to yield a dirty-brown mixture. After the mixture had been stirred for a few minutes, **1** dissolved gradually and the solution changed color to dark green. Complex **2** separated from the concentrated solution (10 mL) in form of large black crystals. Yield 2.1 g (82 %).

Method B: A solution of [$Li_2$(bipy)] in THF (20 mL), freshly prepared from 2,2′-bipyridine (0.5 g, 3.0 mmol) and excess lithium, was added to a suspension of [$YbI_2(thf)_2$] (1.7 g, 2.98 mmol) in THF (25 mL). The reaction proceeded immediately and black colored, crystalline **2** separated from the concentrated solution (15 mL). Yield 1.03 g (73 %). Decomposition: 160°C; $^1$H NMR (200 MHz, [D$_8$]THF, 20°C, TMS): $\delta = 6.54$ (d, $^3J$(H,H) = 6.2 Hz, 2H; CH), 5.28 (d, $^3J$(H,H) = 9.7 Hz, 2H; CH), 5.02 (dd, $^3J$(H,H) = 9.7, 5.3 Hz, 2H; CH), 4.01 (dd, $^3J$(H,H) = 6.2, 5.3 Hz, 2H; CH); IR(Nujol): $\tilde{\nu} = 1590$, 1520, 1480, 1445, 1380, 1345, 1320, 1275, 1265, 1255, 1185, 1150, 1115, 1045, 980, 955, 890, 760, 710, 640, 625, 575, 495 and 425 cm$^{-1}$; elemental analysis calcd (%) for $C_{18}H_{24}N_2O_2Yb$ (473.44): C 45.67, H 5.11, N 5.92, Yb 36.55; found: C 44.42, H 4.05, N 6.17, Yb 36.58.

Received: March 11, 1999 [Z13142IE]
German version: *Angew. Chem.* **1999**, *111*, 2407–2409

**Keywords:** bipyridine · bridging ligands · heterocycles · lanthanides · ytterbium

---

[1] W. Kaim, R. Reinhardt, E. Waldhör, J. Fiedler, *J. Organomet. Chem.* **1996**, *524*, 195–202, and references therein.

[2] S. Herzog, U. Grimm, *Z. Chem.* **1968**, *8*, 186–187.

[3] a) W. J. Evans, D. K. Drummond, *J. Am. Chem. Soc.* **1989**, *111*, 3329–3335; b) W. J. Evans, S. L. Gonzales, J. W. Ziller, *J. Am. Chem. Soc.* **1994**, *116*, 2600–2608; c) M. N. Bochkarev, I. L. Fedushkin, V. I. Nevodchikov, V. K. Cherkasov, H. Schumann, H. Hemling, R. Weimann, *J. Organomet. Chem.* **1996**, *524*, 125–131; d) T. V. Petrovskaya, I. L. Fedushkin, M. N. Bochkarev, H. Schumann, R. Weimann, *Russ. Chem. Bull.* **1997**, *46*, 1766–1768.

[4] H. Bock, J.-M. Lehn, J. Pauls, S. Holl, V. Krenzel, *Angew. Chem.* **1999**, *111*, 1004–1008; *Angew. Chem. Int. Ed.* **1999**, *38*, 952–955.

[5] M. N. Bochkarev, A. A. Trifonov, E. A. Fedorova, N. S. Emelyanova, T. A. Basalgina, G. S. Kalinina, G. A. Razuvaev, *J. Organomet. Chem.* **1989**, *372*, 217–224.

