Magnetic Materials

One-Dimensional Magnetism in Anhydrous Iron and Cobalt Ternary Oxalates with Rare Trigonal-Prismatic Metal Coordination Environment**

Michael B. Hursthouse, Mark E. Light, and Daniel J. Price*

Solid-state coordination chemistry of oxalate (ox) compounds continues to receive much attention, with new structure types being reported for even the simplest binary oxalates.[1] In anhydrous materials complex network structures are formed owing to the high degree of ox^{2-} coordination (bridging up to six metal ions). In contrast hydrates and materials containing additional noncoordinating cations[2] tend have reduced oxalate coordination, linking only two metals with the symmetric bischelating mode as the dominant bridging motif in the network structure. While there are a great many hydrated ternary oxalates very few anhydrous salts are known.[3] Most ternary oxalates are formed at high ox^{2-}:M^{n+} ratios (M = metal center) resulting in simple discrete anionic complexes with $[M(ox)_{2-4}]^{m-}$ compositions although in a few cases the $[M_q(ox)_r]^{m-}$ component forms an extended network structure.[4]

The oxalate dianion is well known to mediate a significant antiferromagnetic exchange interaction when it bridges paramagnetic ions, and transition-metal oxalates[5] have played a key role in the development of molecular-based magnetism. New oxalate-bridged transition-metal networks are likely to provide many new and useful model magnetic systems.

We have used hydrothermal synthesis to produce a new anhydrous ternary metal oxalate; $K_2M(ox)_2$ which comprises

---

[*] Prof. Dr. M. B. Hursthouse, Dr. M. E. Light, Dr. D. J. Price
School of Chemistry
University of Southampton
Highfield, Southampton, SO17 1BJ (UK)
Fax: (+44) 238-059-6805
E-mail: daniel.price@soton.ac.uk

[**] D.J.P. gratefully acknowledges financial support in the form of an Advance Research Fellowship from the EPSRC of the UK. We thank Dr. H. J. Blythe (University of Sheffield) for his assistance with magnetization measurements and Dr. A. L. Hector (University of Southampton) for TGA measurements.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200352406

a network structure in which chains of Fe^{II} or Co^{II} ions are coordinated in a rare trigonal-prismatic environment.

Hydrothermal reaction of mixtures containing MCl_2 (M = Fe, Co), K_2ox, KBr, and H_2O (in an approximately 1:2:25:200 molar ratio) yield crystals of $K_2M(ox)_2$ (M = Fe (**1**), Co (**2**)), and KBr on cooling from 225 °C. Addition of water to the cooled reaction mixture results in the decomposition of the ternary oxalate and the precipitation of $Mox(H_2O)_2$. Experiments show that a minimum potassium-ion concentration of approximately 6 Molar is required to from these products. This situation implies that the chemical potential of potassium ions in these materials is very high, and that neither of these compounds can be crystallized from a solution containing the components in the same stoichiometry as in the solid phases.

Compounds **1** and **2** are isostructural, crystallizing[6] in the space group *P*2/*c*. The asymmetric unit contains one Fe^{II}/Co^{II} ion, three potassium cations and three crystallographically distinct oxalate anions (Figure 1). Each transition-metal center is coordinated by three oxalate ligands in the usual chelating mode. The M^{II} ion has a rare trigonal-prismatic coordination geometry. The O⋯O separations along the triangular face of the prism fall between 2.776–3.005 Å for **1** and 2.711–2.935 Å, for **2**, while the O⋯O distances between these triangular faces are constrained by the oxalate anions and lie in the narrow range 2.643–2.677 Å for both compounds. The degree of distortion from trigonal-prismatic geometry can be characterized by the twist angle φ ($\varphi = 0°$ for a trigonal prism, $\varphi = 30°$ for a trigonal antiprism), we determine $\varphi = 1.68$ and 1.75° for **1** and **2**, respectively. The three potassium environments show considerable variation in their coordination; K3 is six coordinate in a distorted octahedral environment, K1 occupies a distorted square antiprism, and K2 is in an irregular nine-coordinate geometry.

