

Herber and D. C. Figg of Rutgers University for advance communication of their susceptibility results and Professor J. G. Haasnoot of Leiden University for advance communication of their X-ray and EPR results.

**Supplementary Material Available:** Tables SI–SIII, listing full experimental details, anisotropic thermal parameters for non-hydrogen

atoms, and final fractional coordinates and thermal parameters for hydrogen atoms, Tables SIV and SV, listing proton shift parameters at various temperatures in the paramagnetic phase of all iron compounds, and Figure S1, showing NMR spectra of  $\text{Fe}(\text{btr})_2(\text{SCN})_2 \cdot \text{H}_2\text{O}$  at various temperatures (6 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie Inorganique (CNRS, URA 420) and Laboratoire d'Utilisation du Rayonnement Electromagnétique (CNRS, MEN, CEA), Université Paris-Sud, 91405 Orsay, France, and Laboratoire de Chimie des Métaux de Transition (CNRS, URA 419) and Laboratoire de Physique des Milieux Très Condensés (CNRS, URA 782), Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France

## Pressure-Induced Spin-State Crossovers in Six-Coordinate Cobalt(II) Complexes: A Near-Edge X-ray Absorption Study

C. Roux,<sup>1a</sup> J. Zarembowitch,<sup>\*,1a</sup> J. P. Itié,<sup>\*,1b</sup> M. Verdagner,<sup>1c,d</sup> E. Dartyge,<sup>1d</sup> A. Fontaine,<sup>1d</sup> and H. Tolentino<sup>1d</sup>

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The pressure-induced cobalt(II) high-spin (HS) ↔ low-spin (LS) crossover has been investigated at room temperature in six-coordinate complexes of the type  $\text{Co}(\text{H}_2\text{fsa}_2\text{en})\text{L}_2$ , where  $\text{H}_2\text{fsa}_2\text{en}^{2-}$  is the phenolic dianion of the Schiff base resulting from the 2:1 condensation of 3-carboxysalicylaldehyde with 1,2-diaminoethane and L is an axial ligand. The transition was followed at room temperature by near-edge X-ray absorption (XANES) spectroscopy. It was found to require the application of pressures lower than 1.1 GPa for compounds 1 (L = pyridine), 2 (L = 4-*tert*-butylpyridine), and 3 (L =  $\text{H}_2\text{O}$ ), which are known to present a thermally driven spin conversion, and to occur between ~6.5 and ~9.0 GPa for compound 4 (L = 3-methylpyridine), which retains the HS form at any temperature. Plots of the LS fraction ( $n_{\text{LS}}$ ) as a function of pressure could be deduced from the data. The phenomenon was found to be reversible (but for 3, which probably undergoes a slight decomposition under pressure) and the HS → LS transformation to be nearly complete. Moreover, the molecular structures of the two spin forms were shown to be practically independent of pressure and hence of the LS fraction. The differences in transition pressure are discussed in terms of ligand-field strength and of strengthening of intermolecular hydrogen bonds when pressure is applied. The spectral changes associated with the spin conversion are interpreted.

### Introduction

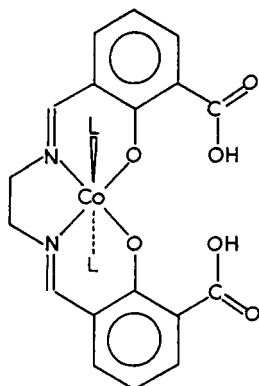
In a number of transition-metal molecular compounds, the ligand-field strength happens to have the same order of magnitude as the mean electron-pairing energy. The metal ion is then capable of undergoing a spin-state interconversion under the effect of an external perturbation.<sup>2–8</sup> The transition from the high-spin (HS) to the low-spin (LS) form is known to be accompanied by a shortening of the metal–ligand distances, which generally leads to a decrease in the molecular volume and hence in the crystal unit-cell volume, the reverse holding true in the case of a LS to HS conversion.<sup>9</sup> Pressure may act as the external perturbation, the system being then thermodynamically governed at constant temperature by  $(\partial G/\partial P)_T$ , which corresponds to volume ( $G =$  Gibbs free energy,  $P =$  pressure). However pressure-induced spin crossovers in solid-state molecular compounds have not yet been

as widely investigated as thermally driven ones. Furthermore, most of the studies reported to date are relative to iron(II) complexes (as examples, see refs. 10–22). Only two of them deal with cobalt(II) compounds, viz. the five-coordinate species  $\text{Co}(\text{nnp})_2(\text{NCS})_2$ , where  $\text{nnp} = N$ -((diphenylphosphino)ethyl)- $N'$ , $N'$ -diethylethylenediamine,<sup>23</sup> and tetrahedral complexes of the type  $\text{Cs}_2\text{CoX}_4$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ).<sup>24</sup>

In this paper, we present the first pressure-induced  $S = 3/2 \leftrightarrow S = 1/2$  transitions in six-coordinate cobalt(II) complexes. The

- (1) (a) Laboratoire de Chimie Inorganique, Université Paris-Sud. (b) Laboratoire d'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud. (c) Laboratoire de Chimie des Métaux de Transition, Université P. et M. Curie. (d) Laboratoire de Physique des Milieux Très Condensés, Université P. et M. Curie.
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**Figure 1.** General formula for compounds 1–4. L = pyridine for 1, 4-*tert*-butylpyridine for 2, H<sub>2</sub>O for 3, and 3-methylpyridine for 4.

