Heat- and Light-Induced Spin Transition of an Iron(II) Polymer Containing the 1,2,4,5-Tetrakis(diphenylphosphanyl)benzene Ligand

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Dedicated to Philipp Gütlich in the occasion of his 70th birthday

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A new iron(II) spin-crossover compound containing a phosphane ligand has been synthesized and characterized by magnetic susceptibility, Mössbauer spectroscopy, and heat capacity and photomagnetic experiments. The $[Fe(tppb)Br_2]$ complex [tppb = 1,2,4,5-tetrakis(diphenylphosphanyl)benzene] exhibits a gradual spin conversion at $T_{1/2}$ = 184 K, and displays at low temperature a partial photoconversion of the low-spin (LS) state into the metastable high-spin (HS) state by irradiating the sample at 530 nm.

Introduction

Iron(II) spin-crossover (SC) compounds have numerous potential applications as display devices, optical switches, and magneto-optical storage systems, since heat- and light-induced spin transitions occur in the solid state without any fatigue.[1] The possibility to convert the spin state by irradiating with light is now reported in a large number of spin-crossover complexes. The major drawback of this process up to now is that optical switching requires that it be carried out at very low temperatures. Nevertheless, it has been theoretically predicted and experimentally confirmed that HS → LS relaxation rates k_{HL} can at least be controlled by the energy difference $\Delta E_{HL}°$ between the lowest vibrational levels of HS and of LS states, and by the change of the metal−ligand bond length Δr_{HL}.[2] In this particular context, iron(II) spin-crossover compounds containing phosphorus atoms are very attractive since a large Δr_{HL} is expected. Unfortunately, to date, spin transition has only been reported for solvated $[FeX_2(dppen)_2]\cdot nS$ compounds with dppen = *cis*-1,2-bis(diphenylphosphanyl)ethylene, X = Cl or Br, and solvent molecules (S) = $CHCl_3$, CH_2Cl_2, or $(CH_3)_2CO$.[3−7] In the particular case of $[Fe(dppen)_2Cl_2]\cdot 2(CH_3)_2CO$, single-crystal structures determined both in HS and LS states showed a large Δr_{HL}(Fe−P) variation (0.3 Å),[4] and relaxation kinetics of the HS → LS conversion that occurs after the LIESST effect were slower than for classical FeN_6 complexes.[7]

In this work, we report the preparation of a new iron(II) spin-crossover complex containing phosphorus atoms with the 1,2,4,5-tetrakis(diphenylphosphanyl)benzene (tppb) ligand (Figure 1). The thermal spin-crossover properties were studied by magnetic susceptibility measurements,

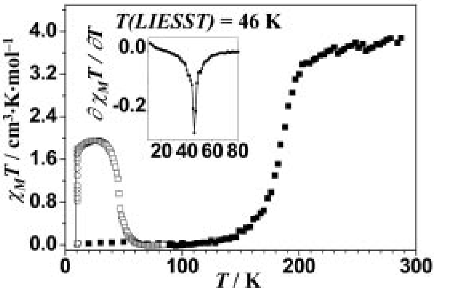

Figure 1. Top left: schematic view of ligand tppb; top right: optimized structure[8] of complex $[Fe(tppb)Br_2]_n$; bottow: molar magnetic susceptibility χ_M vs. temperature *T* before (filled squares), during (unfilled circles) and after (unfilled squares) light irradiation

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Mössbauer spectroscopy, and heat capacity experiments. Photomagnetic investigations are also reported.

