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How to cite

BONHOMMEAU, Sébastien et al. Photoswitching of the Dielectric Constant of the Spin-Crossover Complex [Fe(L)(CN)2]H2O. In: Angewandte Chemie. International edition in English, 2006, vol. 45, n° 10, p. 1625–1629. doi: 10.1002/anie.200503252

This publication URL: https://archive-ouverte.unige.ch/unige:3635
Publication DOI: 10.1002/anie.200503252

Spin-Crossover Complexes

DOI: 10.1002/anie.200503252

Photoswitching of the Dielectric Constant of the Spin-Crossover Complex $[Fe(L)(CN)_2]\cdot H_2O$**

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The interest in bistable molecular materials for information processing has been discussed by several authors.[1] Iron(II) spin-crossover (SCO) compounds[2] are particularly promising in this respect, because the conversion between the high-spin (HS) ($S=2$) and low-spin (LS) ($S=0$) states can be triggered not only by temperature, pressure,[3] and pulsed magnetic fields,[4] but also by irradiation with light.[5] This latter phenomenon—usually called light-induced excited-spin-state trapping (LIESST)—was discovered by Decurtins et al.,[6] who observed a light-induced LS→HS transition involving quantitative trapping of the molecules in the excited HS state at low temperatures (typically below 50 K). Our recent investigations demonstrated that it was feasible to trigger SCO by light even at room temperature by using a nanosecond laser pulse,[7] and potential applications of SCO compounds as active elements in optical devices were also discussed.[8]

Furthermore, we also observed hysteretic bistability in the dielectric properties of SCO materials.[9] The real part of the dielectric constant was found to be significantly different in the two spin states, which suggests that capacitance measurements can be used to "read" the information stored in the bistable system. Taking advantage of this property, we have constructed and patented a prototype of a thermal molecular memory device.[10] Within this context, the existence of a correlation between photomagnetic and dielectric properties would open interesting prospects because switchable dielectric properties and optical addressing are two physical principles widely used for information storage and processing. The possible advantages of using SCO materials for these aims include: a) the short addressing times (picosecond scale on the molecular level),[11] b) photostability over successive cycles, c) low addressing power (on the order of $\mathrm{mW\,cm^{-2}}$), and d) high storage densities (because the LIESST effect is purely molecular).[8,12]

Herein, we report on the observation of the change in dielectric constant upon SCO induced by irradiation with light. A preliminary theoretical approach, based on density functional theory (DFT), to interpret the variation of the dielectric constant with the SCO is also presented. For this study, we selected the SCO complex $[Fe(L)(CN)_2]\cdot H_2O$[13,14] in which L is a Schiff base macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine (L = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene). This molecule was chosen because its critical temperature (T_{LIESST}), defined as the temperature at which the light-induced HS information is erased,[8] is the highest (130 K) ever obtained for a SCO compound.[13] Dynamic dielectric spectroscopy was used to measure the light-induced and thermal variations of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) in the frequency range 10^2–10^6 Hz. The imaginary part ε'' represents the dielectric losses and was found to be small and quasi-independent of temperature for each SCO complex investigated. The real part ε' represents the displacement of the bounded charges under the effect of a time-dependent electric field. We will focus only on this latter physical quantity in the following discussion.

As reported previously,[13–15] the magnetic behavior of $[Fe(L)(CN)_2]\cdot H_2O$ is rather unusual: if the sample is quenched (at a rate of $20\ \mathrm{K\,min^{-1}}$) from 300 to 77 K, the HS state may be "frozen in" and remains stable for several days. The sample transforms into a pure LS state when it is heated up to 150 K. Irradiation with light of the LS state at 10 K leads to an increase in the magnetic susceptibility (LIESST effect) as shown in Figure 1 a. The magnetic behavior of the irradiated sample upon heating ($<1\ \mathrm{K\,min^{-1}}$) is quite complicated. First, a decrease in the $\chi_M T$ value occurs around

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[**] L = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene. Financial support from the Paul Sabatier University (BQR/2004) is acknowledged. DFT calculations have been performed thanks to the facilities provided by CALMIP (Calculs en Midi-Pyrénées, France), CINES (Centre Informatique National de l'Enseignement Supérieur, France), and IDRIS (Institut du Développement et des Ressources en Informatique Scientifique, France). L.M.L.D. thanks the Centro Svizzero di Calcolo Scientifico (CSCS) for the calculation resources allocated in the framework of the CSCS project entitled "Photophysics and Photochemistry of Transition Metal Compounds: Theoretical Approaches" and the Swiss National Science Foundation for financial support.

