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Pressure Effect Investigations on the Spin Crossover Systems $\{Fe[H_2B(pz)_2]_2(bipy)\}$ and $\{Fe[H_2B(pz)_2]_2(phen)\}$

Ana Galet,[b] Ana Belén Gaspar,[a] Gloria Agusti,[a] M. Carmen Muñoz,[b]
Georgii Levchenko,[c] and José Antonio Real*[a]

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Pressure effect studies on the spin crossover behaviour of the mononuclear compounds $\{Fe[H_2B(pz)_2]_2(bipy)\}$(**1**) and $\{Fe[H_2B(pz)_2]_2(phen)\}$(**2**) have been performed in the range of 10^5 Pa–1.02 GPa at variable temperatures (100–310 K). Continuous spin transitions and displacement of its characteristic temperature has been observed for **1** with increasing pressure. Meanwhile the response of **2** under applied pressures is quite unexpected, and can only be understood in terms of a crystallographic phase transition or change in the bulk modulus of the compound.

Introduction

The ability of spin crossover (SCO) materials to change their magnetic, structural, dielectric and optical properties, induced by a variation of temperature and/or pressure or light, has led to an increase in the interest of their potential use in technological applications. Because of their switching properties, SCO materials are potentially useful for rewritable optical, thermal or pressure memories at a nanometric scale.[1–6]

While thermally induced spin crossover behaviour in Fe^{II} complexes is increasingly common, pressure induce high and low spin (HS and LS) Fe^{II} complexes are scarcely reported in the literature. Systematic and detailed studies related to the concerted action of both temperature and pressure variation on SCO compounds have only recently become possible with the development of special hydrostatic pressure cells in connection with magnetic susceptibility, optical and Mössbauer measurements, EXAFS and vibrational spectroscopy.[7–8] Here we present pressure effect investigations on the magnetic behaviour of $\{Fe[H_2B(pz)_2]_2(bipy)\}$(**1**) and $\{Fe[H_2B(pz)_2]_2(phen)\}$ (**2**) complexes carried out in the range of 10^5 Pa–1.2 GPa.

Both **1** and **2** undergo thermal- and light-induced SCO.[9] The thermal spin transition of **2** is more cooperative than that of **1**, as shown by the more abrupt spin transition that takes place with hysteresis (with characteristic temperatures of $T_c\downarrow$ = 165 K and $T_c\uparrow$ = 169 K). Structural data has been previously reported for both the HS and LS states.[10] As illustrated in Figure 1, the structures of **1** and **2** are composed of mononuclear neutral species where the positive charge of the iron(II) ion is neutralized by the coordination of two bidentate dihydrobis(pyrazolyl)borate $[H_2B(pz)_2]^-$ anions; bipy or phen neutral ligands are then used to fill the iron(II) coordination sphere. The molecular structures for both compounds are very similar with Fe–N bond lengths in the 2.212–2.158 Å and 2.007–1.996 Å range for the HS and LS states, respectively. Contrary to **1**, the spin transition of **2** is accompanied by a crystallographic phase transition [$C2/c$ (HS) and $P\bar{1}$(LS)].[10]

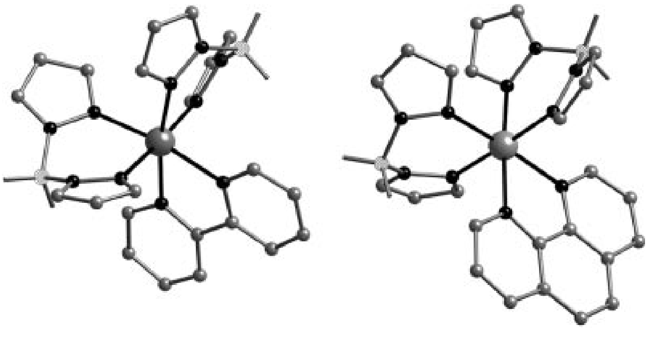

Figure 1. Molecular structure of **1** (left) and **2** (right).

Results and Discussion

Figure 2 gathers a collection of $\chi_M T$ versus T curves (χ_M is the molar magnetic susceptibility, and T the temperature) at different hydrostatic pressures for complex **1**. The measurements have been performed at the rate of 1 K·min^{-1} on single-microcrystals. At 300 K and 10^5 Pa, a $\chi_M T$ value of 3.52 cm^3·K·mol^{-1} indicates a S = 2 spin state configuration

