CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201001398

Crystal-to-Crystal Transformation from a Mononuclear Compound in a Hydrogen-Bonded Three-Dimensional Framework to a Layered Coordination Polymer

Bin Zhang,*[a] Daoben Zhu,*[a] and Yan Zhang[b]

In coordination compounds, the weak interaction of guest molecules, coordination geometry distortion, and coordination number changes can effectively modulate the physical properties of magnetism, absorption, and chirality. Therefore, dynamic molecular crystals capable of crystal-to-crystal transformations, involving changes in the dimensionality, color, and physical properties, are very attractive for their potential applications in molecular devices such as switches and sensors.[1] Because it is usually difficult to obtain high-quality transformed crystals after removal of the bound water or solvent due to collapsing of the framework, only a few crystal-to-crystal transformations have been reported.[2] So far, the crystal-to-crystal transformations were observed between different dimensional coordination polymers, such as 1D to 2D, 1D to 3D, and 2D to 3D.[3] The crystal-to-crystal transformations from 0D polynuclear compounds to 2D and 3D coordination polymers have also been reported.[4] Herein, we present a crystal-to-crystal transformation from 0D mononuclear compound $CuCl_2(1,4\text{-dioxane})_2(H_2O)_2$ (**1**) into 2D coordination polymer $Cu_3Cl_6(1,4\text{-dioxane})_2$ (**2**) accompanied by changes in the crystal color, cell parameters, space group, crystal structure, coordination environments of Cu^{2+}, and magnetic properties.

Blue crystal **1** was obtained from $CuCl_2{\cdot}6H_2O$ in a mixture of 3 N $HCl/CH_3OH/(1,4\text{-dioxane})$ with a yield of 60%. When **1** was heated at an elevated temperature (such as 120 °C for 3 min) or exposure to air with a humidity lower than 50%, it transformed completely into brown crystal **2** and **2** remained stable until 200 °C. During the transformation, the weight loss was 44%. This value is much higher than those reported for crystal-to-crystal transformations with a dimension change from a 0D polynuclear compound: the weight loss was 5.6% from binuclear compound $[Co_2(8\text{-qoac})_2(N_3)_2(H_2O)]$ (8-qoac = quinoline-8-oxyacetate) to 2D coordination polymer $[Co_2(8\text{-qoac})_2(N_3)_2]_n$, 20.7% from hexanuclear compound $[\{Fe^{III}(Tp)(CN)_3\}_4\{Fe^{II}(CH_3CN)(H_2O)_2\}_2]{\cdot}10H_2O{\cdot}2CH_3CN$ (Tp = hydrotris(pyrazolyl)borate) to 1D coordination polymer $[\{Fe^{III}(Tp)(CN)_3\}_4Fe^{II}(H_2O)_2Fe^{II}]$, 21.6% from hexanuclear compound $[\{Fe^{III}(Tp)(CN)_3\}_4\{Co^{II}(CH_3CN)(H_2O)_2\}_2]{\cdot}10H_2O{\cdot}2CH_3CN$ to 3D coordination polymer $[\{Fe^{III}(Tp)(CN)_3\}_2Co^{II}]$.[4] It is also higher than the value observed in porous molecular crystals in which the framework remains the same within transformation involving approximately 10% desolvation of $[Mn_3(HCOO)_6]$ ·solvent or 28% dehydration of $[Co_2(H_{0.67}bdt)_3]{\cdot}20H_2O$ (H_2bdt = 5,5′-(1,4-phenylene)bis(1H-tetrazole)).[5] Attempts to resolvate **2** to obtain pure product **1** have not been successful yet; therefore, desolvation from **1** to **2** is irreversible.

The crystal to-crystal transformation from **1** to **2** was confirmed by the X-ray diffraction experiments. When **1** desolvates into **2**, the space group changes from *C*2/*c* into *C*2/*m* with changes in the cell parameters and crystal structures.

As shown in Figure 1, compound **1** is composed of mononuclear compound $CuCl_2(1,4\text{-dioxane})_2(H_2O)_2$. Each Cu^{2+} is octahedrally coordinated by two Cl^-, two H_2O, and two O atoms (one from each of two 1,4-dioxane molecules in the chair conformation) *trans* to each other. The Cu−O distance to H_2O (1.962(1) Å) is shorter than to the O atom of the 1,4-dioxane molecules (2.615(2) Å). The shortest distance between Cu^{2+} ions is 5.937 Å. There are hydrogen bonds between H_2O and Cl^-: O3−H1···Cl1 2.43 Å/163°, and H_2O and 1,4-dioxane: O3−H2···O1 2.74 Å/166°. The hydrogen bonds form a three-dimensional NaCl framework.