Results and Discussion

Complex $[Fe(tppb)Br_2]_n$ was obtained by mixing equimolar amounts of $FeBr_2$ and tppb in a mixture of chloroform and absolute ethanol (see Exp. Sect.). The elemental analysis (C, H, Cl and Fe) was consistent with the expected composition of a polymeric structure. Crystallization was attempted several times by slow diffusion of solutions of $FeBr_2$ and tppb in ethanol into an H-shaped double-tube glass. An amorphous powder was always obtained, certainly due to the expected low solubility of the polymeric structure. Figure 1 shows a polymeric model built up with the CERIUS 4.0 program.[8] Energy minimization suggests at first a linear organization of the iron(II) atoms along the polymeric chain, with Fe−P bond lengths of 2.5 Å, which are within the 2.3−2.6 Å range reported for $[Fe(dppen)_2Br_2]\cdot 2CHCl_3$ by X-ray diffraction.[4] It also shows that the Fe−Fe distance along the polymer chain is 9 Å, which is longer than that in iron(II)−triazole polymers (3.6 Å[9,10]) since the bridging phosphorus atoms are kept apart by the rigid phenylene structure.

The magnetic properties of $[Fe(tppb)Br_2]_n$ are presented in Figure 1. The value of the molar magnetic susceptibility product with temperature ($\chi_M T$) varies from 3.8 $cm^3\cdot K\cdot mol^{-1}$ at room temperature to nearly 0 $cm^3\cdot K\cdot mol^{-1}$ at 80 K. The room-temperature value is consistent with a high-spin Fe^{II} complex with a $^5T_2$ quintet (assuming octahedral symmetry) ground state. At low temperature, the $\chi_M T$ value corresponds to a low-spin Fe^{II} complex with a $^1A_1$ singlet ground state. The $\chi_M T$ curves recorded in the cooling and warming modes are identical, and no hysteresis is detected. The temperature at which there are equal amounts of HS and LS complexes $T_{1/2}$ is 184 K.

Figure 2 displays the Mössbauer spectra recorded at temperatures of 293 K, 180 K and 80 K. This series of data confirms the occurrence of a temperature-controlled singlet/quintet equilibrium with complete conversion. The single doublet recorded at room temperature is typical of iron(II) in the HS (S = 2) ground state with a quadrupole splitting of $\Delta E_Q = 2.773 \pm 0.007$ $mm\cdot s^{-1}$ and an isomer shift of $\delta = 0.663 \pm 0.004$ $mm\cdot s^{-1}$ relative to natural iron (-0.13 $mm\cdot s^{-1}$). In contrast, at 80 K, the unique doublet found with $\Delta E_Q = 0.740 \pm 0.002$ $mm\cdot s^{-1}$ and $\delta = 0.396 \pm 0.001$ $mm\cdot s^{-1}$ is typical of iron(II) in the LS (S = 0) ground state. At an intermediate temperature (180 K), the inner and outer doublets are observed, as expected. This thermal spin transition was also investigated by DSC techniques. The temperature dependence of the molar heat capacity C_p in the cooling and warming modes was examined in the 120−290 K temperature range. The enthalpy variation associated with the spin transition is $\Delta H = 5.6$ $kJ\cdot mol^{-1}$, and the entropy change is $\Delta S = 31$ $J\cdot mol^{-1}.K^{-1}$. The value for ΔS is smaller than those obtained in strongly cooperative compounds (50−80 $J\cdot mol^{-1}\cdot K^{-1}$)[11]. Since it is very close to the electronic-only value (ΔS_{el}) of 13.4 $J\cdot mol^{-1}$ K^{-1},[1] the weakness of the vibrational component ΔS_{vib} supports the poorly cooperative behavior of $[Fe(tppb)Br_2]_n$.

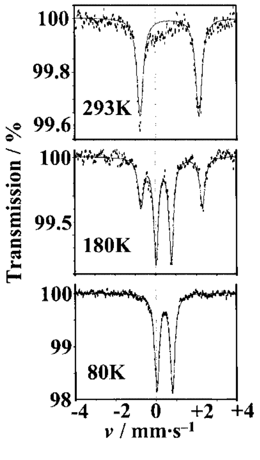

Figure 2. ^{57}Fe Mössbauer spectra for a powder sample of complex **2**; an HS doublet is observed at 293 K, whereas cooling the sample to 80 K gives an LS doublet; at 180 K, both doublets are present with 37% of the HS state