[6] X-ray structure data: Siemens SMART CCD diffractometer, $\omega$ scans, $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), graphite-monochromator, $T = 173$ K, SADABS[10] for absorption correction, structure solution with direct methods (SHELXS-97[11]), refinement against $F^2$ (SHELXL-97[12]) with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters ($U_{iso} = 0.08 \times 10^4$ pm$^2$) on calculated positions. Data collection for **2**: crystal dimensions $0.46 \times 0.42 \times 0.19$ mm, triclinic, $P1$, $a = 1031.60(1)$, $b = 2116.64(2)$, $c = 2138.61(1)$ pm, $\alpha = 118.088(1)$, $\beta = 93.653(1)$, $\gamma = 101.500(1)°$, $V = 3969.40(4) \times 10^6$ pm$^3$, $Z = 3$, $\rho_{calcd} = 1.782 \times 10^3$ kg m$^{-3}$, $\mu = 5.312$ mm$^{-1}$, $F(000) = 2088$, $2.20° \leq 2\theta \leq 55.0°$, $-13 \leq h \leq 13$, $-27 \leq k \leq 27$, $-27 \leq l \leq 16$, 30947 data collected, 23263 unique data ($R_{int} = 0.0266$), 21953 data with $I > 2\sigma(I)$, 1864 refined parameters, three floating origin restraints, GOF ($F^2$) = 1.050, final $R$ indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$), $R_1 = 0.0411$, $wR_2 = 0.1103$, max./min. residual electron density $2.908/-2.593 \times 10^{-6}$ e pm$^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116026. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] C. J. Burns, R. A. Andersen, *J. Am. Chem. Soc.* **1987**, *109*, 941–942.

[8] C. J. Burns, R. A. Andersen, *J. Am. Chem. Soc.* **1987**, *109*, 915–917.

[9] M. H. Chisholm, J. C. Huffman, I. P. Rothwell, P. G. Bradley, N. Kress, W. H. Woodruff, *J. Am. Chem. Soc.* **1981**, 103, 4945–4947.

[10] G. M. Sheldrick, Empirical Absorption Correction Program, Universität Göttingen, **1996**.

[11] G. M. Sheldrick, Program for Crystal Structure Solution, Universität Göttingen, **1990**.

[12] G. M. Sheldrick, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

---

# Tuning of Magnetic Anisotropy in Hexairon(III) Rings by Host–Guest Interactions: An Investigation by High-Field Torque Magnetometry**

Andrea Cornia,* Marco Affronte, Aloysius G. M. Jansen, Gian Luca Abbati, and Dante Gatteschi

Magnetic anisotropy plays a central role in understanding the properties of molecular magnetic clusters, which are often characterized by large ground spin states. The zero field splitting (ZFS) of the multiplets in fact gives rise to important effects, which are now under investigation for many different systems ranging from models for biological clusters to single-molecule magnets.[1–4] In single-molecule magnets the interest is associated with the fact that the magnetic anisotropy drives the spin dynamics of magnetic clusters and leads to slow magnetic relaxation which allows the observation of quantum tunneling of the magnetization at very low temperature.[4]

From an experimental point of view it is necessary to perform measurements on magnetic anisotropy, which so far have been largely based on EPR spectroscopy[5] and inelastic neutron scattering.[6] Direct measurement of the anisotropic magnetization has been hampered by the need for relatively large single crystals. Recently a new technique, cantilever torque magnetometry, has become available, which allows the use of microgram single crystals.[7] Applications of this very sensitive technique in the field of molecular magnetism are quite recent, but they certainly appear to be very promising.[8] Torque magnetometry exploits the mechanical couple acting on a single crystal of a magnetically anisotropic substance in a uniform magnetic field. The couple can be precisely measured by simply anchoring the sample to a tiny metal cantilever and measuring the deflection by a capacitive method.[8a]

We report here on the magnetic anisotropy of the antiferromagnetic iron(III) rings [$LiFe_6(OMe)_{12}(dbm)_6$]$^+$ (**1**) and [$NaFe_6(OMe)_{12}(pmdbm)_6$]$^+$ (**2**), where Hdbm = 1,3-diphenyl-1,3-propanedione and Hpmdbm = 1,3-di(4-methoxyphenyl)-1,3-propanedione (Figure 1). The strong tendency of the $Fe_6(OMe)_{12}$ skeleton to encapsulate alkali metal ions[9] can be exploited to drive the self-assembly of cyclic nanostruc-

---

[*] Dr. A. Cornia, Dr. G. L. Abbati
Dipartimento di Chimica
Università degli Studi di Modena e Reggio Emilia via G. Campi 183
I-41100 Modena (Italy)
Fax: (+39)059-373543
E-mail: acornia@pascal.unimo.it

Dr. M. Affronte
INFM and Dipartimento di Fisica
Università degli Studi di Modena e Reggio Emilia (Italy)

Dr. A. G. M. Jansen
Grenoble High Magnetic Field Laboratory and Centre National de la Recherche Scientifique, Grenoble (France), and Max-Planck-Institut für Festkörperforschung, Stuttgart (Germany)

Prof. D. Gatteschi
Dipartimento di Chimica
Università degli Studi di Firenze (Italy)

[**] This work was in part financially supported through the TMR Program of the European Community under contract no. ERBFMGECT950077.

