Pressure-induced spin-state crossovers at room temperature in iron(II) complexes: comparative analysis; a XANES investigation of some new transitions†

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An attempt to rationalize the behaviour of iron(II) spin-crossover compounds under hydrostatic pressure at room temperature from a comparative analysis of data is reported. The selected pressure-induced spin transitions are those previously described for $Fe(phen)_2(NCS)_2$ [polymorphs I (**a**) and II (**b**)], $Fe(py)_2bpym(NCS)_2$ (**c**) and $Fe(py)_2phen(NCS)_2$ (**d**), and those presented herein for $Fe(Me_2bpy)_2(NCS)_2$ (**1**), $[Fe(2\text{-pic})_3]Cl_2{\cdot}EtOH$ (**2**), $[Fe(2\text{-pic})_3]Cl_2{\cdot}H_2O$ (**3**) and $[Fe(btr)_2(NCS)_2]{\cdot}H_2O$ (**4**) [Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine, 2-pic = 2-(aminomethyl)pyridine, btr = 4,4′-bis-1,2,4-triazole]. All these transitions have been investigated by XANES spectrometry. In this paper, the spectra of compounds **1**–**4** and the resulting n_{LS} *vs.* P plots (n_{LS} = low-spin fraction) are discussed. Transition pressures, $P_{1/2}$, are found to be 0.30 (**1**), 1.32 (**2**), 0.60 (**3**) and 2.04 (**4**) GPa. For compounds **1**, **a**, **b**, **c**, with closely related formulas, $P_{1/2}$ is found to vary quasi-linearly with the transition temperature at atmospheric pressure, $T_{1/2}$, and deviations from linearity are discussed in terms of the variations in entropy and lattice volume associated with the spin change. For compounds **2**, **3** and **d**, the values of $P_{1/2}$ markedly depart from the above trend. This is ascribed either to the change in ligand-field strength resulting from the effects of pressure on the hydrogen-bonding network (**2**, **3**) or the occurrence of a structural phase transition simultaneously with the spin conversion (**d**). In the polymeric two-dimensional compound **4**, pressure is shown to first induce a structural transition to a new high-spin phase, then to produce a very gradual high-spin-to-low-spin transformation of this phase, which results in a comparatively high value of $P_{1/2}$.

In certain transition metal complexes, so-called spin-crossover complexes, metal ions with electronic configurations $3d^4$ to $3d^7$ (and $3d^8$ in some particular cases) can exhibit a thermally induced interconversion between the high-spin (HS) state at higher temperatures and the low-spin (LS) state at lower temperatures.[1–6] As the transition is accompanied by changes in metal–ligand distances ($\Delta R_{HL} = R_{HS} - R_{LS} > 0$) and hence in crystal volume ($\Delta V_{HL} = V_{HS} - V_{LS} > 0$),[3,7] increasing pressure, at a given temperature at which the compound is at least partly in the HS state, is expected to favour the formation of the more compact spin isomer, that is, to trigger the HS-to-LS conversion.

Most of the earlier studies devoted to pressure-induced spin crossovers at constant temperature refer to iron(II)[8–10] and, less frequently, cobalt(II) complexes.[9,10] The aim of the present work is to draw some general inferences on the behaviour of iron(II) spin-crossover compounds under the influence of pressure at room temperature, by trying to rationalize this behaviour on the basis of a comparative analysis of data. Unfortunately, the pressure-induced spin transitions reported in the literature only relate to a small number of different complexes. Moreover, large discrepancies are often observed between the data referring to the same species, which is likely to result mainly from the non-hydrostaticity of the applied pressure in a number of experiments. Such discrepancies were already pointed out, in particular for the most frequently investigated compound, $Fe(phen)_2(NCS)_2$.[8] Therefore, in order to make the comparison of data more reliable, we decided to base our discussion on results obtained under identical conditions (same physical technique, experimental set-up and high-pressure cell), specifically, those we previously reported[8] for several well-documented mononuclear complexes with closely related formulae: $Fe(phen)_2(NCS)_2$ [polymorphs I (**a**) and II (**b**)], $Fe(py)_2bpym\ (NCS)_2$ (**c**) and $Fe(py)_2phen(NCS)_2$ (**d**) (phen = 1,10-phenanthroline, bpym = 2,2′-bipyrimidine, py = pyridine), and those presented in this paper for $Fe(Me_2bpy)_2(NCS)_2$ (**1**), $[Fe(2\text{-pic})_3]Cl_2{\cdot}EtOH$ (**2**), $[Fe(2\text{-pic})_3]Cl_2{\cdot}H_2O$ (**3**) and $[Fe(btr)_2(NCS)_2]{\cdot}H_2O$ (**4**) [Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine, 2-pic = 2-(aminomethyl)pyridine, btr = 4,4′-bis-1,2,4-triazole].

Like species **a**–**d**, compounds **1**–**4** are known to exhibit a thermo-induced spin transition and were chosen as a function of the goal of this work. The study of **1** was undertaken to enrich our earlier investigation on $Fe(L)_2(NCS)_2$ type complexes, this compound being particularly interesting on

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† Dedicated to the memory of Professor Olivier Kahn.

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account of its relatively high transition temperature under atmospheric pressure ($T_{1/2}$), in so far as correlation between the transition pressure at room temperature ($P_{1/2}$) and $T_{1/2}$ was sought. Compounds **2**, **3** and **4** were deliberately selected in order to specify the influence, on pressure-induced spin transitions, of two specific characteristics frequently encountered in spin-crossover compounds, namely the existence of a hydrogen-bonding network (in the three species) and the two-dimensional polymeric character of the structure (in **4**). It should be noted that our choice was also motivated by the fact that **2** and **4** are well-documented complexes. In particular, the crystal structures of the HS and LS forms of **2** and of the HS form of **4** are known. Room temperature pressure-induced spin crossovers were investigated by following the effects of increasing pressure on the near-edge structures of X-ray absorption (XANES) spectra.

Experimental

Syntheses

All syntheses were carried out under argon atmosphere, using previously deoxygenated and dried solvents.

Compound 1. The first stage to prepare this compound consisted in synthesizing the complex $[Fe(Me_2bpy)_3](NCS)_2$. For this purpose, a solution of $FeSO_4{\cdot}7H_2O$ (251.1 mg, 0.91 mmol) in absolute ethanol (20 mL) was gradually added to a solution of 4,4′-bipyridine (Aldrich, 504.5 mg, 2.74 mmol) in the same solvent (50 mL). The mixture was stirred at 70 °C for 1 h. After cooling, it was treated with an excess amount of a saturated aqueous solution of KNCS, then allowed to stand in a refrigerator for a few days. The purple microcrystalline precipitate that very slowly formed was collected by filtration, washed with water and dried under vacuum. The resulting microcrystals were dried for 4 h under vacuum at 85 °C. Removal of water was followed by infrared spectrometry. Compound **1** was then obtained by extracting one Me_2bpy ligand from this complex with acetone, for three weeks, in a Soxhlet apparatus. Anal. calcd. for $C_{26}H_{24}N_6S_2Fe$: C, 57.77; H, 4.48; N, 15.56; S, 11.84; Fe, 10.36; found: C, 57.62; H, 4.37; N, 15.47; S, 11.74; Fe, 10.25.

Compound 2. This compound was prepared as a yellow microcrystalline powder according to the procedure previously described.[11] Anal. calcd. for $C_{20}H_{30}N_6OCl_2Fe$: C, 48.31; H, 6.08; N, 16.90; Cl, 14.10; Fe, 11.27; found: C, 48.18; H, 6.02; N, 16.81; Cl, 14.97; Fe, 11.12.

