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Metal–Ligand Bond Length Changes upon Doublet ↔ Quartet Spin Crossovers in Six-Coordinate Cobalt(II) Complexes: An EXAFS Investigation

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The first direct determination of the metal–ligand bond length changes associated with cobalt(II) quasi-complete spin transitions is reported. A powder EXAFS investigation was performed on two six-coordinate complexes exhibiting an abrupt $S = {}^3/_2 \leftrightarrow S = {}^1/_2$ crossover, $Co(H_2fsa_2en)(H_2O)_2$ (A) and $Co(H_2fsa_2en)(py)_2$ (B), and, for comparison, on a closely related species with a quartet ground state, $Co(H_2fsa_2en)(3\text{-}Mepy)_2$ (C) (H_4fsa_2en = *N*,*N'*-ethylenebis(3-carboxysalicylaldimine), py = pyridine). Two related five-coordinate cobalt(II) compounds, Co(3-MeOsalen)(H_2O) (D) and Co(salen)(py) (E) (salen = *N*,*N'*-ethylenebis(salicylaldiminato) dianion), and two six-coordinate cobalt(III) compounds, $Co(acac)_3$ (F) (acac = acetylacetonato anion) and $[Co(NH_3)_6]Cl_3$ (G), with known crystal structures, were used to check the validity of the data analysis method. The difference between the mean metal–ligand bond distances of the high-spin and low-spin forms was found to be $\overline{\Delta R}$ = 0.09 and 0.12 Å for A and B, respectively. These values are discussed in terms of orbital occupancy and nature of the donor atoms and compared with the available X-ray diffraction data reported for iron(II) and iron(III) spin-crossover compounds. Values of the ligand field splitting parameters $\Delta = 10Dq$ are deduced from $\overline{\Delta R}$, for high- and low-spin forms (Δ_{LS} = 14 400 and 19 800 cm^{-1} and Δ_{HS} = 11 700 and 14 600 cm^{-1} for A and B, respectively).

Introduction

A number of transition-metal complexes, largely including six-coordinate species with d^4, d^5, d^6, and d^7 electronic configurations, have been shown to display a high-spin ↔ low-spin crossover. Such a behavior implies that the crystal field strength is comparable in magnitude with the exchange energy corresponding to the crossover of the high- and low-spin ground states. These spin transitions have been essentially investigated in iron(II), iron(III), and cobalt(II) complexes. They are known to be accompanied by metal–ligand bond length variations:[2,3] the coordination sphere volume diminishes on passing from the high- to the low-spin state and vice versa.

In the case of octahedral compounds, such a structural change can be related to the fact that the high-spin → low-spin conversion results in (i) a lesser occupancy of the formally antibonding e_g orbitals directed toward the ligands and (ii) a greater occupancy of the t_{2g} orbitals, leading to an increased possibility of electron π back-donation from the metal ion to the vacant π^* orbitals of the ligands. Both effects strengthen the metal–donor atom bonds, the latter being expected to make a significant contribution only when the low-spin configuration involves a filled $t_{2g}{}^6$ subshell,[4a] as in cobalt(II) and iron(II) species.

Consequently, metal–ligand bond length variations should be smaller upon the spin crossovers of cobalt(II) complexes ($t_{2g}{}^6e_g{}^1 \leftrightarrow t_{2g}{}^5e_g{}^2$), which involve the transfer of a single electron (ΔS = 1), than in those of iron(II) ($t_{2g}{}^6 \leftrightarrow t_{2g}{}^4e_g{}^2$) and maybe iron(III) ($t_{2g}{}^5 \leftrightarrow t_{2g}{}^3e_g{}^2$) complexes, where two electrons are involved in the orbital population fluctuation (ΔS = 2). However, the changes in bond distances associated with ΔS = 1 and ΔS = 2 processes cannot be compared on these grounds alone. Other factors are expected to possibly influence the extent of these variations. One of them is the ability of the coordination sphere to reorganize, this property being related to the geometry of the coordination core,[5] the existence of intra-[6-9] and/or intermolecular[10,11] steric effects, the ligand rigidity,[12] .... The presence of a Jahn–Teller distortion and the nature of donor atoms (M–N bonds, for instance, being generally far more affected than M–O bonds) also play a part.[13-17] It should be noted that the differences in ionic radii between the high- and low-spin forms of iron(II), iron(III), and cobalt(II) in (pseudo) octahedral environments were estimated by Shannon et al.[18] at 0.16, 0.095, and 0.085 Å, respectively.