---

[a] Prof. B. Zhang, D. Zhu
Organic Solid Laboratory, BNLMS
CMS & Institute of Chemistry
Chinese Academy of Sciences
Beijing, 100190 (P.R. China)
Fax: (+86) 10-62559373
Fax: (+86) 10-62544083
E-mail: zhangbin@iccas.ac.cn
zhudb@iccas.ac.cn

[b] Y. Zhang
Institute of Condensed Matter and Material Physics
Department of Physics, Peking University
Beijing, 100871 (P.R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001398.

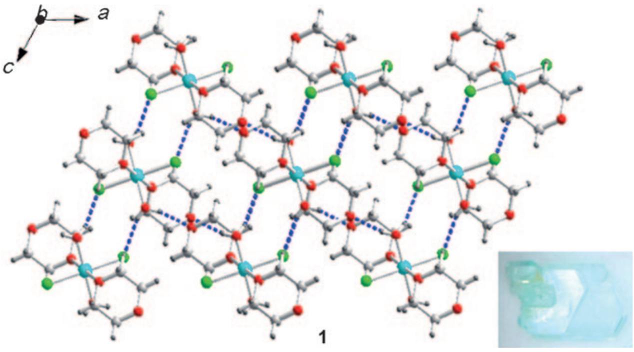


Figure 1. View of the arrangement of discrete mononuclear molecules along the *b* axis in **1**. Cu: blue, C: light gray, O: red, H: gray, Cl: green. Blue dashed lines are hydrogen bonds. Inset: crystal appearance of **1**

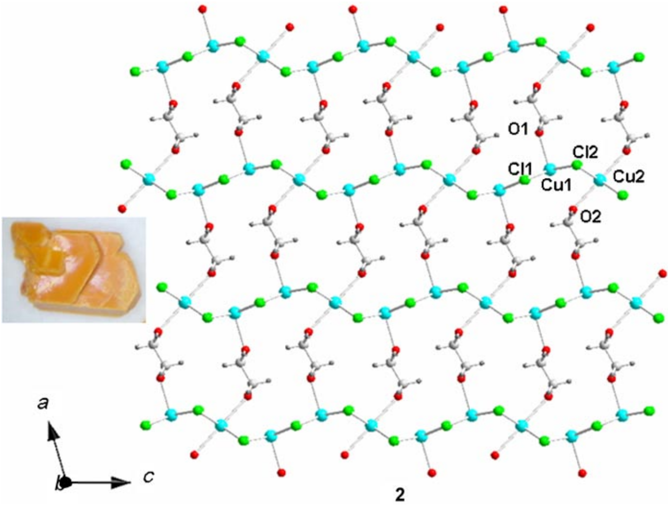
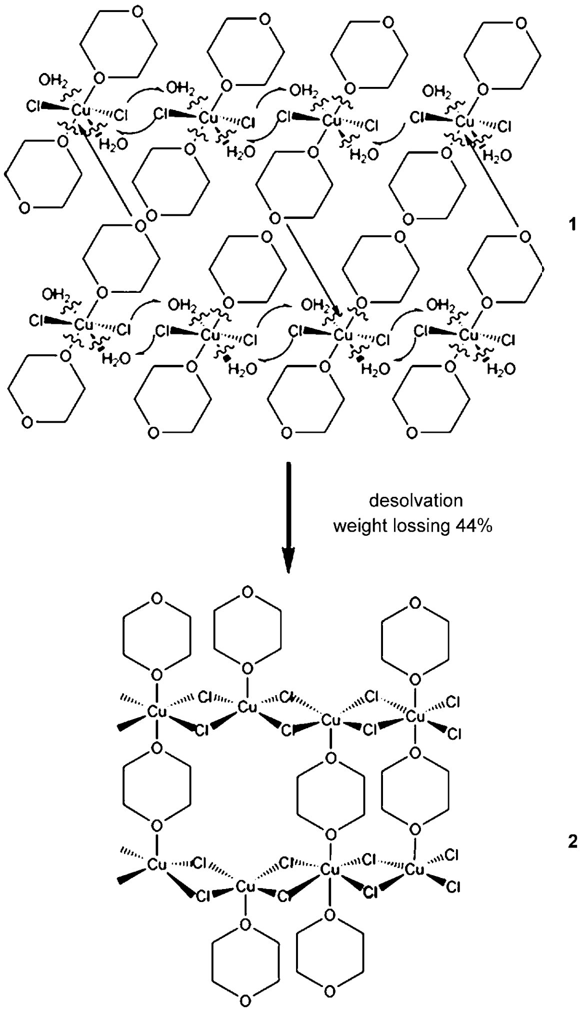


