Polyoxometalates

DOI: 10.1002/anie.201100280

Hexadecacobalt(II)-Containing Polyoxometalate-Based Single-Molecule Magnet**

Masooma Ibrahim, Yanhua Lan, Bassem S. Bassil, Yixian Xiang, Andreas Suchopar, Annie K. Powell, and Ulrich Kortz**

Polyoxometalates (POMs) are a remarkable class of inorganic compounds with enormous structural and compositional diversity and potential applications in various fields, such as catalysis, analytical chemistry, magnetism, nanotechnology, and medicine.[1] In particular lacunary heteropolytungstates of the Keggin and Wells–Dawson type are useful inorganic, diamagnetic ligands allowing for encapsulation of various multinuclear metal-oxo assemblies. Examples of such kinds of structurally, catalytically, and magnetically interesting POMs are the manganese-containing derivative $\{Mn_{14}W_{36}\}$,[2a] the iron-containing derivatives $\{Fe_9W_{12}\}$,[3a] $\{Fe_{13}W_{36}\}$,[3b,c] $\{Fe_{16}W_{48}\}$,[3d] $\{Fe_{28}W_{48}\}$,[3e] the nickel-containing derivatives $\{Ni_9W_{27}\}$,[4a] $\{Ni_8/Ni_9W_{18}\}$,[4b] $\{Ni_{12}W_{35}\}$,[4c] and $\{Ni_{20}W_{34}\}$,[4d] and the copper-containing derivatives $\{Cu_{14}W_{36}\}$[5a] and $\{Cu_{20}W_{48}X\}$ (X = Cl, Br, I).[5b,c] Some transition-metal-containing polyoxomolybdates are also known, such as $\{Fe_{30}Mo_{72}\}$,[6a] $\{V_{30}Mo_{72}\}$,[6b] as well as $\{Co_{16}Mo_{16}\}$ (two types of structures containing 16 cobalt centers, in the form of four tetramers).[7]

The class of cobalt-containing POMs was pioneered by Baker and Pope.[8a,b] Meanwhile a large number of POM-based Co^{II} complexes with nuclearities ranging from 2 to 16 has been reported.[7,9] Our group has reported a nona-cobalt-containing polyanion capped by six antenna-like Co^{II} ions in the solid state,[10a] as well as several polytungstates containing smaller numbers of cobalt ions.[10] Very recently it was shown that $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [9a] is a hydrolytically and oxidatively stable homogeneous water-oxidation catalyst.[11]

During the past decade many high-nuclearity transition-metal-based coordination complexes with interesting electronic and magnetic properties have been prepared.[12] Some cobalt derivatives with nuclearities ranging from 2 to 32 are also known.[13] It is a challenge to encapsulate high-nuclearity magnetic cores in diamagnetic POM shells, in particular by using conventional, soft synthesis methods. We have now succeeded in preparing the tetrameric 36-tungsto-8-phosphate $[\{Co_4(OH)_3PO_4\}_4(PW_9O_{34})_4]^{28-}$ (**1**), containing 16 cobalt(II) centers (Figure 1).