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[a] Institut de Ciència Molecular/Departament de Química Inorgànica, Universitat de València, Edifici de Instituts de Paterna, Apartat de Correus 22085, 46071 València, Spain
[b] Departament de Física Aplicada, Universitat Politécnica de València,
Camí de Vera s/n, 46022, València, Spain
[c] Donetsk Physico-Thechnical Institute, NAS of Ukraine, R. Luxemburg 72, 83114 Donetsk, Ukraine

for the iron(II) ions. $\chi_M T$ remains constant down to 220 K, where it progressively diminishes as a consequence of the spin transition to the S = 0 spin state and attains a value of 0.06 $cm^3 \cdot K \cdot mol^{-1}$ at 100 K. The transition is complete and relatively abrupt. The temperature at which the number of molecules in the HS and LS states is equal, $T_{1/2}$, is 160 K. Application of pressures as high as 0.26 GPa have a strong effect on the $T_{1/2}$ value and shifts it upwards to 210 K. At this pressure, the $\chi_M T$ value at 300 K is slightly lower than that observed at atmospheric pressure which indicates that a small amount of molecules are in the LS state (300 K: 3.42 $cm^3 \cdot K \cdot mol^{-1}$, 97% HS molecules). An increase in the pressure up to 0.4 and 0.5 Gpa results in a displacement of $T_{1/2}$ to 233 K and 255 K, respectively. At room temperature, the $\chi_M T$ value at these two last pressures also decreases to 3.23 $cm^3 \cdot K \cdot mol^{-1}$ and 3.12 $cm^3 \cdot K \cdot mol^{-1}$, respectively.

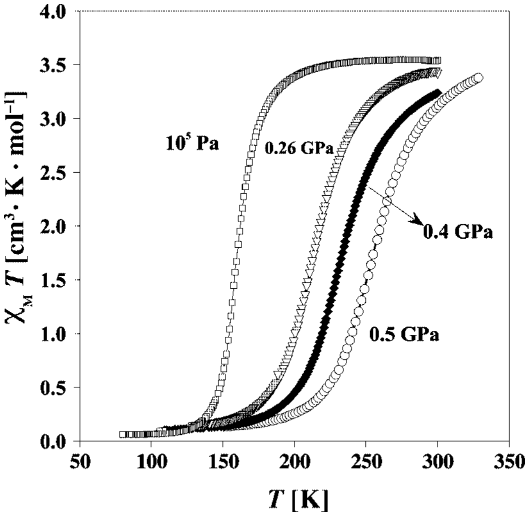

Figure 2. Thermal dependence of $\chi_M T$ at different pressures for **1**.

It is worth mentioning the remarkable continuous character of the spin transition as pressure is increased. The spin crossover takes place in temperature intervals of 150 K, whereas at 10^5 Pa the spin crossover occurs within 70 K. Also, the linear pressure dependence of $T_{1/2}$ for **1** should be noted. The slope of the line in the $T_{1/2}$ versus P plot, $dT_{1/2}/dP$ = 187.5 $K \cdot GPa^{-1}$ (Figure 4), is in the range of values observed for several mononuclear compounds such as $[Fe(abpt)_2(NCS)_2]$ polymorph B,[11] $[Fe(phen)_2(NCS)_2]$ polymorph II,[12] $[Fe(dpa)_2(NCS)_2]$[13] and $[Fe(pic)_3]Cl_2 \cdot EtOH$[14] (Table 1).

Table 1. $dT_{1/2}/dP$ in $K \cdot GPa^{-1}$.

$[Fe(abpt)_2(NCS)_2]$	176
$[Fe(phen)_2(NCS)_2]$ polymorph II	220
$[Fe(dpa)_2(NCS)_2]$	187.5
$[Fe(pic)_3]Cl_2 \cdot EtOH$	150

Figure 3 shows the thermal dependence of **2** for $\chi_M T$ at different pressures. As for **1**, the measurements have been performed on single-microcrystals in the cooling and warming modes at a rate of 1 $K \cdot min^{-1}$. At 300 K and atmospheric pressure, the $\chi_M T$ value is 3.60 $cm^3 \cdot K \cdot mol^{-1}$, which indicates a HS configuration of the iron(II) ions. This value remains virtually constant up to the point of the spin transition, which takes place abruptly at $T_c\downarrow$ = 165 K and $T_c\uparrow$ = 169 K. The application of a hydrostatic pressure of 0.19 GPa dramatically influences the spin crossover behaviour of **2** particularly in the width of the hysteresis loop. Indeed, ΔT_c is equal to 20 K. Meanwhile, at atmospheric pressure ΔT_c is only 4 K. At 0.19 GPa, the critical temperature for the cooling mode is $T_c\downarrow$ = 169 K and for the warming mode it is $T_c\uparrow$ = 189 K. Another remarkable fact is the decrease in the abruptness of the spin transition in the cooling mode. This is in contrast to the transition in the warming mode, which remains steep. A further increase in the pressure up to 0.33 GPa results in a considerable shift of the spin transition to higher temperatures, $T_c\downarrow$ = 238 K and $T_c\uparrow$ = 240 K, with the hysteresis width being very narrow. A complete transformation to a second order phase transition occurs at 0.55 GPa, where $T_{1/2}$ is approximately 270 K. At 1.02 GPa, almost all of the molecules are in the LS state at room temperature. Reversibility of these measurements was checked after a complete relaxation of the pressure because the magnetic behaviour of **2** at 10^5 Pa was perfectly reproducible. Moreover, the magnetic behaviour of **2** in the range of 10^5 Pa–1.02 GPa was investigated in two independent experiments, and the exact same results were obtained.