compounds have the general formula Co(H<sub>2</sub>fsa<sub>2</sub>en)L<sub>2</sub>, H<sub>2</sub>fsa<sub>2</sub>en<sup>2-</sup> being the phenolic dianion of the Schiff base resulting from the 2:1 condensation of 3-carboxysalicylaldehyde with 1,2-diaminoethane and L an axial ligand (cf. Figure 1). The species with L = pyridine (1), 4-*tert*-butylpyridine (2), and H<sub>2</sub>O (3) are known to exhibit the most abrupt thermally induced spin transitions ever reported for cobalt(II) complexes.<sup>25–28</sup> On the other hand, the compound with L = 3-methylpyridine (4) was shown to retain a high-spin ground state down to 4 K.<sup>27</sup>

The spin conversion was followed at room temperature by observing the significant changes in the near-edge structures of X-ray absorption (XANES) spectra, associated with the phenomenon. A diamond-anvil cell designed for X-ray absorption experiments was used to vary the pressure applied to the samples from atmospheric pressure ( $P_{\text{atm}}$ ) to ca. 9 GPa (1 GPa = 10 kbar).

#### Experimental Section

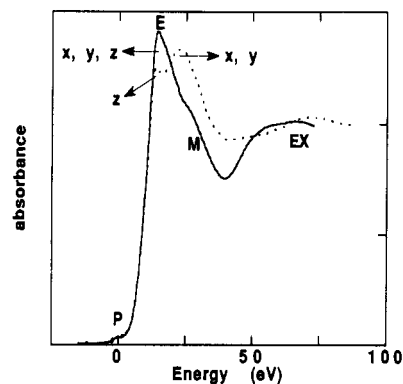
**Syntheses.** The compounds were prepared as previously described.<sup>26–28</sup> They were identified by elemental analysis and infrared spectrometry.

**High-Pressure Cell.** A Block-and-Piermarini diamond-anvil cell<sup>29</sup> was used to generate high pressures. The thickness of the diamond anvils, which also act as windows, was reduced to 1.7 mm in order to decrease the absorption of X-photons. The culet diameter was 800  $\mu\text{m}$ . The samples were loaded in the 500- $\mu\text{m}$ -diameter hole drilled in a 100  $\mu\text{m}$  thick preindented stainless steel (AISI 301) gasket. Silicone oil was used as the pressure-transmitting medium, in order to obtain nearly hydrostatic conditions up to 5 GPa. Above this pressure, the oil begins to freeze and hydrostatic conditions are no more ensured.

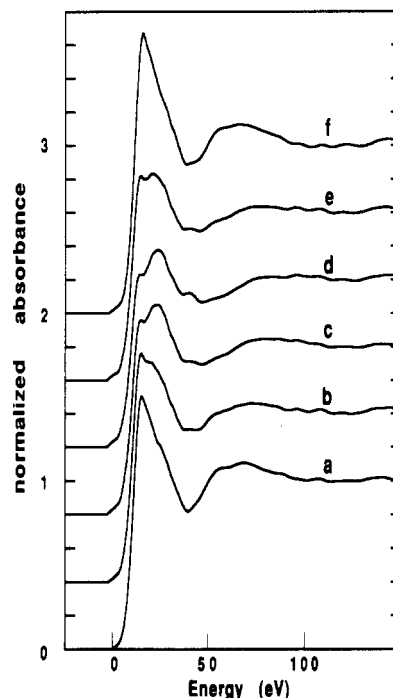
To measure the pressure, a small ruby chip (10–20  $\mu\text{m}$ ) was added to the samples. Pressure measurements were performed by following the shift of the ruby R<sub>1</sub> fluorescence line (at 694.2 nm under atmospheric pressure) excited by the 488-nm line of an air-cooled argon laser. The wavelength calibration was made from the position of the laser plasma line at 696.4 nm. Pressures were calculated by using the linear law  $P = \Delta\lambda/3.65 \text{ GPa}$ .<sup>30</sup> The uncertainty in the pressure values determined by this technique is less than ca. 0.1 GPa in the pressure range where hydrostatic conditions are fulfilled.

**Recording of XANES Spectra.** X-ray absorption experiments were performed at room temperature on the dispersive mode EXAFS station at LURE (Paris-Sud University).<sup>31,32</sup> The DCI storage ring was operated at 1.85 GeV with a typical current of 250 mA. Owing to the strong absorption of the diamonds and to the limited thickness of the samples, the data collection time for one spectrum ranged between 2.7 and 7.5 s according to the compound. In order to increase the statistics, 32 spectra were added for each pressure value.

The spectrometer combines focusing-dispersive X-ray optics, acting as a polychromator, and a position-sensitive detector working under high-flux conditions. The beam probing the sample is made harmonic



**Figure 2.** XANES spectra of 2 at room temperature (—) and 40 K (---) under atmospheric pressure. P = preedge, E = edge, M = multiple-scattering and/or multielectronic excitation range, and EX = EXAFS. x, y, and z stand for  $1s \rightarrow 4p_x$ ,  $MO'$ ,  $1s \rightarrow 4p_y$ ,  $MO'$  and  $1s \rightarrow 4p_z$ ,  $MO'$  transitions, respectively (see the Discussion). These spectra, previously reported,<sup>37</sup> were not normalized.