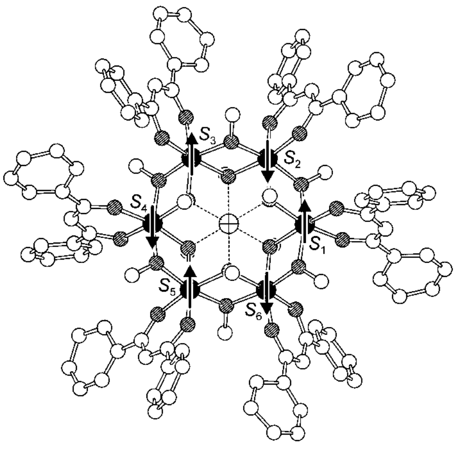

Figure 1. Schematic structure of **1**. Iron atoms: ●, oxygen atoms: ◍, carbon atoms: ○, Li$^+$: ⊕. Hydrogen atoms are omitted for clarity. The arrows represent the spin configuration in the ground $S = 0$ state.

tures as demonstrated by the possibility to halve [Fe$_{12}$(OMe)$_{24}$(dbm)$_{12}$] clusters into hexairon(III) species by reaction with Li$^{I}$ and Na$^{I}$ ions in solution.[10] The hexairon(III) clusters **1** and **2** are particularly well-suited for anisotropic measurements because **1**-PF$_6$ and **2**-ClO$_4$ crystallize in a trigonal space group. Both compounds are antiferromagnetically coupled with an $S = 0$ ground state, but the exchange coupling Fe–Fe interactions differ by almost 50%.[9c] We will show here that the host–guest interactions responsible for the large difference in magnetic coupling also yield a dramatic difference in the magnetic anisotropies.

In Figure 2 we show torque curves recorded on a 0.15 × 0.15 × 0.10 mm single crystal of **1**-PF$_6$ at two different temperatures (1.0 and 0.4 K). The magnetic field $\boldsymbol{B}$ made a $\theta = 3\pi/4$ angle with the sixfold crystal axis. The staircase structure, which becomes more pronounced at low temperature, closely resembles the stepped magnetization curves previously observed in antiferromagnetic rings such as [Fe$_{10}$(OMe)$_{20}$(O$_2$CCH$_2$Cl)$_{10}$].[11] We suggest that the steplike field dependence of magnetic anisotropy originates from spin-level crossing. At low temperature the rings are in the ground $S = 0$ state, while the increasing field induces the crossover from $S = 0$ to $S = 1$, from $S = 1$ to $S = 2$, and so on. For the lowest energy component of each $S$-manifold, the expectation value of the torque signal can be calculated by starting from the spin Hamiltonian given in Equation (a).

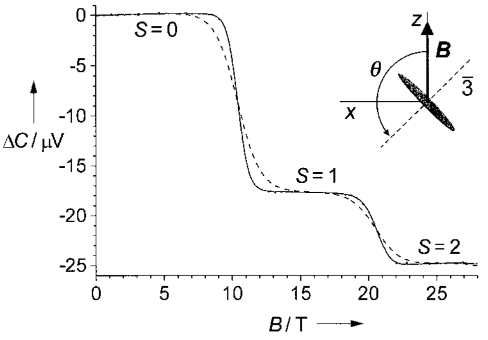

Figure 2. Torque curves recorded on **1**-PF$_6$ at 1.0 K (dashed line) and 0.4 K (solid line) for $\theta_{\mathrm{exp}} = 3\pi/4$. The orientation of the $\bar{3}$ ring axis and of the applied magnetic field $\boldsymbol{B}$ in the adopted coordinate system are also shown.

$$\mathcal{H}_{\mathrm{S}} = \boldsymbol{S} \cdot \boldsymbol{D}_{\mathrm{S}} \cdot \boldsymbol{S} + g\mu_{\mathrm{B}} \boldsymbol{B} \cdot \boldsymbol{S} \qquad \text{(a)}$$

