

Co(II) molecular complexes as a reference for the spin crossover in Fe(II) analogues†

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Received 2nd March 2002, Accepted 2nd May 2002

First published as an Advance Article on the web 17th June 2002

The crystal structures of a series of cobalt(II) molecular complexes, $[\text{Co}(\text{PM-L})_2(\text{NCS})_2]$ [PM = *N*-2-pyridylmethylene, L = 4-(aminobiphenyl) or 4-(phenylethynyl)aniline], are investigated and compared to the analogous iron(II) complexes, $[\text{Fe}(\text{PM-L})_2(\text{NCS})_2]$, already known in the literature. At room temperature, the Co(II) complexes prove to be isostructural with the iron(II) complexes. An interesting point is that the iron complexes, unlike the cobalt complexes, undergo a spin crossover at low temperature. Hence, a comparison of the temperature dependence of the structural properties of the Co(II) and the Fe(II) complexes underlines some structural features of the spin crossover. Comparative deformation of the lattices and thermal expansion tensors are first discussed. Then, new parameters to estimate the distortion and the contraction at the spin crossover of the FeN_6 coordination sphere are presented, thereby allowing the estimation of the reduction of the volume of the octahedron to around 3 \AA^3 (25%). As well, comparative discussions on the intermolecular contact modifications with temperature are proposed. In the above considerations the cobalt series is therefore used as a reference to distinguish between the effects of the spin crossover and the purely thermal effects.

1 Introduction

The conversion from a high spin state to a low spin state in iron(II) complexes is widely studied for the fundamental problems it raises as well as for the many potential industrial applications it offers.^{1–5} The features of such spin conversion which can be induced by temperature, pressure or irradiation effects are known to depend strongly on the structural properties of the complexes. Therefore in order to understand thoroughly this phenomenon, prior to the possible design of spin crossover materials with industrial applications, the structural properties of spin crossover complexes have to be carefully examined.

For a few years, we have been focusing on the $[\text{Fe}(\text{PM-L})_2(\text{NCS})_2]$ family of spin crossover complexes [PM = *N*-2-pyridylmethylene] that shows, depending on the nature of the ligand L, a large diversity within the spin conversion features together with, in a first approach, similarities in structural properties.^{6–9} Nevertheless, a careful comparative examination of the crystal structures of the high spin (room temperature) and low spin (low temperature) states of some complexes of this family showed differences that were connected to the diversity of the spin conversion features.^{8,9} However, the differentiation between the structural modifications owing to the spin crossover from the structural modifications due to the thermal effects is still one of the points requiring further study. To this end, the structural properties of the analogous cobalt family of complexes, $[\text{Co}(\text{PM-L})_2(\text{NCS})_2]$, have been investigated. Indeed, once it had been established that these cobalt complexes do not present a spin conversion, then the comparison of the temperature dependence of the structural properties in the cobalt and iron complexes would hopefully illuminate the structural changes that are induced by the spin conversion in the iron complexes. In such a comparison, the structural properties of the cobalt complexes would be used as a reference for the thermal effect on the iron complexes. Clearly, such an approach is relevant only if the

structural properties of the cobalt and iron complexes are very similar at room temperature. Besides, the latter condition is also required in order to consider a future molecular alloy between the cobalt and iron compounds. This kind of alloy appears interesting to us as it might constitute one possible approach to obtaining materials with a large panel of controlled spin transition features, the proportion of cobalt being inserted being one of the variables.

We report the synthesis and X-ray diffraction study of two cobalt complexes of the above family: (i) $[\text{Co}(\text{PM-BiA})_2(\text{NCS})_2]$, *cis*-bis(thiocyanato)bis[*N*-(2-pyridylmethylene)-4-(aminobiphenyl)]cobalt(II) and (ii) $[\text{Co}(\text{PM-PeA})_2(\text{NCS})_2]$, *cis*-bis(thiocyanato)bis[*N*-(2-pyridylmethylene)-4-(phenylethynyl)aniline]cobalt(II) (Fig. 1). The latter has been obtained with and without inclusion solvent. Crystal structure determinations were performed at room temperature and at low temperature, the latter corresponding to the temperature of the previously published low spin crystal structures of the analogous iron complexes (Table 1). In the present paper the molecular complexes will be named using the scheme *Metal-L*, thereby allowing an immediate understanding of which metal–ligand couple is concerned: $[\text{Co}(\text{PM-BiA})_2(\text{NCS})_2]$ is named as *Co-BiA*, $[\text{Co}(\text{PM-PeA})_2(\text{NCS})_2]$ as *Co-PeA*, $[\text{Co}(\text{PM-PeA})_2(\text{NCS})_2] \cdot 0.5\text{CH}_3\text{OH}$ as *Co-PeA.solv* and the iron analogues are named by replacing *Co* with *Fe*: $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ named as *Fe-BiA* and $[\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2]$ as *Fe-PeA*. *Fe-BiA* may crystallise in an orthorhombic or a monoclinic phase,⁷ the present paper deals only with the monoclinic form.

