Polyoxometalates

A Polyoxometalate Containing the $\{Ni_2N_3\}$ Fragment: Ferromagnetic Coupling in a Ni^{II} μ-1,1 Azido Complex with a Large Bridging Angle**

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Dedicated to Professor M. T. Pope on the occasion of his 70th birthday.

The chemistry of polyoxometalates (POMs) continues to attract much attention, particularly with respect to potential catalytic activity.[1] In the last few years it has also been noted that POMs are ideal models for the study of exchange interactions in magnetic clusters, as they represent a class of well-insulated complexes of controlled nuclearity and topology.[2] The studied clusters have been mainly obtained by filling the vacancies of lacunary Keggin ($\{XW_{11}O_{39}\}$, $\{XW_9O_{34}\}$, $X = Si^{IV}$, P^V, $As^{III/V}$...) or Dawson ($\{P_2W_{17}O_{61}\}$, $\{P_2W_{15}O_{56}\}$) type polyoxotungstates with di- or trivalent first-row transition metals (TMs), which leads to clusters of nuclearity ranging from one to fourteen.[3] Nevertheless, to date, the relevance of POMs in molecular magnetism is limited, partly because only species where the paramagnetic centers are fluoro, oxo, or hydroxo bridged, have been fully characterized; the introduction of larger bridging ligands in a magnetic POM remains a challenge. We are currently exploring the possibility of coupling the paramagnetic ions in the vacancies of POMs by organic or inorganic ligands. Dimeric bis(μ-acetato) lanthanide magnetic complexes have already been obtained.[4] Nevertheless, analogous compounds with TMs replacing the rare-earth cations have not been characterized to date. Considering the high affinity of the azido anion N_3^- for transition metals, such as Cu^{II}, Ni^{II} or Mn^{II},[5] and that N_3^- is certainly one of the most interesting magnetic couplers known in molecular chemistry, we have decided to investigate the interaction of this ligand with magnetic POMs. Very recently, we have shown that the paramagnetic center of a Cu^{II} POM can bind an azido group;[3e] nevertheless, the lack of structural information prevents any investigation of the magnetic properties of the compound obtained.

We report herein the synthesis, the structural characterization, and the magnetic properties of complex $KRb_5[(PW_{10}O_{37})(Ni(H_2O))_2(\mu\text{-}N_3)]\cdot 19\,H_2O$ (**1**), which is the first example of a fully characterized azido polyoxometalate. Moreover, the topology of the $\{Ni(\mu\text{-}1,1\text{-}N_3)Ni\}$ core in **1** is unprecedented, as no corner-sharing azido-bridged Ni^{II} complex has been obtained to date. It follows that the Ni-N-Ni angle θ in **1** is by far the largest observed in azido-ligand bridged Ni^{II} compounds, a feature which should help the understanding of the relationships between structural parameters and the value of the magnetic exchange parameter J for μ-1,1-N_3 complexes.

Compound **1** was obtained by adding solid $K_9[A\text{-}\alpha\text{-}PW_9O_{34}]$ to a hot aqueous solution of Ni^{II} acetate, followed by the addition of an excess of sodium azide. The formation of the $[PW_{10}O_{37}]^{9-}$ ion, as a result of the instability of the $[PW_9O_{34}]^{9-}$ species in solution, is known.[6] Crystal structure analysis of compound **1**[7] shows that **1** can be described as the result of the formal removing of a $\{W_3O_{13}\}$ group from the $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ ion followed by its replacement by a $\{WO_{10}Ni_2(H_2O)_2N_3\}$ fragment (Figure 1). Two crystallographically non-equivalent $[(PW_{10}O_{37})(Ni(H_2O))_2(\mu\text{-}N_3)]^{6-}$ subunits (**1a** and **1b**, containing the ions Ni(1) and Ni(2), respectively) have been found in the unit cell. The dinuclear $\{[Ni(H_2O)]_2N_3\}$ entities are highly similar in **1a** and **1b** (see Figure 1), and will be considered as identical for the forthcoming discussion. The paramagnetic centers are in an axially distorted octahedral environment. Indeed, an elongated Ni–O(PO_3) bond ($d_{Ni\text{-}O} = 2.273(5)$, $2.283(4)$ Å) is observed in the position *trans* to the Ni–OH_2 bond ($d_{Ni\text{-}OH_2} = 2.007(2)$, $2.018(4)$ Å), the remaining Ni-O/N bonds are in the range 1.990(5)–2.081(5) Å. The two paramagnetic centers are bridged by one of the terminal nitrogen atoms of the azido ligand, which connects the

