PERGAMON

Polyhedron 20 (2001) 1279–1283

POLYHEDRON

www.elsevier.nl/locate/poly

A third isolated oxidation state for the family of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ compounds. Synthesis, characterization and single-molecule magnetism properties of $(PPh_4)_2[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ ($x = 3$ or 4)

Mònica Soler [a], Swapan K. Chandra [a], Daniel Ruiz [b], John C. Huffman [a], David N. Hendrickson* [b,1], George Christou* [a,2]

[a] *Department of Chemistry, Indiana University, Bloomington, IN 47405-4001, USA*
[b] *Department of Chemistry, University of California at San Diego, La Jolla, CA 92093-0358, USA*

Received 17 September 2000; accepted 28 October 2000

Abstract

The synthesis and characterization are reported of the two-electron reduced version of the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ family of single-molecule magnets (SMMs). Reduction of the neutral complexes with 2 equiv. of PPh_4I gives the $(PPh_4)_2[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ ($x = 3$ or 4). The crystal structure shows the overall Mn_{12} structure is maintained, with a 2Mn(II), 6Mn(III), 4Mn(IV) trapped oxidation state description. Magnetic characterization indicates a $S = 10$ ground state and retention of SMM behavior. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Single-molecule magnets; Crystal structures; Magnetic characterization

1. Introduction

Research for new single-molecule magnets (SMMs) is of immense interest. SMM behavior is due to a combination of large ground state spin (S) and a negative (easy axis) magnetoanisotropy as gauged by a negative zero-field splitting parameter, D. As a result, there is a significantly large barrier for the relaxation of the cluster's magnetization vector, making them behave as magnetizable magnets. The first and most thoroughly studied SMM was $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2HO_2CCH_3$ (**1**) commonly known as 'Mn_{12}Ac'. It was in 1993 when Mn_{12}Ac was identified as being a nanoscale magnet, the first magnet to contain discrete (magnetically) non-interacting molecular units rather than a 3D extended lattice (metals, metal oxides, etc.); such complexes are now known as SMM [1,2].

The SMM field is now established, and a few additional families of molecules are currently known to function as SMM's. These include $[Mn_4O_3X(O_2CCH_3)_3(dbm)_3]$ ($X = Cl^-$, Br^-, F^-, N_3^-, $CH_3CO_2^-$, etc.) complexes possessing a $S = 9/2$ ground state [3,4] as well as few others Fe_8 [5], Fe_4 [6], Mn_{11} [7] and V_4 [8] species.

For $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2HO_2CCH_3$ (**1**), [1,9,10] the slow magnetization relaxation has been shown to be due to a $S = 10$ ground state spin and an axial zero-field splitting parameter D of -0.50 cm^{-1}. Considerable insight has been obtained from chemical modifications made on the Mn_{12}Ac (**1**) SMM. It was found that ligand exchange of the acetate ligands with a variety of carboxylate ligands resulted in new Mn_{12} complexes with higher solubility in organic solvents [11]. This modification also led to the discovery of Jahn–Teller isomerism in the $[Mn_{12}]$ family [12,13]. Other methods have been used to modify the chemical environment of the Mn_{12}, expanding the chemistry of this family of molecules, including the synthesis of the $[Mn_8Fe_4]$ analogue [14]. Finally, it has also been possi-

---

[1] *Corresponding author.

[2] *Corresponding author. Tel./fax: + 1-812-855-2399; christou@indiana.edu.

PII: S0277-5387(01)00606-4

ble to reduce the $[Mn_{12}]$ with one electron to give $(PPh_4)[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ with a ground state of $S = 19/2$. These one-electron reduced Mn_{12} compounds have been reported also to function as SMMs [10,11,15].

In this paper we report the successful isolation of the two-electron reduced form of the $[Mn_{12}]$ complexes. Furthermore, it is shown that they retain both a high ground state spin value and the resulting SMM properties reported previously for the $[Mn_{12}]^{0,1-}$ species. This provides new information on how changing the spin state and magnetic anisotropy can affect the intrinsic magnetic properties of these important molecules.

