DOI: 10.1002/ejic.200800824

Spin Canting in a Cobalt(II) Radical Complex with an Acentric Counter Anion

Kiyotaka Mitsumoto,[a] Takuya Shiga,[a] Motohiro Nakano,[b] Masayuki Nihei,[a]
Hiroyuki Nishikawa,[a] and Hiroki Oshio*[a]

Keywords: Cobalt / Spin canting / Crystal engineering / Organic radicals / Metamagnets

Cobalt(II) radical complexes with centric and acentric counter anions, [CoCl(bisimpy)(MeOH)$_2$]X [bisimpy = 2,6-bis(4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-1′-oxyl-2′-yl)pyridine; X = PF$_6$ (**1**), and ClO$_4$ (**2**)], crystallize in the centrosymmetric and polar space groups, respectively. Compound **1** is paramagnetic, whereas spin canting in **2** leads to a metamagnetic transition with a critical field of 1300 Oe at 1.8 K.

Introduction

Solids crystallizing in non-centrosymmetric space groups can have tensorial physical properties, such as piezo-electricity, pyro-electricity, and second harmonic generation (SHG).[1] The design of such compounds remains difficult. However, two possible strategies have been proposed for 1D systems:[2] (i) introduction of proper acentric tectons and (ii) combination of chiral tectons. The former may lead to the formation of non-polar crystals due to centrosymmetric packing, and the latter should generate chiral networks. These strategies are appealing to synthetic coordination chemists for designing molecule-based magnetic materials, especially with canted spin systems. On the other hand, combination of metal ions and organic radicals has also been shown to be a good way to construct magnetic materials,[3] among which [Mn(hfac)$_2$(NIT-R)] (Hhfac = hexafluoroacetylacetone, NIT-R = 2-isopropyl-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide) exhibited ferromagnetic ordering at a critical temperature of 7.61 K[4] and [Co(hfac)$_2$-(NITPhOMe)] (NITPhOMe = 4′-methoxyphenyl-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide) has been recognized as the first single-chain magnet.[5] In hybrid spin systems, the sign and amplitude of magnetic interactions depend upon the electronic configurations of metal ions and the coordination modes of radical ligands. Therefore, flexibility in the modification of the ligands is advantageous to designing molecule-based magnetic materials. We prepared hybrid spin systems of [Co^{II}Cl(bisimpy)(MeOH)$_2$]X [bisimpy = 2,6-bis(4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-1′-oxyl-2′-yl)pyridine, X = centric (PF$_6^-$) and acentric (ClO$_4^-$) anions], which crystallized in centric and polar space groups, respectively. We report here the paramagnetic behaviour and spin canting in these complexes, of which the complex with ClO$_4^-$ showed a ferromagnetic transition at 2.7 K.

Results and Discussion

The reaction of CoCl$_2$ with bisimpy and NH$_4$PF$_6$ (or NaClO$_4$) in methanol yielded [Co^{II}Cl(bisimpy)(MeOH)$_2$]X [X = PF$_6$ (**1**), ClO$_4$ (**2**)]. Compounds **1** and **2** crystallize in the monoclinic space group $P2_1/c$ (centric) and in the orthorhombic space group $Pna2_1$ (polar), respectively.[6] They have similar molecular structures, and thus, the same numbering was used for **1** and **2**. An ORTEP diagram of the complex cation of **2** is shown in Figure 1. The ligand bisimpy has two imino nitroxide groups and acts as a tridentate ligand. The cobalt(II) ions in **1** and **2** have a distorted octahedral coordination geometry, and the equatorial coordination sites are occupied by three nitrogen atoms from bisimpy and one chloride ion, and the remaining axial positions are coordinated by two methanol molecules. The distortion of the coordination geometry from the ideal octahedron was quantified by using σ parameters {= $\Sigma|(90 - \theta)|$ [°], θ = bite angles of the two coordinated ligands}, where larger σ values signify larger distortions from the ideal octahedral coordination sphere. The σ parameters were calculated to 81.4 and 84.0 for the complex cations in **1** and **2**, respectively, which means that both cations have similar coordination geometries.