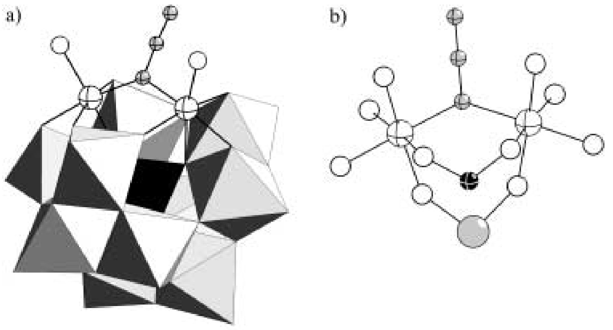

Figure 1. a) Polyhedral and ball-and-stick representation of complex **1**. Light gray octahedra = WO_6; black octahedra = PO_4; white cross-hatched sphere = Ni; empty white sphere = OH_2; gray cross-hatched sphere = N. Selected bonds lengths [Å] and angles [°]: Ni(1)-O 1.990(5)-2.273(5), Ni(2)-O 2.001(5)-2.283(4), Ni(1)-N 2.018(4), Ni(2)-N 2.003(3), Ni(1)···Ni(1) 3.620(6), Ni(2)···Ni(2) 3.639(6), Ni(1)-N-Ni(1) 128.9(4), Ni(2)-N-Ni(2) 129.6(4), N-N-N 172.8(13)–174.1(14). See text for labels. b) Ball-and-stick representation of the $\{[Ni(H_2O)]_2N_3(OPO)(OWO)\}$ fragment. Black cross-hatched sphere = P; gray sphere = W; white sphere = O; white cross-hatched sphere = Ni; gray cross-hatched sphere = N

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paramagnetic centers in an end-on fashion. The two $\mathrm{Ni^{II}}$ cations are related by a mirror plane containing the heteroatom, the azido ligand, and the tungsten atom of the $\{\mathrm{WNi_2}\}$ trinuclear subunit. Finally, the shortest intermolecular $\mathrm{Ni^{II}}\cdots\mathrm{Ni^{II}}$ separation is observed between the Ni(1) and the Ni(2) centers ($d_{\mathrm{Ni(1)\cdots Ni(2)}} = 5.005(1)$ Å). Compound **1** can be compared to the reported complex $[(\mathrm{PW_{10}O_{38}})(\mathrm{Cu(H_2O)})_2]^{7-}$,[6a] for which, a treatment of the magnetic data revealed a mixture of several isomers. Two isomers contain neighboring $\mathrm{Cu^{II}}$ ions, connected through a corner oxygen atom and an edge of their coordination octahedra, the other isomers being constructed of nonadjacent $\mathrm{CuO_6}$ octahedra. From this structure it can be concluded that the azido anion imposes an arrangement in which the paramagnetic pair shares a corner. The $\{[\mathrm{Ni(H_2O)}]_2\mathrm{N_3}\}$ core in **1** can be compared to that found in the copper complex $[\mathrm{Cu_2}(\mu\text{-}1,1\text{-}\mathrm{N_3})\mathrm{L}](\mathrm{ClO_4})_3$ (L = η^8-nitrogen macrocyclic ligand),[8] which is the only $\{\mathrm{M_2}(\mu\text{-}1,1\text{-}\mathrm{N_3})\}$ complex with a longer metal–metal separation ($d_{\mathrm{Cu\text{-}Cu}} = 4.312$ Å) and a larger M-N-M angle (Cu-N-Cu = 146.5°) than **1**. Nevertheless, in this macrocyclic compound, the bridging nitrogen atom of the azido ligand is in an axial position. The IR spectra of **1** is in agreement with an end-on coordination mode of the $\mathrm{N_3^-}$ unit ($\tilde{\nu}_{\mathrm{as}} = 2088\ \mathrm{cm^{-1}}$, $\tilde{\nu}_{\mathrm{s}} = 1301\ \mathrm{cm^{-1}}$), and very similar to that found for the complex postulated to be $\mathrm{H_5K_6[(SiW_9O_{37})Cu_3N_3]}$ ($\tilde{\nu}_{\mathrm{as}} = 2082\ \mathrm{cm^{-1}}$, $\tilde{\nu}_{\mathrm{s}} = 1282\ \mathrm{cm^{-1}}$),[3e] which suggests that the same coordination mode of the azido ligand is adopted in this copper(II) complex. This situation clearly highlights that in aqueous media, the substitution of the terminal water molecules linked to the paramagnetic centers is difficult. Attempts of further azidation on the alkylammonium salts of **1** in organic media need to be performed.