2 Cobalt(II) complexes

2.1 Spin state

The spin state is commonly approximated from the average value of the metal–ligand bond lengths. Years ago, the shortening of the cobalt ligand bond lengths corresponding to the transition from a high spin to a low spin state for the cobalt(II) ion was calculated to be around 0.1 \AA .^{10,11} Actually, the modifications of the bond lengths strongly depend on the nature of the ligand (as shown in Fig. S1 of the ESI).† The

†Electronic supplementary information (ESI) available: histogram of the average of the six cobalt nitrogen bond lengths in CoN_6 octahedra found within the literature from a Cambridge data bank investigation (February 2002). See <http://www.rsc.org/suppdata/jm/b2/b202610d/>

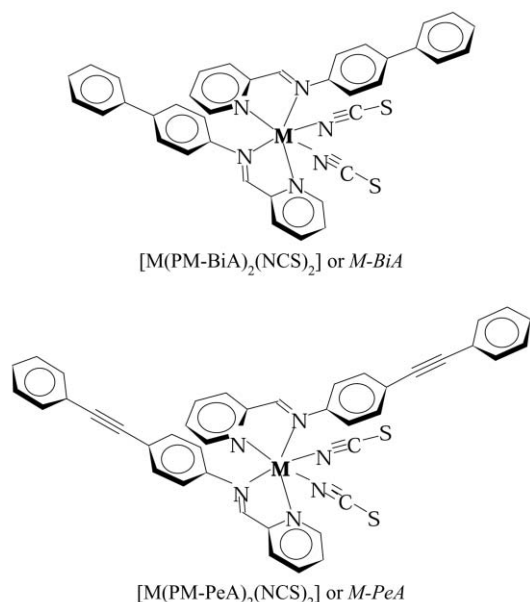


Fig. 1 Molecular diagrams of the [M(PM-L)₂(NCS)₂] complexes (M = Co or Fe): (a) L = BiA and (b) L = PeA.

statistical distribution of the average of the six Co–N bond lengths of the CoN₆ octahedron for the cobalt(II) complexes found within the literature shows a large range from 1.887 Å to 2.258 Å but with two zones centred around two maxima at 1.98 Å and 2.14 Å. These two zones correspond respectively to the low spin state and to the high spin state of the cobalt(II) ion. Table 2 clearly shows that the cobalt ions of interest are in the high spin state at high and low temperatures which confirms that they do not present a thermal spin crossover within the studied temperature range.

2.2 Crystal packing

At room temperature, *Co-BiA* crystallises in the monoclinic *P2₁/c* space group. The asymmetric unit contains one complex, the unit cell therefore contains four entities. Within the *ab* plane the neighbouring entities are related by the screw axis and appear in an antiparallel orientation (Fig. 2). Along the *c* direction, the adjacent complexes form a zigzag. The packing is driven by π – π interactions between neighbouring complexes within the *ab* plane as well as intermolecular hydrogen like contacts involving the NCS branches between neighbouring complexes within the *c* direction. At 120 K, no large modification occurs in the crystal structure of *Co-BiA*. Nevertheless a significant contraction of the unit cell occurs upon cooling