Coordination bond lengths about the cobalt(II) ions in **1** and **2** are in the range of 2.167(3)–2.209(3) Å for the iminyl nitrogen atoms and 2.151(2)–2.138(3) Å for the pyridyl nitrogen atoms. The Co–Cl and Co–O bond lengths are 2.295(1)–2.341(1) Å and 2.120(3)–2.141(2) Å, respectively.

---

[a] Graduate School of Pure and Applied Sciences, University of Tsukuba,
Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan
Fax: +81-29-853-4238
E-mail: oshio@chem.tsukuba.ac.jp
[b] Department of Applied Chemistry, Graduate School of Engineering, Osaka University,
2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan

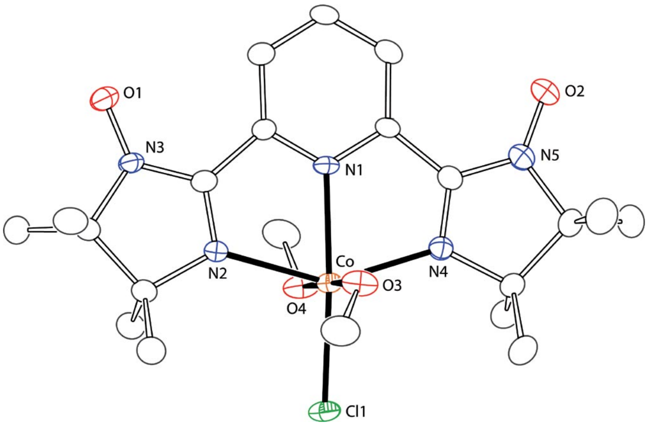

Figure 1. ORTEP diagram of the complex cation in **2**. The same numbering was used for both **1** and **2**. Selected bond lengths [Å] for **1**: Co–O(3) 2.120(3), Co–O(4) 2.141(2), Co–N(1) 2.151(2), Co–N(4) 2.180(3), Co–N(2) 2.205(3), Co–Cl 2.295(1); for **2**: Co–O(3) 2.095(3), Co–O(4) 2.117(3), Co–N(1) 2.138(3), Co–N(4) 2.167(3), Co–N(2) 2.209(3), Co–Cl(1) 2.341(1).

In **1** and **2**, close interatomic distances [2.918(4)–2.822(4) Å] between the oxygen atoms of the imino nitroxyl group and methanol in neighbouring molecules were observed, and hydrogen bonds caused the formation of 1D structures of the complex molecules. Compound **2** has additional intermolecular close contacts [3.956(3) Å] between the coordinated chloride ions and the imino nitroxyl oxygen atoms of neighbouring molecules (Figure 2). Note that neighbouring molecules in the chains are related by glide and twofold screw axes for **1** and **2**, respectively, which is responsible for the different magnetic properties.

Magnetic susceptibility measurements for **1** and **2** were carried out in the temperature range of 1.8–300 K, and $\chi_\mathrm{m}T$ vs. T plots are shown in Figure 3. The $\chi_\mathrm{m}T$ values for **1** gradually increased as the temperature was lowered from 300 K, reaching a maximum value of 4.69 emu mol^{-1} K at 60 K, and then monotonically decreased to 1.8 K. The $\chi_\mathrm{m}T$ value (4.20 emu mol^{-1} K) at 300 K is larger than the Curie constant (2.625 emu mol^{-1} K with $g = 2$) expected for the uncorrelated one Co$^{\mathrm{II}}$ ion ($S = 3/2$) and two radicals ($S = 1/2$), which is due to the orbital contribution of the Co$^{\mathrm{II}}$ ion. The gradual increase of the $\chi_\mathrm{m}T$ values in the high-temperature region suggests the occurrence of an intramolecular ferromagnetic interaction between the Co$^{\mathrm{II}}$ ion and the radical centers.

