Magnetic Properties

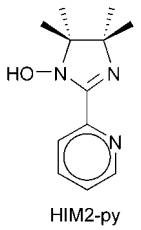
Very Large Ising-Type Magnetic Anisotropy in a Mononuclear Ni^{II} Complex**

Guillaume Rogez, Jean-Noël Rebilly, Anne-Laure Barra, Lorenzo Sorace, Geneviève Blondin, Nadeschda Kirchner, Marc Duran, Joris van Slageren, Simon Parsons, Louis Ricard, Arnaud Marvilliers, and Talal Mallah**

Magnetic anisotropy is one of the crucial parameters governing the magnetic behavior of large spin-clusters. Single-molecule magnetism (SMM) and quantum tunneling of the magnetization in clusters are mainly governed by the nature and the magnitude of the magnetic anisotropy in their ground spin state.[1] One of the main sources of magnetic anisotropy in polymetallic clusters is single-ion anisotropy.[2]

In this respect Ni^{II} complexes are particularly interesting and are frequently used as building blocks of single-molecule magnets.[3] Nonetheless, few studies have been devoted to the magnetic anisotropy of isolated Ni^{II} complexes,[4] with the most recent report concerning a family of pseudotetrahedral dihalobis(triphenylphosphate) complexes.[5]

We report here the preparation, structure, and magnetic properties of a mononuclear octahedral Ni^{II} complex $[Ni(HIM2\text{-}py)_2NO_3]NO_3$ (**1**) with the bidentate ligand HIM2-py. Magnetization versus field measurements at different temperatures, high-field and high-frequency EPR (HF-HFEPR) studies, and frequency domain magnetic resonance spectroscopy (FDMRS) studies indicated the presence of a very large Ising-type anisotropy ($D = -10.1 \pm 0.1\ cm^{-1}$ and $E/|D| = 0.02 \pm 0.01$) never before reported for an isolated Ni^{II} complex.



HIM2-py

The structure of **1** shows that the coordination sphere of the Ni^{II} center contains the four nitrogen atoms of the two HIM2-py ligands in the *cis* positions and the two oxygen atoms of the *O*,*O*′-chelating nitrate (Figure 1). The geometry

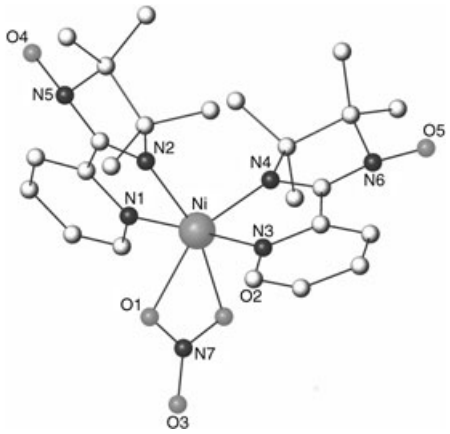


Figure 1. View of the molecular structure of **1**.

around the nickel atom is highly distorted. The Ni–N bond lengths are all different and range from 204.3(9) to 208.9(9) pm, whereas the Ni–O distances are 213.3(8) and 219.4(9) pm. The O1-Ni-O2 angle is very small (59.0°) and is similar to that found in other Ni^{II} complexes that bear an *O*,*O*′-bound nitrate.[6] The bite angles of the other bidentate ligands are 79.6(4)° and are, as expected, far from 90°. We can thus consider that **1** has a symmetry close to C_{2v} with a pseudoprincipal symmetry C_2-rotation axis that bisects the O-Ni-O angle along which it is elongated.

Magnetization versus field measurements between 0 and 5.5 T were performed at different temperatures with a SQUID magnetometer. The $M = f(H/T)$ plots for $T = 2$, 4, 6, and 8 K are not superimposable owing to the presence of magnetic anisotropy within the complex (Figure 2). For $T =$ 2 K and $H = 5.5$ T the observed magnetization value of 1.65 BM ($9.22 \times 10^{-3}\ m^3\,Oe\,mol^{-1}$) is well below the theoretical saturation for an $S = 1$ system ($M_{sat} = 2.2$ BM ($12.29 \times 10^{-3}\ m^3\,Oe\,mol^{-1}$) for $g = 2.2$), as expected in the case of appreciable magnetic anisotropy. The experimental data were fitted by exact diagonalization of the energy matrices corresponding to the spin Hamiltonian $\mathcal{H} = \mu_B \boldsymbol{B}[g]\hat{\mathbf{S}} +$