Compound 3. **3** was obtained by partial dehydration of the complex $[Fe(2\text{-pic})_3]Cl_2{\cdot}2H_2O$, synthesized as reported elsewhere.[12] Removal of one H_2O was carried out by heating the solid at 60 °C for 48 h. The dark green microcrystalline powder thus obtained, very air sensitive, was further handled in a dry inert atmosphere. Anal. calcd. for $C_{18}H_{26}N_6OCl_2Fe$: C, 46.15; H, 5.60; N, 17.95; Cl, 14.94; found: C, 46.33; H, 5.22; N, 17.54; Cl, 15.52.

Compound 4. The syntheses of the btr ligand and compound **4** were performed using the methods described elsewhere.[13,14] The complex was isolated as large colourless crystals. Anal. calcd. for $C_{10}H_{10}N_{14}S_2OFe$: C, 25.97; H, 2.18; N, 42.43; S, 13.84; found: C, 26.33; H, 2.24; N, 42.05; S, 13.51.

XANES spectra recording and processing

Room temperature X-ray absorption experiments were carried out at the iron K-edge (7112 eV) on a dispersive mode EXAFS station at LURE (Paris-Sud University). Samples were examined under pressure in a Block-and-Piermarini diamond anvil cell.[9,15] Using silicon oil as the transmitting medium allowed hydrostatic pressures of up to ~5 GPa to be achieved. Pressure measurements were performed by adding small ruby crystals to the samples, following the shift $\Delta\lambda$ of their R_1 fluorescence line (at 694.2 nm under atmospheric pressure) excited by the 488 nm wavelength of an argon laser, and applying the relation $P\ (\text{GPa}) = \Delta\lambda\ (\text{nm})/3.65$.[16] The uncertainty on the values thus determined is lower than 0.1 GPa. The spectra were recorded over a 200 eV range. To compensate for the effects of the strong absorption of the diamonds and the limited thickness of the samples, a data collection time of 35 s was used for each spectrum, and 16 to 32 spectra were added for each pressure in order to improve the statistics. The experimental resolution was ~1.0 eV and the data reproducibility was better than 0.5 eV. Further details on the experimental setup and conditions have been given elsewhere.[9] Data processing consisted in smoothing and straightening the experimental spectra (which were distorted by diamond absorption in the scanned energy range), calibrating the energy by means of the spectrum of metallic iron and normalizing the absorbance.[17,18]

Magnetic susceptibility measurements

The temperature dependence of the magnetic susceptibility of compound **1** was determined with a Faraday-type magnetometer, calibrated with $Hg[Co(NCS)_4]$. The experimental susceptibility values were corrected for diamagnetic contributions, estimated at $-332 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$.

Results

For each compound, the spectra were recorded first at atmospheric pressure (P_{atm}), then at increasing pressure until no further evolution was observed, and finally at P_{atm} again. The spectra obtained at the onset and the end of a cycle were found to be quite similar for compounds **1** and **2** (showing the reversibility of pressure effects) and to be slightly or markedly different for compounds **4** and **3**, respectively.

The room temperature X-ray absorption spectra of compounds **1**–**4** at P_{atm} and at a pressure where the HS-to-LS transformation is over are depicted in Fig. 1. Taking the K-edge energy of 7112 eV as the origin, the main features of the XANES area are: a strong absorption in the range 14.1–18.5 eV, with a smaller band or a shoulder in the range 26–32 eV, and a very weak pre-edge peak below 1.5 eV. The EXAFS scattering absorption spreads over 60 ± 10 eV within the interval 40–120 eV. The energy values of these structures are given for each compound in Table 1. With increasing pressure, the main absorptions are shifted towards higher energies.

As seen previously,[8,9] the LS fraction (n_{LS}) of iron(II) ions at a given pressure can be determined by comparing the experimental spectrum with linear combinations of the spectra of pure HS ($n_{\text{LS}} = 0$) and LS ($n_{\text{LS}} = 1$) isomers calculated with various n_{LS} values.

At room temperature and $P = P_{\text{atm}}$ compounds **2**, **3** and **4** are in the HS form.[12,19,20] So, for these species, the XANES spectrum of the pure HS isomer is known. On the other hand, on the basis of variable temperature magnetic susceptibility measurements we performed on compound **1** (see Fig. 2, which displays the $\chi_M T$ *vs.* T plot, χ_M being the molar magnetic susceptibility), the spin conversion exhibited by this compound is found to be in progress at room temperature. As the constant value of $\chi_M T$ obtained on extrapolating the experimental values to higher temperatures ($3.70 \pm 0.03\ \text{cm}^3\ \text{mol}^{-1}\ \text{K}$, *i.e.*, $\mu_{\text{eff}} = 5.44 \pm 0.02$ BM) is typical of HS iron(II) ions, the room temperature value of n_{LS} can be obtained from:

$$(\chi_M T)_{\text{RT}} = (\chi_M T)_{\text{LS}}(n_{\text{LS}}) + (\chi_M T)_{\text{HS}}(1 - n_{\text{LS}}) \qquad (1)$$

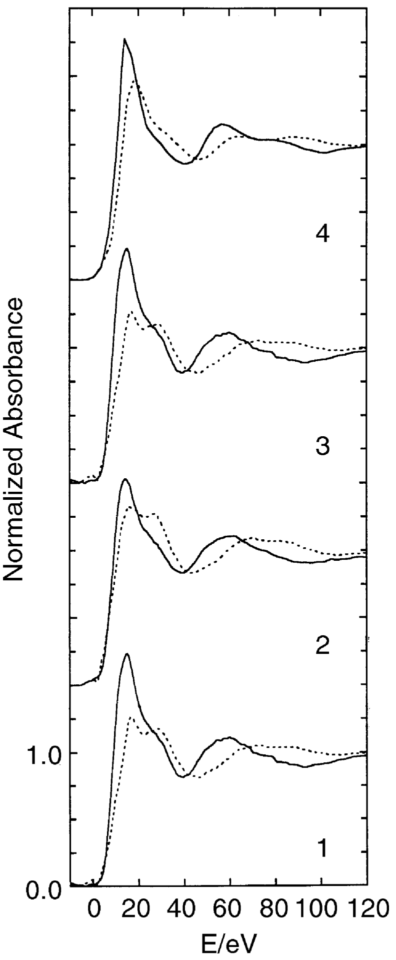

Fig. 1 X-Ray absorption spectra of compounds **1**–**4** at room temperature under the pressures $P = P_{\rm atm}$ (——) and P/GPa = 1.55 for **1**, 4.30 for **2**, 3.30 for **3** and 4.30 for **4** (------). For clarity, the spectra of **2**–**4** are translated upward by applying successive shifts of 1.5 in absorbance.

with $(\chi_M T)_{\rm LS} = 0$, $(\chi_M T)_{\rm RT} = 2.87 \pm 0.02$ cm^3 mol^{-1} K and $(\chi_M T)_{\rm HS} = 3.70 \pm 0.03$ cm^3 mol^{-1} K, yielding $n_{\rm LS} = 0.22 \pm 0.01$. This value was taken into account for spectra simulation. The transition temperature $T_{1/2}$, for which $n_{\rm HS} = n_{\rm LS} = 0.5$, is found to be 270 K.

For all compounds, the XANES spectrum of the pure LS form is assumed to be the one that no longer changes on increasing pressure. Such a hypothesis could be previously substantiated in the case of several iron(II)[8] and cobalt(II)[9,21] complexes.

Table 1 Energies[a,b] of X-ray absorptions (eV) at $P_{\rm atm}$ and high pressures for compounds **1**–**4**

	Pressure/ GPa	Pre-edge	Edge	Shoulder (sh) or peak (p)	EXAFS
1	~0	1.5	15.7	29.0 (p)	60 and ~75
	1.55	0.3	17.0	30.5 (p)	~72 and ~80
2	~0	0.6	14.1	26 (sh)	60
	4.30	0.6	16.0	27.3 (p)	71 and 85
3	~0	−0.5	15.0	27 (sh)	59
	3.30	−0.5	16.7	28.8 (p)	73 and 84
4	~0	0	14.5	27 (sh)	54 and ~77
	4.50	0	18.5	32 (sh)	62 and 90

[a] The energy origin is taken at 7112 eV. [b] Uncertainty is better than ±0.5 eV for pre-edges, edges and additional peaks, ±1 eV for edge shoulders and EXAFS bands.