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

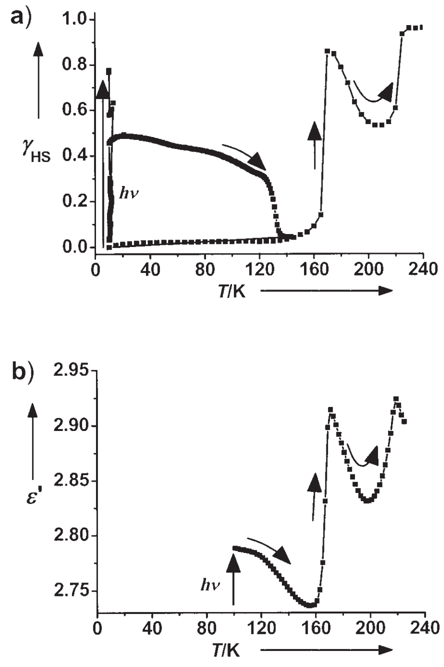

Figure 1. a) Thermal variation of the fraction of high-spin molecules (γ_{HS}) in $[Fe(L)(CN)_2]\cdot H_2O$ obtained through magnetic-susceptibility measurements following irradiation with light at 10 K. b) Thermal variation of the dielectric constant in $[Fe(L)(CN)_2]\cdot H_2O$ following irradiation with light at 100 K.

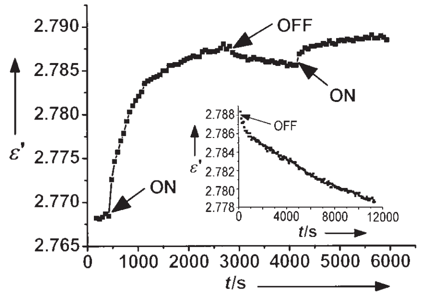

Figure 2. Variation of the dielectric constant of the $[Fe(L)(CN)_2]\cdot H_2O$ complex (initially in a pure LS state) at 100 K upon irradiation with light. The labels "ON" and "OFF" indicate the points at which the light source was switched on and off, respectively. The inset shows the relaxation curve obtained at 115 K following the irradiation at 100 K.

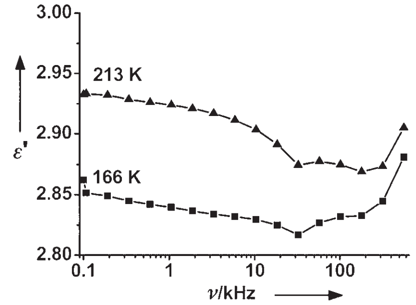

Figure 3. Frequency dependence of the dielectric constant of $[Fe(L)(CN)_2]\cdot H_2O$ at 166 K (squares) and 213 K (triangles). Note that the data reported here and in Figure 1 b were collected in the same experiment.

130 K, which corresponds to the relaxation of the photoinduced HS species. Then, the thermally induced LS-to-HS transformation occurs at about 160 K, which is followed by a decrease in the $\chi_M T$ value around 170 K and a rise around 200 K. Finally, the pure HS state is reached at about 230 K. The change in magnetic properties around 170 K is thought to correspond to a phase transition leading to a 1:1 mixture of LS and HS species. Subsequent slow cooling of the sample ($<1\,K\,min^{-1}$) also yields a population of this 1:1 mixture at around 170 K. Every subsequent (slow) sample heating cycle leads to a pure HS state and every cooling cycle leads to the above-mentioned mixture of spin states.

As it is impossible to observe the LIESST effect at 100 K with this mixture of states,[16] care must be taken to irradiate the sample in its pure LS state. Figure 1 b shows the variation of ε' (measured at 100 kHz) upon irradiation at 100 K and subsequent heating to 230 K. There is a clear similarity between the magnetic and dielectric behavior of the sample (Figure 1 a and b), which proves that the dielectric polarization (dielectric constant) can be photoswitched and allows the light- and thermally induced spin-state changes to be followed as well. Figure 2 displays the temporal evolution of the dielectric constant upon irradiation at 100 K with light. A partial transition of the sample to the HS state occurs, and saturation is reached after approximately 2500 s of illumination. The relaxation from this light-induced metastable state after the laser is switched off is quite slow (Figure 2) and leads to the stable LS state after more than 12000 s at 115 K (inset Figure 2). Any quantitative interpretation of the relaxation rates would be rather doubtful, as the relation between the HS fraction and the dielectric constant is not known, contrary to the case for magnetic susceptibility.