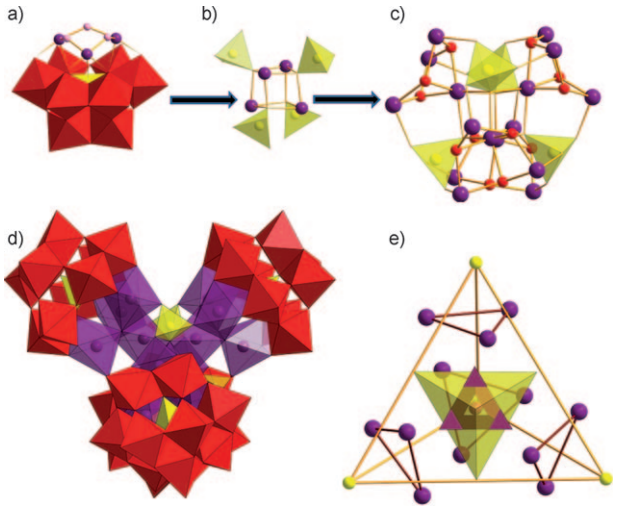

Figure 1. Representations of the various building blocks of **1**: a) $[\{Co(OH)\}_3(A\text{-}\alpha\text{-}PW_9O_{34})]^{6-}$, b) $\{Co_4(PO_4)_4\}^{4-}$, c) $\{Co_{16}(OH)_{12}(PO_4)_4\}^{8+}$, d) polyanion **1**, and e) the tetrahedral building units in **1** formed by connection of the four P heteroatoms of the heteropolyoxometalate units, the four capping P atoms of the phosphate linkers, the four central Co atoms, as well as the four triangular Co_3 groups. Color code: WO_6 red octahedra, CoO_6 violet octahedra, PO_4 yellow tetrahedra, Co violet balls, P yellow balls, O red balls. Protonated oxygen atoms are shown in pink. Images generated by Diamond Version 3.2c (copyright Crystal Impact GbR).

Polyanion **1** was synthesized in a simple one-pot reaction of $CoCl_2{\cdot}6H_2O$ with $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]{\cdot}7H_2O$ in aqueous medium at pH 8 and crystallized as a hydrated sodium–rubidium salt, $Na_{22}Rb_6[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]{\cdot}76H_2O$ (**1a**) in the cubic space group $Fd\bar{3}$. Single-crystal X-ray diffraction analysis on **1a** revealed that **1** comprises a central $\{Co_4O_4\}$ cubane unit which is capped by four tri-cobalt(II)-substituted Keggin fragments $[\{Co(OH)\}_3(A\text{-}\alpha\text{-}$

[*] M. Ibrahim,[+] Dr. B. S. Bassil, Y. Xiang, A. Suchopar, Prof. U. Kortz
Jacobs University, School of Engineering and Science
P.O. Box 750561, 28725 Bremen (Germany)
Fax: (+49) 421-200-3229
E-mail: u.kortz@jacobs-university.de
Homepage: http://www.jacobs-university.de/ses/ukortz
Dr. Y. Lan, Prof. A. K. Powell
Institut für Anorganische Chemie
Karlsruher Institut für Technologie (KIT)
Engesserstrasse 15 Geb. 30.45, 76131 Karlsruhe (Germany)
E-mail: annie.powell@kit.edu
[+] Permanent address: University of Balochistan
Post Code 87300, Quetta (Pakistan)

[**] U.K. thanks the German Science Foundation (DFG-KO-2288/9-1) for research support. M.I. thanks the DAAD and the Higher Education Commission of Pakistan for a doctoral fellowship, and the University of Balochistan, Quetta, Pakistan for allowing her to pursue PhD studies at the Jacobs University. Y.X. acknowledges a fellowship from the Jacobs University Nanofun Research Center. Y.L. and A.K.P. acknowledge support from the DFG Center for Functional Nanostructures.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100280.

$PW_9O_{34})]^{6-}$ and four phosphate linkers, resulting in an assembly with idealized T_d symmetry. Some other tetrameric assemblies comprising 3d metal-containing Keggin tungstophosphates capped by phosphate ions are known, such as $\{Fe_{13}W_{36}\}$[3b,c] and $\{Mn_{14}W_{36}\}$.[2a]