Measurements of the metal–ligand bond length changes (ΔR) accompanying spin conversions are of fundamental interest. (a) The volume difference ΔV between high- and low-spin isomers, which depends on ΔR, is expected to play a prominent part in the spin-crossover mechanism: the larger ΔV, the more cooperative (hence abrupt) the transition and the wider the hysteresis loop should be.[2b,19] (b) The extent of molecular expansion (contraction) is directly or indirectly involved in several theoretical models of spin transition.[20] (c) The vibrational component of the entropy change associated with a spin conversion mainly depends on the frequency variation of metal–ligand vibrations and, consequently, on ΔR.[21] (d) ΔR evaluation can enable one to estimate ligand field strengths when d–d bands cannot be observed in the absorption spectra.[22] (e) Spin interconversion rates and, therefore,

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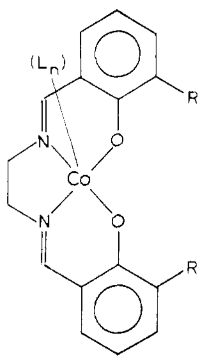

	n	L	R
A	2	H_2O	COOH
B	2	py	COOH
C	2	3-Mepy	COOH
D	1	H_2O	MeO
E	1	py	H

Figure 1. Cobalt(II) compounds studied in this work.

spin-state lifetimes are known to be largely influenced by the extent of the coordination sphere reorganization, in particular by ΔR magnitude[7,15,23] etc.

Bond-length differences between high- and low-spin forms have been determined by X-ray crystal analysis for a number of iron(II) and iron(III) complexes, either by resolving high- and low-temperature structures for spin-crossover species (see Table III in the Results and Discussion) or, more usually, by comparing room-temperature structures for compounds with similar molecular arrangements and differing spin states. Average values ($\overline{\Delta R}$) related to $\Delta S = 2$ processes were found to lie generally in the range 0.14–0.24 Å (0.18–0.20 Å in many cases) for iron(II) complexes[2a,4,6,9,10,24–28] and 0.11–0.15 Å for iron(III) complexes.[12,13,15,16,29–33] Much lower values were obtained for $\Delta S = 1$ processes: for instance, $\overline{\Delta R}$ can be estimated at 0.09 Å for a complete iron(II) $S = 0 \leftrightarrow S = 1$ interconversion[34] and 0.05 Å for a formal iron(III) $S = {}^1/_2 \leftrightarrow S = {}^3/_2$ process.[17] Concerning cobalt(II) complexes, we are aware of only one determination of the metal–ligand bond length changes accompanying a spin transition.[5] However, the higher temperature structural parameters of the five-coordinate species in this study are far from corresponding to the pure $S = {}^3/_2$ isomer and the actual $\overline{\Delta R}$ value is certainly much higher than the one found (0.03 Å). Comparison of metal–ligand bond lengths in some analogous low-[35] and high-spin[36,37] square-pyramidal cobalt(II) compounds leads to $\overline{\Delta R} = 0.08$–$0.09$ Å (see Table II in the Results and Discussion).

In this paper, we report the first direct measurement of $\overline{\Delta R}$ for (quasi) complete spin transitions of cobalt(II) complexes. Two spin-crossover sixfold-coordinated compounds were investigated, namely $Co(H_2fsa_2en)(H_2O)_2$ (A) and $Co(H_2fsa_2en)(py)_2$ (B), where $H_2fsa_2en^{2-}$ is the phenolic dianion of the Schiff base N,N'-ethylenebis(3-carboxysalicylaldimine) and py is pyridine. Both exhibit a discontinous $S = {}^3/_2 \leftrightarrow S = {}^1/_2$ transition, the former at $T_c{\downarrow} = 81.5$ K and $T_c{\uparrow} = 84.6$ K[38] and the latter at $T_c{\downarrow} = 115$ K and $T_c{\uparrow} = 127$ K[39,40] for decreasing and increasing temperatures, respectively. These transitions are the most abrupt ones ever observed for cobalt(II) complexes. As we could not grow crystals of those compounds suitable for X-ray diffraction studies, we turned toward EXAFS (extended X-ray absorption fine structure) spectroscopy. This technique provides the possibility to evaluate the changes in the cobalt atom local environment upon the transition, with use of powder samples.[41] The predominantly high-spin compound $Co(H_2fsa_2en)(3\text{-}Mepy)_2$[40,42] (C) was also investigated for comparison. Moreover, in order to test the validity of the EXAFS data analysis method, we also studied some related cobalt(II) five-coordinate and cobalt(III) six-coordinate complexes, whose structures had already been determined by X-ray diffraction, namely $Co^{II}(3\text{-}MeOsalen)(H_2O)$[36] (D), $Co^{II}(salen)(py)$[35a] (E), $Co^{III}(acac)_3$[43] (F), and $[Co^{III}(NH_3)_6]Cl_3$[44] (G) (salen = dianion of N,N'-ethylenebis(salicylaldimine); acac = acetylacetonato anion). Figure 1 represents the cobalt(II) compounds under study.