Photomagnetic properties were investigated by irradiating the sample in a SQUID cavity coupled to a Krypton Laser through an optical fiber. The compound was first slowly cooled in the dark from room temperature to 10 K, then irradiated for 1 h. The magnetic response was found to increase rapidly until a value of about 1.8 $cm^3\cdot K\cdot mol^{-1}$ was reached (Figure 1). This indicates a partial conversion (50%) of the LS state into the metastable HS state according to the Light-Induced Excited-Spin-State Trapping (LIESST) process.[12] To increase the level of photoexcitation different experiments were performed: an increase in the irradiation time, an increase in the power (up to 30 $mW\cdot cm^{-2}$), and/or a change in the excitation wavelength (488.0−514.5 nm, 647.1−676.4 nm, 752.5−799.3 nm). Unfortunately, the highest photoinduced LS → HS conversion rate remained at around 50%. The light irradiation was then switched off and the critical LIESST temperature value *T(LIESST)* was recorded.[13] In fact, we recently proposed that the capacity of a compound to retain the light-induced HS information may be estimated through the determination of the *T(LIESST)* value.[14] With this procedure, $\chi_M T$ was found to remain constant at low temperature (tunneling domain) and to drop within a few Kelvin when the thermally activated region was reached. The value of *T(LIESST)*, determined as the minimum of the derivative $\partial\chi_M T/\partial T$, was estimated as 46 K (Figure 1). Such a value, in comparison to the other iron(II) spin-crossover complexes from our database,[14] is unfortunately not exceptional. A study of the kinetics in the vicinity of *T(LIESST)* showed that the relaxation curves strongly deviate from single exponentials, with a fast initial decay and a long tail with a much slower decay, typical of a relaxation following a stretched exponential law. This behavior has, in fact, been reported in many other noncooperative spin-crossover complexes and has been attributed to a distribution of activation energies due to some local inhomogeneity of the iron(II) surroundings.[15] In our case, this finding is in good agreement with the gradual character of the thermal spin transition and proves once more the absence of significant cooperativity in the $[Fe(tppb)Br_2]_n$ polymer, certainly because of the long Fe−Fe distances along the chain.

Conclusion

In this work, we have reported the heat- and light-induced spin-crossover properties of a new iron(II) polymeric complex based on a tetraphosphane. This polymer represents an important step towards the design of polynuclear systems combining magnetic interaction and spin conversion under light irradiation. Moreover, it is also a new example of a spin-crossover material involving phosphorus atoms. Synthetic efforts are currently under way to investigate the properties of other complexes based on di- and tetraphosphane ligands.

Experimental Section

General Remarks: All reactions and manipulations were carried out under dry nitrogen. Magnetic susceptibility measurements were carried out by using a MPMS-55 Quantum Design SQUID magnetometer operating at approximately 2 Tesla in the 2−300 K temperature range. Irradiation in the SQUID cavity was done with a 530.9 nm wavelength krypton laser, and the power on the sample was adjusted to 5 $mW\cdot cm^{-2}$. Bulk attenuation of light intensity was limited by the preparation of a thin layer of the compound. Its weight was obtained by comparing its thermal spin-crossover curve with the curve recorded with a heavier sample of the same compound. The heat capacities were measured with a Perkin−Elmer DSC-7 calorimeter, and the cell was cooled to the velocity of 2 $K\cdot min^{-1}$. Elemental analyses were performed by the Service Central d'Analyse (CNRS) in Vernaison, France.

1,2,3,4-Tetrakis(diphenylphosphanyl)benzene: The synthesis of tppb[16] was modified as follows. Ph_2PNa was obtained starting from Ph_2PCl (6 mL, 32 mmol) in THF (50 mL) and Na (1.5 g, 65.2 mmol) while monitoring by ^{31}P NMR spectroscopy. After 10 h at room temperature, the excess sodium was removed and 1,2,4,5-tetrafluorobenzene (0.71 mL, 6.4 mmol) was added. After 1 h at 70 °C and one night at room temperature, ^{31}P NMR spectroscopic data showed completion of the reaction. A few drops of MeOH were then added, the solvent was removed, and the solid extracted with dichloromethane and water. The organic layer was dried with $MgSO_4$, filtered and concentrated. Recrystallization at −18 °C with the addition of a minimum amount of methanol yielded 2.5 g (47%) of the white product, identified by NMR spectroscopy as tppb.[16]