The structure of polyanion **1** can also be viewed as a tetrahedral $\{Co_4(PO_4)_4\}^{4-}$ core with each vertex linked to a $[\{Co^{II}(OH)\}_3(A\text{-}\alpha\text{-}PW_9O_{34})]^{6-}$ unit. The four Co^{II} ions in the cubane unit are coordinated by three μ_3-OH groups of the $[\{Co^{II}(OH)\}_3(A\text{-}\alpha\text{-}PW_9O_{34})]^{6-}$ units and three μ_4-O atoms of three PO_4 linkers. The three "outer" oxygen atoms of each phosphate group link three $[\{Co^{II}(OH)\}_3(A\text{-}\alpha\text{-}PW_9O_{34})]^{6-}$ fragments by three P–O(Co) bonds. All 16 Co^{II} ions in **1** exhibit a distorted octahedral coordination environment with Co–O bond lengths in the range 2.053(19)–2.364(19) Å. Protonated oxygen atoms were identified by bond valence sum (BVS) calculations.[14] All 12 μ_3-oxygen atoms bridging Co ions in **1** are monoprotonated, whereas all the phosphate oxygen atoms are non-protonated, supporting the polyanion formula $[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$. The total charge of **1** is therefore 28− which is balanced in the solid state by 22 sodium and 6 rubidium countercations. The formula is based on three different analytical methods namely single-crystal X-ray diffraction, elemental analysis, and thermogravimetric analysis (TGA). The TGA indicated the presence of 76 crystal waters in **1a** (see Figure S2 in the Supporting Information).

The field of cobalt-based single-molecule magnets (SMMs) has been studied, ever since the first example emerged in 2002.[13b] Since then only a few other examples have been reported.[13e,g,h] POMs possess great potential for stabilizing polynuclear, magnetic metal-oxo aggregates, including SMM assemblies, as has been demonstrated recently.[15] Interestingly, even mono-lanthanide containing heteropolytungstates can behave as SMMs.[16]

We also performed magnetic measurements on a polycrystalline sample of **1a** dispersed in Apiezon grease. The dc magnetic susceptibility data of **1a** under an applied dc field of 1000 Oe in the 1.8–300 K temperature range are plotted in Figure 2. At 300 K, the experimental χT value of **1a** (47.28 $cm^3 K mol^{-1}$) is much higher than the expected value (30.0 $cm^3 K mol^{-1}$) for 16 spin-only high-spin (HS) Co^{II} ions ($S = 3/2$, $g = 2$, $C = 1.875$ $cm^3 K mol^{-1}$) due to a strong orbital contribution of the Co^{II} ions. The χT value for **1a** declines gradually with decreasing temperature and reaches a round minimum of 40.38 $cm^3 K mol^{-1}$ at 45 K. Upon further cooling, the χT value increases rapidly, reaching a maximum of 48.24 $cm^3 K mol^{-1}$ at 5 K, and then falling sharply to 45.97 $cm^3 K mol^{-1}$ at 1.8 K. The decrease of χT above 45 K is due to the spin-orbital coupling of the Co^{II} ions, while the behavior below 45 K indicates overall ferromagnetic coupling between the Co^{II} ions. The final decrease of χT below 5 K is associated with magnetic anisotropy, as all the Co^{II} ions are shielded by diamagnetic POM shells and thus no intermolecular antiferromagnetic interactions are possible. The field dependence of the magnetization at low temperatures for **1a** shows that the magnetization increases abruptly to reach approximately 15 μ_B up to 10 kOe, which is consistent with the presence of ferromagnetic interactions. Above 10 kOe, the magnetization curve increases in a linear fashion to reach 19.3 μ_B with a lack of saturation even at 70 kOe (see Figure 2, inset). This situation is possibly indicative of magnetic anisotropy, which is supported by the non-superposition of the M versus H/T curves (see Figure S3 in the Supporting Information). The experimental $(\chi T)_{max}$ of 48.24 $cm^3 K mol^{-1}$ at 5 K suggests an average g factor of 2.3 and is consistent with all 16 Co^{II} ions each with an effective spin of $^1/_2$ being ferromagnetically coupled to give a ground spin state of $S = 8$. This result is in line with the low-temperature field dependence of the magnetization (see Figure 2), in which the magnetization reaches 19.3 μ_B consistent with 16 high-spin (HS) Co^{II} ions with an effective spin of $^1/_2$ for each Co^{II} center and a g factor of 2.4, further indicating the presence of magnetic anisotropy of the Co^{II} ions.