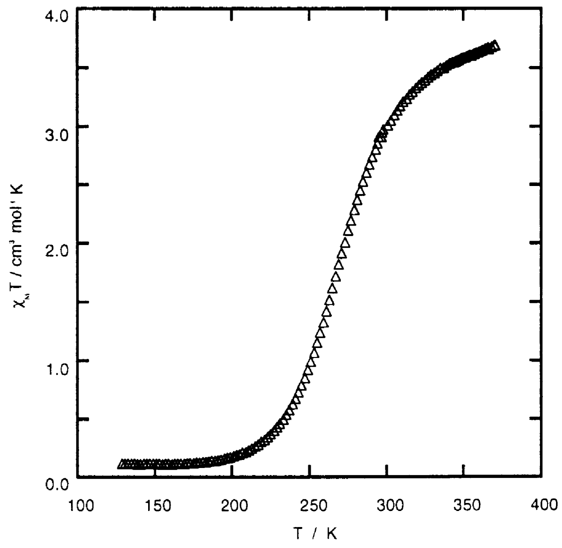

Fig. 2 Temperature dependence of $\chi_M T$ at $P_{\rm atm}$ for compound **1**.

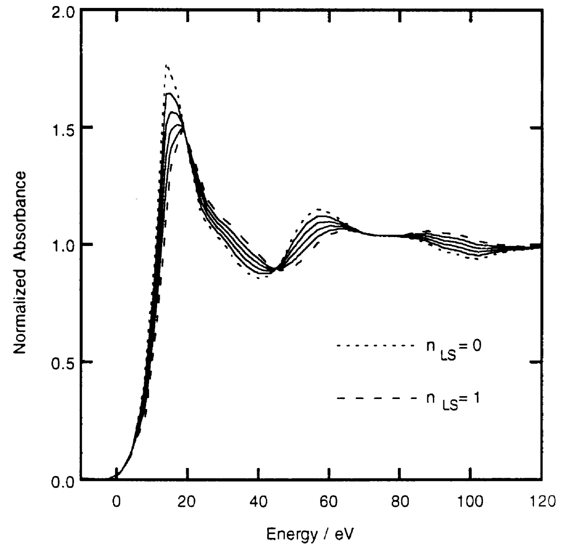

Fig. 3 Spectra of compound **4** simulated for $n_{\rm LS} = 0.2$, 0.4, 0.6, and 0.8 (——) by linear combinations of the spectra of the HS ($n_{\rm LS} = 0$, ------) and LS ($n_{\rm LS} = 1$, – – –) forms.

As an example, the spectra calculated for compound **4** with $n_{\rm LS} = 0.2$, 0.4, 0.6 and 0.8, together with those of the pure HS and LS forms, are shown in Fig. 3. The pressure dependence of $n_{\rm LS}$ found for complexes **1**–**4** is further depicted in Fig. 4.

Discussion

In the following, the XANES data are qualitatively interpreted on the basis of a rather simple molecular orbital approach (a full assignment of the spectra being out of the scope of this work) and an analysis of the resulting $n_{\rm LS}$ *vs.* P plots, together with a general discussion on the dependence of $P_{1/2}$ on $T_{1/2}$, is reported.

X-Ray absorption spectra

K-edge structures originate from transitions of the excited photoelectrons from the 1s core level either to vacant molecular levels of proper symmetry involving metal orbitals or to the continuum.

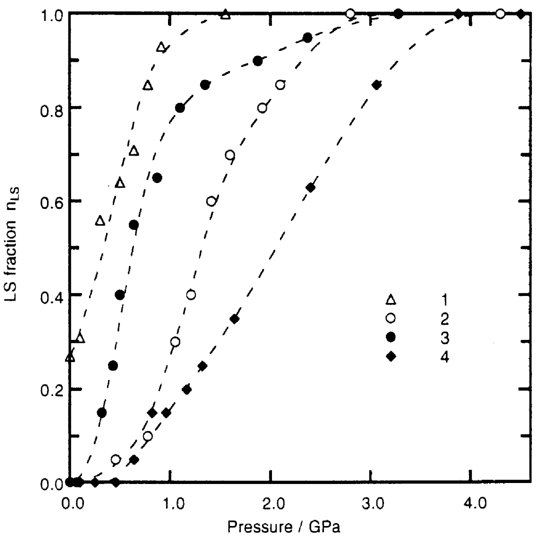

Fig. 4 Pressure dependence of the LS fraction n_{LS} for compounds **1** (Δ), **2** (o), **3** (●) and **4** (◆). Dotted lines are drawn for clarity.

Let us consider the XANES range (to which a review article was recently devoted).[22] For iron(II) complexes, the spectral resolution associated with high-pressure experiments at such a low energy is rather poor. Nevertheless, first approximation assignments with a one-electron model based on electronic dipolar transitions can be made for the most salient absorption features. As these assignments have been detailed elsewhere,[8,22] only the points required for the discussion will be reported hereunder.

Pre-edge features. For octahedral iron(II) complexes, they are ascribed to the transitions:

$$(1s)^2(\ldots)(3d\ \mathrm{MO})^6 \rightarrow (1s')^1(\ldots')(3d\ \mathrm{MO}')^7$$

where the prime sign means that, in the excited state, the molecular levels are relaxed in the core hole. In strictly centrosymmetrical systems, the dipolar transitions are forbidden. The weak absorptions observed in the spectra of six-coordinate complexes may arise from quadrupolar allowed transitions as well as from coordination core distortions with respect to centrosymmetry. It follows that, for compounds **1**–**4**, reliable information on [FeN_6] symmetries cannot be provided by pre-edge structures, all the more as these structures may be altered by data processing.

Nevertheless, two points can be emphasized: (i) the very weak intensity of pre-edge absorptions compared to edge ones shows that, in the four complexes, [FeN_6] cores do not substantially depart from centrosymmetry; (ii) this intensity is found to be still lower for compound $\mathbf{4}_{HS}$ than for compounds $\mathbf{1}_{HS}$–$\mathbf{3}_{HS}$. However, the absorption changes associated with HS-to-LS conversions are too small to be clearly specified.

Edge band. The strong absorption at 16.3 ± 2.2 eV can be at least partly assigned to symmetry-allowed dipolar transitions towards antibonding 4p molecular levels:

$$(1s)^2(\ldots)(3d\,\mathrm{MO})^6(4p\,\mathrm{MO})^0 \rightarrow (1s')^1(\ldots')(3d\,\mathrm{MO}')^6(4p\,\mathrm{MO}')^1$$

Its characteristics depend on both the symmetry of the coordination core and the mean metal–ligand distance. Deviation of [FeN_6] from O_h symmetry is expected to give rise to structures in the band or to some increase in the absorption width, as a consequence of the degeneracy removal of the $4p_{x,y,z}$ MO′. Moreover, a shorter Fe–ligand bond length should result in a lower absorption intensity (the larger metal–ligand orbital overlap reducing the participation of metal orbitals in 4p MO′) and in a shift of the band towards higher energies (owing to the destabilization of molecular antibonding levels). The existence of a shoulder or a peak in the falling part of the edge prevents edge characteristics from being accurately compared. However, a number of reliable qualitative inferences can be drawn by taking these features into account.

Let us first consider [FeN_6] distortion. For compound **1**, the significant narrowing of the edge band observed on going from the HS to the LS form strongly suggests that the spin-crossover process is accompanied by an increase in symmetry of the coordination site. In contrast, the presence of additional shoulders near the absorption maximum in the spectra of $\mathbf{2}_{LS}$ and $\mathbf{4}_{LS}$, compared with the spectra of the corresponding HS isomers, might indicate that the [FeN_6] cores of these species deviate even more from O_h symmetry on undergoing the HS-to-LS conversion.