Table 1 Crystal and experimental data for Co(II) complexes

Compound	<i>Co-BiA</i>		<i>Co-PeA</i>		<i>Co-PeA·solv</i>
Formula	CoC ₃₈ H ₂₈ N ₆ S ₂		CoC ₄₂ H ₂₈ N ₆ S ₂		CoC _{42.5} H ₃₀ N ₆ S ₂ O _{0.5}
<i>T/K</i>	293	120	293	140	293
Crystal dimensions/ mm	0.35 × 0.25 × 0.15	0.50 × 0.25 × 0.15	0.30 × 0.10 × 0.10	0.30 × 0.10 × 0.10	0.30 × 0.10 × 0.10
Crystal description	Orange prism	Orange prism	Orange prism	Orange prism	Orange prism
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>Z</i>	4	4	4	4	4
<i>a/Å</i>	17.664(5)	17.163(1)	15.674(3)	15.674(1)	15.599(5)
<i>b/Å</i>	12.548(5)	12.557(1)	14.599(3)	14.322(1)	14.727(5)
<i>c/Å</i>	17.271(5)	17.270(1)	16.844(3)	16.783(1)	16.870(5)
$\beta/^\circ$	115.91(1)	115.84(1)	93.10(1)	93.36(1)	93.65(5)
<i>V/Å³</i>	3443(2)	3349(1)	3848(1)	3761(1)	3868(2)
μ/mm^{-1}	0.656	0.674	0.593	0.607	0.591
Independent reflections	6038	6828	7746	10487	4924
<i>R</i> _{int} (<i>F</i> ²) (%)	1.1	6.9	11.8	3.5	3.8
Obs. (<i>I</i> > 2σ(<i>I</i>))	4065	4784	3364	7741	2967
<i>R</i> _{obs}	0.038	0.039	0.042	0.039	0.047
<i>wR</i> _{2,all} (<i>F</i> ²)	0.106	0.142	0.112	0.100	0.140

Table 2 Some characteristics of the M^{II}N₆ octahedron geometry (see text) for the studied compounds. Estimated standard deviations are 0.001 Å, 2°, 0.2%, 0.005 Å and 0.1 Å³ respectively

Compound	Spin state	<i>T/K</i>	<i>d</i> ^a /Å	$\Sigma^b P^\circ$	<i>v</i> ^c (%)	<i>d</i> _G ^d /Å	<i>V</i> _p ^e /Å ³
[Co(PM-BiA) ₂ (NCS) ₂]	HS	293	2.129	73	2.8	0.190	12.5
[Co(PM-BiA) ₂ (NCS) ₂]	HS	120	2.125	71	2.4	0.185	12.5
[Co(PM-PeA) ₂ (NCS) ₂]	HS	293	2.134	75	2.7	0.206	12.6
[Co(PM-PeA) ₂ (NCS) ₂]	HS	140	2.136	76	2.9	0.203	12.6
[Co(PM-PeA) ₂ (NCS) ₂]·0.5CH ₃ OH	HS	293	2.131	72	2.7	0.202	12.6
mono-[Fe(PM-BiA) ₂ (NCS) ₂]	HS	293	2.160	80	3.1	0.227	13.0
mono-[Fe(PM-BiA) ₂ (NCS) ₂]	LS	120	1.960	43	1.0	0.056	10.0
[Fe(PM-PeA) ₂ (NCS) ₂]	HS	293	2.159	85	3.4	0.241	13.0
[Fe(PM-PeA) ₂ (NCS) ₂]	LS	140	1.955	56	2.3	0.050	9.7
<i>ortho</i> -[Fe(PM-BiA) ₂ (NCS) ₂] ^f	HS	293	2.174	87	3.8	0.218	13.2
<i>ortho</i> -[Fe(PM-BiA) ₂ (NCS) ₂] ^f	LS	140	1.956	48	1.0	0.045	9.9
[Fe(PM-AzA) ₂ (NCS) ₂] ^g	HS	293	2.160	83	3.4	0.240	13.0
[Fe(PM-AzA) ₂ (NCS) ₂] ^g	LS	110	1.967	47	1.0	0.067	10.0

^aThe average value of the six metal nitrogen distances. ^bThe sum of the deviations from 90° of the 12 *cis* ϕ angles in the coordination sphere. ^cThe deviation of the octahedron from its ideal shape. ^dThe distance between the metal atom and the centre of gravity of the six nitrogen atoms. ^eThe volume of the octahedron. ^fOrthorhombic phase of *Fe-BiA* as reported in ref. 7. ^gReported in ref. 9. AzA = 4-(phenylazo)aniline.

