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Supramolecular Heterotrimetallic Assembly Based on Octacyanomolybdate, Manganese, and Copper

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A unique heterotrimetallic supramolecular assembly has been obtained by following a modular synthetic strategy based on the use of octacyanomolybdate(IV), manganese(III), and copper(II) complexes as building blocks. From a structural standpoint, single-crystal X-ray diffraction reveals the presence of the three different metallic centers that are originally arranged in a one-dimensional fashion. Considering the interchain interaction, the compound is able to be described as a two-dimensional network made up of Mo–CN–Cu–NC–Mo squares that bear pendant Mn complexes. Despite the presence of the Mo/Cu photomagnetic pair and large uniaxial anisotropy, no long-lived metastable state was observed upon light irradiation. Nevertheless, the compound led to novel magnetic materials as well as advances in the study of charge-transfer complexes.

Introduction

Among assorted molecule-based multifunctional materials, there are some that have properties that can be monitored by light.[1] In fact, when considering the very molecular level[2] or bulk assemblies,[3] magnetic properties are particularly well suited to a photoswitching effect. In the field of molecular magnetism, single-molecule magnets (SMM) and single-chain magnets (SCM) are of particular interest and have been extensively studied for more than fifteen years.[4] In fact, designing smart molecular materials that combine light sensitivity with such magnetic behavior to obtain photoswitchable single-molecule or single-chain magnets (SSMMs and SSCMs, respectively) has emerged as one of the challenges among efforts devoted to information handling and storage at the molecular scale.

As part of our continuing research program in molecular photomagnetism and on the bases of a proven modular synthetic strategy conceived in our laboratory,[5] we have carried out the preparation of various oligonuclear complexes that potentially fulfill the key requirements mentioned below to exhibit SSMM or SSCM behavior.

On the one hand, obtaining single-molecule or single-chain magnets may proceed through the control of both the spin S and the uniaxial anisotropy D of the compound since the characteristic anisotropic energy barrier (ΔE) is equal to DS^2 for integer spin values or DS^2–1/4 for half-integer spin values.[6] On the other hand, the rich chemistry of octacyanometalates[7] provides some valuable photomagnetic compounds, among which are the prototypical octacyanomolybdate–copper bimetallic species.[8] For instance, within the large family of compounds that comprise this photomagnetic pair, the paramagnetic complex $Mo^{IV}Cu^{II}_6$[9] presents a ferromagnetic metastable state $Mo^{V}Cu^{I}Cu^{II}_5$ after light irradiation as the result of an intramolecular electron transfer ($Mo^{IV}–Cu^{II} \rightarrow Mo^{V}–Cu^{I}$). Interestingly, this metastable state is persistent up to approximately 300 K. The next step towards SSMM is then to obtain the slow relaxation of the magnetization after irradiation. To this end, one strategy is to associate the photoswitch Mo^{IV}–Cu^{II} and a ternary metallic center to concomitantly increase the spin and the anisotropy.

In the literature, reported examples of heterotrimetallic complexes or assemblies are few.[10] We have recently described the structure and properties of the first heterotrimetallic photoswitchable chain $NiMo_2Cu_7$.[11] However, despite the association of Ni^{2+} with the Mo–Cu photomagnetic switch, the SCM behavior was not observed for this compound after light irradiation. This is most likely due to the elongated octahedral geometry of the nickel center, which led to a positive anisotropic constant value. At this stage, the use of Mn^{III} to replace Ni^{II} and thereby increase the overall uniaxial anisotropy of our systems seemed desirable. Indeed, this ion has already proven its efficiency as an ingredient of both single-molecule and single-chain magnets.[12] Here we report the synthesis, structure, and magnetic properties of a supramolecular assembly that simultaneously involves three different metallic cations: Mo^{IV}, Cu^{II}, and Mn^{III}.