The magnetic behavior of **1** between 2–300 K was investigated (Figure 2). The $\chi_M T$ curve increases continuously upon cooling from 300 K to 31 K, after which $\chi_M T$ rapidly decreases. This pattern is characteristic of ferromagnetic behavior, with a $S = 2$ ground state. The sudden decrease in $\chi_M T$ could be due both to intermolecular interactions and to the zero-field splitting (ZFS) effect on the $S = 2$ state. We considered the Hamiltonian in Equation (1) with $S_1 = S_2 = 1$

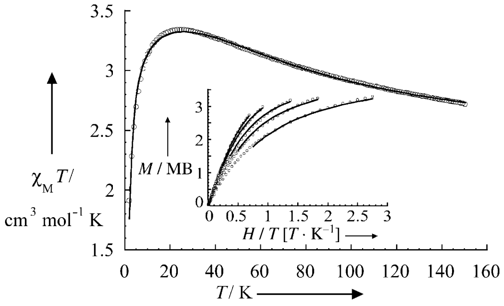

Figure 2. Magnetic susceptibility per mole of compound **1** as a function of temperature between 150 and 2 K. Inset: $M = \mathrm{f}(H/\mathrm{T})$ at 8, 6, 4, 3, and 2 K (from left to right). The solid lines were generated from the best fit parameters given in the text.

$$\hat{H} = -J\hat{S}_1\hat{S}_2 - D(\hat{S}_z^2 - \hat{S}(\hat{S}+1)) \qquad (1)$$

associated to the local spin of the two $\mathrm{Ni^{II}}$ centers, and the axial ZFS Hamiltonian being relative to the $S = 2$ ground state of the cluster.

The $\chi_M T = \mathrm{f}(T)$ curve was fit using the related analytical expression (see Supporting Information). The best fit parameters obtained were $J = 36.4\ \mathrm{cm^{-1}}$, $g = 2.13$, and $D = 5.1\ \mathrm{cm^{-1}}$ ($R = 3.4 \times 10^{-5}$).[9] A fit of the $\chi_M T = \mathrm{f}(T)$ curve considering the Hamiltonian $\hat{H}' = -J\hat{S}_1\hat{S}_2 - zJ'$, where zJ' relates to the interdimer exchange, was also performed, and led to a zJ' value of $-0.62\ \mathrm{cm^{-1}}$ ($J = 27.2\ \mathrm{cm^{-1}}$, $g = 2.21$, $R = 7.10^{-6}$). As this value represents an upper limit, it can then be assumed that intermolecular interactions will vanish at high fields ($H >$ 1.5 T). The variation of the magnetization M with the applied magnetic field H for **1** in the range 0–5.5 T was investigated at 2, 3, 4, 6 and 8 K. The relatively high J value previously found allows the possibility that only the $S = 2$ state is populated at these temperatures to be considered. The best fit of the $M = f(H/T)$ curves in the range $1.5 < H < 5\ \mathrm{T}$ (Figure 2, inset) considering the axial ZFS Hamiltonian $\hat{H}'' = -D(\hat{S}_z^2 - \hat{S}(\hat{S}+1))$ gives $D = 5.9\ \mathrm{cm^{-1}}$ and $g = 2.16$ ($R = 2.10^{-4}$), in good agreement with the values determined by fitting the $\chi_M T = \mathrm{f}(T)$ curve relatively to the H Hamiltonian.[10] It has also to be noticed that the non-superposition of the $M = f(H/T)$ curves clearly indicates that the system is anisotropic. Such large or larger values of D have been reported for dinuclear $\mathrm{Ni^{II}}$ complexes.[11]

