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Pressure effect on a novel spin transition polymeric chain compound

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$[Fe(hyptrz)_3]A_2{\cdot}H_2O$ (hyptrz = 4-(3′-hydroxypropyl)-1,2,4-triazole and A = 4-chlorobenzenesulfonate) represents a novel iron(II) polymeric chain compound. A discontinuous spin transition has been observed by temperature dependent magnetic susceptibility measurements. The spin transition curves are shifted from 181 K to 324 K as the pressure varies from 1 bar to 5.9 kbar. The shapes of these curves are not strongly modified, and this is interpreted as being due to effective cooperative interactions along the chain. This behaviour under pressure can be extended to the family of iron(II)-1,2,4-triazole polymeric chain spin crossover materials.

1 Introduction

Iron(II) spin transition (ST) materials are probably among the most fascinating objects of transition metal chemistry. Their spin state can be changed by several external perturbations such as temperature, pressure and light, from high-spin (HS, $S=2$) to low-spin (LS, $S=0$).[1] Spin transitions ranging from gradual to abrupt but occurring without hysteresis have been classified as continuous, and those with hysteresis as discontinuous.[1] Intensive research efforts have been carried out on one-dimensional polymeric iron(II) ST compounds containing 4-substituted derivatives of 1,2,4-triazole as ligands.[2–10] The structure of these materials was deduced by EXAFS spectroscopy[11] and later confirmed by X-ray single crystal analysis of a copper(II) analogue.[12] The structure comprises chains in which the neighbouring iron(II) ions are triply bridged by 4-substituted-1,2,4-triazole ligands through the nitrogen atoms occupying the 1- and 2- positions. The non-coordinated anions and the eventual solvent molecules are located between the chains.[9] The linear character of these chains has recently been demonstrated in the LS and in the HS state by EXAFS spectroscopy.[13] These materials exhibit discontinuous ST together with a pronounced thermochromic effect, characteristics which suit a potential application in display or memory devices.[2,3,6,9,14] As there is no indication of a crystallographic phase transition accompanying the ST of these materials,[11] the hysteresis loops can be attributed to strong cooperative effects. In the course of our exploration of these materials, we synthesised the compound $[Fe(hyptrz)_3]A_2{\cdot}H_2O$ with hyptrz = 4-(3′-hydroxypropyl)-1,2,4-triazole and A = 4-chlorobenzenesulfonate (see Chart 1) and this paper is devoted to an investigation of its ST features.

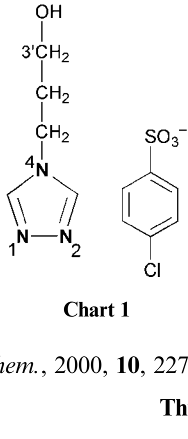

Chart 1

2 Experimental

The ligand hyptrz was synthesised from monoformyl hydrazine, triethylorthoformate and 3-aminopropan-1-ol according to the method of Bayer[15] and obtained as a white solid. Anal. Calcd for $C_5H_9N_3O$: C, 47.23; H, 7.13; N, 33.05; O, 12.58. Found: C, 46.57; H, 7.22; N, 32.71; O, 13.47%. Yield: 41%. Mp: 77 °C. ^1H NMR (200 MHz) (D_2O): 1.97 (t, CH_2), 3.51 (t, CH_2), 4.16 (t, CH_2), 8.44 (s, trz-H). $[Fe(hyptrz)_3]$(4-chlorobenzenesulfonate)$_2{\cdot}H_2O$ was prepared according to a similar procedure for a relative compound[9] and was obtained as a white solid. Anal. Calcd. for $C_{27}H_{37}N_9O_{10}S_2Cl_2Fe$: C, 38.68; H, 4.45; N, 15.03; S, 7.65; Fe, 6.66. Found: C, 38.58; H, 4.43; N, 14.75; S, 6.29; Fe, 6.67%. Yield: 65%. The presence of one water molecule per iron(II) ion was confirmed by TGA analysis.