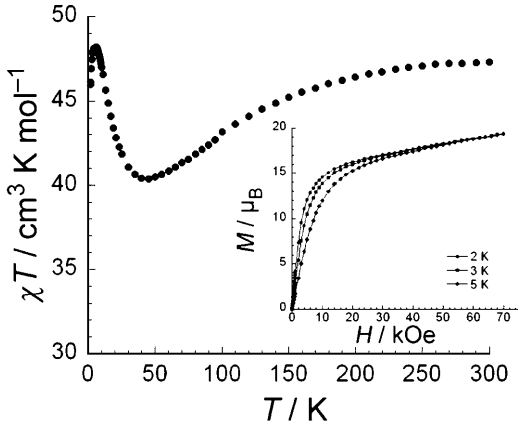

Figure 2. Temperature dependence of the χT product for compound **1a** at 1000 Oe (with χ being the molar susceptibility defined as M/H). Inset: Field dependence of the magnetization of **1a** at the indicated temperatures.

The dynamic properties of **1a** were also investigated using temperature- and frequency-dependent ac susceptibility measurements. The frequency dependence of both in-phase and out-of-phase components can be observed in zero dc field below 6 K, indicating slow relaxation of the magnetization (see Figure 3a,b). In addition, frequency sweeping ac susceptibilities were measured at different temperatures (see Figure 3c,d) and the shape and frequency dependence both indicate that this compound is a SMM. The relaxation time of **1a**, deduced from the data between 1.8 and 3.2 K follows an activated behavior with an energy gap (Δ) of 26.1 K and a pre-exponential factor (τ_0) of 3.5×10^{-8} s (see Figure 4). These parameters are in the region of those reported for cobalt(II) SMMs.[13g,h] Fitting the data using a generalized Debye model[17] leads to $\alpha = 0.10$–0.39 (see Figure 4, inset and Table S1 in the Supporting Information), which proves that there is essentially one dominant relaxation process present in **1a** with a moderate width of the τ distribution.

Moreover, the frequency dependence of the ac susceptibility was also measured at 1.8 K in an applied dc field (see Figure S4 in the Supporting information). With increasing field the relaxation rate $1/\tau$ only slightly shifts on going from zero field to 2000 Oe, indicating that there is no appreciable quantum tunneling effect above 1.8 K.

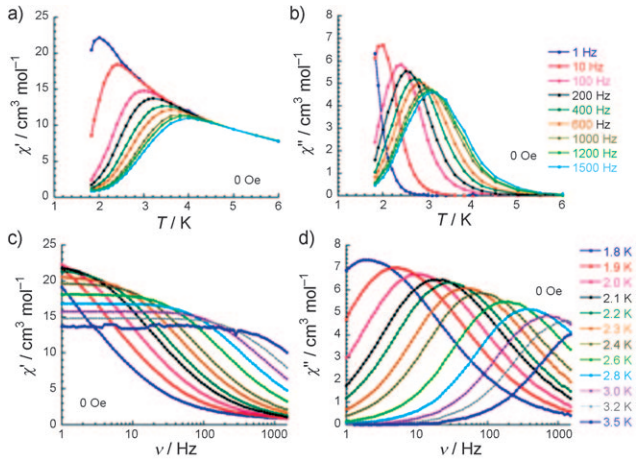

Figure 3. Temperature dependence of the in-phase (a) and out-of-phase (b) components of the ac magnetic susceptibility at different frequencies and frequency dependence of the in-phase (c) and the out-of-phase (d) components of the ac susceptibility at different temperatures for **1a** under zero dc field.

