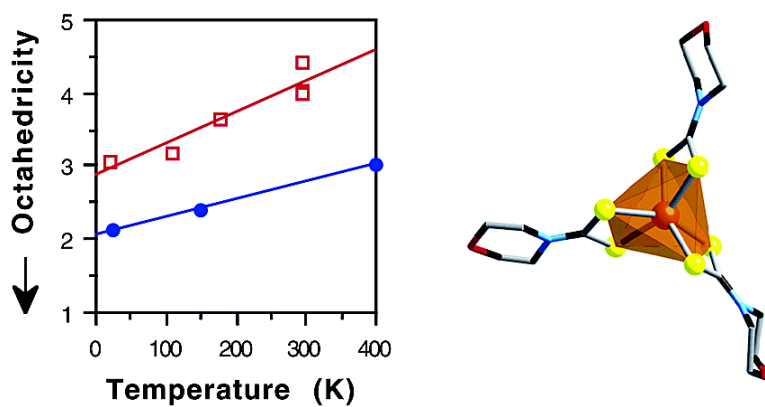


## Relationships between Temperature, Magnetic Moment, and Continuous Symmetry Measures in Spin Crossover Complexes

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## Relationships between Temperature, Magnetic Moment, and Continuous Symmetry Measures in Spin Crossover Complexes

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**Abstract:** A study of the changes in the symmetry of the metal coordination sphere that accompany spin crossover transitions has been carried out. Changes in symmetry have been calibrated by using the *continuous symmetry measures* approach. Different behaviors have been found for several families of complexes, depending on the nature of their ligands. The most remarkable changes take place for trischelate complexes, for which octahedrality, trigonal prismaticity, chirality, bite angle, bond distance, temperature, pressure, magnetic moment, and density are correlated.

In a series of systematic studies of the application of *continuous symmetry measures*<sup>1,2</sup> to the analysis of the molecular and crystal structures of transition metal compounds, we have shown how this conceptually simple, yet powerful, technique allows one to uncover structural trends<sup>3–5</sup> and to identify relationships between molecular symmetry and properties, such as visible absorption or electron spin resonance spectra.<sup>6</sup> In particular, for hexacoordinate complexes, we have shown<sup>4</sup> that a plot of the *distances* of ML<sub>6</sub> coordination spheres to the two ideal structures, the octahedron and the trigonal prism, gives a *symmetry map* in which each distortion pathway occupies a characteristic region. In the present paper, we pursue such investigations by reporting a continuous symmetry analysis of the structure and magnetism dependence on the temperature (or pressure, or irradiation) that accompanies the spin crossover transitions in the families of Fe<sup>II</sup>, Fe<sup>III</sup>, and Co<sup>II</sup> complexes with N<sub>6</sub> or S<sub>6</sub> donor sets. To that end, we have calculated the symmetry measures of each FeX<sub>6</sub> core relative to the octahedron and an ideal trigonal prism, which will be referred to throughout this paper as *S*(O<sub>h</sub>) and *S*(tp), respectively. A value of zero for one such symmetry measure indicates that the MX<sub>6</sub> group has the perfect symmetry (e.g., *S*(O<sub>h</sub>) = 0 indicates a perfect octahedron).

Spin crossover systems appear in the high-spin state at room temperature and undergo a transition to the low-spin state when the temperature is decreased,<sup>7–10</sup> the same transition being

observed under applied pressure at room temperature. Conversely, irradiation of the low-spin state at low temperature converts it to the high-spin state, which has a long enough relaxation time to be studied with a variety of techniques. This phenomenon is known as the light-induced excited spin state trapping (LIESST) effect.<sup>8</sup> In several cases, X-ray structures have been determined at different temperatures, under pressure, or after irradiation at low temperature. Those experiments offer us a valuable data set to analyze the relationships between the symmetry of the metal coordination sphere and physical parameters such as temperature, pressure, magnetic moment, and light irradiation.