It is interesting to compare the above conclusions with those deduced from X-ray structures. The structural data reported in Table 2 refer not only to compounds studied herein, $\mathbf{2}_{HS}$,[23] $\mathbf{2}_{LS}$[23] and $\mathbf{4}_{HS}$,[20a] but also to complexes homologous to compound **1**: $Fe(phen)_2(NCS)_2$ (polymorph II),[24,25] $Fe(bpy)_2(NCS)_2$ (polymorph II)[26] and $Fe(btz)_2(NCS)_2$[25,27] (with bpy = 2,2′-bipyridine and btz = 2,2′-bi-4,5-dihydrothiazine). As suggested from pre-edge intensities, the [FeN_6] core appears to be more distorted in $\mathbf{2}_{HS}$ and likely $\mathbf{1}_{HS}$ than in $\mathbf{4}_{HS}$, where N–Fe–N angles are nearly 90° and Fe–N distances are close to each other. Moreover, an increase in symmetry of this coordination core upon the thermo-induced HS-to-LS conversion is observed for compound **2**, and is expected to occur for compound **1** [this behaviour being a general feature in the family of $FeL_2(NCS)_2$ complexes].[24,26–28] The same trend was evidenced for compounds **3**[12] and **4**[20] from variable-temperature Mössbauer experiments. Therefore, concerning compound **1**, the molecular

Table 2 Crystallographic data related to the coordination cores of compounds **2** and **4**, and of several $FeL_2(NCS)_2$ complexes (like compound **1**)

Compound[a]	Temperature/K	Pressure/GPa	Range/Å of Fe–N distances	Range/deg of N–Fe–N angles[b]	Reference
2	298	~0	2.176–2.220	75.0–76.0	23
	90	~0	1.994–2.031	81.3–81.7	23
4	293	~0	2.125–2.188	89.1–92.1	20
$Fe(phen)_2(NCS)_2$[c]	293	~0	2.057–2.213	76.1–103.2	24
(b)	130	~0	1.958–2.014	81.8–95.3	24
	293	1.00	1.954–2.003	82.5–95.8	25
$Fe(bpy)_2(NCS)_2$[c]	298	~0	2.053–2.181	74.6–100.4	26
(f)	110	~0	1.945–1.969	81.4–91.7	26
$Fe(btz)_2(NCS)_2$	293	~0	2.064–2.176	74.7–97.4	27
	130	~0	1.948–1.982	80.3–91.1	27
	293	0.95	1.947–1.973	80.3–91.9	25

[a] phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine and btz = 2,2′-bi-4,5-dihydrothiazine. [b] Only the angles that would be 90° in strictly O_h symmetry are considered. [c] The data correspond to the polymorph II of the compound.

structures of the LS forms obtained at low temperature under P_{atm} (atmospheric pressure) and at room temperature under high pressure should not significantly differ; for Fe(phen)$_2$(NCS)$_2$ (polymorph II) and Fe(btz)$_2$(NCS)$_2$ (see Table 2), these structures were found not to differ by more than 0.03 Å in Fe–N distances and 1.5° in N–Fe–N angles. In contrast, the coordination site of compounds **2** and **4** should be more distorted with regard to O_h symmetry in the high-pressure LS isomer than in the low-temperature one. This will be confirmed hereafter.

Concerning mean metal–ligand distances: at P_{atm}, where compounds **1**–**4** are fully or mainly in the HS form, these distances can be listed in order of edge energies (see Table 1): **2** > **4** > **3** > **1**. This trend is partly corroborated by the available X-ray diffraction data, which give mean Fe–ligand bond lengths of 2.195, 2.164 and 2.156–2.133 Å for **2**,[23] **4**[20] and the homologous compounds of **1**,[24,26,27] respectively. In a given compound, the shortening of metal–ligand distances associated with the HS-to-LS transition is evidenced by the shift of the edge band towards higher energies (see Table 1) and the attendant absorption reduction. This shortening should be particularly large in compound **4**.

Absorption near 30 eV. This absorption, the energy of which is higher than the ionization energy, is assigned to multiple scattering processes involving photoelectrons with low kinetic energies. The HS-to-LS conversion is found to give rise to a substantial increase in its relative intensity and to a better resolution of the corresponding structures in the spectra of compounds **1**–**3** (see Fig. 1).

The features observed above ~40 eV in the EXAFS region are mainly determined by scattering processes inside the first coordination shell. Their shift towards higher frequencies upon the HS-to-LS transformation illustrates the shortening of metal–ligand distances. Their energy verifies the Natoli rule,[29] which states that ER^2 = constant, E being the resonance energy relative to a given zero energy and R the mean metal–ligand bond length. In the following, this rule will be applied to the structures with well-defined E values (see Table 1).

For compound **1** at P_{atm}, the two absorptions at 60 and ~75 eV can be associated with the Fe–N(Me$_2$bpy) (~2.2 Å) and Fe–N(NCS) (~2.05 Å) bonds, respectively. In the spectrum of $\mathbf{1}_{\text{LS}}$, they merge into a broad band with two scarcely distinguishable close maxima (at ~72 and ~80 eV), which confirms the convergence of Fe–N distances. The Natoli constant found for compound **2** (*vide infra*), the structure of which is known, allows one to estimate the mean value of the Fe–N(Me$_2$bpy) distances in $\mathbf{1}_{\text{HS}}$ and of all the Fe–N distances in $\mathbf{1}_{\text{LS}}$ as 2.19 ± 0.03 Å and 1.95 ± 0.03 Å, respectively. These values are in excellent agreement with those reported for the FeL$_2$(NCS)$_2$ compounds considered in Table 2, 2.18 ± 0.02 Å and 1.97 ± 0.02 Å, respectively.[24–27]

The EXAFS structures of compounds **2** and **3** closely resemble each other. They exhibit a single band around 60 eV for $\mathbf{2}_{\text{HS}}$ and $\mathbf{3}_{\text{HS}}$ and two separate features [corresponding to Fe–N(amine) and Fe–N(pyridine) bonds] at 71 and 85 eV for $\mathbf{2}_{\text{LS}}$ and at 73 and 84 eV for $\mathbf{3}_{\text{LS}}$. This indicates that, in LS isomers, the dispersion of Fe–N distances is higher than in HS isomers, which confirms the decrease in symmetry of the [FeN$_6$] cores during the HS-to-LS conversion. Therefore, at least for compound **2**, the LS form resulting from the effect of pressure is clearly shown to be different from that obtained at low temperature: in the latter, the range of Fe–N distances is narrower than in the HS form (see Table 2) and a single EXAFS structure is observed below 100 eV in the X-ray absorption spectrum.[30] Applying the Natoli rule to the two maxima observed for both $\mathbf{2}_{\text{LS}}$ and $\mathbf{3}_{\text{LS}}$, by using the constant found for $\mathbf{2}_{\text{HS}}$ with E = 60 eV and R (mean value of Fe–N distances) = 2.195 Å,[23] leads to R(Å, ± 0.03) = 2.02 and 1.84 for $\mathbf{2}_{\text{LS}}$ and 1.99 and 1.85 for $\mathbf{3}_{\text{LS}}$. Comparison of these values with those reported for the low-temperature form of $\mathbf{2}_{\text{LS}}$, 2.02 (Fe–amine bond) and 1.99 Å (Fe–pyridine bond),[23] suggests that one of these two metal–ligand bonds (probably the former, on account of the participation of –NH$_2$ groups in a hydrogen-bonding network, *vide infra*) is significantly shortened under pressure effects.