[*] Dr. G. Rogez, J.-N. Rebilly, Dr. G. Blondin, Dr. A. Marvilliers, Prof. T. Mallah
Laboratoire de Chimie Inorganique, UMR CNRS 8613
Université Paris-Sud, Bât 420, 91405 Orsay (France)
Fax: (+33) 1-6915-4754
E-mail: guillaume.rogez@ipcms.u-strasbg.fr
mallah@icmo.u-psud.fr

Dr. G. Rogez
IPCMS-GMI, UMR CNRS 7504
23, rue du Loess, B.P. 43, 67034 Strasbourg Cedex 2 (France)
Fax: (+33) 3-8810-7247

Dr. A.-L. Barra
Laboratoire des Champs Magnétiques Intenses, UPR CNRS 5021
25, avenue des Martyrs, B.P. 166, 38042 Grenoble Cedex 9 (France)

Dr. L. Sorace
UdR INSTM and Department of Chemistry
University of Florence, Polo Scientifico Universitario
Via della Lastruccia 3, 50019 Sesto Fiorentino (Italy)

N. Kirchner, Dr. M. Duran, Dr. J. van Slageren
1. Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57, 70550 Stuttgart (Germany)

Dr. S. Parsons
Department of Chemistry, The University of Edinburgh
West Mains Road, Edinburgh EH9 3JJ (UK)

Dr. L. Ricard
Laboratoire "Hétéroéléments et Coordination", UMR CNRS 7653
Ecole Polytechnique
91128 Palaiseau (France)

[**] We thank the CNRS, the Université Paris XI, and the EPSRC for funding, the LCMI for provision of magnet time, and the EC for financial support (MRTN-CT-2003-504880/RTN Network "QuEMolNa"). The work at Stuttgart was supported by the DFG priority program on molecular magnetism (SPP1137). M.D. acknowledges a NANOTEC fellowship from the Catalan Government. We thank H. Weihe for provision of the SimEPR program and A. Bencini for provision of the AOM program.

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

  DOI: 10.1002/ange.200462294

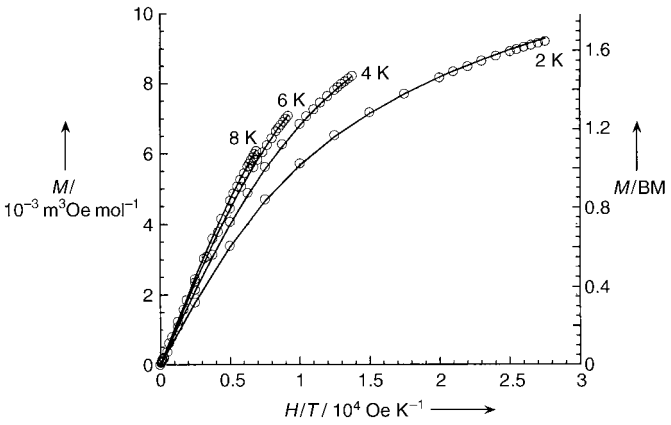


Figure 2. $M = f(H/T)$ plots for complex **1**. The lines correspond to the best fit (see text).

$D[\hat{\mathbf{S}}_z^2 - S(S+1)/3] + E[\hat{\mathbf{S}}_x^2 - \hat{\mathbf{S}}_y^2]$, where D and E are the axial and rhombic anisotropy parameters, respectively, averaged over 120 orientations of the magnetic field.[7] The fitting was performed simultaneously for the four experimental temperatures. The best fit was obtained with $D = -11.2\ \text{cm}^{-1}$, $E/|D| = 0.0$, and $g_{iso} = 2.16$ ($R = 3.7 \times 10^{-5}$). To reduce the variable parameters during the fitting procedure, the **[*g*]** tensor was constrained to be isotropic. Generally, it is not possible to determine the sign of the axial parameter D from the magnetization data as it is possible to find different sets of values for D and $E/|D|$, in which D may be positive or negative, that yield equally satisfactory agreement factors. However, in the case of large D values, low rhombicity, and when the fit is made for different temperatures simultaneously, only one set of parameters is obtained, as in the present case.[8b] All attempts to fit the experimental data using a positive value for D were, indeed, unsuccessful.