It is well known that spin crossover implies a shortening of the metal–ligand distances in the low-spin temperature regime (at low temperature) due to the transfer of the strongly antibonding e<sub>g</sub> electrons to the nonbonding t<sub>2g</sub> set within the metal d-block orbitals. For instance, typical Fe–N distances in bipyridine or phenanthroline Fe<sup>II</sup> complexes are 1.9 and 2.1 Å for the low- and high-spin states, respectively. For the present study, we found it appropriate to distinguish the spin crossover complexes according to the nature of the ligands. Hence, we will consider the following: (a) complexes with only monodentate ligands; (b) trischelate complexes; (c) complexes with two monodentate and two bidentate ligands; and (d) complexes with tridentate ligands.

### Complexes with Only Monodentate Ligands

Probably the best studied Fe<sup>II</sup> spin crossover systems with monodentate ligands are the R–tetrazole complexes. Their structural data and symmetry measures are presented in Table 1. For the case of the methyl–tetrazole derivative, there are two crystallographically independent Fe sites. At low temper-

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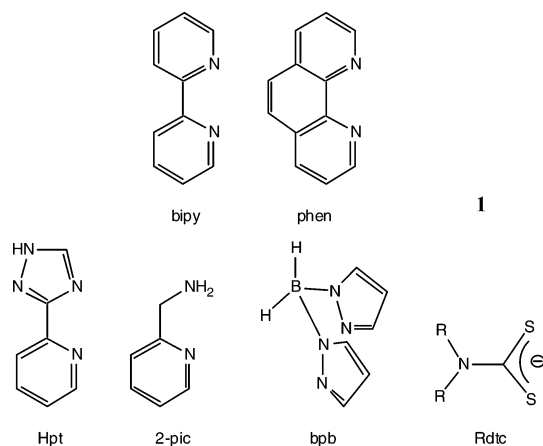
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ature, one of the Fe atoms undergoes a transition to the low-spin state, whereas the other one remains in the high-spin state. By irradiating the compound with light of the appropriate wavelength, Gütllich and co-workers have been able to solve the structure of high-spin-only and low-spin-only isomers at 10 K. In all cases, the spin state is nicely reflected in the average Fe–N distances of about 2.19 Å (high spin) and 2.01 Å (low spin). Despite the large bond length variations involved, the symmetry measures are insensitive to the spin state, indicating practically perfect octahedra in all cases. Hence, we can conclude that the symmetry measures reflect an isotropic contraction of the FeN<sub>6</sub> coordination sphere when going from the high- to the low-spin state (i.e., below the transition temperature).

### Complexes with Three Bidentate Ligands

This family of compounds includes Fe<sup>II</sup> and Fe<sup>III</sup> complexes with ligands shown in **1**, and the corresponding structural and magnetic data are collected in Tables 2 and 3, together with the calculated symmetry measures. At difference with what is found for compounds with monodentate ligands, the value of  $S(O_h)$  for a given compound decreases upon cooling. Differences in  $S(O_h)$  values of between 0.6 and 1.5 are found for the same compound at different temperatures, indicating small but significant distortions, according to our previous experience.<sup>4</sup> It is also seen that the  $S(itp)$  values change in the opposite way, and a good correlation between the two symmetry measures can be found (Figure 1), indicating that these structures are aligned along the Bailar distortion path, the trigonal twist that goes from the octahedron to the trigonal prism through intermediate metaprisms of  $D_3$  symmetry.



More specifically, if we focus on the temperature dependence of the symmetry measures of two dithiocarbamate complexes, tris(4-morpholinedithiocarbamate)iron(III)<sup>28,29,31</sup> and tris(*N,N'*-

**Table 1.** Structural and Continuous Symmetry Data for Hexakis(monodentate) Fe<sup>II</sup> Complexes with R–Tetrazolato Ligands