Figure 2. The structure of layered coordination polymer in **2**. Cu: blue, C: light gray, O: red, H: gray, Cl: green. Inset: appearance of crystal **2**, which was desolvated from **1** in Figure 1

Compound **2** consists of layered coordination polymer of $(CuCl_2)_3$(1,4-dioxane)$_2$ as shown in Figure 2.[6] Cu1 has a square-pyramidal geometry and is coordinated by four Cl^- (two Cl1, two Cl2) in the equatorial plane with a distance of 0.149 Å in the direction of the apex and one O (O1) atom with a Cu–O distance of 2.359(3) Å from the 1,4-dioxane molecule in the chair conformation axially. The weaker Cu–O bonds (O2) 2.823(3) Å complete the distorted octahedra of Cu1. Cu2 is octahedrally coordinated by four Cl2 and two O2 from 1,4-dioxane with Cu–O 2.434(3) Å. Cl1 bridges Cu1 with a Cu1-Cl1-Cu1′ angle of 93.66(4)°, Cl2 connects Cu1 and Cu2 with a Cu1-Cl2-Cu2 angle of 85.26(3)°, the dihedral angle between two $CuCl_4$ in the plane of neighboring Cu1 and Cu2 is 50.11(3)°. The $CuCl_2$ chain is formed along the *c* axis. $CuCl_2$ chains are connected through 1,4-dioxane molecules along the *a* axis and form a long and short brick network with the Schläfli symbols of $(4.6^2)_2(4^2.6^2)$ on the *ac* plane. The Cu···Cu distance bridged by Cl^- is 3.3523(9) Å between two Cu1 and 3.1119(5) Å between Cu1 and Cu2; this is in the same range as reported compounds.[7] The Cu···Cu distance is 6.9577(6) Å between two Cu^{2+} ions connected by 1,4-dioxane molecules. There are no weak interactions, such as hydrogen bonds, between the layers.

The Cu–Cl and Cu–O distances in **1** and **2** are in the same range as those of reported compounds.[7,8] When **1** was heated at 90–160 °C or exposed to dry air, then H_2O and 2/3 of the 1,4-dioxane content desolvated from **1** to form **2**. The transformation suggests that the connecting mode of Cl^- and 1,4-dioxane changed from terminal mode in **1** to bridged mode in **2** and the mononuclear molecule $CuCl_2$(1,4-dioxane)$_2$(H_2O)$_2$ transformed into layered coordination polymer $(CuCl_2)_3$(1,4-dioxane)$_2$ as Scheme 1. It is the first example of crystal-to-crystal transformation from mononuclear molecules to 2D coordination polymer.



Scheme 1. Schematic drawing of the possible route of crystal-to-crystal transformation from **1** to **2**.

Due to the hydrogen bonds in **1** and (μ-Cl)$_2$ bridge in **2**, the magnetic properties of these compounds have been studies. The temperature-dependent magnetization was carried out under a magnetic field of 1000 Oe. On a χ versus T plot of **1**, a broad maximum was observed at 38 K (Figure 3) as observed for Cu^{2+} compounds.[9] At 300 K, the χT value was 0.59 $cm^3 K mol^{-1}$, which is significantly larger than the value of 0.375 $cm^3 K mol^{-1}$ expected for an isolated, spin-only ion with $S=1/2$ and $g=2.00$ and close to the reported value.[10] The χT value decreased smoothly upon cooling and reached 0.01 $cm^3 Kmol^{-1}$ at 2 K. The susceptibility data above 50 K fit the Curie–Weiss law well, giving Curie and Weiss constants of $C=0.690(3)$ $cm^3 Kmol^{-1}$ and $\theta=-66.7(7)$ K, respectively, with $R=1.23\times10^{-4}$. The negative Weiss value means strong antiferromagnetic interactions between Cu^{2+} ions.