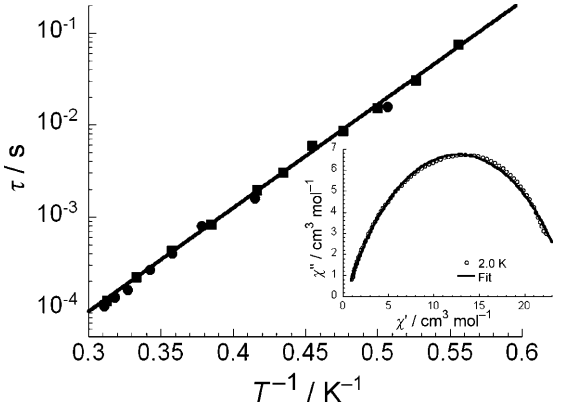

Figure 4. Plot of τ versus $1/T$ for **1a** obtained from ac susceptibilities between 1.8–3.2 K under zero dc field (■ and ● represent experimental data; the solid line is the Arrhenius law). Inset: Cole–Cole plot at 2.0 K (○ represents experimental data; the solid line is the fit with a generalized Debye model.

In summary, we have synthesized the 36-tungsto-8-phosphate $[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$ (**1**) containing 16 cobalt(II) centers by using a simple, one-pot procedure, treating the trilacunary 9-tungstophosphate precursor $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ with Co^{II} ions in phosphate buffer. Polyanion **1** was isolated as a hydrated sodium–rubidium salt $Na_{22}Rb_6[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]\cdot 76H_2O$ (**1a**), which was investigated in the solid state by single-crystal X-ray diffraction, FT-IR spectroscopy, thermogravimetric and elemental analyses, as well as magnetic measurements. Compound **1** represents the largest cobalt aggregate in polyoxotungstate chemistry, and the first example of a cobalt-core-based POM with SMM behavior. The synthesis of **1** demonstrates that conventional synthetic conditions and the use of simple metal salts can lead to the formation of high-nuclearity, magnetic cores stabilized by POM units. Currently we are investigating the interaction of other 3d metal ions with different trilacunary POM precursors.

Experimental Section

1a: $CoCl_2\cdot 6H_2O$ (0.39 g, 1.63 mmol) was dissolved in H_2O (20 mL). Then $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ (0.58 g, 0.20 mmol)[18] was added and the mixture was stirred until a clear, purple solution was obtained. Then Na_3PO_4 (0.50 g, 3.0 mmol) was added in small portions while maintaining the pH value at 8 with HCl_{aq}. The resulting turbid solution was stirred for 1 h at room temperature and then allowed to stand at room temperature until the entire purple precipitate had settled at the bottom of the beaker and was then removed by filtration. Addition of a 1.0 M RbCl (0.55 mL) solution to the filtrate gave a precipitate. The mixture was kept at 30 °C for 10 min, and then filtered. The clear, dark purple filtrate was kept in an open vial at room temperature to allow slow evaporation. After one week a dark purple crystalline product started to appear. Evaporation was allowed to continue until about half the solvent had evaporated. The solid product was then collected by filtration and air dried. Yield 100 mg (15 %).

IR (2 % KBr pellet): $\tilde{\nu} = 3468$ (s), 1630 (s), 1088 (w), 1068 (m), 1026 (m), 940 (s), 884 (w), 816 (m), 703 (w), 679 (w), 611 cm^{-1} (w). Elemental analysis (%) for $Na_{22}Rb_6[\{Co_4(OH)_3PO_4\}_4(A\text{-}\alpha\text{-}PW_9O_{34})_4]\cdot 76H_2O$ (**1a**), calcd: Na 3.94, Rb 4.00, P 1.93, Co 7.35, W 51.57; found Na 3.16, Rb 4.14, P 1.95, Co 7.15, W 51.30.

Received: January 12, 2011
Published online: April 15, 2011

Keywords: cobalt · inorganic synthesis · multinuclear complexes · polyoxometalates · single-molecule magnets

[1] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56–70; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; c) *Chem. Rev.* **1998**, *98*, 1–390 (Special Issue on Polyoxometalates; Ed.: C. L. Hill); d) B. Hasenknopf, K. Micoine, E. Lacôte, S. Thorimbert, M. Malacria, R. Thouvenot, *Eur. J. Inorg. Chem.* **2008**, 5001–5013; e) U. Kortz, A. Müller, J. Van Slageren, J. Schnack, N. S. Dalal, M. Dressel, *Coord. Chem. Rev.* **2009**, *253*, 2315–2327; f) *Eur. J. Inorg. Chem.* **2009**, *34*, 5055–5276 (Issue dedicated to Polyoxometalates; Guest Ed.: U. Kortz); g) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem.* **2010**, *122*, 1780–1803; *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758.