The change in dielectric constant of SCO materials results from structural modifications accompanying the spin-state change. The dielectric constant, and therefore the total polarizability, are always nearly independent of the frequency of the external applied electric field (quasi-static range) within the investigated frequency range (Figure 3). Also, no relaxation process, associated with an orientational polarization of permanent dipole moments, is observed in the ε'' versus frequency curve. Nevertheless, the dielectric constant sometimes increases slightly with temperature once the pure LS or HS state is reached;[9] this phenomenon is typically due to the presence of polar entities, such as water molecules, which are mobile or able to reorient themselves by rotation. These dipoles are able to align more readily with the applied electric field as the molecular mobility increases. In our consideration of the correlation between the macroscopically measurable relative permittivity and the microscopic polarizability, we rule out, in a first approximation, any effect of the dipolar polarization on the observed transition and thereby consider the polarizability to be composed mainly of electronic and ionic contributions. As the HS molecules are larger than the LS ones, their electronic polarizability and hence ε_∞ value should decrease in going from the HS to the LS state. Furthermore, as the HS state has a more ionic nature, the ionic polarizability must also decrease to some extent with the HS→LS spin-state change. Indeed, a decrease of the macroscopically measurable ε' value was observed for most of the investigated SCO compounds during the HS-to-LS transition; the maximal switching magnitude of 0.3 was observed for the compound $[Fe(NH_2trz)_3](NO_3)_2$ (trz = triazole).[9] The title compound $[Fe(L)(CN)_2]\cdot H_2O$ (Figure 1 b) exhibits an ε'_{HS} value of approximately 2.92 and an ε'_{LS} value of approximately 2.74; that is, a difference of 0.18 in the dielectric constants for the LS and HS states.

To gain a deeper insight into the origin of the variation of the dielectric constant upon SCO, a quantum chemical study of the $[Fe(L)(CN)_2]$ complex was performed by using DFT methods. The aim of this study was to determine the dependence on spin state of the microscopic electrical properties by evaluating the electronic polarizability of the molecule in the two spin states. Indeed, the large number of atoms in the SCO complexes prohibits the use of computationally demanding high-level ab initio (i.e. wavefunction-based) methods, whereas DFT methods can be applied efficiently to such large systems. DFT calculations have recently been carried out on several SCO compounds.[17] These studies were aimed at assessing the performance of available density functionals in describing the geometries of the complexes in both spin states, evaluating the HS–LS energy difference, and determining the vibrational spectra. Although the spin-state energetics were often calculated inaccurately, it was shown that DFT methods give structural parameters and vibrational frequencies in good agreement with the experimental data.

The optimized HS geometries were in good agreement with the X-ray structure of $[Fe(L)(CN)_2]\cdot H_2O$ in the HS state.[18] Table 1 gives the metal–ligand distances found for the experimental HS structure and the calculated HS and LS geometries (note that no experimental structural data are available for the LS species). The optimized metal–ligand bonds are approximately 0.2 to 0.3 Å longer in the HS state than in the LS state with the noticeable exception of the Fe–O2 bond, which is approximately 0.7 to 0.8 Å shorter in the HS state. Consequently, the spin-state change is related to a huge structural modification of the iron coordination sphere. The Fe^{II} ion is seven-coordinate in the HS state and six-coordinate in the LS state (Figure 4). This original feature was first suggested by Nelson et al.[14] and corroborated recently by Guionneau et al.[18] through X-ray investigations. It is noteworthy that the same optimized six-coordinate LS geometry was successfully obtained with different basis sets by using the seven-coordinate HS structure as a starting geometry.

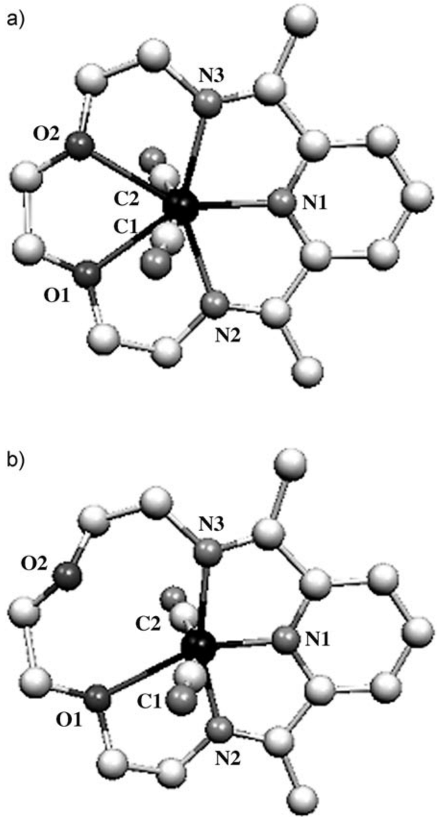

Figure 4. Calculated (B3LYP/6-31G*) optimized structure of the $[Fe(L)(CN)_2]$ complex in the HS (a) and LS (b) states.