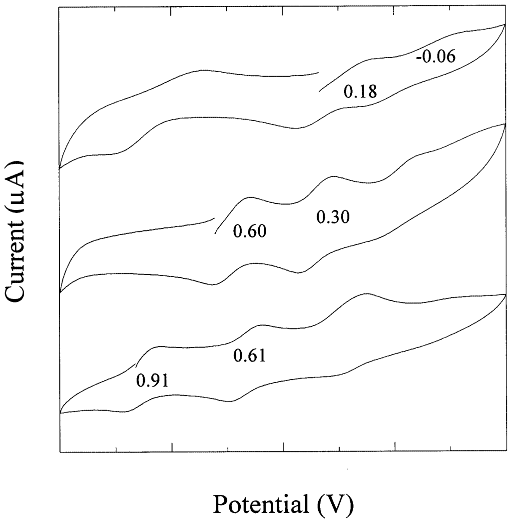

Fig. 1. Cyclic voltammogram at 100 mV s^{-1} for complexes **1**, **2** and **3** in CH_3CN containing 0.10 M $NBu^n_4PF_6$ as supporting electrolyte. The working and auxiliary electrodes were glassy carbon and Pt wire, respectively. The indicated potentials are vs. ferrocene as an internal reference.

Table 1
Electrochemical data for selected $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes[a]

R	E_1 (V)[b]	E_2 (V)[c]
CH_3 (**1**)	+0.18	−0.06
CH_2Cl (**2**)	+0.60	+0.30
$CHCl_2$ (**3**)	+0.91	+0.61
C_6H_5[d]	+0.12	−0.23
C_6H_4-2-NO_2	+0.47	+0.19
C_6H_4-4-NO_2[d]	+0.49	+0.23
C_6H_3-2,4-$(NO_2)_2$ (**5**)	+0.74	+0.45
C_6F_5 (**4**)	+0.64	+0.46

[a] In CH_3CN, unless otherwise indicated; quoted values are DPV peak potentials vs. ferrocene.

[b] First reduction.

[c] Second reduction.

[d] In CH_2Cl_2.

2. Results and discussion

The electrochemical properties of $[Mn_{12}]$ complexes possessing ligands with wide variety of electron-withdrawing capabilities have been studied. $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes with electron-withdrawing groups (R = CH_2Cl (**2**), $CHCl_2$ (**3**), C_6F_5 (**4**) and C_6H_3-2,4-$(NO_2)_2$ (**5**)) were prepared from **1** using the procedure reported elsewhere. The CV in MeCN of **1**, **2** and **3** are shown in Fig. 1. The representative CVs of **2** and **3** show two quasi-reversible one-electron reduction processes at significantly lower potentials than **1**. These values are markedly more positive and more reversible from an electrochemical criteria (forward vs. reverse peak currents and separations) than those for previously reported $[Mn_{12}]$ derivatives (Table 1). The shift of potentials can be correlated with the relative pK_a values of the acids. As the pK_a of the parent acid is decreased, the electron-withdrawing ability of the carboxylate ligands increases, reducing the electron density on the $[Mn_{12}O_{12}]^{16+}$ core and making it easier to reduce. In addition, as the electron-withdrawing ability of the ligand increases, the second reduction becomes more accessible. Therefore, the dianionic species were targeted and subsequently successfully prepared on a large scale using I^- as reducing agent, as previously employed for one-electron reductions [7,11,15]. Thus, addition of two equivalents of PPh_4I, removal of I_2 with hexanes and recrystallization from CH_3CN–Et_2O–hexanes or CH_2Cl_2–hexanes gave dark red–black crystals of $(PPh_4)_2[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$ (**6**), $(PPh_4)_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (**7**), $(PPh_4)_2[Mn_{12}O_{12}(O_2CC_6F_5)_{16}(H_2O)_4]$ (**8**) and $(PPh_4)_2[Mn_{12}O_{12}(O_2CC_6H_3\text{-}2,4\text{-}(NO_2)_2)_{16}(H_2O)_4]$ (**9**) (Eq. (1)).