Owing to the very large anisotropy of the compound, only a few transitions are visible in the HF-HFEPR spectra. The main feature of the spectra is a very intense transition at low field, denoted B_{min}, the others being much weaker and difficult to assign precisely (the assignments reported in Figure 3 were made on the basis of the best simulation

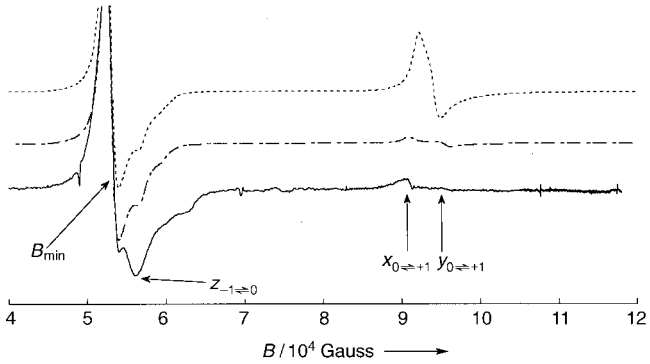


Figure 3. Experimental HF-EPR spectra of **1** at 475 GHz, $T = 5$ K (——) and simulated with $E/|D| = 0.01$, $g_{iso} = 2.17$, and $D = -10.15\ \text{cm}^{-1}$ (– – –) or $D = +10.15\ \text{cm}^{-1}$ (-----). The transitions are identified by the m_S value of the levels between which they occur, considering the quantization axis parallel to the external field.

parameters). Assuming an axial symmetry, the zero-field signal at the lowest frequency provides a direct determination of $|D|$ of about $10\ \text{cm}^{-1}$. On this basis, B_{min}, which occurs at 5.3 T for an incident radiation of 475 GHz, can be assigned to an off-axis turning-point-allowed transition.[5a] No clear evolution of the intensity of the allowed transitions was observed when changing the temperature, which prevents direct determination of the sign of D; nevertheless, the spectra were better reproduced with $D < 0$ (Figure 3). The very high anisotropy of the zero-field splitting tensor prevents determination of the g anisotropy, although the **[*g*]** tensor is most probably strongly axial. We thus used an isotropic value for g ($g_{iso} = 2.17$), which is in the range expected for Ni^{II}. The HF-HFEPR spectra are well reproduced at all frequencies, and the best simulations were obtained with the following values : $g_{iso} = 2.17$, $D = -10.15\ \text{cm}^{-1}$, and $E/|D| = 0.01$ (see Supporting Information).

The most important feature in the FDMRS spectra (Figure 4) is a narrow line at about $10.5\ \text{cm}^{-1}$, which decreases

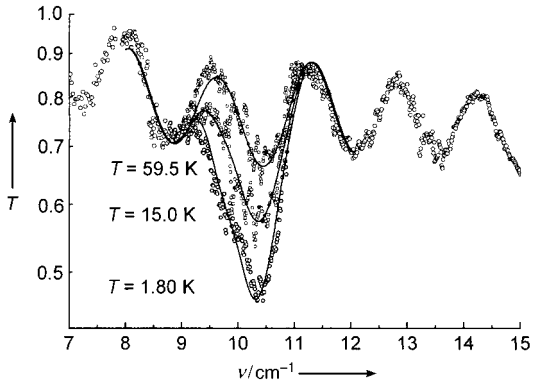


Figure 4. FDMRS spectra of **1** at various temperatures (experimental (○), simulation (——)).

in intensity on raising the temperature. This line is due to magnetic resonance transitions between the m_s levels of the $S = 1$ Ni^{II} ion. The resonance frequencies were obtained from the normalized spectra (i.e. all spectra were divided by the spectrum recorded at the highest temperature). From the line shape it was clear that the resonance line must consist of two overlapping lines owing to the transitions between the $|1\rangle$ and $|0\rangle$ and the $|-1\rangle$ and $|0\rangle$ m_s states, respectively. In an $S = 1$ system the resonance frequencies of these transitions correspond to $|D| - E$ and $|D| + E$, respectively. The resonance frequencies were found to be $\nu_1 = 9.7 \pm 0.1$ and $\nu_2 = 10.3 \pm 0.1\ \text{cm}^{-1}$, respectively. Therefore, it immediately follows that $|D| = 10.0 \pm 0.1\ \text{cm}^{-1}$ and $E = 0.3 \pm 0.1\ \text{cm}^{-1}$. The simulated spectra are also shown in Figure 4. The best fit was obtained using Gaussian line shapes, which means that the line width is determined by distributions in the sample rather than by spin–lattice relaxation.

The sign of D can be obtained from the temperature dependence of the spectra. When $D > 0$, both resonance lines should retain the same intensity. However, if $D < 0$, the intensity of the lowest frequency line should tend to zero upon decreasing the temperature because it is a transition from an excited state.