R	refcode	T (K)	conditions	atom	Fe–N (Å)	$S(O_h)$	$S(itp)$	ref
Me		10	LIESST-100% hs	Fe1	2.177	0.02	16.44	11
		10	LIESST-100% hs	Fe2	2.183	0.02	16.46	
		10	ambient 50% hs	Fe1	1.991	0.00	16.62	
		10	ambient 50% hs	Fe2	2.188	0.01	16.55	
		10	LIESST-100% ls	Fe1	2.031	0.00	16.59	
		10	LIESST-100% ls	Fe2	2.017	0.02	16.48	
Me	juvhen	295		Fe1	2.189	0.02	16.44	12
		295		Fe2	2.180	0.01	16.54	
Me	juvhir	113		Fe1	2.170	0.03	16.46	12
		113		Fe2	2.174	0.02	16.45	
		157		Fe1	2.178	0.02	16.53	
		157		Fe2	2.179	0.02	16.46	
Et	tunbin	295		Fe1	2.183	0.02	16.33	13
		295		Fe2	2.197	0.02	16.42	
Pr	jansas	140		Fe	2.151	0.02	16.62	14
		195		Fe	2.180	0.00	16.68	12
		250		Fe	2.172	0.00	16.68	
		295		Fe	2.175	0.00	16.73	
		295		Fe	2.165	0.00	16.68	15
Pr	nefvid	295		Fe1	2.191	0.01	16.52	16
		130		Fe1	2.187	0.01	16.52	
EtCl	rakzim	295		Fe1	2.208	0.01	16.62	17

dimethyldithiocarbamate)iron(III),<sup>25,26</sup> for which the structure has been solved at several temperatures, we can see that these approach the octahedron as the temperature is lowered, while at the same time they get farther away from the trigonal prism (Figure 2). The unprecedented relationship between symmetry and temperature must be attributed to the change in spin state, as seen by the relationship between the magnetic moment and symmetry measure, illustrated in Figure 3 for three compounds, one with an Fe<sup>II</sup>N<sub>6</sub> core<sup>18–20</sup> and two with Fe<sup>III</sup>S<sub>6</sub> cores.<sup>25,26,28,29</sup> The importance of such changes in the symmetry measures can be calibrated by comparison with those previously reported by Keinan et al.<sup>6</sup> for hexacoordinated Cu(II) complexes, for which the dynamic Jahn–Teller effect at high temperature produces variations in  $S(O_h)$  of less than 0.1 units.

If we recall that spin transitions for complexes with monodentate ligands only are associated with an isotropic contraction of the coordination sphere, we can ask why in this case the spin transition brings about a symmetry change, unequivocally identified as a Bailar twist? We must realize that we are dealing with bidentate ligands now. An important parameter of a bidentate ligand is its *normalized bite*, defined as the ratio between the donor•••donor distance and the average of the

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**Table 2.** Structural, Continuous Symmetry, and Magnetic Data for Tris(bidentate) Fe<sup>II</sup> Complexes with N<sub>6</sub> Cores<sup>a</sup>

ligand <sup>b</sup>	T (K)	Fe–X (Å)	<i>b</i>	$\theta$	<i>S</i> (O <sub>h</sub> )	<i>S</i> (itp)	<i>S</i> (chir)	space group	$\mu$ ( $\mu_B$ ) <sup>c</sup>	refcode	ref
2-pic	295	2.199	1.23	40.8	2.32	9.96	0.45	<i>P bca</i>		apafem	18
	227	2.198	1.23	41.4	2.26	10.28	0.50		apafem01	19	
	199	2.203	1.22	40.3	2.58	9.99	0.56		apafem02		
	171	2.189	1.24	41.7	2.17	10.30	0.45		apafem03		
	148	2.010	1.31	50.1	0.77	13.28	0.10		apafem04		
	115	2.016	1.31	49.8	0.79	13.12	0.11	apafem05			
2-pic	295	2.181	1.24	40.8	2.42	9.99	0.42	<i>P2</i> <sub>1</sub> / <i>c</i>		fepicc02	18
	295	2.195	1.22	40.3	2.57	9.94	0.46		5.1	fepicc20	20
	115	2.091	1.26	44.8	1.57	11.30	0.24		3.4	fepicc03	19
	90	2.013	1.30	49.5	0.86	12.99	0.10		0.9	fepicc21	20
bipy, bpb	139	2.032	1.42 <sup>d</sup>	56.4	0.36	15.82	0.02	<i>C2</i> / <i>c</i>	0.1	neftex	21
			1.27								
	295	2.187	1.40 <sup>d</sup>	51.4	0.74	13.63	0.05		3.7	neftex01	
			1.19								
ptz	250	2.179	1.24	42.6	1.87	10.61	0.61	<i>P bam</i>	5.4	qalmar	22
	95	2.027	1.29	48.9	0.85	12.85	0.30		2.8	qalmar01	