**Figure 3.** Selected XANES spectra obtained for 2 at room temperature under the following increasing and then decreasing pressures: (a)  $P_{\text{atm}}$ ; (b) 0.27 GPa; (c) 0.5 GPa; (d) 1.32 GPa; (e) 0.43 GPa; (f)  $P_{\text{atm}}$ . For clarity, spectra b–f are shifted upward by 0.4, 0.8, 1.2, 1.6, and 2.0 eV, respectively.

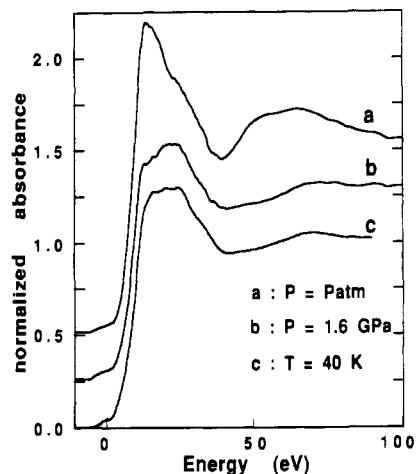
free by using a fused-silica X-ray mirror. Advantages of such a setup for high-pressure experiments (focusing, time resolution, ...) as well as data processing have been discussed elsewhere.<sup>33,34</sup> In the present experiments, the polychromator was a bent crystal of silicon(111) allowing a significant flux of photons ( $2.10^{10} \text{ Hz}$ ) to reach the detector. Because of the relatively low energy of the Co K-edge (7709 eV), the energy band-pass yielded by the bent crystal is limited to about 200 eV, which restricts the spectra to the XANES range.

#### Results

In order to follow the evolution of the spin state as a function of pressure, the XANES spectra of compounds 1–4 were compared with those previously obtained in variable-temperature experiments performed at atmospheric pressure.<sup>35–37</sup> As an example, the

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**Figure 4.** XANES spectra obtained for **1** at room temperature with  $P = P_{\text{atm}}$  (a) and  $P = 1.6$  GPa (b) and at  $T = 40$  K under atmospheric pressure (c). For clarity, spectra b and a are shifted upward by 0.25 and 0.5 eV, respectively.

spectra of the high- and low-spin isomers of **2** carried out at  $T = 295$  and 40 K (with  $P = P_{\text{atm}}$ ), respectively, are given in Figure 2. They show a close similarity to the corresponding spectra obtained in the present room-temperature experiments at atmospheric pressure and  $P = 1.32$  GPa, respectively (see Figure 3). This verifies the fact that using the high-pressure cell does not affect the absorption curves and shows that, for compounds **1**–**3**, the low-spin forms resulting from pressure-induced and thermally induced transitions are likely to have similar molecular structures.

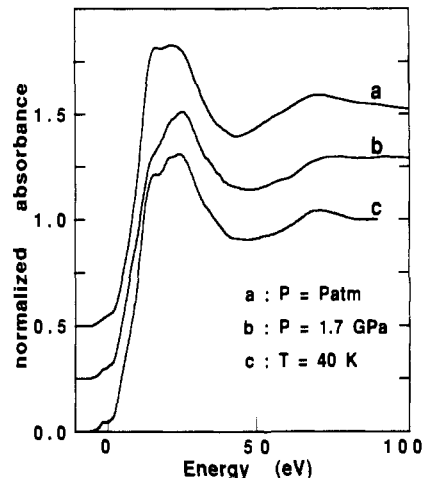
It should be noted that the spectra of HS and LS isomers presented in Figure 2 are typical for all the HS and LS species in this study. In the XANES range, the main features characteristic of HS forms are a strong asymmetrical absorption at  $15 \pm 1$  eV (taking 7709 eV as energy zero) and a shoulder at  $23 \pm 2$  eV; those characteristic of LS forms are a peak at  $15 \pm 2$  eV and a stronger and wide absorption at  $25 \pm 3$  eV.

The experiments were performed first at increasing and then at decreasing pressures ( $P_{\uparrow}$  and  $P_{\downarrow}$ , respectively). In the former case, the onset and the end of the HS  $\rightarrow$  LS conversion occur at pressures we shall call  $P_{\text{onset}\uparrow}$  and  $P_{\text{end}\uparrow}$ , respectively. Between  $P_{\text{onset}\uparrow}$  and  $P_{\text{end}\uparrow}$ , the spectra are indicative of the coexistence of both spin isomers. Similarly, at decreasing pressures, the LS  $\rightarrow$  HS transition takes place between two pressure values referred to as  $P_{\text{onset}\downarrow}$  and  $P_{\text{end}\downarrow}$ . These limit pressures were specified by comparing the spectra with those characteristic of the HS and LS forms. They were corroborated for each experiment by observing the color of the samples through the diamonds under a microscope. A distinct change in color is associated with the spin conversion, the HS isomers being either red-brown (**1**, **3**) or yellow-beige (**2**, **4**) and the LS isomers dark red.

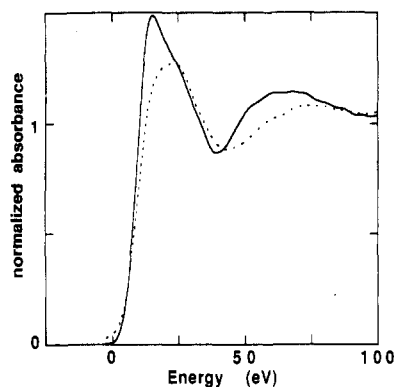
A selection of the spectra relative to compound **2** is given in Figure 3. The transition is found to occur between  $\sim 0.1$  and  $\sim 1.1$  GPa for  $P_{\uparrow}$  and between  $\sim 0.8$  and  $\sim 0.1$  GPa for  $P_{\downarrow}$ .