The axial ZFS tensor $\boldsymbol{D}_{\mathrm{S}}$ has the unique axis along the sixfold molecular axis, which lies in the $xz$ plane of Figure 2, when $\boldsymbol{B}$ is applied along the $z$ axis. The torque vector $\boldsymbol{T}$ is then parallel to the $y$ axis and, in the limit of dominant Zeeman interaction ($B \gg D_{\mathrm{S}}/g\mu_{\mathrm{B}}$), the torque component $T_y = -(\partial E/\partial\theta)_{\mathrm{B}}$ is independent of the magnetic field and simply proportional to the axial ZFS parameter $D_{\mathrm{S}}$ [Eq. (b)].

$$\langle S, -S \,|\, \boldsymbol{T}_y \,|\, S, -S \rangle = D_{\mathrm{S}} S (S - ½) \sin 2\theta \qquad \text{(b)}$$

Notice the angular dependence of $T_y$, which vanishes at $\theta = 0$, $\pi/2$, $\pi$, and $3\pi/2$ and is maximum at $\theta = \pi/4$, $3\pi/4$, $5\pi/4$, and $7\pi/4$.

Abrupt variations of the torque signal are expected at each level crossing as a consequence of Equation (b), and the inflection point of the $S$th step provides directly the critical field $B_{\mathrm{c}}$ required for the transition $S \leftarrow S - 1$. The latter can also be easily calculated from Equation (a) [Eq. (c)].

$$B_{\mathrm{c}} = \frac{\Delta_{\mathrm{S}} + (\cos^2\theta - 1/3)[D_{\mathrm{S}} S (S - 1/2) - D_{\mathrm{S-1}} (S - 1)(S - 3/2)]}{g\mu_{\mathrm{B}}} \qquad \text{(c)}$$

$\Delta_{\mathrm{S}}$ is the energy gap between $S$ and $S - 1$ manifolds in zero magnetic field. Equations (b) and (c) provide a very convenient and general way for evaluating the $D_{\mathrm{S}}$ and $\Delta_{\mathrm{S}}$ parameters in antiferromagnetic clusters. By setting $\theta_{\mathrm{exp}} = \theta - \theta_0$ and $g = 2.00$ the $B_{\mathrm{c}}$ versus $\theta_{\mathrm{exp}}$ plots for the first and second torque steps in **1**-PF$_6$ were fitted to Equation (c) giving $D_1 = 1.16(1)$ cm$^{-1}$, $\Delta_1 = 9.653(3)$ cm$^{-1}$, $\theta_0 = 0.6(4)°$, and $D_2 = 0.295(2)$ cm$^{-1}$, $\Delta_2 = 19.162(4)$ cm$^{-1}$, $\theta_0 = 5.0(7)°$ (Figure 3). It is worth stressing that the precision of the determination is comparable with that usually obtained in HF-EPR experiments. The positive $D_{\mathrm{S}}$ parameters indicate a "hard-axis" anisotropy, which is consistent with the negative sign of

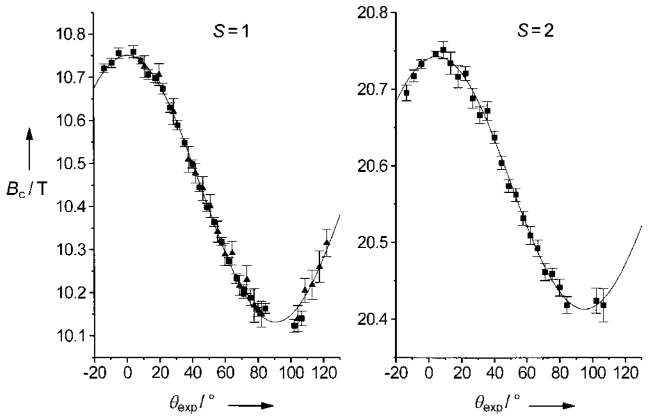

Figure 3. Angular dependence of the inflection point $B_{\mathrm{c}}$ for the two torque steps observed in the field range 0–28 T. The solid lines are the best-fit curves, which correspond to $D_1 = 1.16(1)$ cm$^{-1}$, $\Delta_1 = 9.653(3)$ cm$^{-1}$, $\theta_0 = 0.6(4)°$ ($S = 1$) and $D_2 = 0.295(2)$ cm$^{-1}$, $\Delta_2 = 19.162(4)$ cm$^{-1}$, $\theta_0 = 5.0(7)°$ ($S = 2$). The triplet data obtained on two different samples of **1**-PF$_6$ (▲ and ■) show the good reproducibility of the results.