Results and Discussion

Synthesis and Characterization

By taking advantage of the original stepwise synthetic approach entitled "polynuclear complex as ligand"[11] (i.e.,

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the use of polynuclear complexes as precursors), the building-block heptanuclear compound $[Mo\{Mn^{III}(salen)\}_6]^{2+}$ (generated in situ or previously isolated) [H_2salen = 1,2-bis(salicylideneamino)ethane] can react through its free cyanide ligands with an assembler complex {e.g., $[Cu(cyclam)]^{2+}$; cyclam = 1,4,8,11-tetraazacyclotetradecane}. The choice of the capping ligand as well as its redox compatibility are some key parameters to guarantee an efficient selectivity between the metallic centers and avoid ligand redistribution. The easy-to-prepare cyclam and salen were chosen since they answer to the previous criteria, the selectivity of these ligands with Cu^{II} and Mn^{III} already having been established.[13] Part of the $[Mn(salen)]^+$ units, which are coordinated to the octacyamolybdate core, become labile in the presence of $[Cu(cyclam)]^{2+}$, thus leading to the compound $[Mo(CN)_8\{Cu(cyclam)\}_2Mn(salen)(H_2O)](ClO_4)\cdot 3H_2O\cdot CH_3CN$, denoted $MoMnCu_2$. The system tends to form the thermodynamically stable $MoCu_2$–cyclam[14] 2D network but hopefully an $[Mn(salen)]^+$ unit persists.

The IR spectrum shows intense bands in the cyanide region 2000–2200 cm^{-1} at 2096 and 2115 cm^{-1}. The first band is ascribed to free cyanide Mo–C≡N, whereas the other can be attributed to the envelope of bridged cyanide Mo–C≡N–M (M = Mn^{III} and Cu^{II}). The values typically fall in the range for a Mo^{IV}, which shows that no oxidation to Mo^{V} occurs in the presence of Mn^{III}.[15]

X-ray Structure

The characterization by single-crystal X-ray diffraction reveals that one molybdenum, one manganese, and three different crystallographic copper atoms associated with their respective ligands (cyanide, salen, and cyclam) are present in the asymmetric unit. An ORTEP diagram of the elementary motif with the atom-numbering scheme is shown in Figure 1. The Cu2 and Cu3 ions are located on an inversion center. The structure may be described as $[MoMnCu_2]^+$ chains in a strong interaction. Indeed, a terminal $[Mn(salen)]^+$ complex is connected to an octacyanomolybdate core as well as the [Cu1(cyclam)] complex with apical distances Mn1–N4 and Cu1–N1 equal to 2.333(6) and 2.533(6) Å, respectively. The two other macrocyclic copper complexes (Cu2 and Cu3) bridge the $[MoMnCu]^-$ subunits to form a one-dimensional chain with apical distances Cu2–N2 and Cu3–N3 equal to 2.534(6) and 2.479(6) Å, respectively. Due to the Jahn–Teller effects, the $Cu–N_{ax}$ distances are much longer than the $Cu–N_{eq}$ bond lengths, but they are comparable to those observed in other cyanometalate analogues,[16] for example, $[\{Cu(en)_2\}_3\{W(CN)_8\}_2]H_2O$,[17] with $Cu–N_{ax}$ distances in the range 2.329(6)–2.967(7) Å.

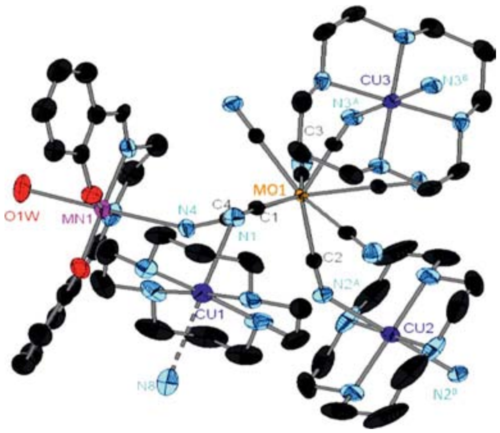

Figure 1. Structure with 30% probability thermal ellipsoids of the heterotrimetallic motif of $MoMnCu_2$. Hydrogen atoms have been omitted. Atoms A and B are related by inversion; symmetry operations: –x, –y, –z.

The chains are parallel to the *c* crystallographic axis (Figure 2). The manganese(III) ion adopts a distorted octahedral environment as a direct consequence of the Jahn–Teller effect.

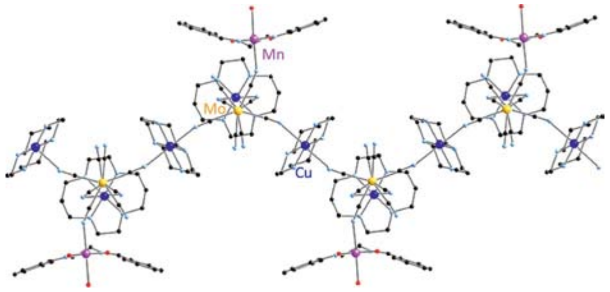

Figure 2. View along the *a* axis of the one-dimensional chain.