Complex **2** showed a different temperature dependence of the $\chi_\mathrm{m}T$ values from that in **1**. The $\chi_\mathrm{m}T$ values slightly increased from 4.19 emu mol^{-1} K at 300 K as the temperature was lowered, reaching the maximum value of 4.26 emu mol^{-1} K at 110 K. Upon further cooling, the $\chi_\mathrm{m}T$ values decreased to the minimum value of 2.34 emu mol^{-1} K at 7.2 K, and then increased to the value of 3.21 emu mol^{-1} K at 3.4 K, from which the values suddenly decreased. The similar coordination geometries about the Co$^{\mathrm{II}}$ ions in **1** and **2** suggests that the amplitude of intramolecular magnetic interactions and the contribution of the orbital term are similar to each other. We think that the

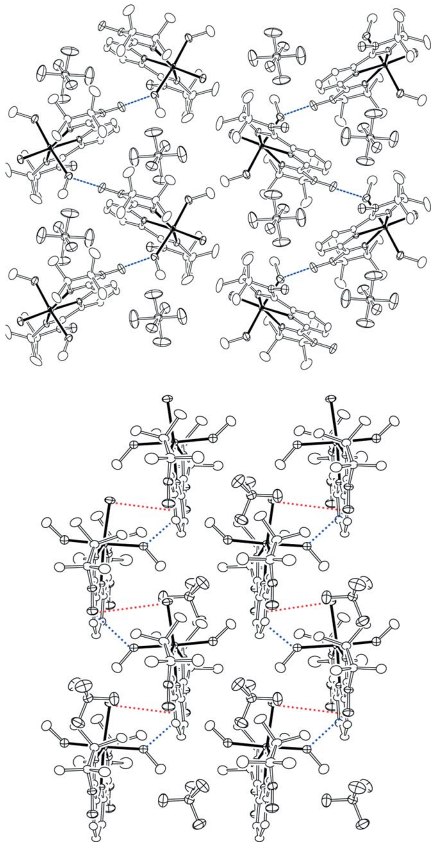

Figure 2. 1D structures in **1** (top) and **2** (bottom). Counter anions are omitted for clarity. Dotted blue lines correspond to hydrogen bonds in **1** and **2**, and red ones in **2** represent close contacts between the chloride ions and the imino nitroxyl oxygen atoms.

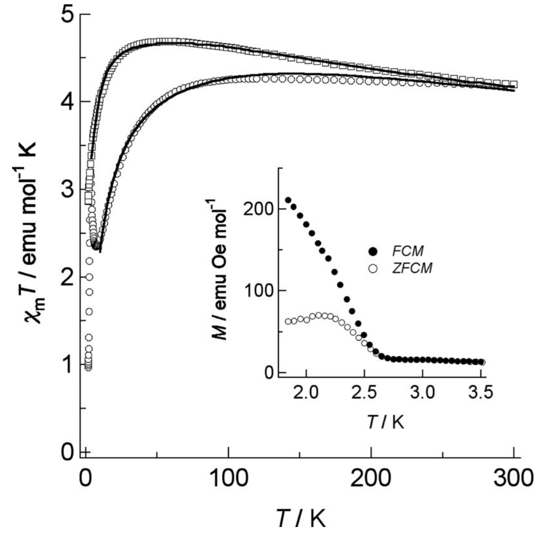

Figure 3. $\chi_\mathrm{m}T$ vs. T plots of **1** (open squares) and **2** (open circles); the solid lines were calculated by using the parameters given in the text. Inset: M vs. T plots for **2**: field-cooled magnetization (FCM) (filled circles) and zero field-cooled magnetization (ZFC) (open circles) measurements.