Figure 5 shows the line intensities in terms of the mode contributions to the magnetic permeability, obtained from the spectral fit, as a function of temperature, together with the calculated behavior using $D<0$ and $D>0$ values. Note that

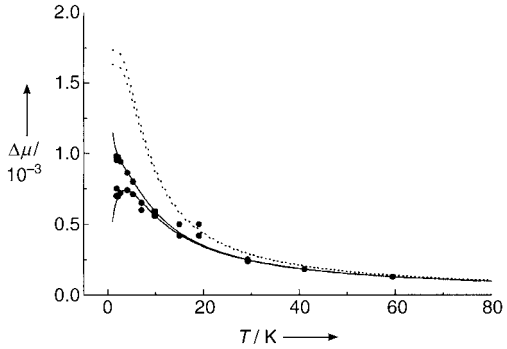


Figure 5. Dependence of the resonance mode contribution to the magnetic permeability $\Delta\mu$ on temperature (experimental $\Delta\mu$ (●); calculations with $D<0$ (——); calculations with $D>0$ (•••••)).

these values are absolute numbers, and that the calculated temperature dependence of the mode contribution is not scaled. Thus, not only does the intensity of the low-frequency line decrease at the lowest temperatures, but the absolute intensities of the mode contributions are also in much better agreement with a negative D parameter. From these calculations it is clear that D must be negative, and therefore $D=-10.0\pm0.1$ cm^{-1} and $E=0.3\pm0.1$ cm^{-1}. These values correspond very well to those found from magnetization and HF-HFEPR measurements. Moreover, this FDMRS experiment confirms unambiguously the negative sign of the D parameter. This is also in agreement with ligand-field-based, second-order-perturbation calculations, which show that a Ni^{II} complex bearing six identical ligands and elongated along a C_2'' axis should possess an Ising-type magnetic anisotropy ($D<0$ and $E/|D|=0$).[8]

To go beyond this qualitative assertion, we used a computer program based on the angular-overlap model that enables the calculation of the spin Hamiltonian parameters if the structure of the complex and the angular-overlap parameters of each ligand are known.[9] However, as the exact parameters for the ligand HIM2-py are not known, we extrapolated them from the data of the literature on similar ligands[10] whilst neglecting the anisotropy of the π-overlap as a first approximation. We checked that assuming a completely anisotropic π-interaction for pyridine did not significantly modify the results. We obtained values of $D=-10.1$ cm^{-1} and $E/|D|=0.10$,[11] in good agreement with the experimental values, even though the estimated rhombic parameter is much larger than the experimental value, as already observed for other systems.[5] Varying the angular overlap parameters slightly does not significantly alter the results of the calculation, although a variation of ±10% around the above-mentioned values of e_σ and e_π leads to proportional changes in the D values (ranging from −9.0 to −11.5 cm^{-1}) and almost no change in the rhombic parameter.

To the best of our knowledge, **1** shows the largest Ising-like magnetic anisotropy ($D<0$) ever reported for an isolated octahedral Ni^{II} complex, thus making it a suitable candidate for use as a building block in polynuclear clusters showing SMM behavior, even though the relative orientation of the local anisotropy axis within the cluster is also crucial.[12] Data obtained from HF-HFEPR spectra, field-dependent magnetization, and FDMRS are in very good agreement (within 10%) and show the complementarity between these techniques for the study of highly anisotropic integer-spin systems, especially for the unambiguous determination of the sign of the D parameter. Moreover, we have shown in this study that careful examination of the molecular structure by relatively easy to perform AOM calculations could allow us to perform a good estimation of the zero field splitting (ZFS) parameters. This may serve as a very useful "prediction tool" in order to help to design complexes with a desired magnetic anisotropy, which could be of great use for the so-called "rational approach" to single-molecule magnets.

Experimental Section

Synthesis of **1**: HIM2-py was synthesized according to published procedures.[13] A deaerated solution of $[Ni(H_2O)_6](NO_3)_2$ (1.4 g, 4.8 mmol) in a mixture of acetonitrile and methanol (70:30 v/v, 40 mL) was added, under an inert atmosphere, to a deaerated solution of HIM2-py (2.1 g, 9.5 mmol) in the same mixture of solvents (50 mL). Crystals of **1** were isolated by slow diffusion of diethyl ether vapor into the mixture (yield = 17%). Elemental analysis calcd (%) for **1**, $C_{24}H_{34}N_8NiO_8$: C 46.40, H 5.51, N 18.03, Ni 9.44; found: C 46.47, H 5.51, N 18.42, Ni 9.13.