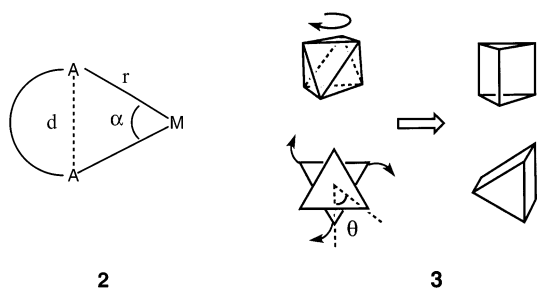
<sup>a</sup> *b* is the normalized bite of the bidentate ligand,  $\theta$  is the trigonal twist angle, *S*(O<sub>h</sub>), *S*(itp), and *S*(chir) are the octahedral, trigonal prismatic, and chirality symmetry measures, respectively, and  $\mu$  is the magnetic moment. <sup>b</sup> For the abbreviations used for the ligands, see **1**. <sup>c</sup> The values of magnetic moment given are only approximate, because in most cases these have been reported only in graphical form. <sup>d</sup> The two values of the normalized bite correspond to the bpb and bipy ligands, in that order.

**Table 3.** Structural, Continuous Symmetry, and Magnetic Data for Tris(dithiocarbamate) Fe<sup>III</sup> Complexes with S<sub>6</sub> Cores

ligand	T (K)	Fe–X (Å)	<i>b</i>	$\theta$	<i>S</i> (O <sub>h</sub> )	<i>S</i> (itp)	<i>S</i> (chir)	space group	$\mu$ ( $\mu_B$ ) <sup>a</sup>	refcode	ref
Bzdtc	295	2.327	1.22	40.2	2.50	8.69	0.46	<i>P2</i> <sub>1</sub>	3.5	bztcfe10	23
	295	2.349	1.21	42.8	2.05	9.82	0.47		bztcfe10		
	150	2.314	1.22	41.0	2.30	8.93	0.41		2.5	bztcfe11	
	150	2.306	1.23	43.5	1.87	10.06	0.40			bztcfe11	
Etdtc	295	2.357	1.21	38.3	2.81	7.43		<i>P2</i> <sub>1</sub> / <i>c</i>	4.3	detcfe	24
	79	2.307	1.23	40.1	2.18	8.43			2.2	detcfe01	
Medtc	400	2.415	1.19	37.6	3.01	7.65	0.85	<i>P bca</i>	4.8	dmtcfe03	25
	295	2.396	1.20	38.3	2.84	7.86	0.81		4.2	dmtcfe	26
	150	2.339	1.22	40.1	2.39	8.50	0.69		2.3	dmtcfe01	26
	25	2.303	1.23	41.2	2.12	8.89	0.60			dmtcfe02	25
HOEtdtc	295	2.390	1.20	34.1	3.63	6.10	0.96	<i>P</i> -1	4.2	hetcfe	27
	150	2.331	1.22	36.5	2.99	6.90	0.77		2.4	hetcfe01	
Morphdtc	295	2.430	1.18	33.4	4.03	6.06	1.02	<i>P</i> -1	5.1	mrdfte	28
	295	2.427	1.19	33.6	3.98	6.10			5.9	mrdfte01	29
	295	2.441	1.18	31.1	4.41	5.08	1.27		5.9	mrdfte05	
	178	2.401	1.20	34.9	3.63	6.58			5.1	mrdfte02	
	110	2.371	1.20	36.7	3.16	7.16			4.4	mrdfte03	
(CH <sub>2</sub> ) <sub>2</sub> CN	20	2.357	1.21	37.1	3.06	7.35		<i>P</i> -1	3.8	mrdfte04	
	210	2.308	1.23	43.7	1.80	11.48			3.2	bogjow	30
	295	2.321	1.22	42.9	1.93	11.17			3.9	bogjow01	