During the last few decades, several groups have tried to understand the relationship between structural parameters and magnetic coupling in μ-1,1-azido bridged complexes (see below). To date, $\mathrm{Ni^{II}}$ compounds containing three and two end-on azido bridging ligands have been reported (see Table 1 for selected $\mathrm{Ni^{II}}$ azido complexes). With three end-on azido bridging ligands, the available structures show a narrow range of Ni-$\mathrm{N_3}$-Ni angle θ ($83.2 \leq \theta \leq 86.9°$), while θ ranged between 94.8 and 104.9° with two end-on azido bridging ligands. For all these compounds, the magnetic coupling was found to be ferromagnetic. In **1**, the θ value is dramatically higher, with an average θ value of 129.3°. It also follows that the Ni⋯Ni separation (3.639(6) Å) is longer than for the previously reported compounds. In 1986, Kahn et al.[12] proposed a spin-polarization model for bis(μ-1,1-$\mathrm{N_3}$) coupled copper(II) dimers, in which the two opposite electrons in the HOMO π_g are localized on the two terminal nitrogen atoms of the azido ligand. For an end-on bridging mode, simultaneous pairing of the two paramagnetic centers would lead to ferromagnetic coupling, irrespectively of the θ value. Nevertheless, based on polarized neutron diffraction studies,[13] Aebersold et al. showed later that a spin-delocalization mechanism in the active-electron approximation must be considered. The coupling would then be ferromagnetic (or antiferromagnetic) under a given θ_{AO} value and antiferromagnetic (or ferromagnetic) above, where θ_{AO} is the angle for accidental orthogonality. This phenomenon was observed by Thompson and co-workers for diazine/azide copper complexes, with $\theta_{\mathrm{AO}} = 108.5°$,[14] but it was established by the same group[15] and Escuer et al.[16] that the antiferromagnetic nature found for diazine/azide copper complexes for $\theta_{\mathrm{AO}} > 108.5°$ was due to the complementary antibonding overlap phenomenon,[17] and not simply to an effect of an increase of the θ

Table 1: Structural parameters and exchange magnetic coupling constant J in **1** and selected di- and tri-μ-1,1-azido bridged nickel(II) complexes.[a]

Compounds	Ni-N-Ni [°]	Ni⋯Ni [Å]	J [cm^{-1}]	Ref.
tri-μ-1,1-azido bridged Ni(II) complexes				
$[Ni_2L^1{}_2(\mu\text{-}N_3)_3]ClO_4$	85.0–86.9	2.896	+30.7	[11]
$[Ni_2L^2{}_2(\mu\text{-}N_3)_3]ClO_4$	86.1–86.5	2.582	+17.2	[20]
di-μ-1,1-azido bridged Ni^{II} complexes				
$[Ni_4(dbm)_4(EtOH)_4(\mu\text{-}N_3)_4]$	94.8–97.7	3.156–3.239	+11.9	[21]
$[\{Ni(terpy)(\mu\text{-}N_3)\}_2]$	101.6	3.274	+22.8	[22]
$[\{Ni_2(Medpt)_2(N_3)_2\}(\mu\text{-}N_3)_2)]$	104	3.470	+46.7	[23]
$[\{Ni(en)_2\}_2(\mu\text{-}N_3)_2](ClO_4)$	104.3	3.369	+20.9	[24]
mono-μ-1,1-azido bridged Ni^{II} complex				
$KRb_5[(PW_{10}O_{37})\{Ni(H_2O)_2\}(\mu\text{-}N_3)]$	129.8–130.6	3.620–3.639	+37	This work

[a] dbm = dibenzoylmethane, L^1 = 1,4,7-trimethyl-1,4,7-triazacyclononane, L^2 = bis(*N*,*N'*-dimethyl-1,4,7-triazacyclononane)calix[4]arene, terpy = 2,2':6,2''-terpyridine; Medpt = methyl(bis(3-aminopropyl)-amine), en = 1,2-ethanediamine.