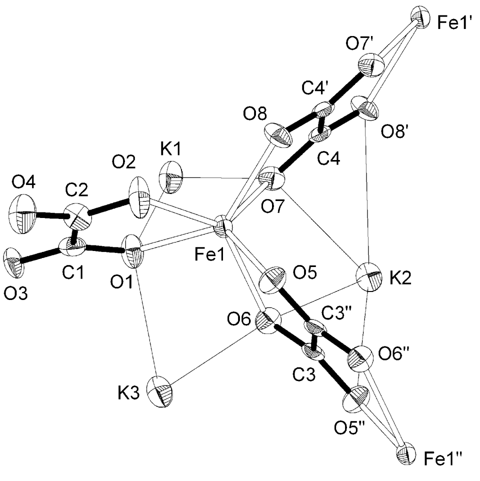

Figure 1. The asymmetric unit of $K_2M(ox)_2$; M = Fe (**1**) and selected symmetry equivalent atoms, showing the trigonal-prismatic coordination of the transition-metal ion and the bridging coordination of two of the oxalate dianions. Thermal ellipsoids are set at 90% probability. Selected bond lengths [Å] an angles [°] for **1** (M = Fe)/**2** (M = Co): M1-O1 2.091(4)/2.059(3), M1-O2 2.107(5)/2.071(3), M1-O5 2.141(7)/2.121(3), M1-O6 2.174(6)/2.151(3), M1-O7 2.138(6)/2.115(3), M1-O8 2.159(6)/2.137(3); O1-M1-O2 78.02(11)/79.87(12), O1-M1-O5 131.36(11)/132.47(12), O1-M1-O6 84.51(10)/84.14(13), O1-M1-O7 90.56(10)/89.36(13), O1-M1-O8 140.94(11)/141.86(12), O2-M1-O5 88.28(11)/87.40(13), O2-M1-O6 139.93(11)/140.74(13), O2-M1-O7 135.08(11)/135.97(13), O2-M1-O8 85.24(11)/84.99(13), O5-M1-O6 76.70(10)/77.47(13), O5-M1-O7 128.52(10)/128.23(13), O5-M1-O8 82.56(10)/80.95(12), O6-M1-O7 80.17(10)/78.90(13), O6-M1-O8 127.97(10)/126.88(13), O7-M1-O8 76.83(10)/77.66(13).

The structure can be considered as infinite chains of transition-metal oxalate, with the formula $[M^{II}(ox)_2]_n^{2n-}$ separated from each other by the potassium cations (Figure 2). These anionic chains contain the two distinct types of oxalate ion, one of which is simply coordinated to a single M ion, while the others bridge two M ions in the common bischelating mode (Figure 1). This results in a zigzag chain running along the *a* axis with M⋯M separations of 5.570(15) for **1** and 5.512(2) Å for **2**.

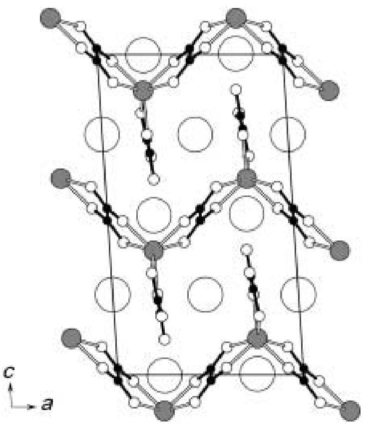

Figure 2. Packing diagram of **1**, viewed along the *b* axis, showing the interdigitation of the $[M(ox)_2]_n^{2n-}$ chains and the relative positions of the potassium counter ions. K large open circles, Fe gray circles, O small open circles, C black circles.

The $[M(ox)_2]_n^{2n-}$ chains pack with the capping oxalate from adjacent chains being interdigitated, which results in layers in the *ac* plane.