<sup>a</sup> The values of the magnetic moment given are only approximate, because in most cases these have been reported only in graphical form. *b* is the normalized bite of the bidentate ligand,  $\theta$  is the trigonal twist angle, *S*(O<sub>h</sub>), *S*(itp), and *S*(chir) are the octahedral, trigonal prismatic, and chirality symmetry measures, respectively, and  $\mu$  is the magnetic moment. For the abbreviations used for the ligands, see **1**.

metal–donor bond distance ( $b = d/r$  in **2**). For a given ligand, the donor···donor distance is approximately constant; hence the decrease in the M–L bond distances that results from the transition from a high- to a low-spin state must imply an increase in the normalized bite. This can be actually seen in the experimental data for several trischelate complexes for which the X-ray structure has been determined in both spin states (Table 2).



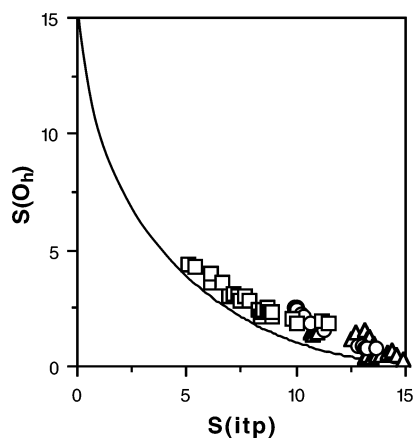
KePERT had shown early on that in trischelate complexes there

is a correlation between the normalized bite of a bidentate ligand and the trigonal twist angle  $\theta$  (**3**).<sup>32</sup> We have recently reported a systematic structural database analysis of hexacoordinate complexes<sup>4,33</sup> and concluded that such a correlation can be expressed by the following equation for the experimental data of complexes with three or more d electrons in the range  $30^\circ < \theta < 60^\circ$ :

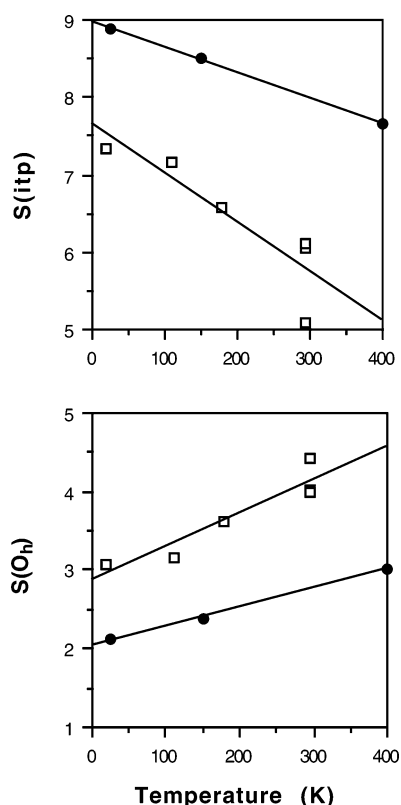
$$\theta = 88.0b - 64.9 \quad (1)$$

Only two exceptions to this rule were found, corresponding to d<sup>5</sup> Fe<sup>III</sup> complexes with encapsulating ligands.<sup>34,35</sup> In summary, small bite ligands favor distortion toward a trigonal prism, driven by the smaller bond angles in this polyhedron (81.8°) as compared to those in the octahedron (90°).