Figure 4 shows the spectra obtained for **1** at  $P = P_{\text{atm}}$  and  $P = 1.6$  GPa and at  $T = 40$  K ( $P = P_{\text{atm}}$ ). It clearly appears that the HS  $\rightarrow$  LS conversion is more complete at high pressure than at low temperature, where a small amount of compound was found to remain in the HS state.<sup>26</sup> For  $P_{\uparrow}$ , the transition takes place between  $P_{\text{onset}\uparrow} \sim 0.6$  GPa and  $P_{\text{end}\uparrow} \sim 1.1$  GPa, and for  $P_{\downarrow}$ , between  $P_{\text{onset}\downarrow} \sim 0.6$  GPa and  $P_{\text{end}\downarrow} \sim 0.3$  GPa.

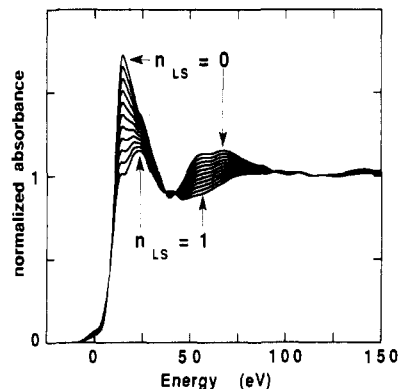
In the case of compound **3**, the spectrum recorded at room temperature and atmospheric pressure (see Figure 5) is indicative of the coexistence of both LS and HS species.  $P_{\text{onset}\uparrow}$  is estimated as  $\sim 0.1$  GPa. Above  $\sim 1.0$  GPa, only the LS form exists. Figure



**Figure 5.** XANES spectra obtained for **3** at room temperature with  $P = P_{\text{atm}}$  (a) and  $P = 1.7$  GPa (b) and at  $T = 40$  K under atmospheric pressure (c). For clarity, spectra b and a are shifted upward by 0.25 and 0.5 eV, respectively.



**Figure 6.** XANES spectra obtained for **4** at room temperature under atmospheric pressure (—) and 10.4 GPa (---).



**Figure 7.** Simulated spectra of **2**, for various values of the LS fraction ( $n_{\text{LS}} = 0.1, 0.2, \dots, 0.9$ ). The spectra were calculated by linear combination of the experimental HS form ( $n_{\text{LS}} = 0$ ) and LS form ( $n_{\text{LS}} = 1$ ) spectra.

**5** also allows comparison of the spectra obtained at 1.7 GPa and at 40 K ( $P_{\text{atm}}$ ). As already observed for **1**, the thermally induced HS  $\rightarrow$  LS conversion is found to be slightly less complete than the pressure-induced one.

Finally, the spectra of the HS and LS forms of **4** are shown in Figure 6. In this case, high pressures are required to induce the transition. This occurs between  $\sim 6.5$  and  $\sim 9.0$  GPa. The fine structures of the LS form absorption that are observed for compounds **1**–**3** are not resolved.

On the basis of the spectra assumed to be those of the HS ( $n_{\text{LS}} = 0$ ) and LS ( $n_{\text{LS}} = 1$ ) species, it is possible by linear combination to simulate the spectra corresponding to different  $n_{\text{LS}}$  values. The

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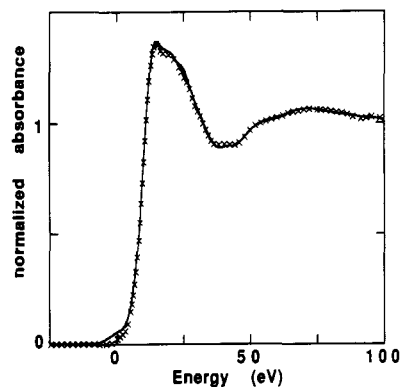


Figure 8. Comparison of the experimental spectrum obtained for 2 at  $P = 0.27$  GPa (X) with the spectrum simulated for  $n_{LS} = 0.5$  (—).

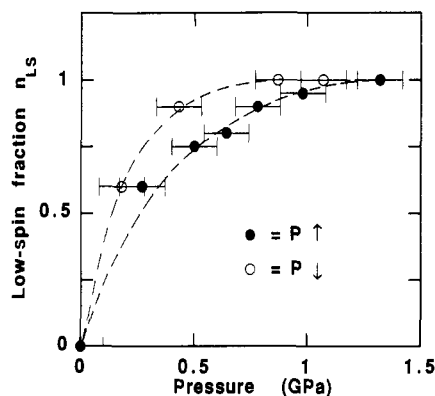


Figure 9. Plots of the LS fraction  $n_{LS}$  as a function of pressure for compound 2, at increasing (●) and decreasing (○) pressures. Dotted lines were drawn for clarity. The experimental points corresponding to a further increase in pressure are located on the upper curve.

results obtained for 2 are presented in Figure 7. The evolution of  $n_{LS}$  as a function of pressure and, consequently, an approximate value for  $P_c$  (defined as the pressure where the HS and LS fractions are  $n_{HS} = n_{LS} = 0.5$ ) can be deduced from the comparison of the experimental spectra with the calculated ones. The very good agreement obtained between these spectra is exemplified in Figure 8. Figure 9 shows the plots of  $n_{LS}$  versus  $P$  determined for 2 at  $P^\uparrow$  and  $P^\downarrow$ .