$\{[Fe(tppb)Br_2]\cdot 0.16CHCl_3\}_n$: The complex was prepared from a solution of tppb (0.1 g, 0.12 mmol) in $CHCl_3$ (20 mL), which was slowly added to a solution of $FeBr_2$ (0.026 g, 0.12 mmol) in warm (45 °C) absolute ethanol (10 mL) in the presence of a few crystals of ascorbic acid (to prevent oxidation of Fe^{II} to Fe^{III}). Upon addition of the ligand, the reaction mixture changed immediately from an orange color to a cloudy mixture, which yielded a yellow precipitate. The powder was then filtered off, washed with a few milliliters of absolute ethanol, and dried under a stream of nitrogen (yield 106 mg, 84%). $C_{54.16}H_{42.16}Br_2Cl_{0.48}FeP_4$ (1049.56): calcd. C 61.98, H 4.05, Cl 1.62, Fe 5.32; found C 61.86, H 4.11, Cl 1.55, Fe 4.93.

Acknowledgments

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[1] P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024−2054; *Angew. Chem.* **1994**, *106*, 2109−2141.

[2] A. Hauser, A. Vef, P. Adler, *J. Chem. Phys.* **1991**, *95*, 8710−8717.

[3] W. Levason, C. McAuliffe, M. Mahfooz Khan, S. M. Nelson, *J. Chem. Soc., Dalton Trans.* **1975**, 1778−1783.

[4] F. Cecconi, M. Di Vaira, S. Midollini, A. Orlandini, L. Sacconi, *Inorg. Chem.* **1981**, *20*, 3423−3430.

[5] E. König, G. Ritter, S. K. Kulshreshtha, J. Waigel, L. Sacconi, *Inorg. Chem.* **1984**, *23*, 1241−1246.

[6] E. König, G. Ritter, S. K. Kulshreshtha, J. Waigel, L. Sacconi, *Inorg. Chem.* **1989**, *28*, 1380−1384.

[7] C.-C. Wu, J. Jürgen, P. K. Gantzel, P. Gütlich, D. N. Hendrickson, *Inorg. Chem.* **1997**, *36*, 5339−5347.

[8] Cerius^2 Molecular Mechanics, Month **1997**. San Diego: Molecular Simulations Inc. **1997**. Energy minimization was done by molecular mechanics technique using the universal force field (UFF), see: A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard, W. M. Skiff, *J. Am. Chem. Soc.* **1992**, *114*, 10024−10035.

[9] A. Michalowicz, J. Moscovici, B. Ducourant, D. Cracco, O. Kahn, *Chem. Mater.* **1995**, *7*, 1833−1842.

[10] M. Verelst, L. Sommier, P. Lecante, A. Mosset, O. Kahn, *Chem. Mater.* **1998**, *10*, 980−985.

[11] P. Gütlich, Y. Garcia, H. A. Goodwin, *Chem. Soc. Rev.* **2000**, *29*, 419−427.

[12] A. Hauser, *Chem. Phys. Lett.* **1986**, *124*, 543−548.

[13] At 10 K, after one hour of photoexcitation, the light irradiation was turned off and the temperature was slowly increased at the rate of 0.3 $K\cdot min^{-1}$, see: J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard, J.-A. Real, O. Kahn, *Chem. Phys. Lett.* **1999**, *313*, 115−120.

[14] S. Marcén, L. Lecren, L. Capes, H. A. Goodwin, J.-F. Létard, *Chem. Phys. Lett.* **2002**, *358*, 87−95.

[15] A. Hauser, J. Adler, P. Gütlich, *Chem. Phys. Lett.* **1988**, *152*, 468−472.

[16] H. Christina, E. McFarlane, W. McForlane, *Polyhedron* **1988**, *7*, 1875−1879.

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