oe and $H_{AC} = 3$ Oe. AC susceptibility studies of other compounds are available as supplementary information.†

Conclusions

Derivatives of the SMM cluster ${[Re^{II}(triphos)(CN)_3]_4[Mn^{II}Cl]_4}$ have been prepared and found to retain the original properties of the parent compound. Compound **2** possesses a 4⁺ charge in contrast to the Re₄Mn₄ cube since negatively charged halogen atoms have been replaced with neutral acetonitrile ligands. In the case of compound **3**, perchlorate anions are used to complete the coordination sphere of three Mn(II) sites with the fourth Mn(II) center being five-coordinate due to the presence of both a methanol and a methoxy ligand. AC susceptometry revealed that a frequency dependency of the χ'' signal was observed for all of the reported derivatives, behavior that is essentially the same as that of the original Re₄Mn₄ cube.

Two additional compounds were obtained from reactions with dicyanamide (dca⁻) and TCNQ⁻⁺. The reaction of the derivative **2** with dca⁻ yielded a discrete cluster (**4**) with dangling dicyanamide ligands, whereas the reaction with LiTCNQ produced a single chain of dimers of Re₄Mn₄ cubes bridged through σ -bonded [TCNQ₂]²⁻ moieties (**5**). Magnetic measurements revealed that both of these compounds exhibit SMM behavior similar to Re₄Mn₄ cube.

The new derivatives reported in this work are air stable and soluble. As such they represent promising candidates for further reactions aimed at tuning their properties and altering their functionalities.

Acknowledgements

This research was supported by the Department of Energy (grant DE-FG03-02ER45999) and the Welch Foundation (A-1449). Funding of the CCD diffractometer (CHE-9807975) by the NSF is gratefully acknowledged.

Notes and references

- 1 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, 365, 141–143.
- 2 R. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, J. Am. Chem. Soc., 1993, 115, 1804–1816.
- 3 A. A. Mukhin, V. D. Travkin, A. K. Zvezdin, S. P. Lebedev, A. Caneschi and D. Gatteschi, *Europhys. Lett.*, 1998, 44, 778.
- 4 M. Shatruk, C. Avendano and K. R. Dunbar, Prog. Inorg. Chem., 2009, 56, 155–334.
- 5 D. Gatteschi and R. Sessoli, Angew. Chem., Int. Ed., 2003, 42, 268-297.
- 6 D. Li, S. Parkin, G. Wang, G. T. Yee, A. V. Prosvirin and S. M. Holmes, *Inorg. Chem.*, 2005, 44, 4903–4905.
- 7 Y. Song, P. Zhang, X. M. Ren, X. F. Shen, Y. Z. Li and X.-Z. You, J. Am. Chem. Soc., 2005, **127**, 3708–3709.
- 8 D. Li, S. Parkin, G. Wang, G. T. Yee, R. Clerac, W. Wernsdorfer and S. M. Holmes, J. Am. Chem. Soc., 2006, **128**, 4214.
- 9 H. J. Choi, J. J. Sokol and J. R. Long, Inorg. Chem., 2004, 43, 1606.
- 10 E. J. Schelter, A. V. Prosvirin and K. R. Dunbar, J. Am. Chem. Soc., 2004, 126, 15004–15005.
- 11 C. P. Berlinguette, D. Vaughn, C. Canada-Vilalta, J. R. Galan-Mascaros and K. R. Dunbar, Angew. Chem., Int. Ed., 2003, 42, 1523–1526.
- 12 C. Raghu, I. Rudra, D. Sen and S. Ramasesha, Phys. Rev. B: Condens. Matter Mater. Phys., 2001, 64, 64419.
- 13 J. H. Yoon, J.-H. Lim, H.-C. Kim and C. S. Hong, *Inorg. Chem.*, 2006, 45, 9613–9615.
- 14 C.-F. Wang, J.-L. Zuo, B. M. Bartlett, Y. Song, J. R. Long and X.-Z. You, J. Am. Chem. Soc., 2006, 128, 7162.
- 15 M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon and R. Clerac, J. Am. Chem. Soc., 2005, 127, 3090.
- 16 D. Li, S. Parkin, G. Wang, G. T. Yee and S. M. Holmes, *Inorg. Chem.*, 2006, 45, 2773–2775.
- 17 S. Wang, J.-L. Zuo, H.-C. Zhou, H. J. Choi, Y. Ke, J. R. Long and X.-Z. You, Angew. Chem., Int. Ed., 2004, 43, 5940–5943.