The characteristic pressure values  $P_{onset}^\uparrow$ ,  $P_{end}^\uparrow$ , and  $P_c^\uparrow$  relative to compounds 1–4 are summarized in Table I. This table also gives the transition critical temperatures in the cooling ( $T_c^\downarrow$ ) and heating ( $T_c^\uparrow$ ) modes for the spin-crossover complexes 1–3,<sup>26–28</sup> along with the values of the mean metal–ligand distances in the HS and LS forms of these compounds, referred to as  $R_{HS}$  and  $R_{LS}$ , respectively.<sup>35,38</sup>

### Discussion

The above results shows that XANES spectra can be used to follow pressure-induced spin transitions, since the X-ray absorption is deeply modified upon the spin-state change. The discussion of the results concerns the interpretation of the spectra, the influence of pressure, and the spin-transition characteristics.

(a) **Interpretation of Edge Structures.** Even if it is possible to draw conclusions about the spin crossover without a detailed understanding of XANES, we propose hereunder a simple analysis of the spectra and of their modifications with the spin change. The interpretation of edge structures is not straightforward. Nevertheless, it is possible to rely on some simple principles.

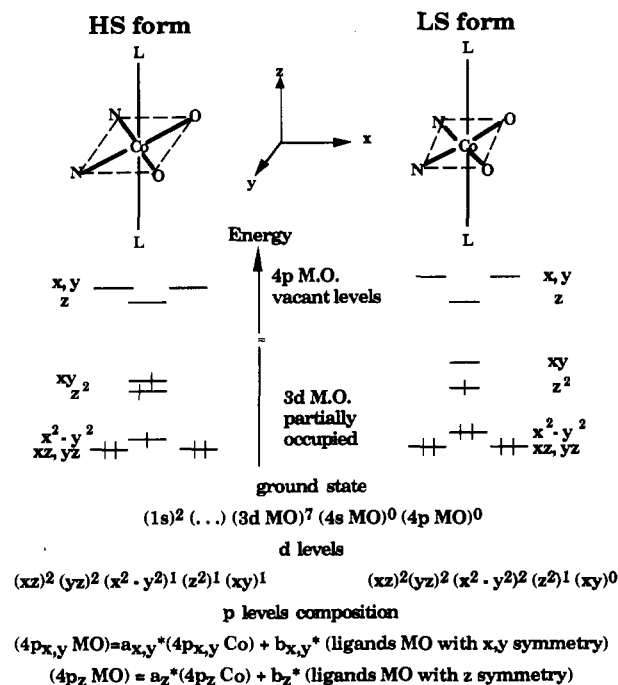
The edge structures originate from transitions of the excited photoelectron from the 1s core level to excited vacant states of proper symmetry. The spectra are therefore closely related to the electronic and stereochemical structures of the complexes. The

Table I. Characteristic Pressures<sup>a</sup> for the Spin Transition in  $\text{Co}(\text{H}_2\text{fsa}_2\text{en})\text{L}_2$  Compounds, Transition Critical Temperatures in the Cooling and Heating Modes ( $P = P_{\text{stim}}$ ) for Compounds 1–3,<sup>b</sup> and Mean Metal–Ligand Bond Lengths  $R$  for HS and LS Isomers<sup>c</sup>

	compd				ref
	1	2	3	4	
	L = py <sup>d</sup>	L = 4- <i>t</i> -Bupy <sup>d</sup>	L = H <sub>2</sub> O <sup>d</sup>	L = 3-Mepy <sup>d</sup>	
$P_{onset}^\uparrow$ , GPa	~0.6	~0.1	~0.1	~6.5	this work
$P_{end}^\uparrow$ , GPa	~1.1	~1.1	~1.0	~9.0	this work
$P_c^\uparrow$ , GPa	~0.8	~0.2	~0.25	~7.5	this work
$T_c^\downarrow$ , K	115	138	81.5	<i>b</i>	26–28
$T_c^\uparrow$ , K	127	154	84.6	<i>b</i>	26–28
$R_{HS}$ , <sup>e</sup> Å	2.02	2.02	1.96	2.04	35, 38
$R_{LS}$ , <sup>e</sup> Å	1.90	1.90	1.88		35, 38

<sup>a</sup>See text. <sup>b</sup>Compound 4 does not exhibit a thermally induced spin transition. <sup>c</sup>Values determined by EXAFS spectroscopy. <sup>d</sup>py = pyridine, 4-*t*-Bupy = 4-*tert*-butylpyridine, 3-Mepy = 3-methylpyridine.

Chart I. Simplified Geometrical and Electronic Structures of the HS and LS Forms of Compounds 1–4<sup>a</sup>



<sup>a</sup>The coordination core deformations are amplified. The energies of the electronic levels are not at scale.

changes in spectra follow the changes in structures. A classical description assigns (i) the preedge structures (P, in Figure 2) to transitions of the 1s excited electron to 3d molecular levels ( $t_{2g}$  and  $e_g$  in  $O_h$  symmetry), (ii) the edge structures (E) to transitions of the 1s electron toward molecular levels built from the mixing of the metal 4p orbitals with the symmetry-adapted combinations of the orbitals of the surrounding ligands, and (iii) the high-energy XANES structures (M) to multiple scattering and/or to multi-electronic excitations (shake-up), with a progressive merge in the EXAFS range (EX). The one-electron picture may be refined by taking into account two-electron transitions, weaker in intensity. Finally, when the dipolar transitions are forbidden for symmetry reasons, quadrupolar transitions become apparent.<sup>39</sup> For allowed transitions, the more important the mixing of metal orbitals with ligand orbitals, the more intense the corresponding transition is.