Experimental Section

Materials. Compounds A and C were obtained by the methods we previously described.[38,42] The syntheses of compounds B, D, E, and G were carried out according to the procedures reported by Torihara et al.,[45] Bailes and Calvin,[46] Diehl and Liggett,[47] and Bjerrum and McReynolds,[48] respectively. Microanalysis data were satisfactory for all the samples. Compound F was a Merck product, utilized without any further purification.

X-ray Absorption Spectroscopy Measurements. The EXAFS spectra at the cobalt K edge were recorded at LURE, the French synchrotron radiation laboratory, on the X-ray absorption spectrometer of the DCI storage ring described by Raoux et al.[49]

The samples were thin sheets of polycrystalline powder with homogeneous depth, compressed between two X-ray-transparent windows. For compounds A–E, the spectra were recorded at both room temperature and 40 K. Spin-crossover complexes were cooled slowly (about 2 °C min^{-1}), so as to avoid the quenching effect that may result in the trapping of significant amounts of high-spin form in the low-spin form at low temperature. Each spectrum was recorded at least twice, the corresponding data being added before analysis.

EXAFS Data Analysis. The first two steps of this analysis were carried out according to a procedure previously described.[50] The first step is the extraction of the EXAFS $\mathbf{k}[\chi(\mathbf{k})]$ vs. $\mathbf{k}$ curves from the absorption spectra ($\ln (I_0/I)$ vs. the incident photon energy $h\nu$), these spectra being corrected by background substracting; here, $\mathbf{k}$ is the wave vector of the photoelectron ejected from the absorbing atom 1s shell and $\chi(\mathbf{k})$ is the EXAFS modulation of the absorption coefficient above the photoionization K edge E_0 ($E_0 = 7725$ eV for cobalt). The second step is a Fourier transformation of $\mathbf{k}^3[\chi(\mathbf{k})][w(\mathbf{k})]e^{-i[\phi(\mathbf{k})]}$ (where $w(\mathbf{k})$ is a filtering-window function and $\phi(\mathbf{k})$ a phase shift coming from the absorbing and back-scattering atoms) from k space to R space, giving the radial distribution functions $\tilde{F}(R)$. A convenient filtering procedure was used to remove the low-frequency background residuals preceding the main peak. This peak alone was analyzed, since it represents the first-coordination-sphere contribution. In all these calculations, EXAFS data were limited upwards to the same $\mathbf{k}$ value of 10.2 $Å^{-1}$, some spectra being much too noisy above this value.

In the present case, the procedure previously described for fitting k-space spectra[50] proved to be inadequate. Because of the large distribution of metal–ligand bond distances in most of the complex cores

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Table I. Mean Metal–Ligand Bond Lengths Deduced from EXAFS Data ($\bar{R}$),[a] Effective Magnetic Moments (μ_e), and Crystallographic Data ($\bar{R}_{cryst}$)[b]

compd	295 K $\bar{R}$, Å	295 K μ_e (μ_B)	40 K $\bar{R}$, Å	40 K μ_e (μ_B)	$\bar{R}_{cryst}$, Å
$Co^{II}(H_2fsa_2en)(H_2O)_2$ (A)	1.96	4.18[c]	1.88	2.33[c]	
$Co^{II}(H_2fsa_2en)(py)_2$ (B)	2.02	4.57[d]	1.90	2.13[d]	
$Co^{II}(H_2fsa_2en)(3\text{-}Mepy)_2$ (C)	2.04	4.31[e]	2.06	3.94[e]	
$Co^{II}(3\text{-}MeOsalen)(H_2O)$ (D)	1.99	4.52[f]	2.02	(4.24)[h]	2.024[j]
$Co^{II}(salen)(py)$ (E)	1.89	2.20[f]	1.92	(1.86)[i]	1.940[k]
$Co^{III}(acac)_3$ (F)	1.88	g			1.893[l]
$[Co^{III}(NH_3)_6]Cl_3$ (G)	1.96	g			1.963[m]

[a] These values were determined by using the Lee and Beni criterion.[51,52] [b] $\bar{R}_{cryst}$ = room-temperature mean values of metal–ligand bond lengths deduced from crystal structures. [c] Reference 38. [d] Reference 40. [e] Reference 42. [f] Reference 54. [g] Compounds F and G are known to be diamagnetic.[55] [h] Value at 87.5 K.[54] [i] Value at 95 K.[54] [j] Reference 36. [k] Reference 35a. [l] Reference 43. [m] Reference 44.