different magnetic behaviour above 10 K is due to intermolecular antiferromagnetic interactions in **2**, and thus, an intermolecular magnetic interaction was included in the analyses of the magnetic data for **2**. The magnetic susceptibility data were analyzed by using a ligand-field theoretical model. The effective Hamiltonian was:

$$\hat{H} = \delta \cdot \left(\hat{L}_Z^2 - \frac{1}{3}\hat{L}^2 \right) - \frac{3}{2}k\lambda\hat{L} \cdot \hat{S}_0 - 2J_{\mathrm{Co-R}} \sum_{i=1}^{2} \hat{S}_0 \cdot \hat{S}_\mathrm{i}$$
$$-2J_{\mathrm{R-R}}\hat{S}_1 \cdot \hat{S}_2 + \mu_0\mu_\mathrm{B}\left(-\frac{3}{2}k\hat{L} + g_e \sum_{i=0}^{2} \hat{S}_i \right) \cdot \left(H - \frac{2zJ'}{\mu_0\mu_\mathrm{B}} M_\mathrm{B} \right)$$
$$M_\mathrm{B} = \left\langle -\frac{3}{2}k\hat{L} + g_e \sum_{i=0}^{2} \hat{S}_i \right\rangle_\mathrm{B}$$

where δ and $\hat{\mathrm{L}}$ are the energy splitting between the $^4A_{2\mathrm{g}}$ and $^4E_\mathrm{g}$ states and an effective angular momentum with a magnitude of $L = 1$, respectively. Spin operators of $\hat{\mathrm{S}}_0$, $\hat{\mathrm{S}}_1$, and $\hat{\mathrm{S}}_2$ stand for the $S_0 = 3/2$ and $S_1 = S_2 = 1/2$ spin states of the cobalt(II) ion and the radical centres, respectively. The parameters of k and λ represent the Stevens orbital reduction factor and the spin-orbit coupling constant, respectively. Two intramolecular exchange coupling constants of $J_{\mathrm{Co-R}}$ and $J_{\mathrm{R-R}}$ were introduced between the $\mathrm{Co^{II}}$ ion and each radical and between the radical centres, respectively. Intermolecular interactions are implemented through a mean field zJ' in conjunction with the molecular magnetization on the counterpart sublattice B, which can be evaluated iteratively. The z and J' values represent the number of neighboring molecules and the intermolecular exchange coupling constant, respectively. The diradical of bisimpy has a triplet spin ground state, which is due to spin-polarization of π-spins on the molecule.[7] The fixed $J_{\mathrm{R-R}}$ value of +4.5 K, which was taken from ref.[7], was used in the calculations. Least-squares calculations by using the data above 10 K yielded $J_{\mathrm{Co-R}}$ = 49.3 K for **1** and $J_{\mathrm{Co-R}}$ = 48.3 K with zJ' = –0.9 K for **2**, where the zJ' value for **1** was found to be negligibly small.[8] In **1** and **2** the magnetic orbitals (pπ) of bisimpy are perpendicular to the equatorial coordination plane, and the high-spin cobalt(II) ion with hexacoordination geometry has unpaired electrons in the d_{xy}, d_{z^2}, and $\mathrm{d}_{x^2-y^2}$ orbitals. The magnetic orbitals of the cobalt(II) ion and bisimpy are, therefore, orthogonal to each other, which is responsible for the occurrence of the intramolecular ferromagnetic interactions.