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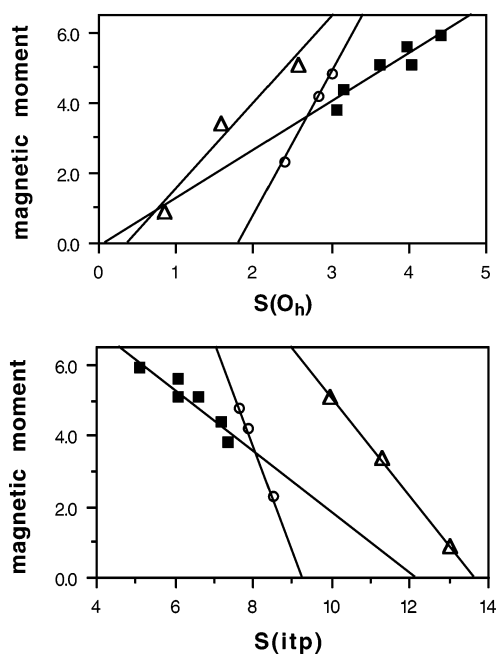


**Figure 1.** Scatterplot of the trigonal prismatic and octahedral symmetry measures of different families of tris- and bischelate Fe complexes:  $[\text{Fe}^{\text{II}}(\text{N-chelate})_3]$  (○),  $[\text{Fe}^{\text{III}}(\text{dithiocarbamate})_3]$  (□), and  $[\text{Fe}^{\text{II}}(\text{N-chelate})_2(\text{NCS})_2]$  (△). The solid line corresponds to the ideal Bailar pathway for the interconversion of the octahedron and trigonal prism.<sup>4</sup>

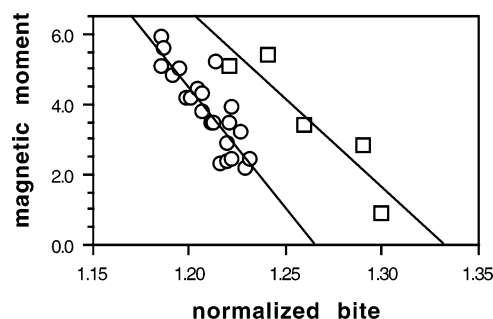


**Figure 2.** Variation of the trigonal prismaticity (above) and octahedrity (below) of the Fe coordination sphere as a function of the temperature for the spin crossover complexes  $[\text{Fe}(\text{morpholine-dtc})_3]$  (□) and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]$  (●).

Because the shortening of the metal–ligand bond distances associated with the transition from the high-spin to the low-spin state induces an increase in the normalized bite of the bidentate ligands, one should expect a significant trigonal twist to accompany the temperature (or pressure- or light-) induced change of the spin state. As an example, for typical Fe–N distances in bipyridine or phenanthroline iron complexes (1.9 and 2.1 Å for low- and high-spin states, respectively), one would expect from eq 1 the twist angle  $\theta$  to vary from  $57^\circ$  (nearly octahedral) to  $45^\circ$  (clearly a  $D_3$  distorted octahedron). In practice



**Figure 3.** Dependence of the magnetic moment (in  $\mu_B$ ) on the octahedral (above) and trigonal prismatic (below) measures of three spin crossover Fe complexes:  $[\text{Fe}(\text{morpholine-dtc})_3]$  (■),  $[\text{Fe}(2\text{-pic})_3]$  (△), and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]$  (○).

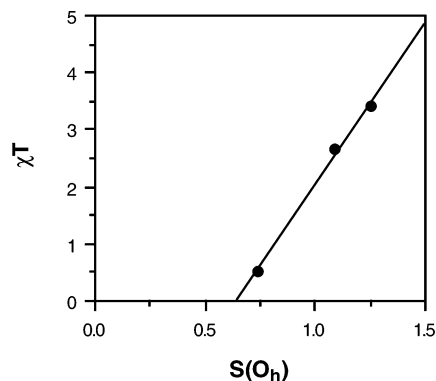


**Figure 4.** Relationship between the magnetic moment and the normalized bite of the bidentate ligand in the families of  $[\text{Fe}^{\text{II}}(\text{N-chelate})_3]$  (○) and  $[\text{Fe}^{\text{III}}(\text{dithiocarbamate})_3]$  (□) complexes.