Table 1: Experimental[16] and calculated Fe–ligand distances [Å] in $[Fe(L)(CN)_2]\cdot H_2O$.[a]

HS state	X-ray[b]	B3LYP/6-31G*	B3LYP/6-311G**
Fe–N1	2.107(2)	2.069	2.096
Fe–N2	2.203(2)	2.225	2.235
Fe–N3	2.203(2)	2.225	2.235
Fe–C1	2.163(3)	2.102	2.120
Fe–C2	2.163(3)	2.102	2.120
Fe–O1	2.334(2)	2.435	2.411
Fe–O2	2.334(2)	2.435	2.411
LS state		**B3LYP/6-31G***	**B3LYP/6-311G****
Fe–N1		1.824	1.832
Fe–N2		1.929	1.937
Fe–N3		2.054	2.067
Fe–C1		1.944	1.958
Fe–C2		1.944	1.958
Fe–O1		2.415	2.409
Fe–O2		3.144	3.149

[a] Calculations were performed on $[Fe(L)(CN)_2]$. [b] X-ray crystal structure obtained at 293 K.

From the optimized structures, the mean (static) electronic polarizability of the complex $\alpha = \frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$ can be determined in both spin states as the analytic second derivative of the energy with respect to the electric field.[19] The calculated values of the LS (α_{LS}) and HS (α_{HS}) mean polarizabilities are given in Table 2. Notably, they increase with the quality of the basis sets and the HS value obtained

Table 2: Calculated values of the HS and LS mean polarizabilities ($\Delta\alpha = \alpha_{HS} - \alpha_{LS}$) for $[Fe(L)(CN)_2]$ (in atomic units).

	α_{LS} [a.u.]	α_{HS} [a.u.]	$\Delta\alpha$ [a.u.]
B3LYP/3-21G	238.99	254.40	15.41
B3LYP/6-31G*	247.40	259.48	12.08
B3LYP/6-311G**	257.50	266.91	9.41
PBE/TZVP	287.52	302.80	15.28

with a given basis set is always higher than its LS counterpart ($\Delta\alpha_{HL} > 0$). This latter trend is also reproduced with the gradient-corrected PBE[20] functional and the TZVP basis set[21] (Table 2). Therefore, the change in the dielectric constant of the SCO compound appears to be correlated with the change in the mean polarizability of the complex. To confirm this result, similar calculations were performed at the B3LYP/6-31G* level for the $[Fe(phen)_2(NCS)_2]$ (phen = phenanthroline)[17c] and $[Fe\{5\text{-}NO_2\text{-sal-N}(1,4,7,10)\}]$ (5-NO_2-sal-N(1,4,7,10) = 1,10-bis(5-nitrosalicylaldehyde)-1,4,7,10-tetraazadecane-*O*,*O′*,*N*,*N′*,*N″*,*N‴*) SCO complexes. The LS and HS polarizabilities obtained for these two complexes are given in Table 3 together with those found for the title complex at the same theoretical level. The calculated electronic polarizabilities and the measured (quasi-static) dielectric constants in $[Fe(L)(CN)_2]\cdot H_2O$ and $[Fe(phen)_2(NCS)_2]$ both increase in going from the LS to the HS state. In contrast, the calculated decrease in the polarizability for $[Fe\{5\text{-}NO_2\text{-sal-N}(1,4,7,10)\}]$ corroborates the previously observed atypical decrease[9] in its dielectric constant upon spin-state change. The electronic polarizability and the dielectric constant of $[Fe\{5\text{-}NO_2\text{-sal-N}(1,4,7,10)\}]$ are indeed higher in the LS state than in the HS state. This counter-intuitive behavior of the dielectric constant is therefore purely of structural origin.

Table 3: Experimental change in the dielectric constant ($\Delta\varepsilon' = \varepsilon'_{HS} - \varepsilon'_{LS}$) and calculated (B3LYP/6-31G*) change in the mean electronic polarizability ($\Delta\alpha = \alpha_{HS} - \alpha_{LS}$) for selected SCO compounds.