In **1** the neighboring molecules in the chain are related by the crystallographic glide operation, which might lead to non-compensating spins on the chains.[9] However, the analysis of the magnetic susceptibility data for **1** suggests negligibly small intermolecular antiferromagnetic interactions, and a long-range order, which is potentially weakly ferromagnetic in nature, was not detected in the measurement temperature range. The chains in **2** locate on the two-fold screw axis, which gives rise to a spin-canting regime in the chain, resulting in an incomplete cancellation of antiferromagnetic intrachain orders. Field-cooled magnetization (FCM) and zero-field-cooled (ZFC) magnetization experiments for **2** were carried out in the temperature range of 3.5–1.8 K and with an applied magnetic field of 10 Oe (Figure 3, inset). The FCM values increased rapidly at 2.7 K with a decrease of temperature. The ZFC magnetization had a maximum value at 2.2 K as the temperature was increased, and then decreased to the same value of the FCM above 2.7 K. This confirmed that the magnetic phase transition occurred at 2.7 K. Field dependences of magnetization were measured at 1.8 K (Figure 4). The magnetization did not saturate upon application of a magnetic field up to 5 T. However, the magnetization curve in the lower magnetic field region showed a sigmoidal increase, characteristic of a metamagnet. Note that a weak ferromagnetic component observed in the magnetic field of ±50 Oe might be due to non-compensating magnetic pathways between the chains. The magnetization abruptly increased at a critical magnetic field (H_c) of 1300 Oe, which is sufficient to overcome the weak interchain antiferromagnetic interactions. Consequently, **2** showed a magnetic field induced phase transition from antiferromagnetic to a ferromagnetic-like state.[10] The low-field magnetization experiments at 1.8 K exhibited a hysteresis loop with a coercive field of 4 Oe and a remnant magnetization of 6.81×10^{-3} emu Oe mol^{-1} (Figure 4, inset).

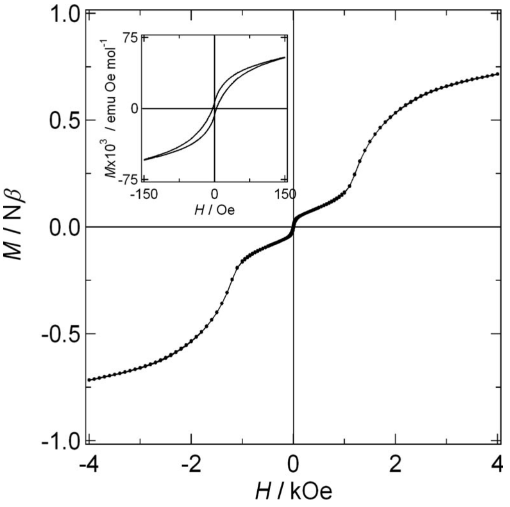

Figure 4. Magnetic field dependence of magnetization for **2** and magnetic hysteresis loop in the low-field region (inset) at 1.8 K.

AC magnetic susceptibility measurements for **2** were performed in a zero magnetic field and in an external magnetic field of 1300 Oe (Figure 5). AC signals in the zero magnetic field did not show a distinct frequency dependence, whereas in the external magnetic field of 1300 Oe, both in- and out-of-phase signals became frequency-dependent. Assuming that the relaxation time (τ) at the peak-top temperature of χ_m'' in the field of 1300 Oe is well approximated by the inverse of the AC frequency [$\tau = \tau_0\exp(\Delta/k_\mathrm{B})$], an Arrhenius plot gave an effective energy barrier for the magnetization reversal of Δ = 58.6 K and a pre-exponential factor of τ_0 = 2.58 × 10^{-16} s.[11] In a magnetic field lower than H_c, the residual magnetic moments due to spin canting on the chains are antiferromagnetically coupled to each other, and this affords a hidden-spin canting situation.[12] In a magnetic field equal to H_c, on the other hand, the amplitude of the applied magnetic field is comparable to the interchain antiferromagnetic interactions, and **2** showed a slow reversal magnetization such as a single-chain magnet.[13]

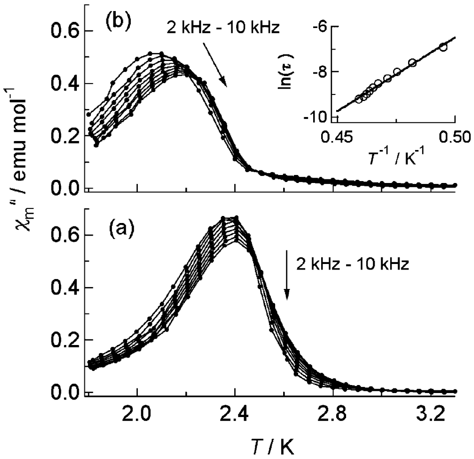

Figure 5. χ_m'' vs. T plots for **2** with a 3 Oe AC field oscillating at 2–10 kHz: zero (a) and 1300 Oe (b) external magnetic field. Inset: Natural logarithm of the relaxation time (τ) vs. the inverse of the temperature plot.