In our case, a one-electron description of the edge mainly based on dipolar transitions allows us to interpret most of the observed phenomena.

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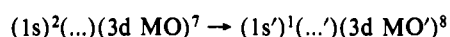
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The simplified electronic and stereochemical structures of the HS and LS forms of the cobalt(II) ( $d^7$ ) complexes are schematized in Chart I.

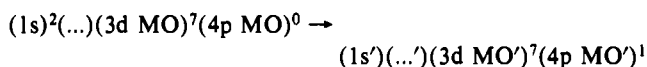
The degeneracy of the 4p levels in the complexes results from a coordination core geometry lower than  $O_h$ , mainly due to an axial elongation demonstrated from magnetic susceptibility measurements<sup>26–28</sup> and evidenced by the room-temperature X-ray diffraction structure of **1**.<sup>40</sup> When passing from the HS to the LS form, the  $3d_{z^2}$  orbital remains similarly populated. By contrast, the  $3d_{xy}$  orbital, which is occupied by one electron in the former case, becomes vacant. It follows that the bond length shortening associated with the spin conversion should mainly concern the equatorial bonds, the axial bonds being much less affected. So, the  $3d_{xy}$ , as well as the  $4p_x$  and  $4p_y$  orbitals are expected to be destabilized and the  $3d_{z^2}$  and  $4p_z$  orbitals to retain practically the same energy. The same reasoning leads to the conclusion that the weight  $a_z^*$  of the metal  $4p_z$  AO is high and remains practically the same in the ( $4p_z$  MO) wave functions of both HS and LS forms, whereas in ( $4p_{x,y}$  MO) wave functions,  $a_{x,y}^*$  is weaker than  $a_z^*$  and still decreases upon the HS to LS conversion (because of a larger participation of ligand orbitals due to shorter distances).

The spectra of the HS forms (see Figures 3–6) are characteristic of distorted octahedral  $Co^{II}$  complexes.<sup>37</sup>

In the preedge area (very weak structures at  $\sim 2$  eV), the transition is



The prime sign reminds us that in the excited state the molecular levels are relaxed in the core hole. The multiplet structures are weak in intensity: the metal first environment is quasi-centrosymmetric, and in a centrosymmetric system, the dipolar transition is forbidden. In the edge area, the allowed transitions are



The strong asymmetrical absorption at  $15 \pm 1$  eV is assigned to the allowed electronic transitions from the 1s level to the first vacant molecular orbitals of p symmetry, i.e. to the transitions  $1s$  to ( $4p_x \text{ MO}'$ ),  $1s$  to ( $4p_y \text{ MO}'$ ), and  $1s$  to ( $4p_z \text{ MO}'$ ). The ( $4p \text{ MO}'$ ) are too close in energy for the transitions to be resolved (see Figure 2). In the higher energy range, the weak shoulder at  $23 \pm 2$  eV may be associated with a multiple-scattering process and/or with a multielectronic excitation, whereas the structures between ca. 40 and 90 eV are clearly single-scattering EXAFS structures.

In the LS state, a similar interpretation is still operative and the modifications of the spectra as compared with those of the HS forms are the following (see Figures 3–6):

The multiplet structures in the preedge are slightly higher in intensity, which can be accounted for by a more distorted coordination core, resulting from the equatorial contraction. The splitting of the edge structures can be assigned to that of the ( $4p \text{ MO}'$ ), now resolved as shown in Chart I; the peak at  $15 \pm 2$  eV may be associated with the  $1s$  to ( $4p_z \text{ MO}'$ ) transition, whereas the wide absorption at  $25 \pm 3$  eV may originate, at least partly, from the  $1s$  to ( $4p_{x,y} \text{ MO}'$ ) transitions, since the  $x,y$  levels are significantly destabilized and shifted toward higher energies (see Figure 2). Furthermore, the decrease in the white-line intensity may be accounted for by two considerations: (i) the different  $1s$  to ( $4p \text{ MO}'$ ) absorptions, which partly overlap in the HS species spectra and add their intensities, are resolved into two different peaks for the LS species, each of them appearing weaker in intensity; (ii) the shorter equatorial metal–ligand distances enhance the admixture of ligand orbitals with  $p_x$  and  $p_y$  metal orbitals in ( $4p_{x,y} \text{ MO}'$ ), as shown above. Consequently, there is a lower participation  $a_{x,y}^*$  of the metal orbitals in the wave function and hence a weaker intensity for the corresponding absorptions. Finally, the HS  $\rightarrow$  LS conversion is found to be associated with

a large shift of the EXAFS structures toward higher energies, which reflects the equatorial shortening of metal–ligand distances. The very peculiar lowering of intensity of the EXAFS first oscillation may be assigned to a larger Debye–Waller factor due to a larger distortion of the coordination core and/or to a probable destructive interference effect, in the LS form, between the signals arising from similar (N, O) scattering neighbors at slightly different distances.