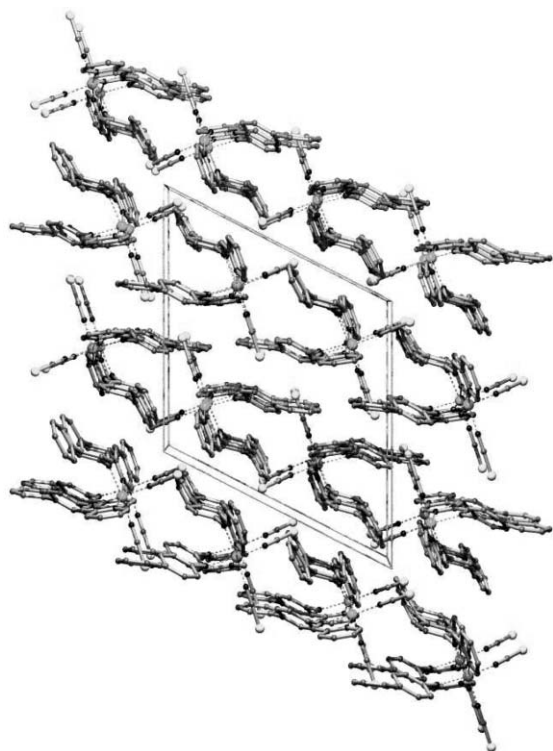


Fig. 2 Crystal packing of *Co-BiA* along *a*.

from 293 K to 90 K corresponding to a decrease of 3.3% of the unit cell volume (Fig. 3). Such a contraction presents a strong anisotropy (Fig. 4): *c* is constant, *b* slightly increases and *a*

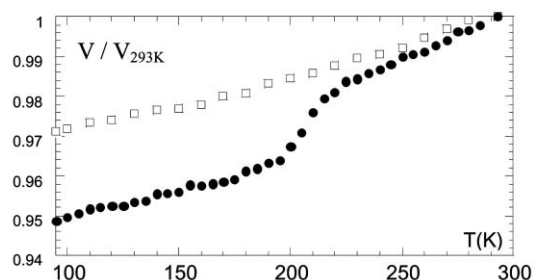


Fig. 3 Relative temperature dependence of the unit cell volumes in *Fe-BiA* (●) and *Co-BiA* (□).

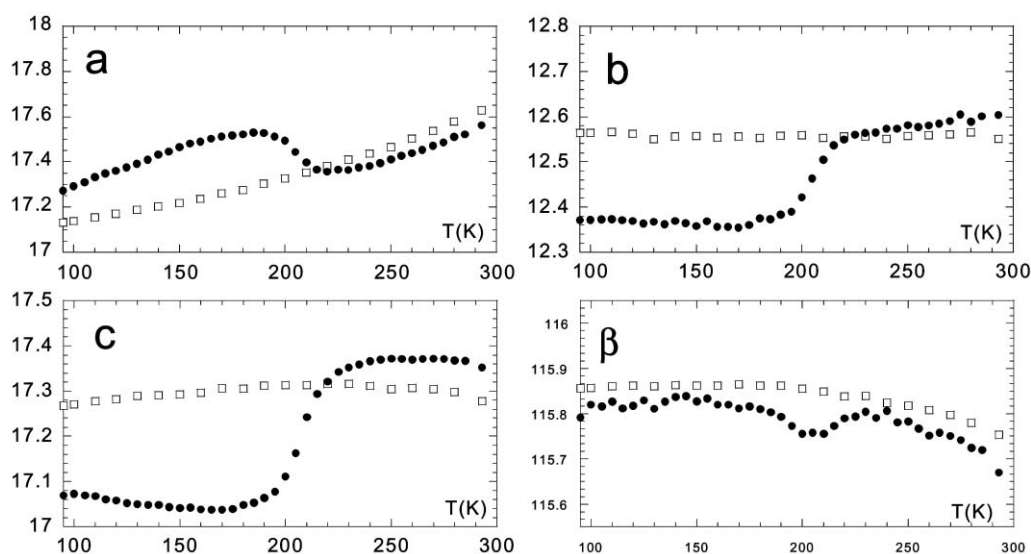


Fig. 4 Comparative temperature dependence of the cell parameters (*a*, *b* and *c* in Å and β in °) in *Fe-BiA* (●) and *Co-BiA* (□).

significantly decreases. The β angle increases when the temperature decreases.

The unit cell parameters are quite different in *Co-PeA* and in *Co-BiA*. Nevertheless, the above description of the *Co-BiA* crystal packing may be used to describe the crystal packing in *Co-PeA*. Such a remark is true either at room temperature or at 140 K. Cooling down the temperature corresponds also for this complex to an anisotropic contraction of the cell with a resulting volume reduction of 2.3%. The crystal packing is similar in *Co-PeA·solv* even though a solvent disordered molecule is present. The observed unit cell volume modification due to the presence of the solvent is weak (0.5%).