The trigonal-prismatic geometry for Fe^{II} and Co^{II} centers is rare. A few examples of high spin $M^{II}O_6$ coordination are known[7,8] but in most cases the M^{II} cation is also found in other coordination geometries within the crystal structure. While both Fe^{II} and Co^{II} stand to lose considerable crystal-field stabilization energy (CFSE) by not adopting an octahedral geometry, repulsion-energy calculations favor a geometry between trigonal-prism and trigonal-antiprism for trischelated metal ions.[9] On these electrostatic arguments we expect the normalized ligand bites (defined as the ratio of the distance between donor atoms on a chelating ligand and the average metal-to-donor-atom separation) of 1.248 and 1.263 for **1** and **2** to have corresponding twist angles of approximately 22°. It is clear that the observed coordination geometry is only formed under exceptional conditions. In this case packing forces in $K_2M(ox)_2$ are responsible for stabilizing the MO_6 trigonal-prismatic geometry in the solid state.

Another unusual feature of these materials is the transition-metal-oxalate chain motif. While a number of "zigzag" oxalate chains are known,[10] in most cases a bidentate amine has been used to cap two *cis*-related coordination sites on the metal center, which prevents further oxalate coordination and a more extensive structure. Only one other example of a chain where an oxalate has a capping function has been reported; $[C_6N_2H_{14}][Zn(ox)_2](H_2O)_3$.[11]

The magnetic susceptibility of **1** shows three distinct features (Figure 3): an abrupt step-like transition at 117(3) K, a broad maximum centered at 18.5(5) K and a "paramagnetic tail" at the lowest experimental temperatures. The transition at 117 K is due to the Verwey transition[12] in magnetite, a common minor impurity from hydrothermal methods[13] (in this case we estimate the magnetite impurity at ≈0.4%). The broad maximum at 18 K is characteristic of the low-dimensional antiferromagnetic behavior[14] expected for **1**, while the "paramagnetic tail" at the lowest temperatures is normally associated with a low level of paramagnetic impurity. In this case defects in the chain may result in paramagnetic-like behavior from "chain ends".[15] The precise behavior of magnetite in the vicinity of the Verwey transition is very sample dependent,[16] being influenced by particle size, purity, crystal orientation and applied field strength. Consequently we exclude the region between 90–120 K from our analysis. At first we attempted to model the observed behavior as a sum of three components; a contribution from the magnetite impurity, a component from a simple linear antiferromagnetically coupled chain[17] plus a small contribution from a paramagnetic impurity. Data below the broad maximum is not well described by this model as the susceptibility is observed to decrease more rapidly than expected. A better fit is obtained by excluding the data below 12 K and fitting with just the 1D antiferromagnetic model plus a magnetite contribution (Figure 3). This approach gives an oxalate-mediated exchange coupling of "$2J/k_B$" $=-4.65(5)$ K and a g value of 2.24(2) for a high spin $S=2$ electronic configuration. The interaction strength is a little weaker compared with other similarly bridged Fe^{II} compounds[18] which range from −7 to −11 K. The low-temperature deviation of the susceptibility could signify either a transition to a long-range ordered antiferromagnetic state (which is not evident in the powder susceptibility measurement) or more interestingly, unusual quantum phase behavior. In particular integer-spin antiferromagnetic chains are predicted to show a "Haldane" gap[19] between a nonmagnetic quantum ground state and the first excited triplet state. While there are several convincing examples of $S=1$ Haldane materials,[20] $S=2$ examples remain unknown. In addition advances in theory now suggest[21] a fundamental difference exists between the ground-state quantum-order of odd and even integer 1D antiferromagnets.

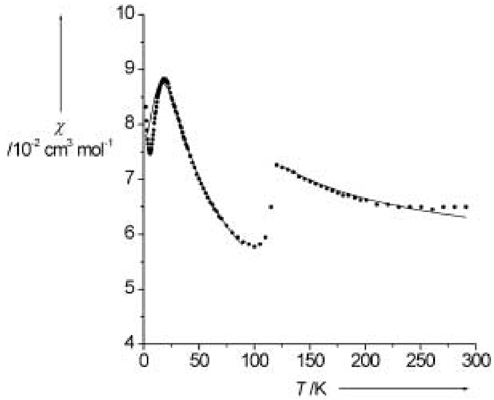

Figure 3. The magnetic susceptibility of **1** showing the three distinct features described in the main text, and the best fit to the data.