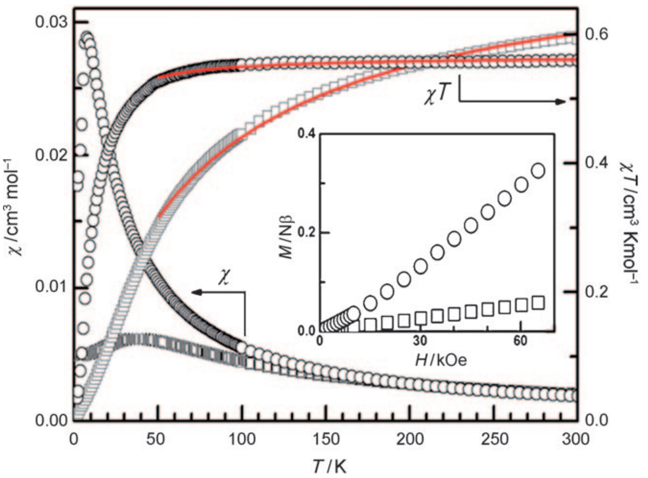


Figure 3. χ versus T and χT versus T plot of **1** (□) and **2** (○) under an applied field of 1000 Oe. The red lines indicate fits to the Curie–Weiss law. Inset: M versus H plot of **1** (□) and **2** (○) at 2 K.

On the χ versus T plot of **2**, a maximum value of 0.0288 $cm^3 mol^{-1}$ was observed at 7.8 K. Below 7.8 K, the χ value decreased and reached 0.0177 $cm^3 mol^{-1}$ at 2 K. At 300 K, the χT value was 0.56 $cm^3 Kmol^{-1}$, in the same range as that obtained for **1**. The χT value remained the same above 80 K, then decreased upon cooling and reached 0.035 $cm^3 Kmol^{-1}$ at 2 K. The susceptibility data above 50 K fit the Curie–Weiss law well, giving Curie and Weiss constants of $C=0.567(1)$ $cm^3 K mol^{-1}$, $\theta=-3.2(1)$ K, respectively, with $R=2.04\times10^{-5}$. The antiferromagnetic interaction in **2** is weaker than in **1**.

The isothermal magnetization was measured at 2 K. No hysteresis loop was observed in **1** and **2**. The isothermal magnetization increased linearly as the field increased and reached 0.06 Nβ at 65 kOe in **1**, 0.33 Nβ at 65 kOe in **2**. These results confirmed that the antiferromagnetic interaction in **1** is stronger than in **2**, although the Cu^{2+} ion is connected by a μ-Cl_2 bridge and a dioxane bridge in **2**. Depending on the crystal structures of **1** and **2**, the weak hydrogen-bonding interactions play as important a role as the Cl and dioxane bridges on molecular magnetism.

In summary, the crystal composed of mononuclear compound **1** in a hydrogen-bonded three-dimension framework can be transformed to a crystal composed of layered coordination polymer (**2**) by desolvation with changes in the crystal composition, color, structure, and magnetism as the antiferromagnetic interaction decreased and the Weiss constants changed from −66.7 (**1**) to −3.2 K (**2**), and the temperature at which a maximum was observed on a χ versus T plot decreased from 38 to 7.8 K. These results show a way to obtain crystals quantitatively by crystal-to-crystal transformation with drastic changes in the molecular formula, crystal structure, crystal color, and magnetism and provides crystalline materials to be used as sensors or switches in the near future.

Experimental Section

Sample preparation: All reagents were commercially and used as received without further purification.

Compound 1: $CuCl_2\cdot4H_2O$ (1.0 mmol) was dissolved in 3 N HCl (1 mL), CH_3OH (5 mL), and 1,4-dioxane (20 mL). Blue block crystals were obtained on the bottom of the beaker in 60% yield after two weeks. Elemental analysis calcd (%) for $C_8H_{20}O_6Cl_2Cu$ (346.70): C 27.72, H 5.81; found: C 27.46, H 5.79. Compound **1** is very unstable to air, so IR characterization was carried out as soon as possible on fresh crystal and a small area of the crystal remained blue during the measurements. IR (micro-IR on a single crystal): 3012–3572 (s, br), 2978 (s), 2960 (s), 2939 (s), 2870 (s), 2762 (m), 2702 (m), 2360 (m), 2334 (m), 2330 (w), 2205 (m), 2179 (m), 2079 (w), 1963 (w), 1932 (w), 1907 (w), 1881 (w), 1656 (s), 1445 (s), 1293 (s), 1250 (s), 1112 (s), 1090 (s), 1021 (w), 892 (m), 861 (s), 823 cm^{-1} (s).