Three nitrogen atoms (two from the salen ligand and one from cyanide) and two oxygen atoms from the Schiff base bind the manganese; a molecule of water completes the coordination sphere with an apical distance of Mn1–O1W of 2.261(6) Å. The Cu1 adopts a square pyramidal geometry (C_{4v}), whereas the other copper ions present an elongated octahedral geometry. A perchlorate anion compensates the overall charge of the species. The analysis of the molybdenum geometry by using SHAPE software[18] shows that the ion adopts a geometry close to the square antiprism. The Mo–C≡N angles are almost linear in contrast to the strongly bent Mn1–N4≡C4, Cu2–N2≡C2 and Cu3–N3≡C3 angles that range from 140.8(5) to 149.7(5)° and a severely bent Cu1–N1≡C1 angle equal to 127.7(5)°. Concerning the crystal packing, it appears that the "terminal" Cu1 shows a distance of 2.918(7) Å to the cyano nitrogen (N8) of another octacyanomolybdate core (interchain interaction). Despite the fact that the distance is longer than the semicoordination distance limit for a Cu–N bond[19] (i.e., 2.78 Å), the structure can be depicted as a supramolecular 2D square-sheet structure extended by Mo–CN–Cu–NC linkage. Four cyano nitrogen atoms of $[Mo(CN)_8]^{4-}$ coordinate to adjacent *trans*-$[Cu(cyclam)]^{2+}$ units to form an octanuclear square unit with an Mo^{IV} ion at each corner and a Cu^{II} ion at the center of each edge. Considering the $[Mn(salen)]^+$ units, the compound can be described as a two-dimensional network made up of Mo–Cu squares that bear pendant manganese complexes. Water molecules and perchlorates are present between the bidimensional planes. The shortest distance found between two paramagnetic centers is equal to 7.919(1) Å (Mn1–Cu2), (Figure 3).

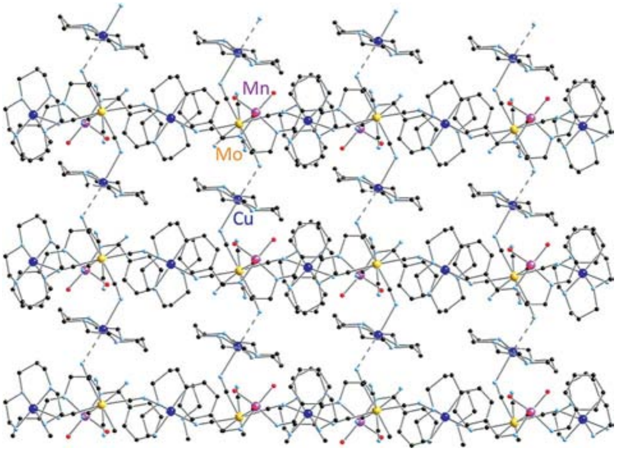

Figure 3. Two-dimensional arrangement showing the intermolecular interaction between the chains (dashed bond type).

The bidimensional structure based on alternative molybdenum and copper with additional pendant manganese complexes is unique. It is reminiscent of an innovative strategy that consists of the use of polynuclear bimetallic complexes as new building blocks for the synthesis of metal-capped squares (i.e., squares with an additional shell of metallic ions).[20]

Magnetic Properties

The magnetic properties are in good agreement with the expected behavior for such paramagnetic systems (Figure 4). The compound behaves as two independent copper atoms (d^9, $S = 1/2$) and one high-spin manganese atom (d^4, $S = 2$), the Mo^{IV} central being diamagnetic (d^2, $S = 0$). $\chi_M T$ is almost constant down to 80 K with a value of 4.22 $cm^3 mol^{-1}$ K. This is almost the theoretical value anticipated for two independent spin 1/2 and one spin 2 with $g = 2.1$ (4.12 $cm^3 mol^{-1}$ K). Below 80 K, the $\chi_M T$ product decreases continually until reaching an $\chi_M T$ value of 2.46 $cm^3 mol^{-1}$ K at 2 K. This decrease can be attributed to the zero-field splitting (ZFS) of the Mn^{III} ions[21] and/or to intermolecular interactions between the chains that form the supramolecular square.