(Table 2), we find changes of  $9\text{--}10^\circ$  in  $\theta$  for  $\text{Fe}^{\text{II}}\text{N}_6$  complexes and of  $2\text{--}6^\circ$  for  $\text{Fe}^{\text{III}}\text{S}_6$  complexes.

The present results unequivocally indicate that a trigonal twist distortion is associated to the transition from high- to low-spin upon lowering the temperature. According to the relationship discussed above between the normalized bite and twist angle, it is clear now that the shorter metal–ligand distances of the low-spin state imply a smaller normalized bite, and hence a larger distortion toward a trigonal prismatic structure. In this regard, it is noteworthy that a fair correlation is found between the experimental magnetic moment and the normalized bite for the two families of compounds studied here (Figure 4). Given the changes in metal–ligand bond distances associated to spin crossover, one should not be surprised to find that, for a given compound, a good correlation is found between its density and its octahedrity at various temperatures (scatterplots provided as Supporting Information): as  $S(O_h)$  decreases, the density increases.

It is worth mentioning that an exception to the general behavior discussed in this section has been identified, corresponding to  $[\text{Fe}(\text{bpb})_2(\text{bipy})]$ . The bpb ligand (**1**) has a rather



**Figure 5.** Dependence of the product  $\chi T$  of  $[\text{Co}(\text{bipy})_3]^+$  salts on the octahedral symmetry measure of the  $\text{CoN}_6$  core.

variable bite, its donor...donor distance is far from being constant and changes from 3.038 Å at high temperature to 2.891 Å at low temperature (i.e., a shortening of 0.14 Å), in contrast with the behavior of the bipy ligand in the same molecule, whose N...N distance increases only 0.08 Å. Consequently, the N–Fe–N bond angles subtended by the bpb ligands remain nearly temperature independent, and only a small trigonal twist results (the average  $\theta$  changes from 56.4° to 51.4°, due mostly to the bipy ligand). These facts indicate that one should not generalize the conclusions of this study to all spin crossover trischelate systems, but only to those with rigid bidentate ligands.

Some authors had previously proposed the existence of synchronous racemization and intersystem crossing in solution,<sup>36</sup> as well as the presence of a trigonal torsion accompanying the spin transition in the solid state.<sup>37</sup> The present symmetry analysis goes a little farther and attributes such a trigonal twist to the constant bite of the bidentate ligands and differentiates it from distortions that accompany the spin transition in the presence of other types of ligands (cf. previous and subsequent sections). The idea that the spin transition can be considered as a “one-dimensional problem in the totally symmetric metal–ligand stretching coordinate,” still present in the minds of many researchers, should probably be abandoned as proposed by Beattie,<sup>7</sup> but only for trischelate complexes.

Although studies of  $d^7$  spin crossover systems are less abundant, we wish to briefly mention here the salts of the  $[\text{Co}(\text{bipy})_3]^{2+}$  cation, which appears in the high-spin state with different counteranions<sup>38,39</sup> but becomes a spin crossover system when incorporated into the cavities of zeolite-Y<sup>40</sup> or in the three-dimensional networks of  $[\text{ACr}(\text{ox})_3]^{2-}$  ( $A = \text{Li}, \text{Na}$ ).<sup>41</sup> Remarkably, both the host lattice and the temperature affect the magnetic behavior of the cation, but the relationship between octahedrality and magnetic moment holds regardless of the nature of the external factors affecting it, as shown in Figure 5.

Among the studied trischelate complexes (Table 2), only one crystallizes in an enantiomorphic space group,<sup>23</sup> which means only one enantiomer is present in the crystal. The study of the

spin and temperature dependence of its chiroptical properties should thus provide new interesting perspectives of the spin crossover systems. The resolution of other enantiopure spin crossover systems and the study of their chiroptical properties seem to be appealing research areas.