Magnetic measurements were carried out over the temperature range 4.2–340 K with a PAR 151 Foner type magnetometer. The hydrostatic high pressure cell with silicon oil as the pressure transmitting medium has been described elsewhere[16] and the hydrostaticity has been established in our earlier studies.[9,17–19] The pressure was measured using the known pressure dependence of a superconducting transition of an inner tin manometer. The data were corrected for the magnetisation of the sample holder and for diamagnetic contributions. With the assumption of a Curie law behaviour for the HS state and a temperature independent susceptibility for the LS state, the HS fraction γ_{HS} may be calculated from the experimentally determined susceptibilities. For the DSC experiments, a Perkin-Elmer DSC 7 instrument working down to 100 K was used. The velocities of heating and cooling were fixed at 2 K min^{-1}. Details of the experimental procedure are described elsewhere.[20]

3 Results

3.1 Magnetic measurements

The temperature dependence of the $\chi_M T$ product (χ_M is the molar magnetic susceptibility corrected for diamagnetic contributions) was measured over the temperature range 4.2–293 K. At room temperature, $\chi_M T$ is equal to 3.60 cm^3 K mol^{-1} which coincides with the expected value for a HS iron(II) ion. $\chi_M T$ is found to decrease gradually down to 190 K and then decreases very rapidly. At 9 K, $\chi_M T$ is equal to 0.15 cm^3 K mol^{-1}, and indicates that iron(II) ions are in the LS state. As the temperature is increased, the same behaviour is observed, with a thermal hysteresis width of 5 K. The transition temperatures are: $T_{1/2}\downarrow = 178$ K and $T_{1/2}\uparrow = 183$ K.

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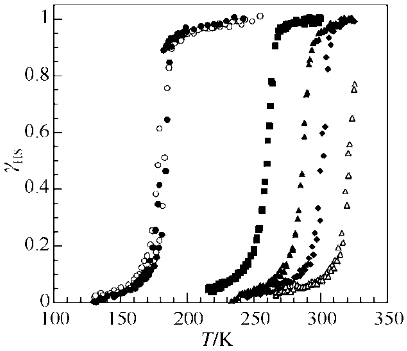

Fig. 1 γ_{HS} as a function of temperature for [Fe(hyptrz)$_3$](4-chlorobenzenesulfonate)$_2$·H_2O over the temperature range 100–350 K, and at different pressures. (●, P = 1 bar; ■, P = 4.1 kbar; ▲, P = 5 kbar; ◆, P = 5.3 kbar; △, P = 5.9 kbar; ○, P = 1 bar after releasing the pressure).

The temperature dependence of the magnetic properties was also investigated under pressure up to nearly 6 kbar. The results are shown in Fig. 1 in the form of the HS molar fraction γ_{HS} as a function of temperature. A shift towards higher temperatures is observed as the pressure increases. The profiles of the curves remain essentially unchanged with the steepness retained at all pressures. However the hysteresis width reveals a non-monotonic character, it first diminishes and is no longer observed at 4.1 kbar, before reappearing at a constant value of 6 K above 5 kbar. The ST was observed at 260 K under 4.1 kbar, at 286 K under 5 kbar, 301 K under 5.3 kbar, and at 324 K under 5.9 kbar. It should be mentioned that for all pressures investigated, the ST curves were not altered by thermal cycling. On releasing the pressure, the same magnetic behaviour as observed at 1 bar was obtained. Fig. 2 shows the pressure dependence of the LS molar fraction at 290 K. From 1 bar up to 4 kbar, no change is observed, whereas above 4 kbar, a dramatic increase of the LS fraction is noticed indicating a HS→LS transition. At 6 kbar, the material is mainly in the LS state, with ~6% of the molecules remaining in the HS state.

3.2 Calorimetric measurements

The temperature dependence of the differential scanning calorimeter (DSC) response below room temperature in the heating mode is shown in Fig. 3. The DSC curve shows an endothermic peak around 185 K, in good agreement with the transition temperature observed for the magnetic measurements at ambient pressure. The enthalpy and entropy variations were determined as $\Delta H = 5.95\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = 32.2\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The experimentally measured entropy variation accounts for an electronic contribution, $R\ln5 = 13.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$, and a vibrational contribution.[1]

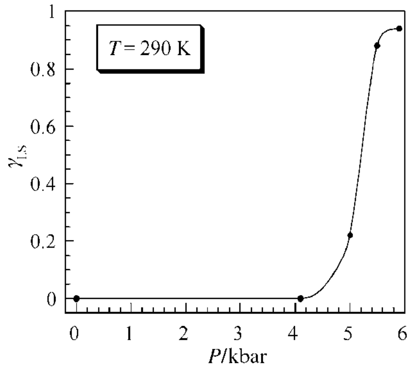

Fig. 2 Pressure dependence of the LS fraction for [Fe(hyptrz)$_3$](4-chlorobenzenesulfonate)$_2$·H_2O at room temperature.