$\Delta C \propto T_y$ in the experimental setting of Figure 2. The $D_1/D_2$ ratio (3.92) can be compared with that resulting from the application of Equation (b) to the $3\pi/4$ curve in Figure 2 (4.27). It follows that the height of neighboring torque steps can indeed be used to determine the whole pattern of ZFS parameters $D_{S-1}/D_S$ in a single field sweep.[8]

The results presented herein provide precious information on the nature of the ground state and on the origin of magnetic anisotropy. The former aspect can be appreciated by looking at the energy spacing of the multiplets. The ratio $\Delta_2/\Delta_1 = 1.985$ shows that the lowest lying $S$-manifolds follow a Landè-type rule $\Delta_S = S\Delta_1$, as already observed in other antiferromagnetic iron(III) rings.[9b, 11] The ZFS tensors $\boldsymbol{D}_S$ can be easily expressed as linear combinations of single-ion ($\boldsymbol{D}_i$) and interaction ($\boldsymbol{D}_{i,j}$) contributions [Eq. (d)].

$$\boldsymbol{D}_S = \sum_{i=1}^{6} [a_S \boldsymbol{D}_i + b_S \boldsymbol{D}_{i,i+1} + c_S \boldsymbol{D}_{i,i+2} + \tfrac{1}{2} d_S \boldsymbol{D}_{i,i+3}] \qquad \text{(d)}$$

The coefficients in Equation (d) are calculated with standard techniques.[12] The expected ratios $a_1/a_2 = c_1/c_2 = 4.410$ and $b_1/b_2 = d_1/d_2 = 4.136$ compare quite well with the experimental value of $D_1/D_2$. Noticeably, a much larger triplet splitting is observed in **2**-ClO$_4$ ($D_1 = 4.32(3)$ cm$^{-1}$) despite the similar molecular geometry of the two compounds.[8]

The $\boldsymbol{D}_{i,j}$ tensors that describe anisotropic pairwise interactions in iron(III) clusters are expected to have mainly a dipolar origin.[12] Dipolar interactions between the pairs of iron(III) ions of the ring can be easily calculated if it is assumed that the individual iron centers can be considered as point dipoles. From this hypothesis we can write Equation (e).

$$D_1 = D_1^{\mathrm{dip}} + D_1^{\mathrm{Fe}} \qquad \text{(e)}$$

In Equation (e) $D_1^{\mathrm{dip}}$ takes the value 1.24 cm$^{-1}$ in **1** and 1.15 cm$^{-1}$ in **2**.[12] Hence, the projected of single-ion anisotropies on the excited triplet, $D_1^{\mathrm{Fe}}$, is $-0.08$ and 3.17 cm$^{-1}$ in the two compounds, respectively. We conclude that the experimental ZFS for **1** is essentially dipolar in origin, while for **2** it is 27 % dipolar only. The small changes in the dipolar values on passing from the lithium to the sodium derivative are not surprising. In fact dipolar contributions depend essentially on the geometry of the hexairon(III) moiety, which is very similar in the two compounds.[9c] On the other hand the single-ion anisotropy depends on the coordination sphere of the individual ions. On the basis of recent ligand-field calculations[13a] we suggest that the larger twist angle[13b] observed in the sodium derivative may explain the larger components of the $D_i$ tensors along the cluster axis ($d_i^{zz} \approx 0.004$ and $-0.147$ cm$^{-1}$ in **1** and **2**, respectively).

These results clearly show that large magnetic rings[10, 14] are important model systems for investigating the origin of magnetic anisotropy in nanoscale clusters. In addition, the possibility of controlling important magnetic parameters in the rings, such as exchange couplings and zero-field splittings, by simply playing with the radius of the alkali metal template extends the potential uses of host–guest chemistry for fine tuning the magnetic properties of single-molecule magnets and for designing new magnetic clusters with preordained magnetic behavior.