At room temperature, the cell parameters^{9,12} and the structural arrangement are very similar when the symmetry of the packing is identical in *Co-BiA* and *Fe-BiA* on one hand and in *Co-PeA* and *Fe-PeA* on the other. The analogous *Fe-L* and *Co-L* complexes may be considered as isostructural at room temperature. In contrast, the low temperature crystal structures of the cobalt and iron complexes are different because of the spin crossover taking place in the iron and not in the cobalt complexes. Despite this difference, *Co-BiA* and *Fe-BiA* adopt, in a first approach, a very similar packing at 120 K. That is not at all the case for the *M-PeA* complexes. Indeed the high spin to low spin transition is accompanied by an increase of the cell symmetry in *Fe-PeA*. In any case, the room temperature similarities of the crystal structures of the cobalt and iron complexes allow us to compare in more detail the temperature dependence of the structural modifications in order to show the structural modification due to the spin crossover in the iron complexes.

3 Comparison with iron(II) analogues

3.1 Deformation of the lattices

3.1.1 Unit cell parameters. Room temperature lattice parameters are similar in the cobalt complexes and their iron analogues. Obviously, the temperature dependence is different due to the spin crossover present in the iron(II) complexes. Consequently, we may use this difference to emphasise the typical effect of the spin crossover on the lattice. Nevertheless, in *Fe-PeA* the spin crossover is accompanied by a modification of the crystal symmetry which makes the comparison of the unit cell parameters temperature dependence of the Co and Fe complexes difficult. Thus, hereafter, we will focus on the *M-BiA* complexes. Fig. 3 and 4 show the comparative temperature dependence of the *Fe-BiA* and *Co-BiA* unit cells.

The temperature dependence of the relative volume of

Co-BiA and *Fe-BiA* (Fig. 3) allows the estimation of the volume reduction due to the spin crossover only, named ΔV_{SC} . Indeed, below the spin transition, in the 200–90 K low temperature range, the rate of volume reduction appears similar in both complexes and so the gap between the two curves represents ΔV_{SC} . In the case of *Fe-BiA*, ΔV_{SC} may thus be estimated to be 2% of the room temperature unit cell volume, which corresponds to 70 Å³. Such a ΔV_{SC} value obtained for *Fe-BiA* confirms the previous estimations of ΔV_{SC} in iron(II) complexes⁹ of the same family based on unit cell parameters temperature dependence: $\Delta V_{SC} \approx 2\%$. It is worthy of note that similar values for ΔV_{SC} have been estimated in tetrazole built spin crossover complexes, [Fe(mtz)₆](PF₆) and [Fe(ptz)₆](BF₄) (mtz = methyltetrazole, ptz = propyltetrazole), even though the structural properties are very different from those of the family currently under study.^{13–15}

These remarks on the volume reduction only reflect the mean changes. Comparison of the *Fe-BiA* and *Co-BiA* cell parameters (Fig. 4) shows without any doubt that the spin crossover is accompanied by an increase of *a* and a strong decrease of *b* and *c* in *Fe-BiA*. On the other hand, it is clear that the increase of the β value is not connected to the spin transition. How is the unit cell parameters temperature dependence correlated to the crystal packing? A way to answer such a question is to calculate the thermal expansion tensors.

3.1.2 *M-BiA* thermal expansion tensors. The thermal expansion tensors are derived from the coefficients of the second order polynomial used to fit the variations of the cell parameters. The elements of the tensor are thus very sensitive to the values of the coefficients. Moreover, to make sense, such a tensor must be calculated within a temperature region without any phase transition. In the case of *Fe-BiA*, where there is a spin crossover around 200 K, the tensor has been calculated within two temperature domains chosen from the unit cell parameters variation curves: [293, 225 K] and [190, 100 K]. Results must be interpreted keeping in mind the above limitations. The three principal thermal expansion vectors are called $\vec{\alpha}_1$, $\vec{\alpha}_2$ and $\vec{\alpha}_3$ and the corresponding magnitude α_1 , α_2 and α_3 . In a monoclinic space group, which is the case in *M-BiA*, $\vec{\alpha}_1$ and $\vec{\alpha}_3$ are in the *ac* plane while $\vec{\alpha}_2$ is parallel to *b* for symmetrical reasons.