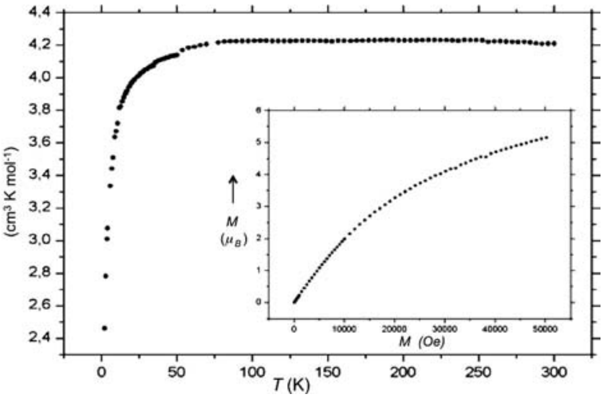

Figure 4. χT versus T plot and first magnetization curve recorded at 2 K (inset).

The evolution of the magnetization as a function of the field at 2 K shows a typical shape for systems that display anisotropy without any saturation even at 5 T (M = 5.16 μ_B).

Considering the configuration of the metallic centers, one could expect a photoswitchable behavior of the chain due to an electron transfer from Mo^{IV} to Cu^{II}[9] or spin transition centered on the molybdenum.[22] Unfortunately, the photomagnetic experiments do not show any change of the magnetic properties after irradiation with a laser (λ = 406 nm) following standard photoexcitation conditions. This result might be justified by a geometrical consideration. Indeed, we have previously shown that the photoswitchable behavior might be strongly correlated to the molybdenum geometry. Thus, an empirical result based on experimental data shows that an intermediate geometry between square antiprism (D_{4d}) and dodecahedron (D_{2d}) is necessary to observe a long-lived photoinduced metastable state. The nature of the HOMO orbital, mainly composed of the d orbitals of the molybdenum atom, might induce and stabilize a high-spin Mo^{IV} excited state (d^2, $S = 1$) after irradiation,[22] when the two orbitals d_{z^2} and $d_{x^2-y^2}$ are close in energy and therefore singly occupied. The system can then undergo a triplet-to-singlet conversion potentially accompanied by an electron transfer from the molybdenum to one copper to obtain a long-lived metastable state Mo^V–Cu^I. In the present case, the molybdenum geometry is obviously not in an intermediate geometry sufficient to stabilize the Mo^{IV} high-spin state and therefore no modification of the magnetic properties is observed after light irradiation.

Conclusion

We have reported here the synthesis and the structure of the first heterotrimetallic compound that contains octacyanomolybdate, manganese, and copper. Considering interchain interactions, the structure might be viewed as an original 2D square-sheet structure with pendant complexes at the corners. The magnetic properties are consistent with the expected paramagnetic behavior. Despite the fact that no photomagnetic effect was detected after light irradiation under the usual experimental conditions, the compound might be viewed as an additional step in the emerging field of paramagnetic compounds based on 4d and 5d transition metals.[23] A great deal of additional work will be required before the potential of this area of molecular (photo)magnetism is fully realized. Nevertheless, heterotrimetallic complexes such as $MoMnCu_2$ have led to novel magnetic materials as well as advances in the study of charge-transfer complexes.

Experimental Section

Measurements: IR spectra were obtained between 4000 and 250 cm^{-1} with a Bio-Rad FTS 165 FTIR spectrometer on KBr pellets. DC magnetic-susceptibility measurements were carried out with a Quantum Design MPMS SQUID susceptometer equipped with a 5 T magnet and operating in a temperature range from 2 to 400 K. The powdered samples [(10 ± 5) mg] were placed in a diamagnetic sample holder and the measurements realized in a 500 Oe applied field using the extraction technique. Before analysis, the experimental susceptibility was corrected from diamagnetism using Pascal constants[24] and from temperature-independent paramagnetism (TIP) of the transition metals.