The magnetism of **2** (Supporting Information) is not complicated by impurities. On cooling **2** shows a broad maximum in χ at 47(2) K followed by a discontinuity at 37 K. The data above 120 K is well described by the Curie–Weiss law with $C=3.66(2)\,cm^{-3}\,K\,mol^{-1}$ and $\theta=-41(1)$ K. The room temperature moment of $5.04\,\mu_B$ is large compared to the spin only expectation for a high-spin configuration, which signifies a substantial orbital contribution. This contribution can be parameterized in an effective g value of 2.60. All the data in the paramagnetic regime above 37 K is very well described by the antiferromagnetic chain model[17] with $S=3/2$, least-squares analysis give a coupling constant "$2J/k_B$" $=-19.5(1)$ K. This value is considerably larger than for comparable oxalate-bridged $Co^{II}O_6$ octahedra.[18a,22] It appears that at 37 K the sample undergoes a magnetic phase transition, to an ordered, essentially 3D antiferromagnetic state. Interchain interactions and single ion anisotropy are likely to be responsible for this dimensionality crossover.

In summary we have demonstrated the synthesis of an uncommon anhydrous ternary oxalate from very concentrated aqueous potassium-ion solutions. The transition-metal environment in these materials is a rare trigonal-prismatic geometry. From a magnetic perspective the simple structure makes these materials good 1D model systems. In particular **1** may be the first serious candidate in which to find the much prized Spin 2 Haldane quantum antiferromagnetic behavior at low temperatures. More sophisticated magnetic studies are underway to establish this latter point.

Experimental Section

Optimal synthesis of $K_2Fe(ox)_2$ (**1**): $FeCl_2(H_2O)_4$ (0.419 g, 2.12 mmol), $K_2ox(H_2O)$ (0.960 g, 5.02 mmol), KBr (5.97 g, 50.2 mmol), and distilled water (7 mL, 390 mmol) were placed in a 23-mL capacity Teflon-lined autoclave and heated to 225 °C for 4 h then cooled back to room temperature over 14 h. The solvent was decanted and ethanol added to the mixture resulting in the precipitation of KBr. Repeated sonication in ethanol and removal of the flocculent precipitate by decanting the fine suspension left a mixture of the product and large crystals of KBr. This mixture of solids was collected by filtration and dried under suction. Glycerol (80 mL) was added to the mixture of solids, and heated to 100 °C, dissolving the KBr. The orange crystalline product was collected by filtration, washed with methanol, and dried in air. (Yield 0.4239 mg, 1.48 mmol, 70%) Magnetization studies (see main text) show Fe_3O_4 impurity at ≈4%. IR diff. refl., KBr matrix: $\tilde{\nu}=3432$ m, 3229 w, 3190 w, 3114 w, 3040 w, 2949 w, 2902 w, 2940 w, 2841 w, 2818 w, 2696 w, 2612 w, 2559 w, 1928 w, 1836 w, 1777 m, 1668 s, 1624 s, 1425 m, 1388 m, 1337 m, 1285 m, 892 w, 801 m, 783 m, 520 m, 504 m, 415 w, 386 cm^{-1} w. UV, diff. refl., $BaSO_4$ matrix, λ nm^{-1} (abs/relative) 2392 (0.073), 2211 (0.065), 1798 (0.080) sh, 1625 (0.088), 1353 (0.087) sh, 1123 (0.092), 412 (0.17), 301 (0.11) sh. Elemental analysis (%) calcd for $K_2FeC_4O_8$: C 15.49; found: C 15.39. Thermogravimetric analysis (TGA; 60% O_2, 40% N_2, 10 °C min^{-1}) single-step decomposition, onset 406 °C, mass lost 29.1%. Expected loss for decomposition to $K_2CO_3+0.5(Fe_2O_3)$, 29.7%.