[2] Q. Wu, Y. Li, Y. Wang, E. Wang, Z. Zhang, R. Clérac, *Inorg. Chem.* **2009**, *48*, 1606–1612.

[3] a) C. P. Pradeep, D. Long, P. Kögerler, L. Cronin, *Chem. Commun.* **2007**, 4254–4256; b) J. Zhao, J. Zhang, S. Zheng, G. Yang, *Inorg. Chem.* **2007**, *46*, 10944–10946; c) C. Pichon, A. Dolbecq, P. R. Mialane, J. Marrot, E. Rivière, F. Sécheresse, *Dalton Trans.* **2008**, 71–76; d) S. S. Mal, M. H. Dickman, U. Kortz, A. M. Todea, A. Merca, H. Bögge, T. Glaser, A. Müller, S. Nellutla, N. Kaur, J. van Tol, N. S. Dalal, B. Keita, L. Nadjo, *Chem. Eur. J.* **2008**, *14*, 1186–1195; e) B. Godin, Y. Chen, J. Vaissermann, L. Ruhlmann, M. Verdaguer, P. Gouzerh, *Angew. Chem.* **2005**, *117*, 3132–3135; *Angew. Chem. Int. Ed.* **2005**, *44*, 3072–3075.

[4] a) J. M. Clemente-Juan, E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-Garcia, *Inorg. Chem.* **1999**, *38*, 55–63; b) C. Pichon, P. Mialane, A. Dolbecq, J. Marrot, E. Rivière, B. S. Bassil, U. Kortz, B. Keita, L. Nadjo, F. Sécheresse, *Inorg. Chem.* **2008**, *47*, 11120–11128; c) H. Zhang, Y. Li, Y. Lu, R. Clérac, Z. Zhang, Q. Wu, X. Feng, E. Wang, *Inorg. Chem.* **2009**, *48*, 10889–10891; d) S. T. Zheng, J. Zhang, J. M. Clemente-Juan, D.-Q. Yuan, G.-Y. Yang, *Angew. Chem.* **2009**, *121*, 7312–7315; *Angew. Chem. Int. Ed.* **2009**, *48*, 7176–7179.

[5] a) P. Mialane, A. Dolbecq, J. Marrot, E. Rivière, F. Sécheresse, *Angew. Chem.* **2003**, *115*, 3647 – 3650; *Angew. Chem. Int. Ed.* **2003**, *42*, 3523 – 3526; b) S. S. Mal, U. Kortz, *Angew. Chem.* **2005**, *117*, 3843 – 3846; *Angew. Chem. Int. Ed.* **2005**, *44*, 3777 – 3780; c) S. S. Mal, B. S. Bassil, M. Ibrahim, S. Nellutla, J. van Tol, N. S. Dalal, J. A. Fernández, X. López, M. J. Poblet, R. Ngo Biboum, B. Keita, U. Kortz, *Inorg. Chem.* **2009**, *48*, 11636 – 11645.

[6] a) A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. X. Trautwein, V. Schünemann, *Angew. Chem.* **1999**, *111*, 3435 – 3439; *Angew. Chem. Int. Ed.* **1999**, *38*, 3238 – 3241; b) A. Müller, A. M. Todea, M. Dressel, J. van Slageren, H. Bögge, M. Schmidtmann, M. Luban, L. Engelhardt, M. Rusu, *Angew. Chem.* **2005**, *117*, 3925 – 3929; *Angew. Chem. Int. Ed.* **2005**, *44*, 3857 – 3861.