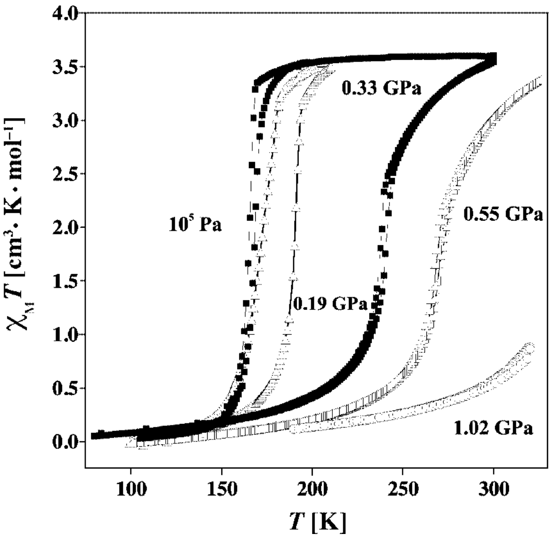

Figure 3. Thermal dependence of $\chi_M T$ at different pressures for **2**.

Figure 4 displays the pressure dependence of the average T_c^{av} values calculated as $T_c^{av} = (T_c^{down} + T_c^{up})/2$ for **2**. As it can be seen, there is a strong nonlinearity in the case of compound **2** that contrasts the almost linear dependence observed for **1**. This is an unexpected result in view of the fact that the mean field theory of phase transitions in SCO compounds predicts a decrease in the hysteresis width and in the slope of the transition curve with an increase in the pressure. The hysteresis vanishes at a critical pressure, and at even higher pressures the transition transforms into a second order continuous phase transition.[7,8,15] However, there are several SCO systems in which the effect of pressure on the SCO behaviour cannot be adequately described by this theory. Occurrence of structural phase transitions and/or a change in the bulk modulus of the materials under the applied pressure has been proposed for the observed anomalous behaviour (e.g. increase in the hysteresis width, nonlinear behaviour of $T_c(P)$ versus P).[5,7,8,16]

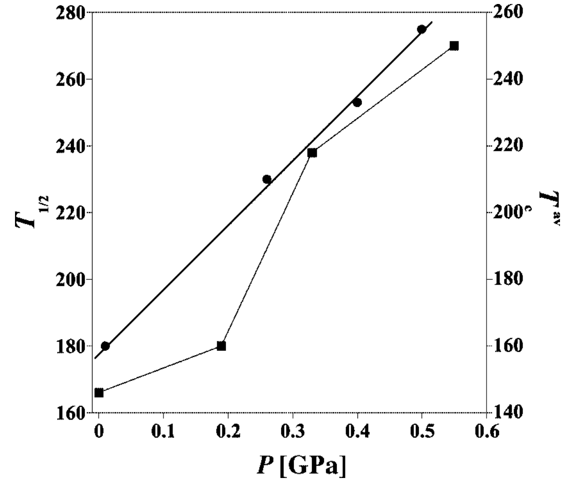

Figure 4. $T_{1/2}$ versus P plots for **1** (filled circles) and T_{av} versus P plot for **2** (filled squares). The straight line corresponds to the linear fit for **1**.

As mentioned above, the crystallographic phase transition that involves the space group change $C2/c$ (HS) ↔ $P\bar{1}$(LS) takes place concomitantly with the thermally induced HS ↔ LS spin transition in **2**. The response of **2** under the applied pressures increases the hysteresis width at 0.19 GPa, and the nonlinear behaviour of $T_{1/2}$ versus P could be due to the occurrence of a crystallographic phase transition under these applied pressures. The unexpected pressure effects will be understood from the crystal structure determination under applied pressure and, of course, at variable temperature.

Experimental Section

Synthesis of 1 and 2: Single-crystals of both compounds were obtained as discussed previously in the literature.[9]

Magnetic Susceptibility Measurements Under Hydrostatic Pressure: The variable-temperature magnetic susceptibility measurements were performed on small single-crystals with a Quantum Design MPMS2 SQUID susceptometer equipped with a 5.5 T magnet and operated at 1 T and 1.8–375 K. The hydrostatic pressure cell was made of hardened beryllium bronze with silicon oil as the pressure-transmitting medium, and was operated in the pressures range 10^5 Pa–1.2 GPa (accuracy $\approx \pm 0.025$ GPa). Cylindrically shaped powder sample holders with dimensions of 1 mm in diameter and 5–7 mm in length were used. The pressure dependence of the superconducting transition temperature of the built-in pressure sensor, which is made of high purity tin, was used to measure the pressure.[17] Experimental data were corrected for diamagnetism with Pascal's constants.

Acknowledgments

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