Compound 2: Blue crystals of **1** were heated at 120 °C for 3 min or exposed to air and brown crystals of **2** were obtained with a yield of 100%. Elemental analysis calcd (%) for $C_8H_{16}O_6Cl_6Cu_3$ (579.53): C 16.58, H 2.78; found: C 16.59, H 2.86; IR (micro-IR on a single crystal): 3416 (m, br), 2979 (m), 2916 (w), 2858 (w), 1614 (w), 1444 (m), 1435 (m), 1370 (vw), 1289 (m), 1254 (s), 1112 (s), 1079 (m), 1033 (m), 893 (m), 857 (vs), 616 cm^{-1} (m).

Physical characterizations: Thermogravimetric analysis was carried out on Shimadzu DTG-60 Analyzer with 10 °C min^{-1} from room temperature to 600 °C. There are two main mass losses in **1**: 44% from 60 to 80 °C, and 17% from 180 to 200 °C. There is one main mass loss in **2**: 30% from 180 to 220 °C.

X-ray diffraction data was collected at 293 K on a Nonius KappaCCD diffractometer with graphite monochromated $Mo_{K\alpha}$ ($\lambda=0.71073$ Å) radiation.[11] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELX program,[12] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms of H_2O in **1** were found by difference Fourier and refined isotropically. Hydrogen atoms of dioxane were located by calculations and refined isotropically. Crystallographic data of **1**: $C_8H_{20}Cl_2CuO_6$; $M_r=346.68$; monoclinic; space group $C2/c$; $a=17.4816(4)$, $b=7.5763(2)$, $c=11.8672(3)$ Å, $\beta=119.238(1)°$; $V=1371.52(6)$ Å^3; $Z=4$; $\rho_{calcd}=1.679$ $g cm^{-3}$; $\mu=1.994$ mm^{-1}, 10876 measured data, 1577 unique; $R_{int}=0.0575$; $R_1=0.0254$ for 1363 observations of $I\geq2\sigma(I_0)$, $wR_2=0.0627$ for all data, GOF = 1.061. Crystallographic data of **2**: $C_8H_{16}Cl_6Cu_3O_4$; $M_r=579.53$; monoclinic; space group $C2/m$; $a=7.8677(3)$, $b=12.0410(5)$, $c=9.1884(4)$ Å; $\beta=106.371(2)°$; $V=7835.17(6)$ Å^3; $Z=2$; $\rho_{calcd}=2.305$ $g cm^{-3}$; $\mu=4.751$ mm^{-1}; 7679 measured data; 1001 unique; $R_{int}=0.0686$; $R_1=0.0280$ for 735 observations of $I\geq2\sigma(I_0)$; $wR_2=0.0612$ for all data; GOF = 0.986.

CCDC-759714 (**1**) and 765426 (**2**) contain 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.

Powder X-ray diffraction patterns were obtained on a Rigaku RINT2000 diffractometer at room temperature with $Cu_{K\alpha}$ radiation in a flat-plate geometry. Magnetization measurements were performed on a tightly packed polycrystalline sample in a capsule on a Quantum Design MPMS 7XL SQUID system. Susceptibility data were corrected for diamagnetism of sample by Pascal constants ($-191.4\times10^{-6}\,cm^3mol^{-1}$ for **1**, $-286.2\times10^{-6}\,cm^3mol^{-1}$ for **2**, and $-95.4\times10^{-6}\,cm^3mol^{-1}$ for one Cu atom in **2**) and background by experimental measurements were performed on the sample holder.

Acknowledgements

The authors thank Prof. Zheming Wang and Song Gao of the College of Chemistry and Molecular Engineering, Peking University, for their kind helps in X-ray experiments and valuable discussions. This work was supported by CMS-LX200906, NSFC no. 20673120, 20873154, and MOST 2006CB932102, 2006CB601001 of China.

Keywords: coordination polymers • copper • crystal engineering • hydrogen bonds • magnetic properties

---

[1] a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; b) J. J. Vittal, *Coord. Chem. Rev.* **2007**, *251*, 1781–1795; c) J. Zhang, X. Huang, X. Chen, *Chem. Soc. Rev.* **2009**, *38*, 2385–2396; d) C. B. Aakeröy, N. R. Champness, C. Janiak, *CrystEngComm* **2010**, *12*, 22–43.