[7] a) C. du Peloux, A. Dolbecq, P. Mialane, J. Marrot, E. Riviere, F. Sécheresse, *Angew. Chem.* **2001**, *113*, 2521 – 2523; *Angew. Chem. Int. Ed.* **2001**, *40*, 2455 – 2457; b) Y. Ma, Y. G. Li, E. B. Wang, Y. Lu, X. Xu, X. L. Bai, *Transition Met. Chem.* **2006**, *31*, 262 – 267.

[8] a) L. C. W. Baker, T. P. McCutcheon, *J. Am. Chem. Soc.* **1956**, *78*, 4503 – 4510; b) L. C. W. Baker, V. E. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, L. L. Koh, *J. Am. Chem. Soc.* **1966**, *88*, 2329 – 2331.

[9] a) T. J. R. Weakley, H. T. Evans, Jr., J. S. Showell, G. F. Tourné, C. M. Tourné, *J. Chem. Soc. Chem. Commun.* **1973**, *139–140*; b) T. J. R. Weakley, *J. Chem. Soc. Chem. Commun.* **1984**, 1406 – 1407; c) C. M. Tourné, G. F. Tourné, F. Zonnevijlle, *J. Chem. Soc. Dalton Trans.* **1991**, 143 – 155; d) J. R. Galán-Mascarós, C. J. Gómez-García, J. J. Borrás-Almenar, E. Coronado, *Adv. Mater.* **1994**, *6*, 221 – 223; e) M. D. Ritorto, T. M. Anderson, W. A. Neiwert, C. L. Hill, *Inorg. Chem.* **2004**, *43*, 44 – 49; f) J. M. Clemente-Juan, E. Coronado, A. Forment-Aliaga, J. R. Galán-Mascarüs, C. Giménez-Saiz, C. J. Gómez-García, *Inorg. Chem.* **2004**, *43*, 2689 – 2694; g) L. Lisnard, P. Mialane, A. Dolbecq, J. Marrot, J. M. Clemente-Juan, E. Coronado, B. Keita, P. de Oliveira, L. Nadjo, F. Sécheresse, *Chem. Eur. J.* **2007**, *13*, 3525 – 3536.

[10] a) B. S. Bassil, S. Nellutla, U. Kortz, A. C. Stowe, J. van Tol, N. S. Dalal, B. Keita, L. Nadjo, *Inorg. Chem.* **2005**, *44*, 2659 – 2665; b) U. Kortz, N. K. Al-Kassem, M. G. Savelieff, N. A. Al Kadi, M. Sadakane, *Inorg. Chem.* **2001**, *40*, 4742 – 4749; c) B. S. Bassil, U. Kortz, A. S. Tigan, J. M. Clemente-Juan, B. Keita, P. De Oliveira, L. Nadjo, *Inorg. Chem.* **2005**, *44*, 9360 – 9368; d) B. S. Bassil, M. H. Dickman, M. Reicke, U. Kortz, B. Keita, L. Nadjo, *Dalton Trans.* **2006**, 4253 – 4259; e) N. H. Nsouli, A. H. Ismail, I. S. Helgadottir, M. H. Dickman, J. M. Clemente-Juan, U. Kortz, *Inorg. Chem.* **2009**, *48*, 5884 – 5890; f) B. S. Bassil, M. Ibrahim, S. S. Mal, A. Suchopar, R. Ngo Biboum, B. Keita, L. Nadjo, S. Nellutla, J. van Tol, N. S. Dalal, U. Kortz, *Inorg. Chem.* **2010**, *49*, 4949 – 4959.

[11] Q. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill, *Science* **2010**, *328*, 342 – 345.