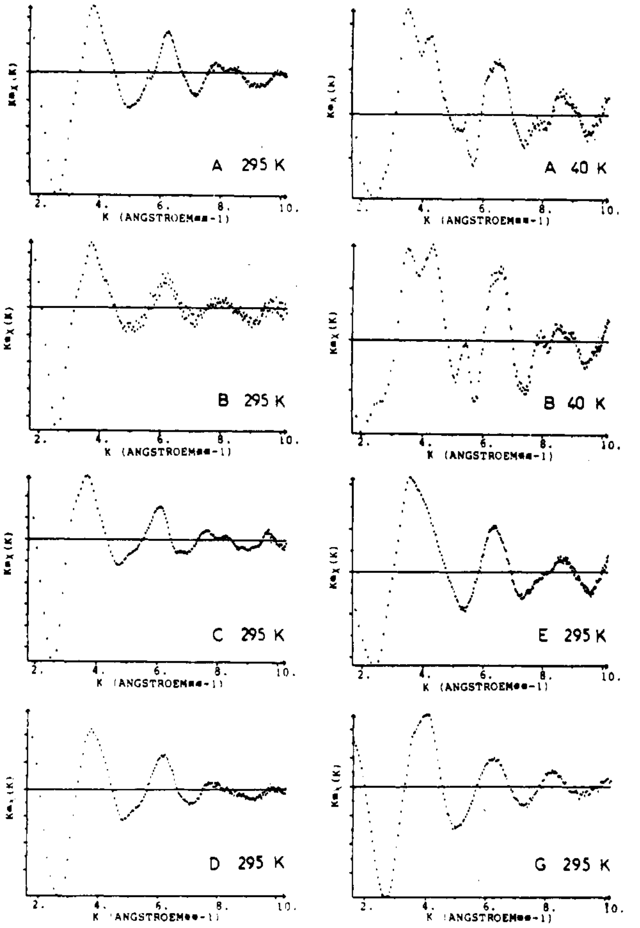

Figure 2. k-Space spectra $\mathbf{k}[\chi(\mathbf{k})]$ (in arbitrary units) vs. $\mathbf{k}$ (in $Å^{-1}$) for the compounds $Co^{II}(H_2fsa_2en)(H_2O)_2$ (A) and $Co^{II}(H_2fsa_2en)(py)_2$ (B) at 295 and 40 K and for the compounds $Co^{II}(H_2fsa_2en)(3\text{-}Mepy)_2$ (C), $Co^{II}(3\text{-}MeOsalen)(H_2O)$ (D), $Co^{II}(salen)(py)$ (E), and $[Co^{III}(NH_3)_6]Cl_3$ (G) at 295 K.