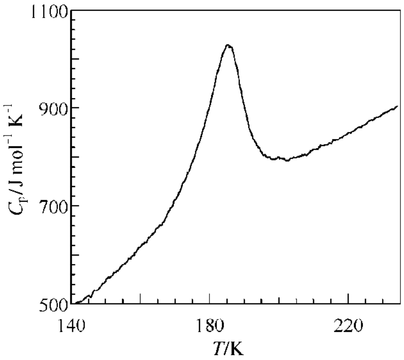

Fig. 3 DSC curve for [Fe(hyptrz)$_3$](4-chlorobenzenesulfonate)$_2$·H_2O below room temperature.

4 Discussion and conclusions

The present material reveals a discontinuous ST with a small thermal hysteresis width of 5 K, which is an uncommon feature for an iron(II)-1,2,4-triazole chain compound, with the hysteresis width being typically around 10 K.[5–9] Its thermodynamic parameters confirm the weak cooperative character of the spin transition. The entropy variation is less than one half of the values found for the cooperative ST chain compounds [Fe(NH$_2$trz)$_3$](CH$_3$SO$_3$)$_2$·H_2O, 60 J mol^{-1} K^{-1} and [Fe(NH$_2$trz)$_3$](NO$_3$)$_2$, 66 J mol^{-1} K^{-1} where NH$_2$trz stands for 4-amino-1,2,4-triazole.[21,22]

The pressure experiments were carried out in order to gain insight into the origin of the cooperative behaviour developed by [Fe(hyptrz)$_3$](4-chlorobenzenesulfonate)$_2$·H_2O. Upon applying pressure, the position of the curves is shifted to higher temperatures, as a result of the increased stability of the LS state compared with the smaller volume for the LS iron(II) ion. However, the sharpness of the transition is not strongly modified. This behaviour does not correspond to what is generally observed for mononuclear compounds which exhibit a discontinuous spin transition. In this case, a flattening of the ST curves together with a variation in the hysteresis width with increasing pressure is observed.[17,23]

Thus, application of pressure does not appear to increase the cooperativity of [Fe(hyptrz)$_3$](4-chlorobenzenesulfonate)$_2$·H_2O. Assuming that pressure, as a consequence of the one-dimensional character of the material, has little effect along the chain direction, this supports the idea that the hysteresis originates from intrachain interactions. The cooperativity of this material may therefore be attributed primarily to short range interactions which result from the presence of triazole molecules which link the Fe(II) centres, allowing the effective propagation of the molecular distortions involved in the spin transition. This is in contrast with [Fe(Htrz)trz](BF$_4$) (Htrz = 4*H*-1,2,4-triazole and trz = 1,2,4-triazolato), for which long range interactions arising from interaction between infinite chains, are mainly responsible for the significant hysteresis observed (~50 K).[2] These assumptions for [Fe(hyptrz)$_3$](4-chlorobenzenesulfonate)$_2$·H_2O should be checked by applying a recent model developed for linear chain compounds.[24]

It is of interest to note that at room temperature, the application of pressure on the present compound up to nearly 6 kbar provokes an abrupt HS→LS transition. This transition is associated with a dramatic colour change from white in the HS state to violet in the LS state, making this material potentially suitable for an application such as a pressure sensor or display.

In the present work, the application of pressure was of particular interest in the sense that the behaviour of the ST curves under pressure allowed us to conclude that the cooperativity of this material, stems from intrachain interactions. The conservation of the shape of the ST curves under pressure was also observed on another iron(II) ST polymeric chain compound, $[Fe(hyetrz)_3](3\text{-nitrobenzenesulfonate})_2$ (hyetrz = 4-(2'-hydroxyethyl)-1,2,4-triazole).[6] In this case, an unprecedented shift of the transition curves on the whole temperature range was observed. In addition, the hysteresis width was retained independent of the pressure in the range of 1 bar–8.9 kbar.[9] The same behaviour was observed for the ST chain compounds $[Fe(NH_2trz)_3](CH_3SO_3)_{2-2x}(CF_3SO_3)_{2x}$ but in this case as a consequence of an internal pressure[8] induced by the variation of the position and the nature of the non-coordinated anions in the lattice.[25] This behaviour under pressure seems to be typical for this class of materials.

Acknowledgements

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