$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + 2PPh_4I \rightarrow (PPh_4)_2[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x] + I_2 \qquad (1)$$

These compounds have been characterized by IR, ^1H NMR, ^{19}F NMR, elemental analysis, CV, DPV, magnetic studies and, in the cases of **6** and **7**, crystallography.

2.1. X-ray crystallography

The crystal structures of $(PPh_4)_2[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$ (**6**) and $(PPh_4)_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (**7**) were obtained and confirmed the retention of the same structure as observed in the neutral and monoanionic species. The clusters are trapped-valence [2Mn(II), 6 Mn(III), 4 Mn(IV)] species in the solid state. In both cases the structure shows two PPh_4^+ cations and the anion $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{2-}$ ($x = 3$ (**6**) and $x = 4$ (**7**)). A plot of the dianion of complex **7** is shown in Fig. 2, where Mn9 and Mn11 are

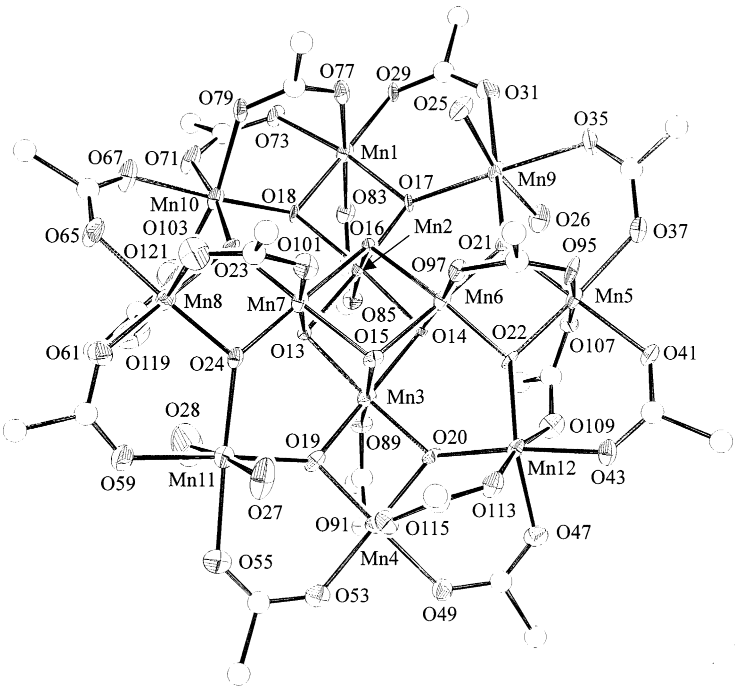

Fig. 2. ORTEP representation of the anion of complex **7** showing 50% probability ellipsoids. For clarity, all hydrogen and chlorine atoms have been omitted.

Mn(II) ions. The assignment of Mn(II)/Mn(III)/Mn(IV) sites is based on relative Mn–O bond distances, bond valence sum calculations [16] (Table 2) and the presence of Jahn–Teller (JT) axial elongations at the six Mn(III) sites. In both structures, the two added electrons are located in the outer ring on two Mn(II) (formerly Mn(III)) ions rather than reducing two Mn(IV) ions in the central cubane. This can be explained by the same argument used for the one-electron reduction product [15], i.e. the two electrons are located in the outer ring to avoid the strain that would be introduced into the rigid $[Mn(IV)_4O_4]^{8+}$ central cubane from the formation of JT-elongated Mn(III) ions. Complex **7** has four H_2O ligands that are located in Mn9 and Mn11 which are the two Mn(II) ions. Complex **6** only has three H_2O ligands, two of them on a Mn(II) ion and the third one on a Mn(III) ion. Several other $[Mn_{12}]$ complexes have shown this feature of only possessing three H_2O molecules in the solid state.