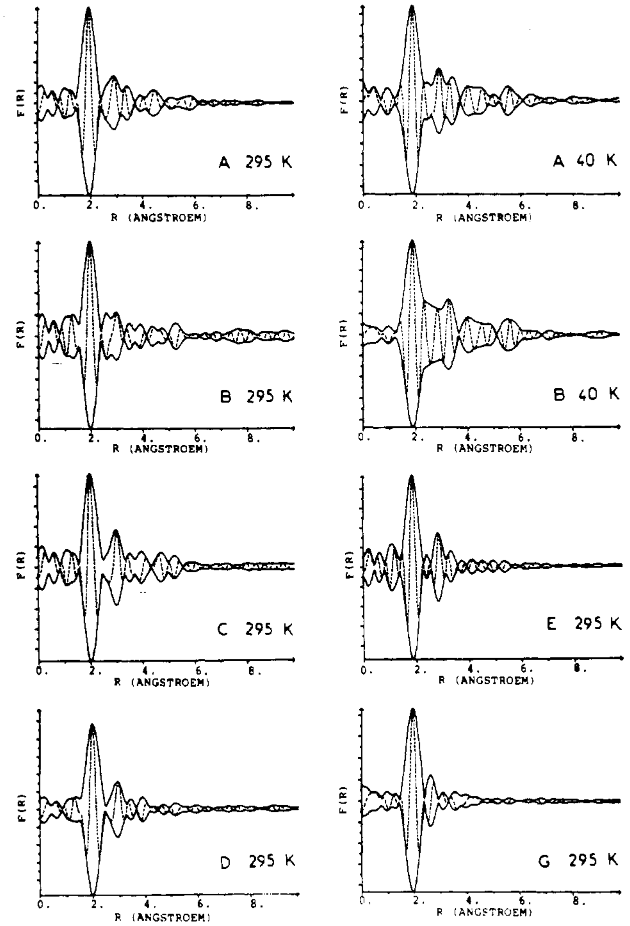

Figure 3. R-Space spectra FT $[\mathbf{k}^3[\chi(\mathbf{k})][w(\mathbf{k})]e^{-i[\phi(\mathbf{k})]}]$ (in arbitrary units) vs. $\mathbf{R}$ (in Å), deduced from the experimental data given in Figure 2: (solid line) modulus; (broken line) imaginary part of the Fourier transform.

(compounds A,[38] B,[40] C,[40,42] D,[36] and E[35a] were shown to be axially distorted) and the mixing of nitrogen and oxygen contributions in the unresolved wide peaks, single-shell fits were not satisfactory. However, axial and equatorial bond lengths are not sufficiently different for two shells to be distinguished among the six (or five) metal first neighbors. Moreover, the limited data range did not permit the use of many fitting parameters.

So, we determined the mean length $\bar{R}$ of cobalt–ligand bonds by using the Lee and Beni criterion.[51] This method has been described, discussed, and widely used by Goulon et al.[52] The $\bar{R}$ value is obtained when the modulus and imaginary part maxima of the phase-corrected $\tilde{F}(R)$ functions coincide. The adjustable parameter is E_0, which appears in the expression of the photoelectron wave vector $\mathbf{k} = [2m_e/\hbar^2(h\nu - E_0)]^{1/2}$. Calculations were performed by using the phase parameters tabulated by Teo et al.[53]

Results and Discussion

The EXAFS spectra $\mathbf{k}[\chi(\mathbf{k})]$ vs. $\mathbf{k}$ recorded at room temperature for compounds A–E and G, and also at 40 K for both spin-crossover species A and B, are shown in Figure 2. Figure 3 gives the modulus and imaginary part of the corresponding Fourier transforms FT $[\mathbf{k}^3[\chi(\mathbf{k})][w(\mathbf{k})]e^{-i[\phi(\mathbf{k})]}]$ in the R space. For compounds C–E, the low-temperature data were not represented, since they were very close to the room-temperature data, as expected. The values obtained for the mean length of co-

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Table II. Available Metal–Ligand Bond Lengths (Å) in Five- and Six-Coordinate Cobalt(II) Complexes Formed with salen and salen-Type Ligands

compd	spin state[a]	$(Co–N)_{eq}$[b]	$(Co–O)_{eq}$	$(Co–N)_{ax}$[c]	$(Co–O)_{ax}$	$\bar{R}$[d]	$\overline{\Delta R}$[e]	ref
Co(3-MeOsalen)(H_2O) (D)	HS	2.05	1.95		2.12	2.02		36
Co(salen)(py) (E)[f]	LS	1.90	1.90	2.10		1.94		35a
Co(salbn)(py)[f]	LS	1.87[g]	1.90_5[g]	2.14		1.94		35b
Co(salphen)(2-MeImd)[f]	HS	2.08[g]	1.97_5[g]	2.07		2.04		37
Co(H_2fsa_2en)(H_2O)$_2$ (A)	HS					1.96	0.09	this work
	LS					1.88		
Co(H_2fsa_2en)(py)$_2$ (B)	HS					2.02	0.12	this work
	LS					1.90		
Co(H_2fsa_2en)(3-Mepy)$_2$ (C)	HS					2.04		this work

[a] HS = high spin; LS = low spin. [b] eq = equatorial. [c] ax = axial. [d] Average metal–ligand bond lengths. [e] Values corresponding to complete high-spin ↔ low-spin conversions. [f] Abbreviations: salen = *N,N'*-ethylenebis(salicylaldimine) dianion; py = pyridine; salbn = *N,N'*-butylenebis(salicylaldimine) dianion; salphn = *N,N'-o*-phenylenebis(salicylaldimine) dianion; 2-MeImd = 2-methylimidazole. [g] Mean value.

balt–ligand bonds ($\bar{R}$) are listed in Table I. This table also gives the effective magnetic moments (μ_e) of cobalt(II) compounds (cobalt(III) species F and G are known to be diamagnetic[55]) and the mean R values deduced from the X-ray diffraction structures of reference complexes ($\bar{R}_{cryst}$).