(b) **Influence of Pressure.** The application of increasing pressure to the HS systems first decreases the crystal unit-cell volume, which leads to a shortening of intermolecular spacing and hence to an increase of the lattice strain. When the pressure becomes high enough to force a structural rearrangement to occur, then the LS form, where the lattice strain is weaker due to the smaller volume of molecules, is thermodynamically stabilized and a HS  $\rightarrow$  LS conversion takes place.

For compounds **1–3**, which are known to exhibit thermally driven spin crossovers,<sup>25–28</sup> the transition takes place at relatively low pressures ( $P_c \approx 0.2$  to 0.8 GPa; see Table I), being complete at 1.0–1.1 GPa. On the other hand, in the case of compound **4**, which retains the HS state down to 4 K at  $P_{\text{atm}}$ ,<sup>27</sup> a pressure as high as ca. 7.5 GPa is required for half the HS molecules to be converted into LS molecules. In this case, the spin change can be explained as follows.<sup>41</sup> Let us call  $\Delta E$  the ligand-field splitting, under atmospheric pressure, between the lowest lying HS and LS terms:  $\Delta E = E(^4A_{2g}) - E(^2A_{1g})$ .<sup>27</sup> Applying a pressure  $P$  results in an energy change  $P(\Delta V) = P(V_{\text{HS}} - V_{\text{LS}})$ , where  $\Delta V$  is the volume difference of the crystal in the HS and LS forms, at constant temperature, with respect to one molecule. Therefore, the effective splitting, concerning the conditions for the thermal equilibrium under pressure, becomes

$$\Delta E_P = (E_P)_{\text{HS}} - (E_P)_{\text{LS}} = \Delta E + P\Delta V \quad (1)$$

Here  $\Delta E$  is negative, since the ground state is  $^4A_{2g}$  at atmospheric pressure (for **4**,  $\Delta E$  was evaluated as  $-598 \text{ cm}^{-1}$ ).<sup>27</sup> The term  $P(\Delta V)$ , which is correlated to  $R_{\text{HS}} - R_{\text{LS}}$ , is positive. So, for  $P = P_{\text{atm}}$ , eq 1 gives  $\Delta E_P \approx \Delta E < 0$ . Magnetic measurements<sup>27</sup> show that, at room temperature, the HS ground state essentially is populated. When  $P$ , and consequently  $P(\Delta V)$ , increases at constant temperature, the LS state is more and more stabilized with regard to the HS one. For a sufficiently large  $P$  value,  $\Delta E_P$  becomes positive. The ground state is then LS and its thermal population increases with  $P$ .

For compounds presenting a thermally induced spin crossover, the transition pressure ( $P_c$ ) is expected to be correlated with the transition temperature ( $T_c$ ), which depends on the ligand-field splitting: the higher  $T_c$ , the lower  $P_c$  should be. This can be understood by considering again eq 1.<sup>41</sup>  $\Delta E$  is now positive since, in spin-crossover complexes, the lowest lying LS level acts as the ground state. For compounds **1–3**, the thermal population of the excited HS state, at room temperature and atmospheric pressure, is nearly complete.<sup>25–28</sup> Since  $P\Delta V > 0$ , applying pressure at constant temperature leads to an increase in  $\Delta E_P$  and accordingly to a stabilization of the LS state with respect to the HS one. The higher  $\Delta E$  (and hence  $T_c$ ), the lower the pressure ( $P_c$ ) required for  $\Delta E_P$  to result in a thermally half-populated LS state will be. This statement is confirmed when comparing the  $P_c \uparrow$  and  $T_c \downarrow$  values relative to the parent compounds **1** and **2** (see Table I), i.e.,  $\sim 0.8$  GPa and 115 K for **1** and  $\sim 0.2$  GPa and 138 K for **2**. The same trend can also be observed from the data reported by Pebler<sup>17</sup> for  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  and  $\text{Fe}(\text{phen})_2(\text{NCSe})_2$  (where phen = 1,10-phenanthroline), viz.,  $P_c \uparrow = 1.35$  and 0.9 GPa, and  $T_c \downarrow = 182$  and 235 K, respectively. In the same way, the very low  $P_c \uparrow$  value at room temperature (slightly higher than 0.12 GPa) that can be estimated for  $[\text{Fe}(\text{phy})_2](\text{BF}_4)_2$ <sup>22</sup> (where phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone) is certainly correlated with the relatively high  $T_c \downarrow$  value (277 K) found for this complex. The low  $P_c \uparrow$  value of  $\sim 0.25$  GPa obtained for **3**,

(40) Charpin, P.; Nierlich, M.; Vigner, D.; Lance, M.; Thuéry, P.; Zarembovitch, J.; d'Yvoire, F. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 429.

(41) This discussion concerning the energy change induced by the application of pressure was suggested by one of the reviewers, whom we wish to thank.

though the thermally-induced spin transition of this compound is centered around  $T_c^\downarrow = 81.5$  K and  $T_c^\uparrow = 84.6$  K, might result from the strengthening under the influence of increasing pressure of the intermolecular hydrogen bonds that are likely to exist at  $P_{\text{atm}}$ , which would increase the ligand field.<sup>42</sup>

As seen above, the similarity of the high-pressure and low-temperature XANES spectra of compounds 1–3 shows that the LS forms obtained at increasing pressure and decreasing temperature are likely to have the same molecular structure. So, in both cases, the HS to LS conversion should mainly result in a shortening of equatorial bonds (*vide supra*). On the contrary, it is clear that pressure must strongly modify intermolecular interactions. This effect is expected to be all the more pronounced, as compounds 1–4 may develop intermolecular hydrogen bonds through the carboxylic substituents of the Schiff base ligand and, additionally for 3, the two coordinated water molecules. Moreover, it seems worth emphasizing that since the experimental spectra obtained for different pressures can be closely reproduced from linear combinations of the HS form and LS form spectra (see Figures 7 and 8), the molecular structures of both spin isomers may be considered to be practically independent of pressure and hence of the LS fraction.