2.2. Magnetism studies

The ground state spin values for **6**, **7**, **8** and **9** were determined from the fitting of the reduced magnetization data ($M/N\mu_B$) versus H/T data in the 10–70 kG and 1.80–4.00 K ranges. In Fig. 3 is presented the plot of the reduced magnetization data for complex **7**; fitting of these data gives $S = 10$, $D = -0.27$ cm^{-1} (-0.39 K) and $g = 2.00$. For the other three complexes, the fitting values are in the same range ($S = 10$, $D = -0.26$ cm^{-1}, $g = 1.94$ for **6**; $S = 10$, $D = -0.28$ cm^{-1}, $g = 2.01$ for **8** and $S = 10$, $D = -0.28$ cm^{-1}, $g = 1.94$ for **9**). The ground state spin is thus similar to the $S = 10$ or 19/2 values for the neutral and monoanionic complexes, respectively, but the anisotropy decreases on reduction as the Mn(III) content decreases; Jahn–Teller distortions of the latter are the main contributor to the anisotropy of the molecule. The $S(D)$ values for the three oxidation levels are: $[Mn_{12}]$, 10 (ca. -0.5 cm^{-1});

Table 2
Bond valence sums for each Mn atom in the complex $(PPh_4)_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]\cdot 4CH_2Cl_2\cdot H_2O$ [a]

Atom	Mn(II)	Mn(III)	Mn(IV)
Mn(1)	3.265804	**2.987141**	3.136055
Mn(2)	4.225385	3.864844	**4.057512**
Mn(3)	4.230319	3.869356	**4.062249**
Mn(4)	3.382426	**3.093812**	3.248043
Mn(5)	3.27541	**2.995927**	3.145278
Mn(6)	4.168696	3.812991	**4.003074**
Mn(7)	4.151116	3.796911	**3.986193**
Mn(8)	3.287366	**3.006863**	3.15676
Mn(9)	**2.144883**	1.961866	2.059668
Mn(10)	3.416894	**3.125339**	3.281142
Mn(11)	**2.087613**	1.909482	2.004673
Mn(12)	3.366642	**3.079375**	3.232886

[a] The bold value is the one closest to the actual charge for which it was calculated. The oxidation state of a particular atom can be taken as the nearest whole number to the bold number.

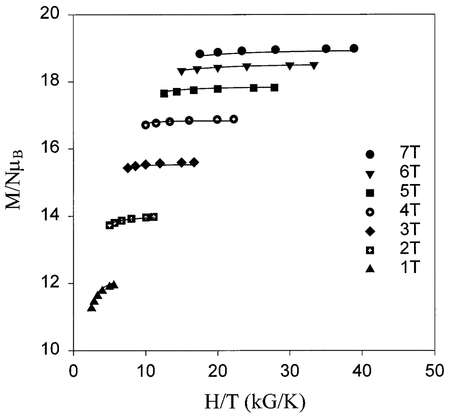

Fig. 3. Plot of the reduced magnetization ($M/N\mu_B$) vs. H/T for complex **7** at the indicated fields. The solid lines are fits to the appropriate expression; see text for the fit parameters.

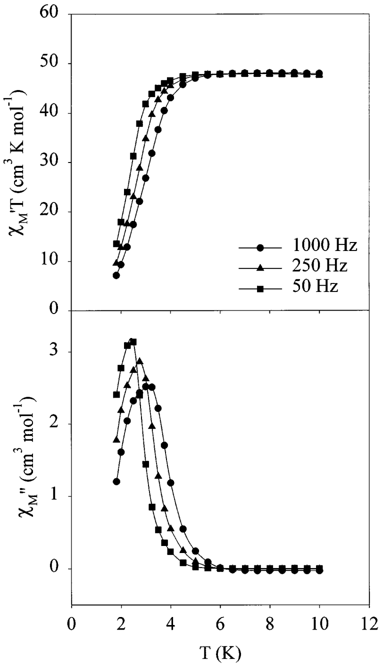

Fig. 4. Plots of the in-phase and out-of-phase ac magnetic susceptibility (χ''_M) for complex **7** at the indicated oscillation frequencies of the applied field.