Perusal of Table I shows that, for the octahedral reference complexes F and G, EXAFS $\bar{R}$ values do not deviate by more than 0.01 Å from $\bar{R}_{cryst}$ values, which points out the validity of Lee and Beni's criterion[51] and the suitability of the phase parameters used for calculations. The reproducible discrepancies observed at room temperature for compound D and particularly for compound E are likely to be mainly associated with the significant axial elongation of the coordination cores (see Table II): indeed, the thermal vibrations of apical ligands are then expected to be large, which is well-known to smear out the relevant EXAFS signals. This explanation is supported by the fact that, for both compounds, the $\bar{R}$ value at 295 K is found to be in excellent agreement with the mean *equatorial* metal–ligand bond length determined by single-crystal X-ray diffraction (see Table II). Furthermore, comparison of the low-temperature EXAFS data related to compounds D and E with the corresponding room-temperature X-ray diffraction data clearly shows that, for these complexes, the coordination sphere contraction with decreasing temperature is negligible, being lower than the uncertainty on the EXAFS results.

The spin transitions of compounds A and B have been shown not to be quite complete.[38,40] By assuming a linear variation of the mean cobalt–ligand bond lengths as a function of the high-spin fraction, the value of $\overline{\Delta R}$ associated with a complete spin conversion was estimated to be 0.09 Å for compound A and not to differ significantly from the experimental value (0.12 Å) for compound B. Some comments can be made about these results.

On the basis of magnetic susceptibility measurements, A and B are expected to exhibit a tetragonal elongation.[38,40] As seen above for compounds D and E, it follows that room-temperature $\bar{R}$ values may be underestimated, which would lead to $\overline{\Delta R}$ values somewhat lower than the actual ones.

The main difference between cobalt(II) high- and low-spin configurations is that the $d_{x^2-y^2}$ orbital is occupied in the former case and empty in the latter. This orbital points toward the Schiff base O and N donor atoms. It follows that the bond-length variations accompanying a spin conversion are expected to specially concern the equatorial bonds, axial bonds being much less affected. This feature is exemplified by comparing the room-temperature X-ray structures of the closely related high- and low-spin cobalt(II) square-pyramidal compounds, given in Table II. $\overline{\Delta R}_{eq}$ is found to lie in the range 0.10–0.14 Å, while axial cobalt–ligand bonds vary by +0.02 to −0.07 Å when passing from low- to high-spin species.

A survey of the variations in crystallographic parameters associated with spin-multiplicity changes shows that, for a given metal ion, bond-length differences depend on the nature of the donor atoms. For instance, comparison of the structural data for the four square-pyramidal complexes in Table II leads to $\Delta R_{eq} \simeq$ 0.15–0.21 Å for Co–N bonds and 0.04–0.05 Å for Co–O bonds. Similar results were also obtained for iron(III) compounds including Schiff bases derived from salicylaldehyde as ligands.[15-17] Moreover, such an observation was reported, to a higher degree, for a family of compounds involving Fe^{II}–P and Fe^{II}–Cl bonds, $\overline{\Delta R}$ being found as high as 0.28–0.45 Å for the former bonds and as low as ~0–0.03 Å for the latter.[6,9] The influence of donor atoms is known to depend on their σ- and π-bonding ability. Phosphorus, which is a strong π-acceptor atom, largely favors the metal-to-ligand π back-bonding in the low-spin form, thus leading to small values of R_{LS} and consequent large values of ΔR. Conversely, chlorine, which is a weak π donor, nearly acts as a weak σ donor atom, which results in rather small ΔR values. In the equatorial plane of compounds A and B, Co–N bonds are then expected to be much more affected than Co–O bonds by the $S = {}^3/_2 \leftrightarrow S = {}^1/_2$ interconversion. The possibility for these bonds to lengthen or shorten is doubly facilitated. On the one hand, the Schiff base coordination site is not closed (in contrast with that of porphyrin complexes, for instance), which authorizes tilted positions for the aromatic rings. On the other hand, the $-(CH_2)_2-$ bridge is flexible and may twist. However, it should be noted that the existence of intermolecular hydrogen bonds may somewhat oppose these molecular deformations.

As expected (vide supra), the $\overline{\Delta R}$ values obtained for compounds A and B are significantly or somewhat lower than those reported for iron(II) and iron(III) $\Delta S = 2$ spin conversions, respectively (see Table III, which gives the available structural data arising from variable-temperature single-crystal X-ray diffraction studies of spin-crossover complexes). In particular, the fact that a ratio on the order of ${}^1/_2$ is found between the $\overline{\Delta R}$ values relating to cobalt(II) ($\Delta S = 1$) and iron(II) ($\Delta S = 2$) spin changes is quite satisfying, the low-spin states of both metal ions being similarly stabilized by the existence of a filled t_{2g} subshell.[4a]

Owing to the molecular shape of A and B complexes and to the fact that axial bond lengths are expected not to be appreciably modified upon the spin conversion, the values obtained for $\overline{\Delta R}$ are likely to result in rather small changes in molecular volumes. This may partly explain why both spin transitions, though being the most abrupt ones obtained for cobalt(II) complexes, are far from being as sharp as those reported for many iron(II) complexes.