Preparations: The ligand cyclam (1,4,8,11-tetraazacyclotetradecane) is commercially available. The ligand H_2salen [1,2-bis(salicylideneamino)ethane] and the complex $K_4[Mo(CN)_8]\cdot 2H_2O$ were synthesized according to protocols already published in the literature.[25,26] The complex $[Mn(salen)(H_2O)](ClO_4)$[16] was obtained by a modified procedure of the literature methods. The synthesis of $[Mo\{Mn(salen)_6\}](ClO_4)_2\cdot 5H_2O$ was inspired by protocols published for analogous compounds.[15,12c]

***Caution!** Perchlorate salts should be handled with great caution as they are potentially explosive.*

$[Mn(salen)(H_2O)](ClO_4)$: Manganese(III) acetate dihydrate (2.000 g, 7.460 mmol) in methanol (60 mL) was added to a solution of H_2salen (2.000 g, 7.460 mmol) in methanol (100 mL). Sodium perchlorate (1.584 g, 10.983 mmol) dissolved in water (40 mL) was added to the resulting brown solution. The solution was stirred for 20 min before being filtered. Brown needles were collected a few days later. (70% yield). $[Mn(C_{16}H_{14}N_2O_2)(H_2O)](ClO_4)$: calcd. C 43.80, H 3.68, N 6.38; found C 43.58, H 3.80, N 6.23.

$[Mo(CN)_8\{Mn(C_{16}H_{14}N_2O_2)\}_6](ClO_4)_2\cdot 5H_2O$ = $[Mo\{Mn(salen)\}_6](ClO_4)_2$: $[Mn(salen)(H_2O)](ClO_4)$ (0.353 g, 0.805 mmol) was dissolved in H_2O/CH_3CN (20 mL, 1:1 mixture). $K_4[Mo(CN)_8]\cdot 2H_2O$ (0.100 g, 0.201 mmol) in water (10 mL) was then slowly added. The mixture was stirred for 10 min before filtering an eventual brown precipitate. A few days later, brown crystals were obtained from the filtrate (12% yield). $[Mo(CN)_8\{Mn(C_{16}H_{14}N_2O_2)\}_6]$ $(ClO_4)_2\cdot 5H_2O$, C 49.26, H 3.76, N 11.11, Mo 3.81, Mn 13.08, Cl 2.81; found C 50.22, H 3.74, N 11.21, Mo 3.57, Mn 12.67, Cl 3.40. IR (KBr): $\tilde{\nu}$ = 2093, 2104.8, and 2118 (CN asymmetric stretching), 1088 (ν_{Cl-O}) cm^{-1}.

$[Mo(CN)_8\{Cu(C_{10}H_{24}N_4)\}_2Mn(C_{16}H_{14}N_2O_2)](ClO_4)\cdot 3H_2O\cdot CH_3CN$ = MoMnCu$_2$: $[Mn(salen)(H_2O)](ClO_4)$ (0.353 g, 0.805 mmol) was dissolved in H_2O/CH_3CN (20 mL, 1:1 mixture). $K_4[Mo(CN)_8]\cdot 2H_2O$ (0.100 g, 0.201 mmol) in water (10 mL) was then slowly added. The mixture was stirred for 10 min before filtering an eventual brown precipitate and adding $[Cu(cyclam)](ClO_4)_2$ previously formed by the in situ reaction of $Cu(ClO_4)_2$ (0.074 g, 0.201 mmol) and cyclam (0.044 g, 0.221 mmol) in H_2O/CH_3CN (10 mL, 1:1 mixture). After 10 min of stirring, the mixture was filtered and the filtrate allowed to stand in the dark. A few days later, brown plates were obtained (31% yield). $[Mo(CN)_8\{Cu(C_{10}H_{24}N_4)\}_2Mn(C_{16}H_{14}N_2O_2)](ClO_4)\cdot 3H_2O\cdot CH_3CN$: calcd. C 41.00, H 5.31, N 19.75, Mo 7.12, Cu 9.43, Mn 4.08, Cl 2.63; found C 40.05, H 5.33, N 19.37, Mo 7.10, Cu 9.31, Mn 4.03, Cl 2.79. IR (KBr): $\tilde{\nu}$ = 2096 and 2115 (CN asymmetric stretching) cm^{-1}.