- 19 H. Miyasaka, H. Takahashi, T. Madanbashi, K. Sugiura, R. Clerac and H. Nojiri, *Inorg. Chem.*, 2005, 44, 5969.
- 20 A. L. Barra, P. Debrunner, D. Gatteschi, C. E. Schulz and R. Sessoli, *Europhys. Lett.*, 1996, 35, 133.
- 21 E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer and K. R. Dunbar, J. Am. Chem. Soc., 2007, 129, 8139–8149.
- 22 A. V. Palii, S. M. Ostrovsky, S. I. Klokishner, B. S. Tsukerblat, E. J. Schelter, A. V. Prosvirin and K. R. Dunbar, *Inorg. Chim. Acta*, 2007, 360, 3915–3924.
- 23 D. E. Freedman, D. M. Jenkins, A. T. Iavarone and J. R. Long, J. Am. Chem. Soc., 2008, 130, 2884–2885.
- 24 S. L. Bartley and K. R. Dunbar, Angew. Chem., Int. Ed. Engl., 1991, 30, 448–450.
- 25 G. M. Finniss, E. Canadell, C. Campana and K. R. Dunbar, Angew. Chem., 1996, 108, 2946–2774.
- 26 S. L. Bartley and K. R. Dunbar, Angew. Chem., 1991, 103, 447–450.
- 27 S. L. Bartley and K. R. Dunbar, Angew. Chem., Int. Ed. Engl., 1991, 30 448–450
- 28 C. Campana, K. R. Dunbar and X. Ouyang, Chem. Commun., 1996, 2427–2428.
- 29 S. L. Bartley, M. J. Bazile, R. Clerac, H. Zhao, X. Ouyang and K. R. Dunbar, *Dalton Trans.*, 2003, 2937–2944.
- 30 X. Ouyang, C. Campana and K. R. Dunbar, *Inorg. Chem.*, 1996, 35, 7188–7189.
- 31 C. E. Uzelmeier, S. L. Bartley, M. Fourmigué, R. Rogers, G. Grandinetti and K. R. Dunbar, *Inorg. Chem.*, 1998, 37, 6706–6713.
- 32 S. L. Bartley, S. N. Bernstein and K. R. Dunbar, *Inorg. Chim. Acta*, 1993, 213, 213–231.
- 33 K. E. Funck, M. G. Hilfiger, C. P. Berlinguette, M. Shatruk, W. Wernsdorfer and K. R. Dunbar, *Inorg. Chem.*, 2009, 48, 3438–3452.
- 34 C. P. Berlinguette and K. R. Dunbar, Chem. Commun., 2005, 2451-2453.
- 35 J. Kim, J. M. Lim and Y. Do, Eur. J. Inorg. Chem., 2003, 2563-2566.
- 36 Y.-Z. Zheng, M.-L. Tong, W. Xue, W.-X. Zhang, X.-M. Chen, F. Grandjean and G. J. Long, *Angew. Chem., Int. Ed.*, 2007, 46, 6076–6080.

- 37 H.-B. Xu, B.-W. Wang, F. Pan, Z.-M. Wang and S. Gao, Angew. Chem., Int. Ed., 2007, 46, 7388–7392.
- 38 M. Viciano-Chumillas, S. Tanase, I. Mutikainen, U. Turpeinen, L. J. de Jongh and J. Reedijk, *Inorg. Chem.*, 2008, 47, 5919–5929.
- 39 P. Albores and E. Rentschler, Inorg. Chem., 2008, 47, 7960-7962.
- 40 Y.-L. Bai, J. Tao, W. Wernsdorfer, O. Sato, R.-B. Huang and L.-S. Zheng, J. Am. Chem. Soc., 2006, 128, 16428–16429.
- 41 J. Tao, Y.-Z. Zhang, Y.-L. Bai and O. Sato, *Inorg. Chem.*, 2006, **45**, 4877–4879.
- 42 H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita and R. Clerac, J. Am. Chem. Soc., 2006, 128, 3770–3783.
- 43 Z. Lin, Z. Li and H. Zhang, Cryst. Growth Des., 2007, 7, 589-591.
- 44 H. Miyasaka, K. Nakata, K. Sugiura, M. Yamashita and R. Clerac, Angew. Chem., Int. Ed., 2004, 43, 707–711.
- 45 W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson and G. Christou, *Nature*, 2002, 416, 406–409.
- 46 R. Bagai, W. Wernsdorfer, K. A. Abboud and G. Christou, J. Am. Chem. Soc., 2007, 129, 12918–12919.
- 47 E. J. Schelter, J. K. Bera, J. Bacsa, J. R. Galan-Mascaros and K. R. Dunbar, *Inorg. Chem.*, 2003, 42, 4256–4258.
- 48 M. T. Costello, P. W. Schrier, P. E. Fanwick and R. A. Walton, *Inorg. Chim. Acta*, 1993, 212, 157–163.
- 49 S. K. Hoffmann, P. J. Corvan, P. Singh, C. N. Sethulekshmi, R. M. Metzger and W. E. Hatfield, J. Am. Chem. Soc., 1983, 105, 4608–4617.
- 50 H. Zhao, R. A. Heintz and K. R. Dunbar, J. Am. Chem. Soc., 1996, 118, 12844–12845.
- 51 B. J. Hathaway, D. G. Holah and A. E. Underhill, J. Chem. Soc., 1962, 2444–2448.
- 52 J. L. Manson, C. R. Kmety, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, 1999, 38, 2552–2553.
- 53 H. Zhao, R. A. Heintz, X. Ouyang and K. R. Dunbar, *Chem. Mater.*, 1999, **11**, 736–746.
- 54 E. Ruiz, A. Rodriguez-Fortea, S. Alvarez and M. Verdaguer, *Chem.-Eur. J.*, 2005, **11**, 2135–2144.
- 55 K. R. Dunbar, E. J. Schelter, A. V. Palii, S. M. Ostrovsky, V. Y. Mirovitskii, J. M. Hudson, M. A. Omary, S. I. Klokishner and B. S. Tsukerblat, J. Phys. Chem. A, 2003, 107, 11102–11111.