The electronic spectra of A and B complexes did not allow one to determine the ligand field splitting parameters $\Delta = 10Dq$; indeed, in spite of many attempts, no d–d band has been observed so far in these spectra. However, knowing the mean metal–ligand bond length changes $\overline{\Delta R}$ associated with the spin transition, one can obtain an estimate of Δ from the approximate expression recently established by Hitchman:[22]

$$\Delta \simeq \frac{\bar{R}_0 f N \overline{\Delta R}}{nm}$$

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Table III. Comparison of Average Metal–Ligand Bond Distances (Å) between the High- and Low-Spin Forms of Six- and Five-Coordinate Spin-Crossover Compounds[a]

compd[b]	donor atom set	spin conversion	$\bar{R}$(HT)[c]	$\bar{R}$(LT)[c]	$\overline{\Delta R}$[d]	ref
$Fe^{II}(bpy)_2(NCS)_2$	N_6	$S = 0 \leftrightarrow S = 2$	2.14[e]	2.02[e]	0.12	24
$[Fe^{II}(2\text{-pic})_3]Cl_2 \cdot EtOH$	N_6	$S = 0 \leftrightarrow S = 2$	2.195	2.013	0.182	25
$[Fe^{II}(2\text{-pic})_3]Cl_2 \cdot MeOH$	N_6	$S = 0 \leftrightarrow S = 2$	2.198[f]	2.016	0.23[g]	26
$[Fe^{II}(6\text{-Mepy})_3tren](PF_6)_2$	N_6	$S = 0 \leftrightarrow S = 2$	2.213	2.093[h]	0.15[g]	10
$[Fe^{II}_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$	N_6[i]	$S = 0 \leftrightarrow S = 2$	2.174	2.031	0.143	28
$[Fe^{II}(dppen)_2Cl_2] \cdot 2(CH_3)_2CO$	P_4Cl_2	$S = 0 \leftrightarrow S = 2$	2.510	2.310	0.200	6
$[Fe^{II}(hptpd)Br](BPh_4) \cdot CH_2Cl_2$	P_4Br	$S = 0 \leftrightarrow S = 1$	2.261[f]	2.229[h]	0.09[g]	34
Fe(salen)(NO)	N_3O_2	$S = {}^1/_2 \leftrightarrow S = {}^3/_2$	1.950[f]	1.910	0.05	17
$Fe^{III}(Me_2dtc)_3$	S_6	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$	2.396[f]	2.339[h]	0.14[g]	31
$Fe^{III}(Et_2dtc)_3$	S_6	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$[l]	2.357[f]	2.306	0.11[g]	13
$[Fe^{III}((4\text{-mp})cdt)_3] \cdot CH_2Cl_2$	S_6	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$	2.427[f]	2.371[h]	0.15[g]	33
$[Fe^{III}(OEP)(3\text{-Clpy})_2](ClO_4)$	N_6	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$	2.074[f]	2.007	0.12[g]	12
$Fe^{III}(TPP)(NCS)py$[j]	N_6	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$	2.040[f]	1.978	0.12[g]	56
$NH_4[Fe^{III}(3,5\text{-Cltsa})_2] \cdot 1.5H_2O$[k]	$N_2O_2S_2$	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$	2.144[f]	2.069[h]	0.13[g]	57a
$K[Fe^{III}(3,5\text{-Cltsa})_2] \cdot 1.5H_2O$[k]	$N_2O_2S_2$	$S = {}^1/_2 \leftrightarrow S = {}^5/_2$ $S = {}^1/_2 \leftrightarrow S = {}^5/_2$	2.092[f] 2.136[f]	2.022[h] 2.048[h]	0.23[g] 0.15[g]	57b
$Co^{II}(nnp)(NCS)_2$	N_4P	$S = {}^1/_2 \leftrightarrow S = {}^3/_2$	2.09[f]	2.06	~0.06[g]	5