[12] Recent, representative examples include: a) M. Murrie, H. Stoeckli-Evans, H. U. Güdel, *Angew. Chem.* **2001**, *113*, 2011 – 2014; *Angew. Chem. Int. Ed.* **2001**, *40*, 1957 – 1960; b) M. Murugesu, C. E. Anson, A. K. Powell, *Chem. Commun.* **2002**, 1054 – 1055; c) M. Murugesu, R. Clérac, C. E. Anson, A. K. Powell, *Inorg. Chem.* **2004**, *43*, 7269 – 7271; d) M. Murugesu, R. Clérac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem.* **2005**, *117*, 6836 – 6840; *Angew. Chem. Int. Ed.* **2005**, *44*, 6678 – 6682; e) T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem.* **2007**, *119*, 902 – 906; *Angew. Chem. Int. Ed.* **2007**, *46*, 884 – 888; f) E. E. Moushi, C. Lampropoulos, W. Wernsdorfer, V. Nastopoulos, G. Christou, A. J. Tasiopoulos, *J. Am. Chem. Soc.* **2010**, *132*, 16146 – 16155; g) T. C. Stamatatos, D. Foguet-Albiol, W. Wernsdorfer, K. A. Abbouda, G. Christou, *Chem. Commun.* **2011**, *47*, 274 – 276.

[13] a) E. K. Brechin, S. G. Harris, A. Harrison, S. Parsons, A. G. Whittaker, R. E. P. Winpenny, *Chem. Commun.* **1997**, 653 – 654; b) E. C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, L. N. Zakharov, R. D. Sommer, A. L. Rheingold, M. Ledezma-Gairaud, G. Christou, *J. Appl. Phys.* **2002**, *91*, 7382 – 7384; c) G. Aromí, A. S. Batsanov, P. Christian, M. Helliwell, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco, R. E. P. Winpenny, *Chem. Eur. J.* **2003**, *9*, 5142 – 5161; d) G. N. Newton, G. J. T. Cooper, P. Kögerler, D. L. Long, L. Cronin, *J. Am. Chem. Soc.* **2008**, *130*, 790 – 791; e) K. W. Galloway, A. M. Whyte, W. Wernsdorfer, J. Sanchez-Benitez, K. V. Kamenev, A. Parkin, R. D. Peacock, M. Murrie, *Inorg. Chem.* **2008**, *47*, 7438 – 7442; f) Y. Bi, X.-T. Wang, W. Liao, X. Wang, X. Wang, H. Zhang, S. Gao, *J. Am. Chem. Soc.* **2009**, *131*, 11650 – 11651; g) F. Klöwer, Y. Lan, J. Nehrkorn, O. Waldmann, C. E. Anson, A. K. Powell, *Chem. Eur. J.* **2009**, *15*, 7413 – 7422; h) M. Murrie, *Chem. Soc. Rev.* **2010**, *39*, 1986 – 1995, and references therein.

[14] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244 – 247.

[15] a) C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y. F. Song, D. L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin, L. Cronin, *Angew. Chem.* **2008**, *120*, 5691 – 5694; *Angew. Chem. Int. Ed.* **2008**, *47*, 5609 – 5612; b) J.-D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekalle, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez, W. Wernsdorfer, *Angew. Chem.* **2009**, *121*, 3123 – 3127; *Angew. Chem. Int. Ed.* **2009**, *48*, 3077 – 3081.

[16] a) M. A. Al Damen, J. Clemente-Juan, E. Coronado, C. Martí-Gastaldo, A. Gaita-Ariño, *J. Am. Chem. Soc.* **2008**, *130*, 8874 – 8875; b) B. S. Bassil, M. H. Dickman, B. von der Kammer, U. Kortz, *Inorg. Chem.* **2007**, *46*, 2452 – 2458.

[17] a) H. Miyasaka, R. Clérac, K. Mizushima, K. Sugiura, M. Yamashita, W. Wernsdorfer, C. Coulon, *Inorg. Chem.* **2003**, *42*, 8203 – 8213; b) R. Clérac, H. Miyasaka, M. Yamashita, C. Coulon, *J. Am. Chem. Soc.* **2002**, *124*, 12837 – 12844; c) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090 – 3099.

[18] *Inorganic Syntheses*, *Vol. 27* (Ed.: A. P. Ginsberg), Wiley, New York, **1990**, p. 100.