[Mn$_{12}$]$^{1-}$, 19/2 (ca. -0.4 cm^{-1}); [Mn$_{12}$]$^{2-}$, 10 (ca. -0.3 cm^{-1}). This implies that the two-electron reduced Mn$_{12}$ complexes might also function as SMMs, if they have a sufficiently large barrier to the reversal of the magnetization that they display slow magnetization relaxation (reorientation) rates. The calculated barriers are: [Mn$_{12}$], U ca. 72 K; [Mn$_{12}$]$^{1-}$, U ca. 56 K; [Mn$_{12}$]$^{2-}$, U ca. 39 K ($U = S^2|D|$ for integer and $(S^2 - 1/4)|D|$ for half-integer spins).

Ac magnetic susceptibility studies at zero dc field and 3.5 G ac field were carried out to determine the slow magnetization relaxation rates for these complexes (**6**, **7**, **8** and **9**). The observation of a frequency-dependent out-of-phase ac magnetic susceptibility signal at zero dc field is an indicator that a molecule functions as a SMM. In the ac susceptibility experiment, the ac magnetic field is oscillated at a particular frequency and a non-zero χ''_M is observed when the magnetic moment of the molecule cannot relax (reorient) fast enough to keep in-phase with the oscillating field. The position of the out-of-phase ac susceptibility peak maximum is the temperature at which the relaxation rate of the molecule equals the oscillating field. The upper panel of Fig. 4 shows the plot of the in-phase component of the ac susceptibility versus temperature ($\chi'_M T$ vs. T) while the lower panel is a plot of the out-of-phase susceptibility versus temperature (χ''_M versus T) for complex **7**. Frequency-dependent out-of-phase ac susceptibility signals have been observed for all the complexes reported here (**6**, **7**, **8** and **9**), which indicates that all of them function as SMMs. In all cases one peak is observed in the range of 2–4 K range, lower than the 4–6 K and 6–8 K ranges for the χ''_M peaks in the monoanionic and neutral complexes, respectively (Fig. 5). This is consistent also with the change in S and D values on progressive reduction. The value of $\chi'_M T$ at this

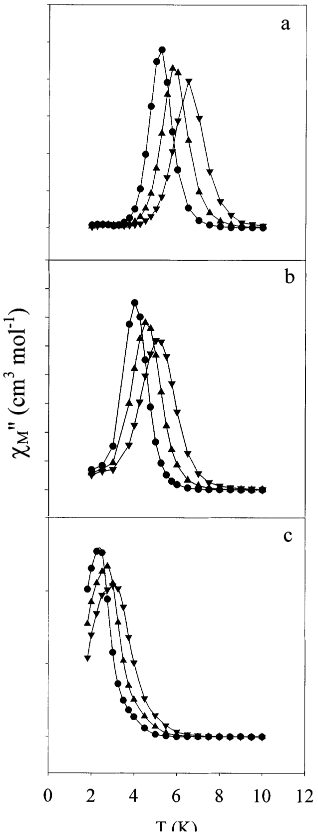

Fig. 5. Plot of the out-of-phase peaks ac magnetic susceptibility (χ''_M) for the series [Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_{16}$(H$_2$O)$_4$] (**3**) (a), (PPh$_4$)$_2$-[Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_{16}$(H$_2$O)$_4$] (b) and (PPh$_4$)[Mn$_{12}$O$_{12}$(O$_2$CCHCl$_2$)$_{16}$(H$_2$O)$_4$] (**7**) (c) at 1000 Hz (▼), 250 Hz (▲) and 50 Hz (●).

low-temperature plateau in Fig. 4 can be used also to estimate the ground state for complex **7**. If it is assumed that only the ground state of complex **7** is thermally populated in the 5–10 K range, then the value of $\chi'_M T$ indicates a $S = 10$ ground state with $g = 1.9$.