[2] a) C. H. Hu, U. Englert, *Angew. Chem.* **2005**, *117*, 2321–2323; *Angew. Chem. Int. Ed.* **2005**, *44*, 2281–2283; b) C. J. Adams, H. M. Colquhoum, P. C. Crawford, M. Lusi, A. G. Orpen, *Angew. Chem.* **2007**, *119*, 1142–1146; *Angew. Chem. Int. Ed.* **2007**, *46*, 1124–1128.

[3] a) J. D. Ranford, J. J. Vittal, D. Wu, X. Yang, *Angew. Chem.* **1999**, *111*, 3707–3710; *Angew. Chem. Int. Ed.* **1999**, *38*, 3498–3501; b) E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858–2861; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798–2801; c) S. K. Ghosh, W. Kanebo, D. Kiriya, M. Ohba, S. Kitagawa, *Angew. Chem.* **2008**, *120*, 8843–8847; d) Z. Duan, Y. Zhang, B. Zhang, D. Zhu, *J. Am. Chem. Soc.* **2009**, *131*, 6934–6935.

[4] a) X. Cheng, W. Zhang, X. Chen, *J. Am. Chem. Soc.* **2007**, *129*, 15738–15739; b) Y. Zhang, T. Liu, S. Kanegawa, O. Sato, *J. Am. Chem. Soc.* **2009**, *131*, 7942–7943; c) Y. Zhang, T. Liu, S. Kanegawa, O. Sato, *J. Am. Chem. Soc.* **2010**, *132*, 912–913.

[5] a) D. Maspoch, D. Ruiz-Molina, K. Wurst, N. Domingo, M. Cavallini, F. Biscarini, J. Tejada, C. Rovira, J. Veciana, *Nat. Mater.* **2003**, *2*, 190–195; b) Z. M. Wang, B. Zhang, H. Fujiwara, H. Kobayashi, M. Kurmoo, *Chem. Commun.* **2004**, 417–418; c) W. H. Zhu, Z. M. Wang, S. Gao, *Dalton Trans.* **2006**, 765–768; d) Z. Wang, Y. Zhang, M. Kurmoo, T. Liu, S. Vilminot, B. Zhao, S. Gao, *Aust. J. Chem.* **2006**, *59*, 617–628; e) W. Ouellette, A. V. Prosvirin, K. Whitenack, K. R. Dunbar, J. Zubieta, *Angew. Chem.* **2009**, *121*, 2174–2177; *Angew. Chem. Int. Ed.* **2009**, *48*, 2140–2143.

[6] J. C. Barnes, T. J. Weakley, *Acta Crystallogr. Sect. B* **1977**, *33*, 921–923.

[7] a) T. Chivers, Z. Gu, L. Thompson, *Chem. Commun.* **2005**, 2339–2341; b) T. Luo, H. Tsai, S. Yang, Y. Liu, R. Yadav, C. Su, C. Ueng, L. Lin, K. Lu, *Angew. Chem.* **2005**, *117*, 6217–6221; *Angew. Chem. Int. Ed.* **2005**, *44*, 6063–6067.

[8] F. A. Cotton, *Advanced Inorganic Chemistry*, Wiley, New York, **1999**, p. 865.

[9] a) J. Darriet, M. S. Haddad, E. N. Duesler, D. N. Hendrickson, *Inorg. Chem.* **1979**, *18*, 2679–2682; b) J. L. Manson, M. M. Conner, J. A. Schlueter, T. Lancaster, S. J. Blundell, M. L. Brooks, F. L. Pratt, T. Papageorgiou, A. D. Bianchi, J. Wosnitza, M. Whangbo, *Chem. Commun.* **2006**, 2894–2896; c) J. L. Manson, J. A. Schlueter, K. A. Funk, H. I. Southerland, B. Twamley, T. Lancaster, S. J. Blundell, P. J. Baker, F. L. Pratt, J. Singleton, R. D. McDonald, P. A. Goddard, P. Sengupta, C. D. Batista, L. Ding, O. C. Lee, M. Whangbo, I. Franke, C. Baines, D. Trial, *J. Am. Chem. Soc.* **2009**, *131*, 6733–6747.

[10] a) O. Kahn, *Molecular Magnetism*, Wiley, New York, **1993**, p. 10; b) R. L. Carlin, A. L. van Duyneveldt, *Magnetic Properties of Transition Metal Compounds*; Springer, New York, **1977**, p. 69.

[11] Otwinowski & Minor, *Denzo and Scalepack*, **1997**.

[12] SHELX-97, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), **1997**.

Received: May 21, 2010