In contrast with the above assignments, the interpretation of the EXAFS structures observed for the polymeric complex **4** is not self-evident. In the spectrum of $\mathbf{4}_{\text{HS}}$, the energies of these structures do not directly reflect the mean values of Fe–N(btr) and Fe–N(NCS) distances, 2.184 and 2.125 Å, respectively.[20] Nevertheless, it may be reasonably inferred that the two resonances at 54 and ~77 eV for $\mathbf{4}_{\text{HS}}$ and at 62 and 90 eV for 4_{LS} are at least partly associated with Fe–N(btr) and Fe–N(NCS) bonds, respectively. Therefore, as for compounds **2** and **3**, the range of Fe–N distances appears to be more extended in the LS species than in the HS one. This is consistent with our above finding regarding the increase in distortion of metal environment on passing from the HS to the LS isomer under the effects of pressure, and confirms that the molecular structures of the high-pressure and low-temperature forms of $\mathbf{4}_{\text{LS}}$ are different.

n_{LS} *versus P* plots—dependence of $P_{1/2}$ on $T_{1/2}$

Fig. 4 shows the pressure dependence of n_{LS} for compounds **1**–**4**. The relevant data are collected in Table 3: P_{onset} and P_{end} are the pressures corresponding to the onset and the end of the HS-to-LS transformation and $P_{1/2}$ is the pressure at which $n_{\text{LS}} = 0.5$.

At the transition temperature under a given pressure P, $(T_{1/2})_{\text{P}}$, the Gibbs free energies of the HS and LS forms of a spin-crossover system are equal. It follows that:

$$(\Delta G_{\text{HL}})_{\text{P}} = (G_{\text{HS}})_{\text{P}} - (G_{\text{LS}})_{\text{P}} = 0$$

which can be expressed as:

$$(\Delta H_{\text{HL}})_0 + P(\Delta V_{\text{HL}})_{\text{P}} - (T_{1/2})_{\text{P}}(\Delta S_{\text{HL}})_{\text{P}} = 0 \qquad (2)$$

$(\Delta H_{\text{HL}})_0$ is the enthalpy difference between the two spin isomers at P_{atm}; $(\Delta V_{\text{HL}})_{\text{P}}$ and $(\Delta S_{\text{HL}})_{\text{P}}$ are the variations in volume and entropy associated with the complete spin-state conversion. By assuming that ΔS_{HL} does not markedly vary with increasing pressure (only the small entropy fraction resulting from changes in intermolecular vibrational modes is expected to be significantly altered) and by taking into account the relation $(\Delta H_{\text{HL}})_0/\Delta S_{\text{HL}} = (T_{1/2})_0$, where $(T_{1/2})_0$ is the transition temperature at P_{atm}, eqn. (2) may be written as:

$$(T_{1/2})_0 - (T_{1/2})_{\text{P}} + P\left[\frac{(\Delta V_{\text{HL}})_{\text{P}}}{\Delta S_{\text{HL}}}\right] = 0 \qquad (3)$$

In our experiments, the transition temperature is room temperature (T_{amb}) under the pressure $P_{1/2}$, and hence:

$$P_{1/2} = [(T_{\text{amb}} - (T_{1/2})_0]\left[\frac{\Delta S_{\text{HL}}}{(\Delta V_{\text{HL}})_{\text{P}}}\right] \qquad (4)$$

Table 3 Characteristic pressures (GPa) of the HS-to-LS conversion for compounds **1**–**4**

	P_{onset} (±0.02)	P_{end} (±0.05)	$P_{1/2}$ (±0.02)
1	—[a]	1.20	0.30
2	0.15	2.80	1.32
3	0.10	3.30	0.60
4	0.50	3.90	2.04

[a] At room temperature and $P = P_{\text{atm}}$, part of this complex is already converted into the LS form ($n_{\text{LS}} = 0.22$).

This equation shows that, for compounds with similar $\Delta S_{HL}/(\Delta V_{HL})_P$ ratios at the pressure $P_{1/2}$, this pressure should depend linearly on $(T_{1/2})_0$. However, the decrease of ΔV_{HL} with increasing pressure, which is expected to originate from the higher compressibility of HS isomers compared with LS ones, is generally unknown. Therefore, to a first approximation, the dependence of $P_{1/2}$ on $(T_{1/2})_0$ in iron(II) complexes, illustrated in Fig. 5, will be discussed in terms of ΔS_{HL} and of the change in volume at P_{atm}, $(\Delta V_{HL})_0$ (hereafter denoted ΔV_{HL}). As the linear dependence of $P_{1/2}$ in terms of $(T_{1/2})_0$ (hereafter denoted $T_{1/2}$) implies that spin conversion is the only effect of pressure, three groups of compounds will be considered, according to whether this condition is fulfilled (compounds A) or whether, in addition, pressure produces molecular distortions (compounds B) and/or structural phase transitions (compounds C).

Compounds A (1, a, b, c). As expected from the fact that the HS-to-LS conversion of **1** is in progress at room temperature, $P_{1/2}$ is found to be rather weak, 0.30 ± 0.02 GPa. As the spin change proceeds up to ~1.20 GPa, its cooperativity appears to be much lower than that of the spin transitions of the polymorphs I (**a**) and II (**b**) of the homologous compound $Fe(phen)_2(NCS)_2$, in which the whole process occurs within a range of ~0.6 and ~0.7 GPa, respectively.[8] It should be noted that the same applies to the thermally induced spin crossovers of these compounds, which extend over more than 150 K for **1** (see Fig. 2), ~10 K for **a** and ~70 K for **b**.[24] This is not surprising, since a spin conversion is expected to be all the more abrupt as the associated change in volume is less conveniently accommodated by the lattice,[3] which should not substantially depend on the control parameter.

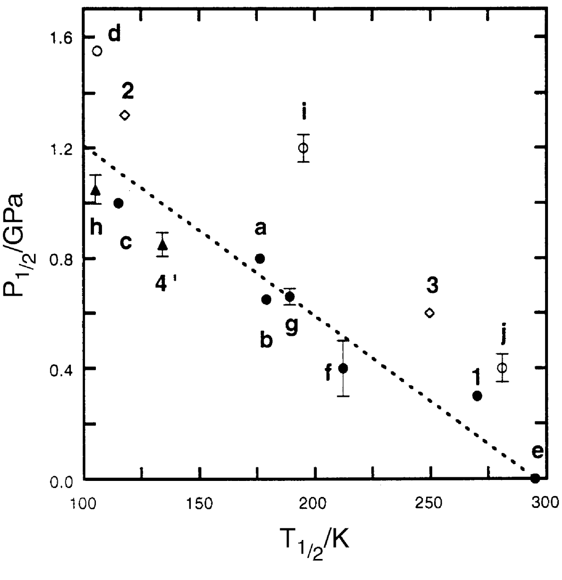

Fig. 5 Dependence of spin-transition pressures at room temperature ($P_{1/2}$) on spin-transition temperatures at P_{atm} ($T_{1/2}$) for iron(II) complexes, either mononuclear of A-type (●), B-type (◇) and C-type (o) or polymeric (▲), namely: $Fe(Me_2bpy)_2(NCS)_2$ (**1**), $[Fe(2\text{-}pic)_3]Cl_2{\cdot}EtOH$ (**2**),[40,41] $[Fe(2\text{-}pic)_3]Cl_2{\cdot}H_2O$ (**3**),[12] $Fe(phen)_2(NCS)_2$ polymorph I(**a**),[8,31] $Fe(phen)_2(NCS)_2$ polymorph II (**b**),[8,31] $Fe(py)_2bpym(NCS)_2$ (**c**),[8,33] $Fe(py)_2phen(NCS)_2$ (**d**),[8,33] $Fe(bpy)_2(NCS)_2$ polymorph II (**f**),[26,37] $Fe(PM\text{-}AzA)_2(NCS)_2$ (**g**),[39] $[Fe(hyetrz)_3](3\text{-nitrophenylsulfonate})_2$ (**h**),[55] $Fe[HB\{3,5\text{-}(CH_3)_2pz\}_3]_2$ (**i**),[10,57] $[Fe(phy)_2](BF_4)_2$ (**j**).[59,60] **e** is the point ($P = P_{atm}$, $T = T_{amb}$). **4′** represents the hypothetical behaviour of $[Fe(btr)_2(NCS)_2]{\cdot}H_2O$ (**4**) in the absence of a pressure-induced structural phase transition.[53] For thermal spin transitions occurring in two steps or with hysteresis, $T_{1/2}$ is taken as the average of the two $T_{1/2}$ values. For clarity, error bars are omitted when uncertainties on $P_{1/2}$ values are as low ±0.02 GPa.