Optimal synthesis of $K_2Co(ox)_2$ (**2**): As for **1** but with the following reagent quantities: $CoCl_2(H_2O)_6$ (0.29 g,1.2 mmol), $K_2ox(H_2O)$ (0.59 g, 3.2 mmol), KBr (15.96 g, 134.1 mmol), and distilled water (5 mL, 280 mmol). (Yield 123 mg, 33 %) IR diff. refl., KBr matrix: $\tilde{\nu} = 3436$ m, 3230 w, 3206 w, 3157 w, 3122 w, 3080 w, 3042 w, 2940 w, 2900 w, 2829 w, 2699w, 2620 w, 2561 w, 2512 w, 2427 w, 2376 w, 1931 w, 1672 s, 1626 s, 1428 m, 1385 m, 1340 m, 1285 m, 1135 br m, 894 w, 806 m, 783 m, 518 m, 505 m, 420 cm^{-1} w. UV, diff. refl., $BaSO_4$ matrix, $\lambda\, nm^{-1}$ (abs/relative) 1805 (0.055) sh, 1614 (0.062), 1350 (0.072) sh, 1095 (0.088), 549 (0.10), 496 (0.080) sh, 293 (0.12). Elemental analysis (%) calcd for $K_2CoC_4O_8$: C 15.34; found: C 15.07. TGA (60 % O_2, 40 % N_2, 10 °C min^{-1}) single-step decomposition, onset 353 °C, mass lost 28.6 %. Expected loss for decomposition to $K_2CO_3 + 0.333\,(Co_3O_4)$, 30.3 %.

Field-cooled magnetic-susceptibility measurements were performed between 2 and 290 K in applied fields of 200 and 1000 G. A diamagnetic correction of $-92 \times 10^{-6}\ cm^3 mol^{-1}$ was estimated from Pascal's constants.[23]

Received: July 17, 2003 [Z52406]

Keywords: chain structures · hydrothermal synthesis · iron · magnetic properties · O ligands

---

[1] a) R. E. Dinnebier, S. Vensky, M. Panthöfer, M. Jansen, *Inorg. Chem.* **2003**, *42*, 1499–1507; b) E. Jeanneau, N. Audebrand, D. Louër, *Acta Crystallogr. Sect. C* **2001**, *57*, 1012–1013; c) D. J. Price, A. K. Powell, P. T. Wood, *Polyhedron* **1999**, *18*, 2499–2503; d) D. Yu. Naumov, A. Virovets, N. V. Podberezskaya, E. V. Boldyreva, *Acta Crystallogr. Sect. C* **1995**, *51*, 60–62; e) A. N. Christensen, P. Norby, J. C. Hanson, *Z. Kristallogr.* **1994**, *209*, 874–877.

[2] a) W. Ollendorf, F. Weigel, *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 263–269; b) S. Natarajan, R. Vaidhyanathan, C. N. R. Rao, S. Ayyappan, A. K. Cheetham, *Chem. Mater.* **1999**, *11*, 1633–1639; c) R. Vaidhyanathan, S. Natarajan, A. K. Cheetham, C. N. R. Rao, *Chem. Mater.* **1999**, *11*, 3636–3642; d) H. Hernandez-Molina, F. Lloret, C. Ruiz-Perez, M. Julve, *Inorg. Chem.* **1998**, *37*, 4131–4135.

[3] a) M. Jaber, R. Faure, H. Loiseleur, *Acta Crystallogr. Sect. B* **1978**, *34*, 429–431; b) J. D. Donaldson, M. T. Donoghue, C. H. Smith, *Acta Crystallogr. Sect. B* **1976**, *32*, 2098–2101; c) J.-C. Trombe, P. Thomas, C. Brouca-Cabarrecq, *Solid State Sci.* **2001**, *3*, 309–319.