X-ray crystallographic data: Nonius KappaCCD diffractometer, ϕ and ω scans, $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), graphite monochromator, $T=150$ K, structure solution with SIR97,[14] refinement against F^2 (SHELXL97)[15] with anisotropic thermal parameters for all non-hydrogen atoms; hydrogen positions calculated with riding isotropic thermal parameters. Data collection for **1**: crystal dimensions $0.20\times0.18\times0.16$ mm^3, orthorhombic, $P2_12_12_1$, $a=10.9890(10)$, $b=13.2620(10)$, $c=20.2230(10)$ (Å), $V=2947.2(4)$ Å^3, $Z=4$, $\rho_{calcd}=1.400$ g cm^{-3}, $\mu=0.717$ cm^{-1}, $F(000)=1304$, $\theta_{max}=30.03°$, hkl ranges: −15 to 15; −18 to 18; −28 to 28, 8518 data collected, 8518 unique data, 7020 data with $I>2\sigma(I)$, 379 parameters refined, GOF(F^2) = 1.015, final R indices ($R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $R1=0.0378$, $wR2=0.0971$, Flack parameter 0.027(9), max/min residual electron density 0.541(0.057)/−0.463(0.057) e Å^{-3}. CCDC-251946 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Magnetization measurements were performed on a Quantum Design MPMS5 SQUID magnetometer. The powder obtained from ground crystals of **1** was sealed in parafilm to avoid any orientation of the sample. Data were corrected for the parafilm contribution, and diamagnetism was estimated from Pascal constants.

HF-HFEPR experiments were performed at the High Magnetic Field Laboratory, Grenoble, France, using a previously described apparatus.[16] We used ground crystals (about 30 mg) pressed to form a pellet to reduce torquing effects under high magnetic fields. A simulation program is available from Dr. H. Weihe; for more information see http://sophus.kiku.dk/software/epr/epr.html.[17]

Frequency domain magnetic resonance spectroscopic (FDMRS) measurements were performed on a homebuilt spectrometer described in the literature.[18] Spectra were recorded at various temper-

atures on a pressed powder pellet of 155 mg with a diameter of 1 cm and a thickness of 1.82 mm.

Received: October 13, 2004
Published online: February 11, 2005

Keywords: angular-overlap model · EPR spectroscopy · FDMR spectroscopy · magnetic properties · nickel

[1] R. Sessoli, D. Gatteschi, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268, and references cited therein.

[2] 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) G. L. Abbati, L.-C. Brunel, H. Casalta, A. Cornia, A. C. Fabretti, D. Gatteschi, A. K. Hassan, A. G. M. Jansen, A. L. Maniero, L. Pardi, C. Paulsen, U. Segre, *Chem. Eur. J.* **2001**, *7*, 1796; c) D. Gatteschi, L. Sorace, *J. Solid State Chem.* **2001**, *159*, 253; d) D. Collison, M. Murrie, V. S. Oganesyan, S. Piligkos, N. R. J. Poolton, G. Rajaraman, G. M. Smith, A. J. Thomson, G. A. Timco, W. Wernsdorfer, R. E. P. Winpenny, E. J. L. McInnes, *Inorg. Chem.* **2003**, *42*, 5293.

[3] a) N. Vernier, G. Bellessa, T. Mallah, M. Verdaguer, *Phys. Rev. B* **1997**, *56*, 75; b) C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer, R. E. P. Winpenny, *Chem. Commun.* **2001**, 2666; c) S. T. Ochsenbein, M. Murrie, E. Rusanov, H. Stoeckli-Evans, C. Sekine, H. U. Güdel, *Inorg. Chem.* **2002**, *41*, 5133; d) M. Moragues-Cánovas, M. Helliwell, L. Ricard, E. Rivière, W. Wernsdorfer, E. Brechin, T. Mallah, *Eur. J. Inorg. Chem.* **2004**, 2219.