In Fig. 5, the ($P_{1/2}$, $T_{1/2}$) set related to compound **1** (0.32 GPa, 270 K) can be compared with the corresponding data reported for other mononuclear metal complexes of the type $FeL_nL'_m(NCS)_2$ (L = bidentate ligand, $n = 1$ or 2): **a** (0.80 GPa,[8] 176.2 K[31,32]), **b** (0.65 GPa,[8] 178.8 K[31,32]) and **c** (1.00 GPa,[8] 115 K[32,33]). These compounds are good candidates for comparison purposes: they neither include solvent molecules nor exhibit intermolecular hydrogen bonds. Moreover, as seen above, the molecular structure of their LS form should depend little on the control parameter of the spin transition (pressure or temperature).

As expected from eqn. (4), the four experimental points related to the above compounds are not far from being on a straight line going through the point **e** ($P_{1/2} = P_{atm} = {\sim}0$ GPa, $T_{1/2} = T_{amb}$). The dotted line drawn in Fig. 5, the slope of which is taken as the mean slope of the four lines joining **e** to the experimental points, is consequently defined by the relationship:

$$P_{1/2}(\text{GPa}) = 1.83 - 6.2 \times 10^{-3}\ T_{1/2}\ (\text{K}) \qquad (5)$$

and will be used as a reference to facilitate the following discussion.

ΔV_{HL} was estimated at 18 Å^3 per molecule for compound **b**[27] and should be greater for compound **a** in consequence of the larger value of ΔR_{HL} on spin-state change (0.24 Å,[34] compared to 0.16 Å[24]). Moreover, the ΔS_{HL} values we determined for the two polymorphs on the basis of DSC measurements were also found to follow the same trend (46 ± 4 and 36 ± 4 J K^{-1} mol^{-1} for the complete HS-to-LS transformation of **a** and **b**, respectively).[35,36] This was foreseeable, since ΔS_{HL} is mainly of vibrational origin and hence is also expected to increase with ΔR_{HL}. The fact that $P_{1/2}(\mathbf{a}) > P_{1/2}(\mathbf{b})$ suggests that, in this case, the entropic effect overbalances the volumic one.

Regarding compound **c**, only the ΔS_{HL} value related to the solvate **c**·0.25py was reported, 56 ± 4 J K^{-1} mol^{-1}.[33] As this value presumably includes the additional contribution of an order–disorder transition of non-coordinated pyridine molecules (these being anticipated to show a positional disorder in the HS phase on the basis of the large thermal coefficient of their atoms),[33] the ΔS_{HL} and hence ΔV_{HL} values of **c** are likely not to significantly deviate from those of compounds **a** and **b**.

For compound **1**, ΔV_{HL} and ΔS_{HL} are still unknown. However, the fact that the representative point in Fig. 5 lies slightly above the straight line suggests some similarity between this species and complex **a**.

Two additional points corresponding to A-type compounds can be added to Fig. 5. They concern the polymorph II of $Fe(bpy)_2(NCS)_2$ (**f**) and the complex $Fe(PM\text{-}AzA)_2(NCS)_2$ (**g**), with PM-AzA = *N*-(2′-pyridylmethylene)-4-(azophenyl)aniline. For **f**, which was shown not to exhibit any structural phase transition under pressures lower than ~3 GPa,[26] $T_{1/2} = 212$ K[37] and $P_{1/2}$ can be approximated to be 0.4 ± 0.1 GPa from the pressure dependence of the absorption spectra.[26] The behaviour of this compound, in Fig. 5, appears to be similar to that of compound **b**, both representative points lying slightly under the straight line. This may be explained if one considers that: (i) ΔV_{HL} values are likely to be close to each other, owing to the proximity of the ΔV values (the global variation ΔV including both ΔV_{HL} and lattice thermal contraction), which are 32.8[26] and 29.8[24] Å^3 per molecule, respectively, for ~82 % of the HS-to-LS conversion; (ii) the ΔS_{HL} values related to these polymorph II complexes, synthesized by the same "precipitation" method, should not significantly differ, since the values determined for the corresponding polymorphs I, prepared by the same "extraction" method, have the same order of magnitude (48 ± 4[38] and 46 ± 4[35,36] J K^{-1} mol^{-1}, respectively, from DSC measurements). Regarding compound **g**, which exhibits a thermal spin transition without any structural phase change around

$T_{1/2} = 189$ K,[32,39] $P_{1/2}$ can be estimated as 0.66 ± 0.03 GPa by interpolating to $n_{LS} = 0.5$ the room temperature values of n_{LS} under various pressures.[39] It is worth noticing that, in Fig. 5, points **g** is on the straight line.

Compounds B (2, 3). The pressure-induced spin conversion of the ionic solvate **2** occurs between 0.15 and 2.80 GPa (with $P_{1/2} = 1.32 \pm 0.02$ GPa). The cooperativity of the process is close to that found for compound **1** (see Fig. 4), despite the less gradual character of the thermo-induced spin crossover of **2**, compared to **1**. It should be noted that, for compound **2**, the thermal process takes place in two steps.[40,41] This was ascribed to some ordering of HS and LS molecules,[42] which might imply short range quasi-antiferromagnetic interactions.[2,43] Such a behaviour was not observed in the pressure-induced spin change and the assumption that it might have escaped detection because of experimental uncertainty has to be ruled out, owing to the fact that the additional step observed at P_{atm} in the n_{HS} *vs.* T plot vanishes on applying a pressure as low as ~0.1 GPa.[44]

In Fig. 5, the point corresponding to compound **2** ($P_{1/2} =$ 1.32 GPa, $T_{1/2} = 118$ K[45]) lies significantly above the straight line. This deviation could be partly accounted for by the volumic and entropic data: ΔV_{HL} is small (15.5 Å^3 per metal atom)[46] compared with the values reported for **b** (18 Å^3) and other mononuclear Fe(II) complexes (typically ~25 Å^3);[3,47] ΔS_{HL} is rather large (50.59 J K^{-1} mol^{-1}),[2,41] in consequence of the additional contribution (8.97 J K^{-1} mol^{-1}) of the orientational order–disorder transition of EtOH molecules (these being distributed over three sites in the HS form and occupying only one site in the LS form).[7,48] However, as the high-pressure and low-temperature LS $[Fe(2\text{-pic})_3]^{2+}$ cations have been shown to be structurally different (*vide supra*), $P_{1/2}$ and $T_{1/2}$ values do not strictly correspond to the same HS-to-LS transition, which very likely mainly explains the apparent high value of $P_{1/2}$. It should be noted that the alteration of the spin-changing cations under pressure can be ascribed to the high sensitivity of the hydrogen-bonding network to pressure effects and the subsequent alteration of the ligand-field strength.[49] In particular, the substantial shortening of Fe–N(amine) bonds (0.18 ± 0.03 Å, *vide supra*) in the high-pressure LS phase, compared with the low-temperature one, is likely to result from the strengthening of $-NH_2\cdots Cl$ hydrogen bonds, leading to an increase in the electron density at the N atoms and hence to a strengthening of the corresponding coordination bonds.