[a] This table only contains data arising from variable-temperature single-crystal X-ray diffraction studies. [b] Abbreviations: bpy = 2,2′-bipyridine; 2-pic = 2-picolylamine; $(6\text{-Mepy})_3$tren = tris[4-(6-methyl-2-pyridyl)-3-aza-3-butenyl]amine; Ettrz = 4-ethyl-1,2,4-triazole; dppen = *cis*-1,2-bis(diphenylphosphino)ethylene; hptpd = hexaphenyl-1,4,7,10-tetraphosphadecane; salen = *N*,*N*′-ethylenebis(salicylaldiminato) dianion; R_2dtc = *N*,*N*′-dialkyldithiocarbamato anion; (4-mp)cdt = 4-morpholinecarbodithioato anion; OEP = octaethylporphyrinato dianion; TPP = *meso*-tetraphenylporphinato dianion; 3,5-Cltsa = 3,5-dichlorosalicylaldehyde thiosemicarbazonato anion; nnp = *N*-[2-(diphenylphosphino)ethyl]-*N*′,*N*′-diethylethylenediamine. [c] Highest (HT) and lowest (LT) temperature data, not necessarily associated with the pure high- and low-spin species. [d] Average metal–ligand bond length differences between pure high- and low-spin forms. [e] Low-accuracy data; *R* factor = 0.21 (295 K) and 0.19 (~100 K). [f] Lower limit corresponding to an incomplete low-spin → high-spin conversion. [g] Value estimated for complete high-spin ↔ low-spin interconversion, by assuming a linear variation of $\bar{R}$ as a function of the high-spin fraction (deduced from effective magnetic moment). [h] Upper limit corresponding to an incomplete high-spin → low-spin conversion. [i] Environment of the only iron atom that exhibits a spin transition in this trinuclear molecule. [j] In this compound, there are two crystallographically independent molecular sites; iron(III) atoms undergo a spin transition in one of them only. [k] In this class of compounds, there are two crystallographically independent iron(III) atoms, both presenting a spin-crossover behavior in the potassium salt but only one of them in the ammonium salt. [l] The nature of the spin transition could not be determined in that case but is assumed to be of the type $S = {}^1/_2 \leftrightarrow S = {}^5/_2$ as in the homologous methyl derivative.

Here $\bar{R}_0$ is the initial mean metal-ligand bond distance, f the force constant of the corresponding symmetric stretching mode, N the number of ligand atoms bound to the metal ion, m the number of electrons involved in the spin change, and n a parameter defined by the fact that Δ is assumed to be inversely proportional to the nth power of $\bar{R}_0$. In the present cases $n \simeq 5$.[22,24] Satisfying f mean values can be estimated for the low-spin form of A (1.4071 mdyn Å^{-1}) and B (1.4395 mdyn Å^{-1}) complexes. They are deduced from the force constants calculated by Bigotto et al.[58] for the square-planar low-spin cobalt(II) compound formed with the Schiff base *N*,*N*′-ethylenebis(acetylacetone imine) dianion. It follows that

$$\Delta_{LS} \simeq 14400 \text{ cm}^{-1} \text{ (A)},\ 19800 \text{ cm}^{-1} \text{ (B)}$$

and, since Δ_{HS}/Δ_{LS} was assumed to nearly vary as $[(\bar{R}_0)_{LS}/(\bar{R}_0)_{HS}]^5$, that

$$\Delta_{HS} \simeq 11700 \text{ cm}^{-1} \text{ (A)},\ 14600 \text{ cm}^{-1} \text{ (B)}$$

Δ values are larger for the pyridine adduct than for the water adduct. This may account for the fact that the spin transition critical temperature of the former compound is higher than that for the latter one.[38,40] Moreover, since the electron mean pairing energy π of the metal ion is such that $\Delta_{HS} < \pi < \Delta_{LS}$ for a given compound, the above results are found to be in agreement with the range estimated for π in d^7 metal complexes by Machado[60] (14000–20000 cm^{-1}). To our knowledge, no Δ evaluation was reported so far for low-spin six-coordinate cobalt(II) species. In contrast, a number of data concern compounds with a spin-quartet ground state.[61–66] They lie between ≃6100 and ≃11 300 cm^{-1}. As expected, the Δ_{HS} values obtained for A and B complexes are found to be higher than the upper limit of this energy range. It should be noted that very few reliable data related to the crystal field splitting parameter in the high-spin form of spin-crossover cobalt(II) compounds are available, for comparison with the present results. A value of 13 800 cm^{-1} was deduced from the electronic spectrum of $Co(pvdh)_3Br_2$ (pvdh = pyruvaldehyde dihydrazone).[67]

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Supplementary Material Available: Listings of all the experimental **k**[χ(**k**)] vs. **k** data (26 pages). Ordering information is given on any current masthead page.

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