3. Conclusions

Electron-withdrawing carboxylate ligands have made possible the addition of a second electron to the $[Mn_{12}O_{12}]$ core. Two crystal structures have been obtained showing that both electrons are going on to Mn(III) ions, reducing them to Mn(II). All members of this family of neutral, one-electron reduced and two-electron reduced Mn_{12} complexes behave as single-molecule magnets. The two-electron reduced Mn_{12} complexes show faster relaxation processes than the neutral or one-electron reduced complexes. The $[Mn_{12}]$ family of SMMs has been extended and now provides three oxidation levels for the study of this important new phenomenon. The ability to synthetically control the S and D values of a family of molecules is necessary if the directed synthesis is to be achieved of complexes that display single-molecule magnetism at higher temperatures. In particular, the $[Mn_{12}]^{2-}$ versus $[Mn_{12}]$ comparison provides an invaluable opportunity to study how the magnetic properties and quantum tunneling behavior of equivalent spin ($S = 10$) system vary with magnetoanisotropy.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 182/1822. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Science Foundation.

References

[1] R. Sessoli, D. Gatteschi, G. Christou, D.N. Hendrickson, Nature 365 (1993) 141.

[2] R. Sessoli, H.-L. Tsai, A.R. Schake, S. Wang, J.B. Vincent, K. Folting, D. Gatteschi, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 115 (1993) 1804.

[3] S.M.J. Aubin, M.W. Wemple, D.M. Adams, H.-L. Tsai, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 118 (1996) 7746.

[4] S.M.J. Aubin, N.R. Dilley, L. Pardi, J. Krystek, M.W. Wemple, L.-C. Brunel, M.B. Maple, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 120 (1998) 4991.

[5] A.-L. Barra, P. Debrunner, D. Gatteschi, C.E. Schulz, R. Sessoli, Europhys. Lett. 35 (1996) 133.

[6] A.-L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, J. Am. Chem. Soc. 121 (1999) 5302.

[7] H.J. Eppley, S.M.J. Aubin, M.W. Wemple, D.M. Adams, H.-L. Tsai, V.A. Grillo, S.L. Castro, Z. Sun, K. Folting, J.C. Huffman, D.N. Hendrickson, G. Christou, Mol. Cryst. Liq. Cryst. 305 (1997) 167.

[8] S.L. Castro, Z. Sun, C.M. Grant, J.C. Bollinger, D.N. Hendrickson, G. Christou, J. Am. Chem. Soc. 120 (1998) 2365.

[9] A.L. Barra, D. Gatteschi, R. Sessoli, Phys. Rev. B 56 (1997) 8192.

[10] S.M.J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L.-C. Brunel, A.L. Rheingold, G. Christou, D.N. Hendrickson, Inorg. Chem. 38 (1999) 5329.

[11] H.-L. Tsai, H.J. Eppley, N. de Vries, K. Folting, G. Christou, D.N. Hendrickson, J. Chem. Soc., Chem. Commun. (1994) 1745.

[12] Z. Sun, D. Ruiz, E. Rumberger, C.D. Incarvito, K. Folting, A.L. Rheingold, G. Christou, D.N. Hendrickson, Inorg. Chem. 37 (1998) 4758.

[13] Z. Sun, D. Ruiz, N.R. Dilley, M. Soler, J. Ribas, K. Folting, M.B. Maple, G. Christou, D.N. Hendrickson, Chem. Commun. (1999) 1973.

[14] S.M.J. Aubin, Z. Sun, I.A. Guzei, A.L. Rheingold, G. Christou, D.N. Hendrickson, Chem. Commun. (1997) 2239.

[15] H.J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 117 (1995) 301.

[16] (a) I.D. Brown, D. Altermatt, Acta Crystallogr., Sect. B 41 (1985) 244. (b) W. Liu, H.H. Throp, Inorg. Chem. 32 (1993) 4102.