For compound **3**, the X-ray absorption spectra recorded at P_{atm} and high pressure closely resemble those of compound **2** (see Fig. 1). Nevertheless, the resulting n_{LS} *vs.* P plots of the two species are different (see Fig. 4). That of **3** first takes place a little more abruptly (from ~0.10 to ~0.8 GPa), then becomes much more inflected (up to 3.30 GPa, where the spin transformation comes to an end). The latter characteristic is not observed in the thermo-induced spin transition of this compound,[12] the last part of the HS-to-LS conversion being then found to proceed rather rapidly as a function of the triggering parameter. It is worth noticing that this transition exhibits an extremely wide thermal hysteresis of 91 K ($T_{1/2}\downarrow = 204$ K, $T_{1/2}\uparrow = 295$ K), which can be easily shown, from the reported data, to be a "real" hysteresis, and not an "apparent" one resulting from the removal of non-coordinated water molecules in the warming mode and the subsequent HS-to-LS conversion of the anhydrate species in the cooling mode.

The surprising shape of the n_{LS} *vs.* P plot in the high pressure range is very likely to result from the progressive departure of water molecules above ~0.8 GPa. This statement is supported by the following remarks. The formation of the anhydrate $[Fe(2\text{-pic})_3]Cl_2$, known to exhibit a thermal spin transition around 115 K,[12,50] that is at a temperature much lower than that reported for **3** (249.5 K),[12,32] is expected to increase the pressure required for a full HS-to-LS transformation and hence to decrease the values of n_{LS} at a given pressure (which is observed). Moreover, the X-ray absorption spectrum obtained after releasing the pressure appears to be somewhat different from the initial spectrum at P_{atm} (lower edge intensity, slight shifts of edge and EXAFS structures towards higher energies), showing that compound **3** was altered in an irreversible way under pressure effects. Finally, although these alterations indicate a rather slight shortening of Fe–N distances, the common characteristics of the two spectra (edge energies close to each other, absorption near 30 eV appearing as a shoulder and EXAFS area with a single maximum) strongly suggest that the final compound is also in the HS form at P_{atm}, as expected for the non-solvated species $[Fe(2\text{-pic})_3]Cl_2$.

In Fig. 5, the behaviour of compound **3** is like that of compound **2**, the corresponding point ($P_{1/2} = 0.60 \pm 0.02$ GPa, $T_{1/2} = 249.5$ K) lying significantly above the dotted line. As the spectrum of LS $[Fe(2\text{-pic})_3]Cl_2$, used to calculate LS fractions, closely resembles that of $\mathbf{2}_{LS}$ (see Fig. 1) and consequently is expected not to significantly differ from that (hypothetical) of $\mathbf{3}_{LS}$, the resulting error on n_{LS} and hence $P_{1/2}$ values should not be large enough to justify such a deviation. On the other hand, as seen above for compound **2**, the relatively high value of $P_{1/2}$ can be related to the distortion of LS $[Fe(2\text{-pic})_3]^{2+}$ cations under pressure. As this distortion has been demonstrated to be similar to that found for **2**, it can also be explained on the basis of the effects of pressure on the hydrogen-bonding network. In spite of the absence of crystal structure, the existence of such a network in compound **3** is beyond doubt, this property (strongly suggested from the chemical formula) being a general feature in the family of compounds $[Fe(2\text{-pic})_3]X_2\cdot n S$, with X = Cl, Br and nS = MeOH, EtOH, $2H_2O$.[2] The removal of water molecules might indirectly result from the strengthening of $-NH_2\cdots Cl$ bonds, through the subsequent weakening of the hydrogen bonds involving these molecules.

Compounds C (4, d): mononuclear and polymeric species. The two-dimensional structure of the well-documented polymeric spin-crossover compound **4**[20,51,52] consists of layers of iron(II) ions, in which each ion is linked to its four closest neighbours by bidentate btr ligands acting as bridges. The NCS^- anions are *N*-coordinated in *trans* positions, whereas the water molecules, located between the layers, are weakly hydrogen-bonded to non-coordinating nitrogen atoms lying in the neighbouring layers. Only the structure of $\mathbf{4}_{HS}$ could be determined.[20a] All our attempts to obtain that of $\mathbf{4}_{LS}$ failed to succeed, the HS-to-LS transition causing crystals to shatter.

As seen in Fig. 4, the pressure-induced spin transformation exhibited by compound **4** takes place over a comparatively extended pressure range (0.50–3.90 GPa). Moreover, the corresponding point ($P_{1/2} = 2.04 \pm 0.02$ GPa, $T_{1/2} = 134$ K[20,32]), which is not shown in Fig. 5, would be very far above the straight line. These findings are all the more surprising as the thermo-induced spin crossover of **4** is highly cooperative[20] and the low temperature at which it takes place ($T_{1/2}\downarrow = 123.5$ K, $T_{1/2}\uparrow = 144.5$ K) is consistent with the fact that the ligand-field strength of the HS form ($10D_q^{HS} = 11\,600$ cm^{-1})[20] is close to the lower limit of the range (11 500–12 500 cm^{-1}) defined for iron(II) spin-crossover compounds.[2]

The unexpected behaviour of compound **4** under pressure cannot result from the experimental conditions, the hydrostaticity of the pressure, in particular, being guaranteed up to ~5 GPa. Moreover, it cannot originate from the possible removal of the lattice water molecules of the compound, since samples were not found to be whitish coloured (which is typical of the presence of even a small amount of the anhydrous species) after a pressure cycle. It should be noted that the large entropy variation associated with the thermo-induced spin change (~76 J K^{-1} mol^{-1})[51,52] could not by itself entirely account for the abnormally elevated $P_{1/2}$ value, all the more as the entropic effect should be at least partly compensated by the high value of ΔV_{HL} suggested by the XANES data, through the discussion on ΔR_{HL}.

It follows that the n_{LS} *vs.* *P* curve is very likely to largely relate to a new species arising from a structural phase transition. This finding is by no means surprising, given the structure of compound **4**: applying pressure is expected to increase the deviation of the (SCN)N–Fe–N(btr) angles from 90° as a consequence of the reduction of inter-layer distances and to distort the quasi-planar arrangement of the Fe–N(btr) bonds. Evidence was already provided, from X-ray absorption data, of the formation under pressure of a LS form less symmetrical than that obtained at low temperature. In other respects, the slightly lower energies and higher intensities of the XANES edge observed in the pressure range ~0.25–1.0 GPa, compared with the edge at P_{atm}, reveal a small increase in the mean metal–ligand distance. This shows that, in the new HS phase that forms, the HS state is stabilized with regard to the initial HS species. If the point ($P_{1/2} = 2.04$ GPa, $T_{1/2}$) corresponding to this phase were on the straight line drawn in Fig. 5, the value of $T_{1/2}$ would be found to be negative, which is typical of a fully HS state. It should be noted that the closer proximity of the layers under pressure is also expected to cause a strengthening of hydrogen bonds (as supported by the persistent presence of water molecules, these being in contrast easily removed at P_{atm}),[20,51] and consequently to result in an increase in the ligand-field strength (and hence in a stabilization of the LS state) through a strengthening of metal-to-ligand π-back bonding.[49] It clearly appears that this effect is overbalanced by the symmetry lowering effect.

Jeftic *et al.*[53] reported an investigation, by optical measurements, of the effect of pressure (from P_{atm} to 0.16 GPa) on the thermal hysteresis loop associated with the spin transition of compound **4**. Both $T_{1/2}\downarrow$ and $T_{1/2}\uparrow$ were found to increase linearly with pressure, which does rule out the assumption of a structural phase transition in the explored pressure range. However, an extrapolation of the data to $T_{1/2} = T_{amb}$ leads to a value of $P_{1/2}$ (0.85 ± 0.02 GPa) much lower than the one found in the present work, in agreement with our conclusion concerning the existence of a new phase under higher pressures.

In a recent study, performed in a wider pressure range (P_{atm}–1.05 GPa) by magnetic susceptibility measurements, Garcia *et al.* clearly demonstrated the existence of the pressure-induced transformation of $\mathbf{4}_{HS}$ into a fully HS new phase.[54] In keeping with our above finding, the process is shown to set in at a pressure slightly lower than 0.3 GPa and to come to an end at $P = 1.05$ GPa.