In *Co-BiA*, the direction corresponding to the main expansion, $\vec{\alpha}_1$, is close to the crystallographic axis *a* and then corresponds more or less to the π - π interactions within the crystal packing. The direction of least expansion, $\vec{\alpha}_3$, is close to *c* and

corresponds to the intermolecular hydrogen like contacts. The temperature dependence of the corresponding magnitudes (Fig. 5a) shows that α_2 and α_3 vary slightly while α_1 decreases so that the sum of these three magnitudes, α_V , follows the α_1 decrease. Thus, this suggests that the intermolecular space corresponding to the π - π interactions is more affected by the temperature than the hydrogen like contacts direction. The bulk modulus, α_V^{-1} , reflects the ability of the unit cell to deform: the smaller the value the more deformable is the cell. For *Co-BiA*, unsurprisingly, the bulk modulus at 293 K ($\alpha_V^{-1} = 4790$ K) is much lower than at 100 K ($\alpha_V^{-1} = 10\,540$ K) and of the same order of magnitude as the values usually obtained for molecular crystals in this temperature domain.¹⁶

In *Fe-BiA*, the directions in the high temperature range are similar to those found for *Co-BiA*. The spin transition significantly affects these directions: the direction of main expansion, $\vec{\alpha}_1$, close to *a* at high temperature is close to *c* in the low temperature range and *vice versa* for the direction of less expansion, $\vec{\alpha}_3$. Thus, in the low temperature domain (low spin state) the hydrogen like contact interactions are more affected by the temperature while it is the π - π interactions which are more affected by the temperature in the high temperature (high spin state) domain. Moreover, the spin crossover also induces a significant change in the magnitudes (Fig. 5b) corresponding to a drop in α_V . As a consequence, α_V^{-1} is quite different on both sides of the spin crossover ($\alpha_V^{-1} = 4290$ K at 225 K and $\alpha_V^{-1} = 5760$ K at 190 K). But the interesting point may be that α_V^{-1} at 293 K is smaller in *Fe-BiA* ($\alpha_V^{-1} = 3840$ K) than in *Co-BiA* (4790 K), showing that the iron complex unit cell is more sensitive to deformation than the cobalt complex one; similar data on other iron spin crossover complexes are needed to go expand this interpretation.

3.2 $M^{II}N_6$ octahedron deformation

The following discussions refer to Table 2.

The spin crossover from LS to HS in the iron(II) complexes corresponds to an increase of the Fe–N bond lengths and a distortion of the octahedron.^{1,2,17–19} The first one is usually characterised by the average value of the six metal nitrogen distances, denoted *d* here, and the second one has been more recently characterised by the Σ parameter,^{8,20} that is the sum of the deviations from 90° of the 12 *cis* ϕ angles in the coordination sphere:

$$\Sigma = \sum_{i=1}^{12} |90 - \phi_i|$$

Nevertheless, it would be interesting to find a structural parameter which takes into account both the variations in bond length and the distortion of the octahedron. We propose here two new parameters corresponding to this definition. The first one, denoted d_G , is the distance between the metal atom and the centre of gravity of the six nitrogen atoms. The second one, noted ν , represents the deviation of the octahedron from its ideal shape.²¹ It has been defined using the formula:

$$\nu = 100 \left(1 - \pi \frac{V_p}{V_s} \right)$$

where V_p is the volume of the octahedron and V_s is the volume of the circumscribed sphere. This parameter, expressed as a percentage, increases with the distortion and must be equal to zero for a regular octahedron. To sum up, if *d* concerns only the dimensions of the octahedron, the distortion is directly estimated by the values of Σ , ν or d_G although the last two also contain information on the dimensions. The requirements to validate these parameters are first that their variations should be drastic at the spin crossover and secondly that they must not depend on purely thermal variations. The cobalt series we studied in this