angle as initially supposed. Previously Mikuriya et al. had reported that no significant magnetic coupling occurs in the only single-bridged azido end-on complex $[Cu_2(\mu\text{-}1,1\text{-}N_3)L](ClO_4)_3$;[8] however, for this compound, the azido ligand is in an axial position, and this lack of magnetic coupling is quite understandable considering that the unpaired electrons of the Cu^{II} centers are localized in the $d_{x^2-y^2}$ orbitals. Our results (i.e. a ferromagnetic coupling occurring in a dimeric μ-1,1 azido complex with a θ value of 129.3°) provides empirical evidence for a positive answer to the question posed by Kahn et al. "Can the 1,1-azido group be considered as an almost universal ferromagnetic coupler?".[13] At least, we can say that this assumption must be true for nickel(II) complexes; nevertheless, MO calculations must be performed to verify that no countercomplementarity effect arises from the long O-P-O and O-W-O bridges connecting the divalent centers. Owing to the lack of available compounds, no clear correlation between θ and J for Ni^{II} azido bridged compounds could be found to date. Nevertheless, our work verifies the Ruiz et al. DFT B3LYP calculations,[18] which proposed that, even at high θ angles, Ni^{II} dimers could be ferromagnetically coupled. Obtaining single crystals of **1** suitable for polarized neutron diffraction studies would be helpful in further understanding of the magnetic exchange mechanism in μ-1,1-azido bridged complexes. Additionally, the synthesis of analogous μ-1,1-N$_3$/POMs complexes with other divalent transition metals must be performed.

Experimental Section

1: $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.220 g, 0.88 mmol) was dissolved at 60 °C in water (10 mL). Then, a sample of $K_9[A,\alpha\text{-}PW_9O_{34}]{\cdot}16H_2O$[19] (1.07 g, 0.37 mmol) was added as a solid. NaN$_3$ (0.087 g, 1.34 mmol) in water (10 mL) of was added dropwise to the resulting yellow solution. The solution was stirred for 10 min and allowed to cool to room temperature. Solid RbCl (0.750 g, 6.2 mmol) was then added. A precipitate (0.2 g) was removed by filtration after 30 min, and the filtrate let to evaporate overnight. Green yellow crystals of **1** were then collected by filtration and washed with ethanol and diethyl ether. Yield: 0.4 g (30 %, based on $\{PW_9O_{34}\}$). Elemental analysis calcd (%) for $KRb_5[(PW_{10}O_{37})(Ni(H_2O))_2(\mu\text{-}N_3)]{\cdot}19H_2O$: W 53.05, Ni 3.40, N 1.21, K 1.13, Rb 12.33; found: W 53.05, Ni 3.42, N 1.26, K 0.93, Rb 12.25. IR (KBr pellet): $\tilde{\nu}$ = 2088(s), 1620 (s), 1301(w), 1053(s), 950(s), 905(s), 877(s), 809(s), 692(s), 509(m), 365(m) cm^{-1}.

Magnetic susceptibility measurements were carried out with a Quantum Design SQUID Magnetometer with an applied field of 1000 G. The independence of the susceptibility value with regard to the applied field was checked at room temperature. The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables and from temperature-independent paramagnetism (TIP). The analytical expression used for the fit of the $\chi_M T = f(T)$ curve is given as Supporting Information.

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[1] For reviews on polyoxometalates, see the special issue, *Chem. Rev.* **1998**, *98*, 1–387 (Guest Ed.: C. Hill).

[2] J. M. Clemente-Juan, E. Coronado, *Coord. Chem. Rev.* **1999**, *193–195*, 361.

[3] For examples of magnetic POM/TM Keggin complexes see: a) H. Y. Woo, H. So, M. T. Pope, *J. Am. Chem. Soc.* **1996**, *118*, 621; b) K. Wassermann, R. Palm, H.-J. Lunk, J. Fuchs, N. Steinfeldt, R. Stösser, *Inorg. Chem.* **1995**, *34*, 5029; c) J. M. Clemente-Juan, E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-Garcia, *Inorg. Chem.* **1999**, *38*, 55; d) U. Kortz, I. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, *Inorg. Chem.* **2002**, *41*, 6412; e) P. Mialane, A. Dolbecq, J. Marrot, E. Rivière, F. Sécheresse, *Angew. Chem.* **2003**, *115*, 3647; *Angew. Chem. Int. Ed.* **2003**, *42*, 3523; for POM/TM Dawson complexes: f) X. Zhang, T. M. Anderson, Q. Chen, R. G. Finke, *Inorg. Chem.* **2001**, *40*, 418; g) C. J. Gómez-Garcia, J. J. Borrás-Almenar, E. Coronado, L. Ouahab, *Inorg. Chem.* **1994**, *33*, 4016.