### *Experimental Section*

Single-crystal samples of [LiFe$_6$(OMe)$_{12}$(dbm)$_6$]PF$_6$ (trigonal space group $R\bar{3}$, $a = 14.523(2)$ Å, $\alpha = 84.35(1)^\circ$ at 298 K) were synthesized as reported in reference [9c]. A water-cooled electromagnet equipped with a $^3$He cryostat (Grenoble High Magnetic Field Laboratory) was used to obtain magnetic fields up to 28 T, with field-sweep rates in the range 400–600 G s$^{-1}$. The selected single crystal ($\approx 3$ μg) was mounted on a Cu–Be cantilever with silicon grease. The field-induced deflection of the cantilever was detected by measuring the variation in the capacitance of the torquemeter, $\Delta C \propto T_y$, with a sensitive electronic bridge. The magnetic field was applied in the $(1\bar{1}0)$ crystal plane, and the orientation of the unique $\bar{3}$ molecular axis ($\theta_{\mathrm{exp}} = 0$) was determined accurately by following the height of the first torque step as a function of $\theta$ (see Eq. (b)).

Received: March 1, 1999 [Z13093IE]
German version: *Angew. Chem.* **1999**, *111*, 2409–2411

**Keywords:** cluster compounds · host–guest chemistry · iron · magnetic properties · spin crossover

---

[1] A. Boussac, J.-J. Girerd, A. W. Rutherford, *Biochemistry* **1996**, *35*, 6984.

[2] O. Horner, E. Rivière, G. Blondin, S. Un, A. W. Rutherford, J.-J. Girerd, A. Boussac, *J. Am. Chem. Soc.* **1998**, *31*, 7924.

[3] C. E. Dube, R. Sessoli, M. P. Hendrich, D. Gatteschi, W. H. Armstrong, *J. Am. Chem. Soc.*, in press.

[4] W. Wernsdorfer, R. Sessoli, *Science* **1999**, *284*, 133.

[5] a) A.-L. Barra, D. Gatteschi, R. Sessoli, G. L. Abbati, A. Cornia, A. C. Fabretti, M. G. Uytterhoeven, *Angew. Chem.* **1997**, *109*, 2423; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 2329; b) A.-L. Barra, L.-C. Brunel, D. Gatteschi, L. Pardi, R. Sessoli, *Acc. Chem. Res.* **1998**, *31*, 460.

[6] a) H. U. Güdel, U. Hauser, A. Fürrer, *Inorg. Chem.* **1979**, *18*, 10; b) R. Caciuffo, G. Amoretti, A. Murani, R. Sessoli, A. Caneschi, D. Gatteschi, *Phys. Rev. Lett.* **1998**, *81*, 4744.

[7] a) M. J. Naughton, J. P. Ulmet, M. Chaparala, *Bull. Am. Phys. Soc.* **1996**, *41*, 302; b) S. Uji, M. Chaparala, S. Hill, P. S. Sandhu, J. Qualls, L. Seger, J. S. Brooks, *Synth. Met.* **1997**, *85*, 1573.

[8] a) A. Cornia, A. G. M. Jansen, M. Affronte, *Phys. Rev. B*, submitted; b) J. A. A. J. Perenboom, J. S. Brooks, S. O. Hill, T. Hathaway, N. S. Dalal, *Physica B* **1998**, *246/247*, 294; c) J. A. A. J. Perenboom, J. S. Brooks, S. O. Hill, T. Hathaway, N. S. Dalal, *Phys. Rev. B* **1998**, *58*, 330.

[9] a) A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467; b) A. Caneschi, A. Cornia, A. C. Fabretti, S. Foner, D. Gatteschi, R. Grandi, L. Schenetti, *Chem. Eur. J.* **1996**, *2*, 1379; c) G. L. Abbati, A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, W. Malavasi, L. Schenetti, *Inorg. Chem.* **1997**, *36*, 6443.

[10] A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, *Angew. Chem.* **1999**, *111*, 1372; *Angew. Chem. Int. Ed.* **1999**, *38*, 1295.

[11] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.* **1994**, *116*, 823.

[12] A. Bencini, D. Gatteschi, *EPR of Exchange-Coupled Systems*, Springer, Berlin, **1990**.

[13] a) A.-L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.*, **1999**, *121*, 5302; b) E. L. Muetterties, L. J. Guggenberger, *J. Am. Chem. Soc.* **1974**, *96*, 1748.

[14] S. P. Watton, P. Fuhrmann, L. E. Pence, A. Caneschi, A. Cornia, G. L. Abbati, S. J. Lippard, *Angew. Chem.* **1997**, *109*, 2917; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2774.