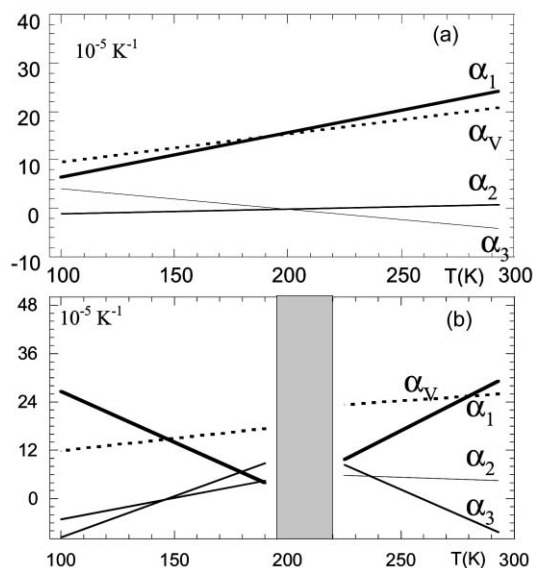


Fig. 5 Thermal expansion tensors in *Co-BiA* (top) and *Fe-BiA* (bottom).

paper is used to fulfill the last requirement. The volume of the octahedron, V_p , is also investigated.

Each of these parameters is similar at room temperature for all of the Co(II) complexes (Table 2). Relatively high values of Σ , ν or d_G indicate a noticeable distortion. Moreover, no significant variation of these parameters occurs when cooling down the temperature. We may however note that the values of ν are less coherent than the others. Besides, the calculated volume of the octahedron, V_p , is identical for all the cobalt compounds whatever the temperature. If the CoN₆ octahedron geometry is not temperature dependent on the contrary the FeN₆ octahedron geometry is different at high and low temperatures.

Consequently, the variation of these parameters from high to low temperature in the iron complexes may be attributed to the spin crossover only. As already known the decrease in d and Σ are very large at the spin crossover. This is also the case for ν which significantly decreases and thus shows the convergence towards an ideal octahedron in the low spin state. However, the variation of this parameter may be different from one complex to another: three of the iron complexes present a threefold decrease of ν while one, *Fe-PeA*, shows a much smaller decrease of this parameter, a similar remark being true for the Σ parameter variations. It may be worth noting that the magnetic properties of the *Fe-PeA* complex are different from those of the other studied iron complexes; it is indeed the only one of the series to present a very large thermal hysteresis.⁷ On the other hand the d_G distance variation is similar in all the complexes. Interestingly, d_G is almost the same for all the iron complexes in the high spin state. The fourfold decrease due to the spin crossover means that the iron atom significantly moves towards the centre of the octahedron. Hence, both ν and d_G are representative of the octahedron geometry modification at the spin crossover because they present a large variation at the spin crossover but no dependence on the temperature. In any case, the benefit of looking at ν or d_G is that they take into account the expansion and the distortion of the octahedron at the same time, unlike the other commonly used parameters d and Σ .

The variation of V_p is almost the same for all the iron complexes below the spin crossover. To our knowledge, the decrease of the octahedron volume due to the thermal spin crossover had never been calculated. In view of the non dependence of V_p on the temperature within the cobalt series, the contraction of the FeN₆ octahedron at the spin crossover can be estimated to be around 3 Å³, which corresponds to 25% of the room temperature value. Not surprisingly, this value is identical to the octahedron volume modification observed in the photoinduced spin conversion of the iron(II) complexes: [Fe(phen)₂(NCS)₂].²²

3.3 NCS branches

The intermolecular contacts involving the sulfur atoms of the NCS branches and hydrogen atoms have been suspected to be strongly connected to the features of the spin crossover in the [Fe(PM-L)₂(NCS)₂] series.^{8,9} Table 3 reports one of the

Table 3 Characteristics and temperature dependence of the shortest intermolecular sulfur hydrogen contact in the studied *Co-L* complexes and comparison with the same contacts in the *Fe-L* complexes. Such a contact concerns S4 (x, y, z) and H127 ($x, \frac{1}{2} - x, \frac{1}{2} - y$). H127 is linked to the sp² benzylic carbon atom

Complex	C-S...H/°	S...H-C/°	S...H/Å	S...C/Å
<i>Co-BiA</i> (293 K)	114	161	2.88	3.759
<i>Co-BiA</i> (120 K)	117	161	2.83	3.732
<i>Fe-BiA</i> (293 K)	107	157	3.03	3.901
<i>Fe-BiA</i> (120 K)	118	151	2.94	3.796
<i>Co-PeA</i> (293 K)	95	153	3.10	3.918
<i>Co-PeA</i> (140 K)	93	150	3.03	3.911
<i>Fe-PeA</i> (293 K)	93	150	3.08	3.917