Conclusions

Cobalt(II) radical complexes with symmetric and asymmetric counter anions crystallized in the centrosymmetric and polar space groups, respectively, and the latter space group caused canted ferromagnetism. Spin canting can arise from single-ion magnetic anisotropy and/or asymmetric exchange interaction (Dzyaloshinsky–Moriya interaction). Both mechanisms are allowed in compounds crystallizing in a non-symmetric space group. The acentric counterion ClO_4^- caused **2** to crystallize in the non-symmetric space group of *Pna*2$_1$.

Experimental Section

General: Chemicals were obtained from standard sources and were used as received. Unless otherwise stated, the reactions were carried out under dry nitrogen.

[CoCl(bisimpy)(MeOH)$_2$]PF$_6$ (1): Anhydrous $CoCl_2$ (14 mg, 0.11 mmol) in methanol (1 mL) was added to bisimpy (40 mg, 0.11 mmol) in methanol (2 mL); after stirring for 10 min, NH_4PF_6 (15 mg, 0.11 mmol) in methanol (1 mL) was added. The mixture was concentrated to 1 mL on a hot plate, and then cooled to room temperature, affording red square plates of **1**. Yield: 23 mg (33%). $C_{21}H_{35}ClCoF_6N_5O_4P$ (660.89): calcd. C 38.11, H 5.48, N 10.58; found C 37.77, H 5.30, N 10.42.

[CoCl(bisimpy)(MeOH)$_2$]ClO$_4$ (2): Compound **2** was obtained in a similar manner as **1** by using $NaClO_4$ instead of NH_4PF_6. Yield: 15 mg (48%). $C_{21}H_{35}Cl_2CoN_5O_8$ (615.38): calcd. C 40.99, H 5.73, N 11.38; found C 41.05, H 5.69, N 11.38.

Acknowledgments

This work was supported by TARA projects, University of Tsukuba, and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

---

[1] a) H. Zhao, Z.-R. Qu, Q. Ye, B. F. Abrahams, Y.-P. Wang, Z.-G. Liu, Z. Xue, R.-G. Xiong, X.-Z. You, *Chem. Mater.* **2003**, *15*, 4166–4168; b) S. Ohkoshi, H. Tokoro, T. Matsuda, H. Takahashi, H. Irie, K. Hashimoto, *Angew. Chem. Int. Ed.* **2007**, *46*, 3238–3241; c) O. R. Evans, W. Lin, *Chem. Mater.* **2001**, *13*, 3009–3017; d) K. T. Holman, A. M. Pivovar, M. D. Ward, *Science* **2001**, *294*, 1907–1911; e) C. Dhenaut, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault, H. L. Bozec, *Nature* **1995**, *374*, 339–342; f) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522.

[2] A. Jouaiti, M. W. Hosseini, N. Kyritsakas, *Chem. Commun.* **2002**, 1898–1899.

[3] a) A. Caneschi, D. Gatteschi, P. Rey, R. Sessoli, *Acc. Chem. Res.* **1989**, *22*, 392–398; b) C. Benelli, D. Gatteschi, *Chem. Rev.* **2002**, *102*, 2369–2387; c) D. Luneau, P. Rey, *Coord. Chem. Rev.* **2005**, *249*, 2591–2611; d) N. Koga, S. Karawsawa, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1384–1400; e) O. Kahn, *Acc. Chem. Res.* **2000**, *33*, 647–657 and references are therein.

[4] A. Caneschi, D. Gatteschi, P. Rey, R. Sessoli, *Inorg. Chem.* **1988**, *27*, 1756–1761.

[5] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760–1763.