X-ray Crystallography: Suitable crystals for X-ray crystallography were directly obtained from the reaction medium. A single crystal of the compounds was selected rapidly, mounted onto a glass fiber, and transferred into a cold nitrogen gas stream. Intensity data were collected with a Bruker–Nonius Kappa-CCD with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit-cell parameters determination, data collection strategy, and integration were carried out with the Nonius EVAL-14 suite of programs.[27] The structure was solved by direct methods with the SIR-92 program[28] and refined anisotropically by full-matrix least-squares methods with the SHELXL-97 software package.[29]

Crystal data for $C_{46}H_{71}ClCu_2MnMoN_{19}O_9$: M_r = 1347.63 $g\,mol^{-1}$, triclinic, space group $P\bar{1}$; a = 10.4734(9) Å, b = 14.2226(18) Å, c = 19.581(2) Å; α = 94.189(8)°, β = 91.152(8)°, γ = 96.147(9)°; V = 2891.1(6) $Å^3$; Z = 2; 13001 independent reflections [R(int) = 0.0467], $R1$ = 0.0680, $wR2$ = 0.1819. R_1 was calculated for observed data and wR_2 for all data.

CCDC-804618 (for "**MoMnCu$_2$**") contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) P. Gütlich, Y. Garcia, T. Woike, *Coord. Chem. Rev.* **2001**, *219–221*, 839; b) F. Varret, A. Bleuzen, K. Boukheddaden, A. Bousseksou, E. Codjovi, C. Enachescu, A. Goujon, J. Linares, N. Menendez, M. Verdaguer, *Pure Appl. Chem.* **2002**, *74*, 2159; c) O. Sato, *Acc. Chem. Res.* **2003**, *36*, 692.

[2] a) I. Ciofini, P. P. Lainé, M. Zamboni, C. A. Daul, V. Marvaud, C. Adamo, *Chem. Eur. J.* **2007**, *13*, 5360–5377; b) I. Ciofini, C. Adamo, Y. Teki, F. Tuyèras, P. P. Lainé, *Chem. Eur. J.* **2008**, *14*, 11385–11405; c) I. Matsumoto, I. Ciofini, P. P. Lainé, Y. Teki, *Chem. Eur. J.* **2009**, *15*, 11210–11220.

[3] a) O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem.* **2007**, *46*, 2152; b) A. Bousseksou, G. Molnár, G. Matouzenko, *Eur. J. Inorg. Chem.* **2004**, 4353–4369.

[4] a) D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, *265*, 1054; b) G. Aromi, E. K. Brechin, *Synthesis of 3d Metallic Single- Molecule Magnets*, Springer, Berlin, **2006**, vol. *122*/**2006**, pp. 1–67; c) M. Andruh, J. P. Costes, C. Diaz, S. Gao, *Inorg. Chem.* **2009**, *48*, 3342; d) R. Sessoli, A. K. Powell, *Coord. Chem. Rev.* **2009**, *253*, 2328.

[5] a) V. Marvaud, C. Decroix, A. Scuiller, J. Vaissermann, C. Guyard, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* **2003**, *9*, 1677–1691; b) V. Marvaud, C. Decroix, A. Scuiller, F. Tuyèras, C. Guyard, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdaguer, *Chem. Eur. J.* **2003**, *9*, 1692–1705; c) F. Tuyèras, A. Scuiller, C. Guyard-Duhayon, M. Hernandez-Molina, F. Fabrizi de Biani, M. Verdaguer, T. Mallah, W. Wernsdorfer, V. Marvaud, *Inorg. Chim. Acta* **2008**, *361*, 3505–3518.

[6] G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66–71.

[7] P. Przychodzen, T. Korzeniak, R. Podgajny, B. Sieklucka, *Coord. Chem. Rev.* **2006**, *250*, 2234.

[8] a) A. Bleuzen, V. Marvaud, C. Mahonière, B. Sieclucka, M. Verdaguer, *Inorg. Chem. Forum Article* **2009**, *48*, 3453–3466; b) G. Rombaut, M. Verelst, S. Golhen, L. Ouahab, C. Mathoniere, O. Kahn, *Inorg. Chem.* **2001**, *40*, 1151; c) S. Ohkoshi, N. Machida, Y. Abe, Z. J. Zhong, K. Hashimoto, *Chem. Lett.* **2001**, *4*, 312; d) S. Ohkoshi, H. Tokoro, T. Hozumi, Y. Zhang, K. Hashimoto, C. Mathonière, I. Bord, G. Rombaut, M. Verelst, C. Cartier dit Moulin, F. Villain, *J. Am. Chem. Soc.* **2006**, *128*, 270.

[9] J.-M. Herrera, V. Marvaud, M. Verdaguer, J. Marrot, M. Kalisz, C. Mathonière, *Angew. Chem. Int. Ed.* **2004**, *43*, 5468.