shortest sulfur–hydrogen intermolecular contacts. First, at room temperature, characteristics of this contact are similar in *Fe-BiA* and *Co-BiA* on one hand and in *Fe-PeA* and *Co-PeA* on the other, thereby confirming the similarity of the *Co-L* and *Fe-L* crystal structures. There is no temperature dependence of these characteristics for the cobalt complexes. On the contrary, significant modifications occur in *Fe-BiA* and a complete change of the intermolecular network occurs in *Fe-PeA* at low temperature, after the spin crossover. This may be connected to the modification of the intramolecular angle (SC)N–Fe–N(CS). Indeed, if this angle is almost identical at room temperature in *Co-BiA*, *Co-PeA*, *Fe-BiA*, and *Fe-PeA* (96.6(1)°, 96.4(1)°, 96.3(1)° and 96.2(1)° respectively), it presents no temperature dependence in the cobalt complexes (96.4(1)°, 96.3(1)°) while significant differences occur after the spin crossover in the iron complexes (90.5(1)°, 90.4(1)°). The comparison of the cobalt and iron complexes structures shows that the role of the intermolecular sulfur hydrogen contact in the spin crossover must be elucidated. Further work is in progress.

4 Concluding remarks

The crystal structures of the cobalt complexes and their iron analogues are thus very similar at room temperature. Upon cooling the temperature, the cobalt complexes do not undergo a spin conversion contrary to the iron complexes. Differences in the low temperature crystal structures heighten the contrast and enable one to identify the structural modifications due to the spin conversion in the iron complexes. For instance, the unit cell variation comparison gives us the cell volume reduction due to the spin crossover only ($\Delta V_{SC} = 2\%$).

The present study shows that careful structural analysis may yet bring relevant information in the field of spin crossover. For example, a debated question²³ may be formulated as follows: “is the deformation or the expansion of the FeN₆ octahedron the relevant parameter in the study of the spin crossover phenomenon?”. We have first confirmed the parameter Σ as being relevant to estimate the FeN₆ octahedron deformation at the spin crossover. Then, we have proposed and tested two new parameters, ν and d_G , which take into account both the deformation and the expansion. In the same context, the experimental systematic determination of the bulk modulus, α_V^{-1} , appears promising. At last, on the basis of the present study, we have also confirmed²² that from the high spin state to the low spin state the volume of the FeN₆ octahedron is reduced by 3 Å³ (25 %).

5 Experimental

5.1 Synthesis

The compound *cis*-bis(thiocyanato)bis(*N*-(2-pyridylmethylene)aminobiphenyl)cobalt(II), [Co(PM-BiA)₂(NCS)₂], was prepared following the synthetic procedure previously published for the [Fe(PM-BiA)₂(NCS)₂] complex.⁷ The Schiff base *N*-(2-pyridylmethylene)aminobiphenyl, PM-BiA was synthesized from 2-pyridinecarbaldehyde and aminobiphenyl. A [Co(PM-BiA)₂(NCS)₂] powder sample was obtained from the addition of cobalt(II) thiocyanate to PM-BiA ligand in methanol solution. Anal. Calcd for CoC₃₈H₂₈N₆S₂: C, 65.98; H, 4.08; N, 12.15; S, 9.27; Co, 8.51. Found: C, 65.67; H, 4.12; N, 12.19; S, 9.46; Co, 8.15%. Single crystals were obtained by slow diffusion in methanol of PM-BiA and Co(NCS)₂, using a glass H-tube.

5.2 Single crystal X-ray diffraction

Details of the data collections and processes can be found in Table 1.

Co-PeA·solv and *Co-PeA* single crystals co-exist within the same batch without any difference in morphology that can be

seen under the microscope. Samples were cooled at a rate of 2 K min⁻¹. All the structural determinations and refinement based on full-matrix least squares on F^2 were performed using the SHELX-97 programs.²⁴ Calculation and figures were made with PLATON.²⁵ All the above software being used within the WINGX package.²⁶ In *Co-BiA* and *Co-PeA*, H atoms were treated according to the riding model during refinement with isotropic displacement corresponding to the atom they are linked to. In *Co-PeA*, the H atomic positions were refined freely. Calculation of the V_p , d_G and v parameters to characterise the symmetry of the MN₆ octahedron were performed using IVTON.²⁷

CCDC reference numbers 181918–181922.

See <http://www.rsc.org/suppdata/jm/b2/b202610d/> for crystallographic data in CIF or other electronic format.

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