Finally, it should be noted that the existence of pressure-induced spin transitions for compounds that do not present a thermally driven spin conversion, as is the case for 4, has already been reported through several examples (e.g., see refs 10, 16, 17, 19, and 20). So, applying pressure proves to be a more efficient way to induce spin changes than varying temperature.

**(c) Spin-Transition Characteristics.** For compounds 1, 2, and 4, the spectra obtained at  $P_{\text{atm}}$  before pressure was applied and after pressure was released are quite similar. The slight difference observed in the case of 3 is indicative of the presence of some more LS species in the HS matrix after the first pressure loop was over; this might result from the formation under pressure of a small amount of the LS planar compound  $\text{Co}(\text{H}_2\text{fsa}_2\text{en})$ , by removal of the two coordinated water molecules of 3. So, in this series of compounds, pressure-induced transitions are found to be reversible, except of course when pressure induces a chemical modification.

In spite of this reversibility, the compounds do not behave in the same way at increasing and decreasing pressures. This is

illustrated in Figure 9, which shows the variation of the LS fraction  $n_{\text{LS}}$  as a function of pressure for compound 2. Obtaining a given  $n_{\text{LS}}$  value requires a lower pressure at  $P^\downarrow$  than at  $P^\uparrow$ . However, the existence of two branches for  $n_{\text{LS}}$  vs  $T$  plots is likely not to be indicative of the existence of a hysteresis effect. When pressure is again applied after a first cycle, this actually leads to  $n_{\text{LS}}$  values ( $n_{\text{LS}}, P^\uparrow$ )<sub>2</sub> lower than those obtained upon the first application of pressure ( $n_{\text{LS}}, P^\uparrow$ )<sub>1</sub> and very close to those determined from the experiments performed at decreasing pressure ( $n_{\text{LS}}, P^\downarrow$ )<sub>1</sub>. This can be observed, for example, in the following data: for 2, at  $P \approx 0.43$  GPa, ( $n_{\text{LS}}, P^\uparrow$ )<sub>1</sub>  $\approx 0.70$ , ( $n_{\text{LS}}, P^\downarrow$ )<sub>1</sub>  $\approx 0.90$ , and ( $n_{\text{LS}}, P^\uparrow$ )<sub>2</sub>  $\approx 0.90$ ; for 1, at  $P \approx 0.40$  GPa, ( $n_{\text{LS}}, P^\uparrow$ )<sub>1</sub>  $\approx 0.05$ , ( $n_{\text{LS}}, P^\downarrow$ )<sub>1</sub>  $\approx 0.40$ , and ( $n_{\text{LS}}, P^\uparrow$ )<sub>2</sub>  $\approx 0.40$ . So, it clearly appears that the compounds are likely to undergo some irreversible modification upon the first application of pressure. The nature of this modification is not clear at the moment. A possible hypothesis might be the formation of intermolecular hydrogen bonds, which could be retained after the first pressure release. This would explain the lower pressures required for the spin conversion at decreasing ( $P^\downarrow$ )<sub>1</sub> and then increasing ( $P^\uparrow$ )<sub>2</sub> pressures. It is worth noting that the thermally induced spin transitions of compounds 1–3 were found to present a hysteresis, with a width of  $\sim 12$  K for 1,  $\sim 16$  K for 2, and  $\sim 3$  K for 3.<sup>26–28</sup>

Table I shows that, at  $P^\uparrow$ , the spin conversion presented by 1–3 occurs in a pressure range of  $\sim 0.5$ ,  $\sim 1.0$ , and  $\sim 0.9$  GPa, respectively. For 4, the transition is more gradual, taking place within  $\sim 2.5$  GPa. This may arise from the fact that the high pressure required for the spin change ( $P_c \approx 7.5$  GPa) is no longer hydrostatic and is likely to produce a larger amount of crystal imperfections, which is expected to reduce the domain size and hence to lower the cooperativity of the phenomenon.

Finally, it can be seen from Figures 2–5, on the basis of a comparison between the relative intensities of the peaks at  $25 \pm 3$  and  $15 \pm 2$  eV in the low-temperature and high-pressure spectra, that the spin conversion of compounds 1–3 is much closer to completeness when obtained under the effect of pressure than when resulting from a decrease in temperature. At low temperature, the residual HS fraction in the LS matrix was estimated, from magnetic susceptibility measurements, to be 6% for 1,<sup>26</sup> 8% for 2,<sup>27</sup> and 9% for 3.<sup>28</sup> This shows that increasing pressure can lead to a spin conversion that is not far from being complete, which justifies the set of spectra represented in Figure 7, the simulation of which was based on the knowledge of the spectra of pure HS and LS forms.

(42) Claude, R.; Zarembowitch, J.; Philoche-Levisalles, M.; d'Yvoire, F. *New J. Chem.*, in press.