[4] a) D. J. Price, A. K. Powell, P. T. Wood, *J. Chem. Soc. Dalton Trans.* **2000**, 3566–3569; b) C. Boudaren, J. P. Auffredic, M. Louër, D. Louër, *Chem. Mater.* **2000**, *12*, 2324–2333; c) T. Bataille, D. Louër, *Acta Crystallogr. Sect. C* **1999**, *55*, 1760–1762.

[5] a) C. Mathoniere, C. J. Nuttall, S. G. Carling, P. Day, *Inorg. Chem.* **1996**, *35*, 1201–1206; b) G. de Munno, R. Ruiz, F. Lloret, J. Faus, R. Sessoli, M. Julve, *Inorg. Chem.* **1995**, *34*, 408–411; c) S. Decurtins, H. W. Schmalle, P. Schneuwly, H. R. Oswald, *Inorg. Chem.* **1993**, *32*, 1888–1892; d) M. Julve, M. Verdaguer, A. Gleizes, M. Philochelevisalles, O. Kahn, *Inorg. Chem.* **1984**, *23*, 3808–3818.

[6] Unit cell parameters and data for **1** and **2** were collected on a Bruker Nonius Kappa CCD diffractometer mounted at the window of a rotating anode generator following standard procedures. Structures were solved by direct methods and refined by a full-matrix least-squares on F^2. All atoms were refined anisotropically. Crystal data for **1**, $K_2Fe(C_2O_4)_2$, 120(2) K, monoclinic, *P*2/*c* (no. 13), $a = 8.5207(3)$, $b = 6.8846(2)$, $c = 14.6912(6)$ Å, $\beta = 93.8105(16)°$, $V = 859.90(5)$ Å^3, $Z = 4$, $\rho_{cald} = 2.419\ g cm^{-3}$, $\theta_{max} = 27.48°$, $\mu(0.71073\ Å) = 3.274\ mm^{-1}$. 4840 reflections collected, 1508 unique reflections [1446 $I > 2\sigma(I)$] were used in the refinement. Final *R* values: *R* (all data/$2\sigma(I)$) 0.0346/0.0333, *wR*2 (all data/$2\sigma(I)$) 0.0847/0.842 for 138 parameters. Largest residual peak (hole) 0.879 (−0.496) e Å^{-3}. For **2**, $K_2Co(C_2O_4)_2$, 120(2) K, monoclinic, *P*2/*c* (no. 13), $a = 8.4505(2)$, $b = 6.9084(2)$, $c = 14.6600(4)$ Å, $\beta = 93.3359(8)°$, $V = 854.39(4)$ Å^3, $Z = 4$, $\rho_{cald} = 2.171\ g cm^{-3}$, $\theta_{max} = 25.02°$, $\mu(0.71073\ Å) = 3.663\ mm^{-1}$. 4364 reflections collected, 1008 unique reflections [924 $I > 2\sigma(I)$] were used in the refinement. Final *R* values: *R* (all data/$2\sigma(I)$) 0.0383/0.0342, *wR*2 (all data/$2\sigma(I)$) 0.0705/0.0693 for 138 parameters. Largest residual peak (hole) 0.324 (−0.337) e Å^{-3}. CCDC-215206 (**1**) and CCDC-215207 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] For Fe^{II}; M. Ijjaali, G. Venturini, R. Gerardin, B. Malaman, C. Gleitzer, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 983–998.

[8] For Co^{II}; a) J. Darriet, L. Elcoro, A. El Abed, E Gaudin, J. M. Perez-Mato, *Chem. Mater.* **2002**, *14*, 3349–3363; b) M.-H. Whangbo, H.-J. Koo, K.-S. Lee, O. Gourdon, M. Evain, S. Jobic, R. Brec, *J. Solid State Chem.* **2001**, *160*, 239–246; c) H.-C. zur Loye, K. E. Stitzer, M. D. Smith, A. El Abed, J. Darriet, *Inorg. Chem.* **2001**, *40*, 5152–5156.