[4] a) U. Kortz. *J. Cluster Sci.* **2003**, 205; b) P. Mialane, A. Dolbecq, E. Rivière, J. Marrot, F. Sécheresse, *Eur. J. Inorg. Chem.* **2004**, 33.

[5] For a review on Ni^{II} and Mn^{II} azido-bridge complexes, see J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193–195*, 1027.

[6] a) C. J. Gómez-Garcia, E. Coronado, P. Gómez-Romero, N. Casañ-Pastor, *Inorg. Chem.* **1993**, *32*, 89; b) R. C. Howell, F. G. Perez, S. Jain, W. DeW. Horrocks, Jr., A. L. Rheingold, L. C. Francesconi, *Angew. Chem.* **2001**, *113*, 4155; *Angew. Chem. Int. Ed.* **2001**, *40*, 4031.

[7] Crystal data and structure refinements for **1**: a green yellow crystal (0.22 × 0.12 × 0.03 mm) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using Mo$_{K\alpha}$ monochromatized radiation (λ = 0.71073 Å). Monoclinic, space group $P2_1/m$, a = 12.3390(1), b = 16.4182(2), c = 25.6887(4) Å, β = 94.926(1)°, V = 46165.2(2) Å^3, Z = 4, ρ_{calcd} = 4.245 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 27.682 mm^{-1}, $F(000)$ = 5780, 35791 reflections measured, of which 13587 were independent, 764 refined parameters, R_1 = 0.0573, wR_2 = 0.1214. Data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggen-

stein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413547.

[8] M. Mikuriya, S. Kida, I. Murase, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1355.

[9] $R = [\Sigma(\chi_M T_{\text{calcd}} - \chi_M T_{\text{obs}})^2 / \Sigma(\chi_M T_{\text{obs}})^2]$.

[10] An analogous fit in the range $0 < H < 5$ T gave $g = 2.14$ and $D = 5.6$ cm^{-1} ($R = 3.3 \times 10^{-4}$).

[11] P. Chaudhuri, T. Weyhermüller, E. Bill, K. Wieghardt, *Inorg. Chim. Acta* **1996**, *252*, 195.

[12] M.-F. Charlot, O. Kahn, M. Chaillet, C. Larrieu, *J. Am. Chem. Soc.* **1986**, *108*, 2574.

[13] M. A. Aebersold, B. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I. von Seggern, F. Tuczek, L. Öhrström, A. Grand, E. Lelièvre-Berna, *J. Am. Chem. Soc.* **1998**, *120*, 5238.

[14] S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.* **1995**, *34*, 2356.

[15] L. K. Thompson, S. S. Tandon, F. Lloret, J. Cano, M. Julve, *Inorg. Chem.* **1997**, *36*, 3301.

[16] A. Escuer, R. Vicente, F. A. Mautner, M. A. S. Goher, *Inorg. Chem.* **1997**, *36*, 1233.

[17] V. McKee, M. Zvagulis, C. A. Reed, *Inorg. Chem.* **1985**, *24*, 2914.

[18] E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, *120*, 11122.

[19] R. Contant, *Can. J. Chem.* **1987**, *65*, 568.

[20] P. D. Beer, M. G. B. Drew, P. B. Leeson, K. Lyssenko, M. I. Ogden, *J. Chem. Soc. Chem. Commun.* **1995**, 929.

[21] a) M. A. Halcrow, J. C. Huffman, G. Christou, *Angew. Chem.* **1995**, *107*, 971; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 889; b) M. A. Halcrow, J.-S. Sun, J. C. Huffman, G. Cristou, *Inorg. Chem.* **1995**, *34*, 4167.

[22] M. G. Barandika, R. Cortes, L. Lezama, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Chem. Soc. Dalton Trans.* **1999**, 2971.

[23] A. Escuer, R. Vicente, J. Ribas, X. Solans, *Inorg. Chem.* **1995**, *34*, 1793.

[24] R. Cortes, J. I. Ruiz de Larramendi, L. Lezama, T. Rojo, K. Urtiga, M. I. Arriortua, *J. Chem. Soc. Dalton Trans.* **1992**, 2723.