[4] a) B. E. Myers, L. G. Polgar, S. A. Friedberg, *Phys. Rev. B* **1972**, *6*, 3488; b) Y. Ajiro, S. A. Friedberg, N. S. VanderVen, *Phys. Rev. B* **1975**, *12*, 39; c) R. L. Carlin, C. J. O'Connor, S. N. Bhatia, *J. Am. Chem. Soc.* **1976**, *98*, 3523; d) L. A. Pardi, A. K. Hassan, F. B. Hulsbergen, J. Reedijk, A. L. Spek, L.-C. Brunel, *Inorg. Chem.* **2000**, *39*, 159; e) J. Mroziński, A. Skorupa, A. Pochaba, Y. Dromzée, M. Verdaguer, E. Goovaerts, H. Varcammen, B. Korybut-Daszkiewicz, *J. Mol. Struct.* **2001**, *559*, 107; f) A. Mašlejová, R. Boča, L. Dlháň, R. Herchel, *J. Magn. Magn. Mater.* **2004**, *272–276*, 380; g) R. Boča, *Coord. Chem. Rev.* **2004**, *248*, 757.

[5] a) J. Krzystek, J.-H. Park, M. W. Meisel, M. A. Hitchman, H. Stratemeier, L.-C. Brunel, J. Telser, *Inorg. Chem.* **2002**, *41*, 4478; b) S. Vongtragool, B. Gorshunov, M. Dressel, J. Krzystek, D. M. Eichhorn, J. Telser, *Inorg. Chem.* **2003**, *42*, 1788.

[6] T. Astley, M. A. Hitchman, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1997**, *50*, 145.

[7] O. Horner, E. Rivière, G. Blondin, S. Un, A. W. Rutherford, J.-J. Girerd, A. Boussac, *J. Am. Chem. Soc.* **1998**, *120*, 7924.

[8] a) F. E. Mabbs, D. Collison, *Electron Paramagnetic Resonance of d Transition Metal Compounds*, Elsevier, Amsterdam, **1992**; b) G. Rogez, PhD thesis, Université Paris-Sud, Orsay (France), **2002**.

[9] A. Bencini, I. Ciofini, M. G. Uytterhoeven, *Inorg. Chim. Acta* **1998**, *274*, 90.

[10] a) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, *2nd ed.*, Elsevier, Amsterdam, **1984**; b) A. Bencini, C. Benelli, D. Gatteschi, *Coord. Chem. Rev.* **1984**, *60*, 131.

[11] The parameters for aromatic polyamines were estimated by considering that in these systems e_o and e_π and the ratio e_o/e_π are slightly higher than for the corresponding monoamine.[10b] For the *O*,*O*′-bound nitrate, we used the values reported for another complex with similar structure.[6] We used $B = 860\ cm^{-1}$, $C/B = 3.9$, and $\xi = 630\ cm^{-1}$ for the Racah parameters and the spin–orbit constant, and $e_o(N1_{pyr}) = e_o(N3_{pyr}) = 4400\ cm^{-1}$, $e_\pi(N1_{pyr}) = e_\pi(N3_{pyr}) = 400\ cm^{-1}$, $e_o(N2_{im}) = e_o(N4_{im}) = 4600\ cm^{-1}$, $e_\pi(N2_{im}) = e_\pi(N4_{im}) = 500\ cm^{-1}$, $e_o(O1_{nitrate}) = 3300\ cm^{-1}$, $e_\pi(O1_{nitrate}) = 400\ cm^{-1}$, $e_o(O2_{nitrate}) = 3200\ cm^{-1}$, and $e_\pi(O2_{nitrate}) = 300\ cm^{-1}$ for the angular-overlap parameters.

[12] J. van Slageren, R. Sessoli, D. Gatteschi, A. A. Smith, M. Helliwell, R. E. P. Winpenny, A. Cornia, A.-L. Barra, A. G. M. Jansen, E. Rentschler, G. A. Timco, *Chem. Eur. J.* **2002**, *8*, 277; b) D. Collison, V. S. Oganesyan, S. Piligkos, A. J. Thomson, R. E. P. Winpenny, E. J. L. McInnes, *J. Am. Chem. Soc.* **2003**, *125*, 1168.

[13] J. N. Helbert, P. W. Kopf, E. H. Pointdexter, B. E. Wagner, *J. Chem. Soc. Dalton Trans.* **1975**, 998.

[14] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data.

[15] G. M. Sheldrick, SHELXL-97, Universität Göttingen, Germany, **1997**.

[16] A.-L. Barra, L.-C. Brunel, J. B. Robert, *Chem. Phys. Lett.* **1990**, *165*, 107.

[17] J. Glerup, H. Weihe, *Acta Chem. Scand.* **1991**, *45*, 444.

[18] J. van Slageren, S. Vongtragool, B. Gorshunov, A. A. Mukhin, N. Karl, J. Krzystek, J. Telser, A. Müller, C. Sangregorio, D. Gatteschi, M. Dressel, *Phys. Chem. Chem. Phys.* **2003**, *5*, 3837.