[9] D. L. Kepert, *Inorganic Stereochemistry*, Springer, Berlin, **1982**.

[10] a) J.-H. Luo, M.-C. Hong, Y.-C. Liang, R. Cao, *Acta Crystallogr. Sect. E* **2001**, *57*, m361-m362; b) J. Y. Lu, T. J. Schroeder, A. M. Babb, M. Olmstead, *Polyhedron* **2001**, *20*, 2445–2449; c) D. Deguenon, G. Bernardinelli, J.-P. Tuchages, P. Castan, *Inorg. Chem.* **1990**, *29*, 3031–3037.

[11] R. Vaidhyanathan, S. Natarajan, C. N. R. Rao, *J. Chem. Soc. Dalton Trans.* **2001**, 699–706.

[12] F. Walz, *J. Phys. Condens. Matter* **2002**, *14*, R285-R340.

[13] M. Molinier, D. J. Price, P. T. Wood and A. K. Powell, *J. Chem. Soc. Dalton Trans.* **1997**, 4061–4068.

[14] L. J. de Jongh, A. R. Miedema, *Adv. Phys.* **2001**, *50*, 947–1170.

[15] K. Kojima, A. Keren, L. P. Le, G. M. Luke, W. D. Wu, Y. J. Uemura, K. Kiyono, S. Miyasaka, H. Takagi, S. Uchida, *Phys. Rev. Lett.* **1995**, *74*, 3471–3474.

[16] a) V. A. M. Brabers, F. Walz, H Kronmüller, *Phys. Rev. B* **1998**, *58*, 14163–14166; b) J. M. Honig, *J. Alloys Compd.* **1995**, *229*, 24–39.

[17] W. Hiller, J. Strähle, A. Datz, M. Hanack, W. E. Hatfield, L. E. ter Haar, P. Gütlich, *J. Am. Chem. Soc.* **1984**, *106*, 329–335.

[18] a) J. Glerup, P. A. Goodson, D. J. Hodgson, K. Michelsen, *Inorg. Chem.* **1995**, *34*, 6255–6264; b) D. Armentano, G. de Munno, F. Lloret, M. Julve, J. Curély, A. M. Babb, J. Y. Lu, *New J. Chem.* **2003**, *27*, 161–165.

[19] a) F. D. Haldane, *Phys. Lett. A* **1983**, *93*, 464–468; b) F. D. Haldane, *Phys. Rev. Lett.* **1983**, *50*, 1153–1156.

[20] a) W. J. L. Buyers, R. M. Morra, R. L. Armstrong, M. J. Hogan, P. Gerlach, K. Hirakawa, *Phys. Rev. Lett.* **1986**, *56*, 371–374; b) Y. Ajiro, T. Goto, H. Kikuchi, T. Sakakibara, T. Inami, *Phys. Rev. Lett.* **1989**, *63*, 1424–1427; c) N. Metoki, Y. Koike, Y. Matsuoka, T. Kobayashi, M. Yamashita, *J. Magn. Magn. Mater.* **2001**, *226–230*, 414–416.

[21] a) M. A. Ahrens, A. Schadschneider, J. Zittartz, *Europhys. Lett.* **2002**, *59*, 889–895; b) U. Schollwock, O. Golinelli, T. Jolicoeur, *Phys. Rev. B* **1996**, *54*, 4038–4051; c) T. Kennedy, H. Tasaki, *Phys. Rev. B* **1992**, *45*, 304–307.

[22] a) V. B. Kursigerski, V. V. Spasojeviæ, N. Dj. Lazarov, D. S. Markoviæ, V. M. Matić, S. P. Sovilij, M. Guillot, *Solid State Commun.* **2003**, *126*, 319–322; b) O. Castillo, A. Luque, P. Román, F. Lloret, M. Julve, *Inorg. Chem.* **2001**, *40*, 5526–5535.

[23] See for example: O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.