Our experimental data (see Fig. 4) allows us to specify that, from ~0.5 to 1.05 GPa, the formation of the new phase at the expense of the original one competes with the HS-to-LS conversions of the two phases, leading to the presence of ~15% of LS form at $P = 1.05$ GPa. Moreover, evidence is provided of the spin transition of the new phase alone (shown to proceed up to $P = 3.90$ GPa), which completes the results reported in ref. 54. This transition is very gradual, as expected for a fully HS species.[8,9] After releasing the pressure, the X-ray absorption spectrum of the final HS form is found to closely resemble that of the initial species. However, a slight shift of the structures to lower energies and a very small increase in the edge intensity can be observed (see Fig. 6), showing a partial trapping of the pressure-induced new HS phase (also detected in ref. 54).

Concerning the influence of the polymeric character of a compound on the value of $P_{1/2}$, it is interesting to note that, in Fig. 5, the point **4′** ($P_{1/2} = 0.85$ GPa,[53] $T_{1/2} = 134$ K[20,32]), which would correspond to the pressure-induced spin transition of the initial phase of compound **4** (see above), is close to the straight line. So, in the absence of a structural phase transition, the behaviour of **4** would not differ from that of the A-type mononuclear species taken herein into account. The pressure dependence of the thermal spin transition reported for the polymeric complex [Fe(hyetrz)$_3$](3-nitrophenylsulfonate)$_2$ (**h**),[55] with hyetrz = 4-(2′-hydroxyethyl)-1,2,4-triazole, leads to a similar result. The linear extrapolation to room temperature of the variation of $T_{1/2}$ in terms of pressure gives $P_{1/2} = 1.05 \pm 0.05$ GPa. As $T_{1/2} = 105$ K at P_{atm},[32] the point **h**, in Fig. 5, is also found not to significantly deviate from the straight line.

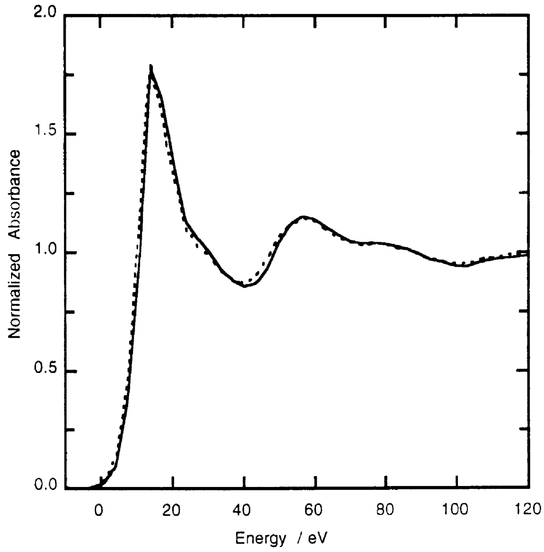

Fig. 6 X-ray absorption spectra obtained for compound **4** at P_{atm} before (——) and after (······) applying a pressure of 4.50 GPa.

Let us now consider the case of the complex Fe(py)$_2$(phen)(NCS)$_2$ (**d**). In Fig. 5, the corresponding point ($P_{1/2} = 1.55$ GPa,[8] $T_{1/2} = 106$ K[33]) lies far above the straight line. Therefore, the behaviour of this compound is quite different from that of the parent complex Fe(py)$_2$(bpym)(NCS)$_2$ (**c**). This may be related to the unusual values of ΔS_{HL} and ΔV_{HL} found for the solvate [Fe(py)$_2$(phen)(NCS)$_2$]·0.5py:[33] ΔS_{HL} is as low as 37 ± 5 J K^{-1} mol^{-1}, in spite of the disorder of lattice pyridine molecules in the HS isomer[56] and hence of the possible occurrence of an order–disorder transition on cooling, and ΔV_{HL} is only 6–7 Å^3 per metal atom.[56] These surprising values show that the HS-to-LS conversion of the solvate is very likely to be coupled with a structural phase transition. The same should hold for **d** since, in both cases, the crystals shatter upon the spin change.

A similar situation is encountered for the two complexes Fe[HB(3,5-(CH$_3$)$_2$pz)$_3$]$_2$ (**i**), where pz = 1-pyrazolyl group, and [Fe(phy)$_2$](BF$_4$)$_2$ (**j**), where phy = 1,10-phenanthroline-2-carbaldehydephenylhydrazone. Regarding compound **i**, which exhibits a thermo-induced spin transition around $T_{1/2} = 195$ K,[57] $P_{1/2}$ can be determined to be as high as 1.20 ± 0.05 GPa[58] from the n_{HS} *vs.* *P* plot reported by Hannay *et al.*[10] (it should be emphasized that the relevant data were obtained under the same experimental conditions as those we used in the present work). Concerning compound **j**, for which $T_{1/2}$ was found to be 281 ± 1 K at P_{atm} by various physical measurements,[59] $P_{1/2}$ can be approximated to 0.40 ± 0.05 GPa from the estimate of the variation of $T_{1/2}$ as a function of pressure, 30 ± 2 K GPa^{-1}.[60] In Fig. 5, points **i** and **j** appear to be far above the dotted line, which can be accounted for by the coupling in compounds **i** and **j** of the spin-changing process with a structural phase transition. For **i**, the occurrence of this transition was suggested by the reduction of crystals into a finely divided powder after a thermal cycle from room temperature to ~100 K and back;[57]

for **j**, it was evidenced from X-ray powder diffraction data and from the abnormally high value obtained for ΔS_{HL} (86 ± 4 J K^{-1} mol^{-1}).[59]

Conclusions

XANES spectrometry proves to be a powerful technique to investigate pressure-induced spin conversions: it allows one not only to get n_{LS} *vs.* P curves, but also to follow the main structural alterations of molecules under pressure effects.

For compounds like **1**, **a**, **b**, **c**, in which these alterations only originate from the spin change, a quasi-linear dependence of the transition pressure at T_{amb}, $P_{1/2}$, on the transition temperature at P_{atm}, $T_{1/2}$, is established. So, an approximate value of $P_{1/2}$ ($\pm 0.1_5$ GPa) may be estimated from $T_{1/2}$. Substantial deviations from linearity may be observed in the following situations: (1) the application of pressure produces additional molecular distortions; (2) a pressure-induced structural phase transition takes place; (3) the change in crystal volume (ΔV_{HL}) and/or entropy (ΔS_{HL}) associated with the spin conversion significantly deviates from the usual values of ~18 to 25 Å^3 molecule^{-1} and ~35 to 50 J K^{-1} mol^{-1}, respectively. The first situation, where $P_{1/2}$ and $T_{1/2}$ do not relate to the same HS-to-LS process, is observed in particular for complexes with bridging hydrogen bonds, like compounds **2** and **3**. Molecular distortions are then very likely to result from the strong alteration of the hydrogen-bonding network under pressure and the subsequent modification of the ligand-field strength. The second situation is illustrated by compound **4**, in which increasing pressure first results in a structural transition to a new HS phase, then to the HS-to-LS transformation of this phase. Concerning the third situation, unusual values of ΔS_{HL} and/or ΔV_{HL} may have various origins. For instance, they may be associated with the occurrence of a structural phase change simultaneously with the spin-crossover process, as seen for compound **d**, or with the order–disorder transition of counter-ions or lattice solvent molecules (which is expected to result in relatively high values of ΔS_{HL}). Let us mention that the weak influence of the polymeric character of a compound on the value of $P_{1/2}$, found for two complexes, should be corroborated with additional data.

Therefore, we may conclude that, despite the little amount of reliable data related to pressure-induced spin transitions at room temperature, interesting generalities can be drawn from the comparative analysis of these data. However, it is clear that our conclusions now have to be further supported by new examples.

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