	$\Delta\varepsilon'$	α_{LS} [a.u.]	α_{HS} [a.u.]	$\Delta\alpha$ [a.u.]
$[Fe(L)(CN)_2]\cdot H_2O$	0.18	247.40	259.48	12.08
$[Fe(phen)_2(NCS)_2]$	0.015[9]	414.33	469.78	55.45
$[Fe\{5\text{-}NO_2\text{-sal-N}(1,4,7,10)\}]$	−0.13[9]	351.71	343.52	−8.19

In summary, photoswitching of the dielectric constant has been demonstrated experimentally for the SCO compound $[Fe(L)(CN)_2]\cdot H_2O$ and correlated through DFT calculations with the change in electronic polarizability that accompanies the spin transition. The electrical detection of a photoinduced spin-state change promises new opportunities for the use of SCO compounds as switchable capacitors in electronic devices for information storage and processing. Further research is necessary to enhance the changes in the dielectric constant of SCO compounds upon irradiation with light. Such tailoring of the relative permittivity might be possible, for example, by the introduction of highly polarizable (i.e. voluminous) atoms into these materials. Moreover, the relationship between the permittivity change and the structural and electronic changes accompanying the SCO must also be investigated in detail.

Experimental Section

Measurements of the dielectric constant were performed by using a Novocontrol BDS 4000 broad-band dielectric spectrometer for which the frequency of the external electric field applied to the sample was scanned between 10^2 and 10^6 Hz. Irradiation was carried out by applying an Ar^+ laser beam (457 –514 nm) on the polycrystalline sample located between a stainless steel electrode and an ITO (indium–tin oxide) electrode deposited on a glass plate, which allows uniform irradiation of the whole sample surface. The dielectric powder sample sandwiched between the two electrodes was ca. 100 μm thick with an effective diameter of 10 mm. The diameter of the laser beam was adjusted to slightly larger than that of the sample to ensure complete irradiation of the sample, and the power density at the sample was ca. 0.5 $mW\,mm^{-2}$.

DFT calculations were performed with the Gaussian 03 program package.[22] The Becke three-parameter hybrid functional B3LYP[23] was used with three different basis sets: 3-21G, 6-31G*, and 6-311G**. Calculations were also performed at the PBE/TZVP level.[20,21] The X-ray crystal structure was used as the starting point for the optimization of the HS geometry. As the low-temperature structure is not known because of the structural instability of the single crystals at low temperature, the optimized HS structure was used to initialize the optimization of the LS structure. The structures were optimized without constraints. The MOLDEN[24] and the MOLEKEL[25] software packages were used to visualize the calculated molecular structures. After completion of the optimization, the vibrational frequencies (within the harmonic approximation) and the static polarizability tensor were calculated. The optimized LS and HS geometries correspond to true minima since real frequencies were obtained in all cases.

Received: September 13, 2005
Revised: December 5, 2005

Keywords: density functional calculations · dielectric constant · magnetic properties · photophysics · spin crossover

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[1] a) O. Kahn, C. J. Martinez, *Science* **1998**, *279*, 44; b) C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541; c) J. K. Gimzewski, C. Joachim, *Science* **1999**, *283*, 1683.

[2] a) P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem.* **1994**, *106*, 2109; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024; b) “Spin Crossover in Transition Metal Compounds I–III” (Ed.: P. Gütlich, H. A. Goodwin): *Top. Curr. Chem.* **2004**, 233 – 235.

[3] V. Ksenofontov, A. B. Gaspar, P. Gütlich, *Top. Curr. Chem.* **2004**, *235*, 23.

[4] A. Bousseksou, K. Boukheddaden, M. Goiran, J.-P. Tuchagues, F. Varret, *Top. Curr. Chem.* **2004**, *235*, 65.

[5] A. Hauser, *Top. Curr. Chem.* **2004**, *234*, 155.

[6] S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* **1984**, *105*, 1.

[7] S. Bonhommeau, G. Molnár, A. Galet, A. Zwick, J.-A. Real, J. J. McGarvey, A. Bousseksou, *Angew. Chem.* **2005**, *117*, 4137; *Angew. Chem. Int. Ed.* **2005**, *44*, 4069.

[8] J.-F. Létard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.* **2004**, *235*, 221.

[9] A. Bousseksou, G. Molnár, P. Demont, J. Menegotto, *J. Mater. Chem.* **2003**, *13*, 2069.