[10] a) D. Visinescu, J.-P. Sutter, C. Ruiz-Perez, M. Andruh, *Inorg. Chim. Acta* **2006**, *359*, 433; b) C. P. Berlinguette, K. R. Dunbar,

Chem. Commun. **2005**, *19*, 2451; c) H.-Z. Kou, B. C. Zhou, S. Gao, R.-J. Wang, *Angew. Chem. Int. Ed.* **2003**, *42*, 3288; d) R. Gheorghe, M. Andruh, J.-P. Costes, B. Donnadieu, *Chem. Commun.* **2003**, 2778–2779; e) D. Visinescu, A. M. Madalan, M. Andruh, C. Duhayon, J.-P. Sutter, L. Ungur, W. Van den Heuvel, L. F. Chibotaru, *Chem. Eur. J.* **2009**, *15*, 11808–11814; f) R. Gheorghe, A. M. Madalan, J. P. Costes, W. Wernsdorfer, M. Andruh, *Dalton Trans.* **2010**, *39*, 4734–4736.

[11] J. Long, L.-M. Chamoreau, C. Mathonière, V. Marvaud, *Inorg. Chem.* **2009**, *48*, 22–24.

[12] a) T. Lis, *Acta Crystallogr., Sect. B* **1980**, *36*, 2042; b) G. Christou, *Polyhedron* **2005**, *24*, 2065; c) H. Miyasaka, R. Clérac, W. Wernsdorfer, L. Lecren, C. Bonhomme, K. Sugiura, M. Yamashita, *Angew. Chem. Int. Ed.* **2004**, *43*, 2801; d) H. J. Choi, J. J. Sokol, J. R. Long, *J. Phys. Chem. Solids* **2004**, *65*, 839.

[13] R. D. Hancock, A. E. Martell, *Chem. Rev.* **1989**, *89*, 1875.

[14] J. Larionova, R. Clérac, B. Donnadieu, S. Willemin, C. Guérin, *Cryst. Growth Des.* **2003**, *3*, 267.

[15] P. Przychodzen, K. Lewinski, M. Balanda, R. Pelka, M. Rams, T. Wasiutynski, C. Guyard-Duhayon, B. Sieklucka, *Inorg. Chem.* **2004**, *43*, 2967–2974.

[16] a) E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, J. M. Moreno, A. Pajunen, *J. Chem. Soc., Dalton Trans.* **2000**, *50*, 5; b) H. Z. Kou, H. M. Wang, D. Z. Liao, P. Cheng, Z. H. Jiang, S. P. Yan, X. Y. Huang, G. L. Wang, *Aust. J. Chem.* **1998**, *51*, 661.

[17] D. F. Li, S. Gao, L. M. Zheng, W. Y. Sun, T. Okamura, N. Ueyama, W. X. Tang, *New J. Chem.* **2002**, *26*, 485.

[18] D. Casanova, M. Llunel, P. Alemany, S. Alvarez, *Chem. Eur. J.* **2005**, *11*, 1479.

[19] F. Valach, *Polyhedron* **1999**, *18*, 699.

[20] J. Long, L.-M. Chamoreau, V. Marvaud, *Dalton Trans.* **2010**, *39*, 2188–2190.

[21] B. J. Kennedy, K. S. Murray, *Inorg. Chem.* **1985**, *24*, 1552.

[22] M.-A. Arrio, J. Long, C. Cartier dit Moulin, A. Bachschmidt, V. Marvaud, A. Rogalev, C. Mathonière, F. Wilhelm, P. Sainctavit, *J. Phys. Chem. C* **2010**, *114*, 593–600.

[23] X.-Y. Wang, C. Avendano, K. R. Dunbar, *Chem. Soc. Rev.* **2011**, *40*, 3213–3238.

[24] O. Kahn, *Molecular Magnetism*, Wiley-VCH, Weinheim, **1993**.

[25] H. Diehl, C. C. Hach, *Inorg. Synth.* **1950**, *3*,196.

[26] J. G. Leipoldt, L. C. D. Bok, P. J. Cilliers, *Z. Anorg. Allg. Chem.* **1974**, *409*, 343.

[27] A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J. Appl. Crystallogr.* **2003**, *36*, 220.

[28] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[29] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.

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