[6] Crystal data for **1**: $C_{21}H_{35}N_5ClCoF_6O_4P$, 660.89 g mol^{-1}, monoclinic $P2_1/c$, a = 10.2864(12), b = 26.122(3), c = 11.3897(13) Å, β = 111.063(2)°, V = 2856.0(6) Å^3, Z = 4, T = 200 K, $R1$ = 0.0638, Rw = 0.0759 (all, obsd.). Crystal data for **2**: $C_{21}H_{35}N_5Cl_2CoO_8$, 615.37 g mol^{-1}, orthorhombic *Pna*2$_1$, a = 17.039(4), b = 14.977(4), c = 10.774(3) Å, V = 2749.6(12) Å^3, Z = 4, T = 200 K, $R1$ = 0.0337, Rw = 0.0606 (all, obsd.). CCDC-692610 (for **1**) and -692611 (for **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.

[7] H. Oshio, M. Yamamoto, T. Ito, H. Kawauchi, N. Koga, T. Ikoma, S. Tero-Kubota, *Inorg. Chem.* **2001**, *40*, 5518–5525.

[8] In the analyses of the magnetic data for **1** and **2**, the g value was fixed to 2.0. Note that the orbital term of the cobalt(II) ion was included as the effective angular momentum term. The least-squares calculation for **1** yielded δ = 580.0 K, λ = –275.1 K, and k = 0.70, and the same parameter set was used for **2**.

[9] A. A. Leitch, J. L. Brusso, K. Cvrkalj, R. W. Reed, C. M. Robertson, P. A. Dube, R. T. Oakley, *Chem. Commun.* **2007**, 3368–3370.

[10] D. K. Price, S. R. Batten, B. Moubaraki, K. S. Murray, *Polyhedron* **2003**, *22*, 2161–2167.

[11] The contribution of three-dimensional magnetic interactions cannot be excluded, even when applying the magnetic field of H_c, which leads to an unrealistic τ_0 value. The non-linearity of the Arrhenius plot also suggests competing relaxation mechanisms in these temperature and field regions. The crossover between these mechanisms may cause overestimation of Δ and τ_0 values.

[12] a) X.-Y. Wang, L. Wang, Z.-M. Wang, G. Su, S. Gao, *Chem. Mater.* **2005**, *17*, 6369–6380; b) E.-Q. Gao, A.-L. Cheng, Y.-X. Xu, M.-Y. He, C.-H. Yan, *Inorg. Chem.* **2005**, *44*, 8822–8835; c) H. H. Ko, J. H. Lim, H. C. Kim, C. S. Hong, *Inorg. Chem.* **2006**, *45*, 8847–8849; d) M.-H. Zeng, W.-X. Zhang, X.-Z. Sun, X.-M. Chen, *Angew. Chem. Int. Ed.* **2005**, *44*, 3079–3082; e) S. Mossin, H. Weihe, H. O. Sørensen, N. Lima, R. Sessoli, *Dalton Trans.* **2004**, 632–639; f) H.-L. Sun, Z.-M. Wang, S. Gao, *Inorg. Chem.* **2005**, *44*, 2169–2176; g) K. Bernot, J. Luzon, R. Sessoli,

A. Vindigni, J. Thion, S. Richeter, D. Leclercq, J. Larionova, A. van der Lee, *J. Am. Chem. Soc.* **2008**, *130*, 1619–1627.

[13] a) L. M. Toma, R. Lesscouëzec, F. Lloret, M. Julve, J. Vaissermann, M. Verdaguer, *Chem. Commun.* **2003**, 1850–1851; b) L. M. Toma, F. S. Delgado, C. Ruiz-Pérez, R. Carrasco, J. Cano, F. Lloret, M. Julve, *Dalton Trans.* **2004**, 2836–2846; c) L. M. Toma, R. Lesscouëzec, S. Vriel, R. Llusar, C. Ruiz-Pérez, J. Veissermann, F. Lloret, M. Julve, *Dalton Trans.* **2007**, 3690–3698.

Received: August 18, 2008