[10] A. Bousseksou, C. Vieu, J.-F. Létard, P. Demont, J.-P. Tuchagues, L. Malaquin, J. Menegotto, L. Salmon, EP1430552, **2004**.

[11] C. Brady, J. J. McGarvey, J. K. McCusker, H. Toftlund, D. N. Hendrickson, *Top. Curr. Chem.* **2004**, *235*, 1.

[12] Besides the purely molecular LIESST effect, macroscopic domain switching by light pulses in solid spin-crossover materials has also been evidenced,[26] even at room temperature.[7] Freysz and co-workers reported that within the hysteresis loop, $[Fe(PM\text{-}BiA)_2(NCS)_2]$ (PM-BiA = *N*-(2-pyridylmethylene)-4-aminobiphenyl) was converted from the LS state into a pure HS state within the 8-ns light pulse and that the system relaxed to a mixture of HS/LS molecules in approximately 1 s.[26] However, more research is necessary to clarify the main characteristics

(domain size, switching times, and switching power) of this recently discovered phenomenon.

[13] a) S. Hayami, Z.-z. Gu, Y. Einaga, Y. Kobayasi, Y. Ishikawa, Y. Yamada, A. Fujishima, O. Sato, *Inorg. Chem.* **2001**, *40*, 3240; b) J. S. Costa, P. Guionneau, J.-F. Létard, *J. Phys. Conf. Ser.* **2005**, *21*, 67.

[14] S. M. Nelson, P. D. A. Mcllroy, C. S. Stevenson, E. König, G. Ritter, J. Waigel, *J. Chem. Soc. Dalton Trans.* **1986**, 991.

[15] E. König, G. Ritter, J. Dengler, S. M. Nelson, *Inorg. Chem.* **1987**, *26*, 3582.

[16] H. Liu, A. Fujishima, O. Sato, *Appl. Phys. Lett.* **2004**, *85*, 2295.

[17] a) G. Baranovic, *Chem. Phys. Lett.* **2003**, *369*, 668; b) G. Brehm, M. Reiher, S. Schneider, *J. Phys. Chem. A* **2002**, *106*, 12024; c) V. K. Pálfi, T. Guillon, H. Paulsen, G. Molnár, A. Bousseksou, *C. R. Chim.* **2005**, *8*, 1317; d) H. Paulsen, A. X. Trautwein, *Top. Curr. Chem.* **2004**, *235*, 197; e) H. Paulsen, A. X. Trautwein, *J. Phys. Chem. Solids* **2004**, *65*, 793; f) H. Paulsen, L. Duelund, H. Winkler, H. Toftlund, A. X. Trautwein, *Inorg. Chem.* **2001**, *40*, 2201; g) H. Paulsen, H. Winkler, A. X. Trautwein, H. Grunsteudel, V. Rusanov, H. Toftlund, *Phys. Rev. B* **1999**, *59*, 975; h) M. Reiher, *Inorg. Chem.* **2002**, *41*, 6928; i) A. Fouqueau, S. Mer, M. E. Casida, L. M. Lawson Daku, A. Hauser, T. Mineva, F. Neese, *J. Chem. Phys.* **2004**, *120*, 9473; j) A. Fouqueau, M. E. Casida, L. M. Lawson Daku, A. Hauser, F. Neese, *J. Chem. Phys.* **2005**, *122*, 044110; k) L. M. Lawson Daku, A. Vargas, A. Hauser, A. Fouqueau, M. E. Casida, *ChemPhysChem* **2005**, *6*, 1393.

[18] P. Guionneau, J. S. Costa, J.-F. Letard, *Acta Crystallogr. Sect. C* **2004**, *60*, m587.

[19] M. Frisch, M. Head-Gordon, J. Pople, *Chem. Phys.* **1990**, *141*, 189.

[20] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.

[21] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

[22] Gaussian 03 (Revision B.05): M. J. Frisch et al., see Supporting Information.

[23] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) *Becke3LYP Method References and General Citation Guidelines*, Gaussian *News*, **1994**, *5*, 2.

[24] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.

[25] a) MOLEKEL 4.3: P. Flükiger, H. P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Manno, Switzerland, **2000–2002**; b) S. Portmann, H. P. Lüthi, *Chimia* **2000**, *54*, 766.

[26] a) E. Freysz, S. Montant, S. Létard, J.-F. Létard, *Chem. Phys. Lett.* **2004**, *394*, 318; b) J. Degert, N. Lascoux, S. Montant, S. Létard, E. Freysz, G. Chastanet, J.-F. Létard, *Chem. Phys. Lett.* **2005**, *415*, 206.