### Complexes of the Type $[\text{Fe}(\text{chelate})_2(\text{NCS})_2]$ : Pressure and Symmetry

$\text{Fe}^{\text{II}}$  complexes with two N-donor bidentate and two thiocyanato ligands form one of the families that has been most studied in regard to their spin crossover behavior (see Table 4). In addition to the temperature dependence of the magnetic susceptibility, in a couple of cases<sup>42</sup> also the application of pressure has been shown to produce a spin transition. As for the symmetry changes associated with the spin crossover transition, these compounds behave in a way similar to that of the trischelate compounds discussed above, even though there are some differences to be discussed. The decreased Fe–N bond lengths that accompany the change from the high- to the low-spin state induce a decreased bite angle and a trigonal twist, as can be seen in Figure 1, where the symmetry measures of these compounds are plotted alongside those of the trischelate analogues. In that figure, one can appreciate that deviations from the octahedral geometry are less pronounced in this case due to the presence of two monodentate ligands. Hence, while the chelate angles decrease (by 5–7°) from the low- to high-spin state (i.e., with increasing temperature) as happens for the trischelate family, the N–Fe–N bond angle subtended by the thiocyanato ligands evolves in the opposite direction (increases by 3–6°), thus compensating in part the tendency to twist toward the trigonal prism. Consequently, the ranges of  $\theta$  and  $S(O_h)$  values are significantly reduced relative to those of the trischelates. As found for the trischelates, the octahedrality and the density of a given spin crossover compound are nicely correlated, both increasing with temperature (scatterplot provided as Supporting Information).

For those cases in which the spin transition is induced by an applied pressure, the expected dependence of octahedrality on pressure is found (Figure 6). What is remarkable is that the symmetry measure of those two compounds at high pressure is practically coincident with the values that correspond to ambient pressure and low temperature. It is thus tempting to conclude that there is some equivalence between pressure and temperature, as far as the effect of these parameters on molecular symmetry is concerned. Interestingly enough, by equating the linear dependences of  $S(O_h)$  for a given compound on temperature and pressure, we obtain the same expression for the equivalence between those two variables for the two compounds studied,<sup>42,45,46</sup> where  $T_{\text{eq}}$  is the temperature that produces an effect equivalent to the application of a pressure  $P$ :

$$T_{\text{eq}} (\text{K}) = 313 - 185P (\text{GPa}) \quad (2)$$

At present, this is just a suggestion to be checked when more

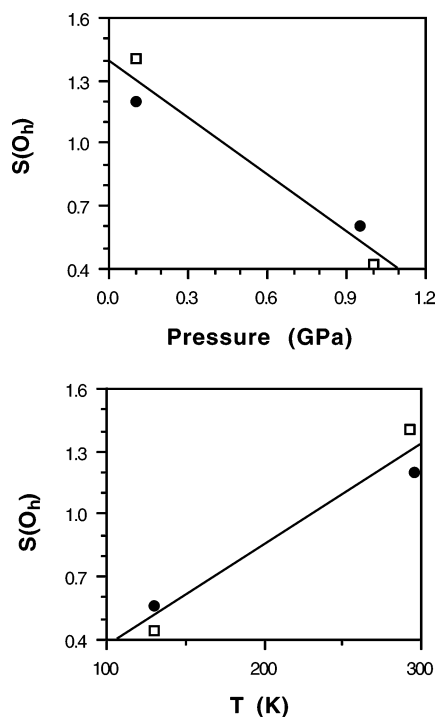
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**Table 4.** Structural, Continuous Symmetry, and Magnetic Data for Bis(bidentate)bis(thiocyanate) Fe<sup>II</sup> Complexes

T (K)	Fe-X (Å)	b	θ	S(O <sub>h</sub> )	S(tp)	S(chir)	space group	μ (μ <sub>B</sub> ) <sup>a</sup>	refcode	ref
30 <sup>b</sup>	2.143	1.235	45.6	1.48	10.68	0.27	<i>P bcn</i>			43
30	1.983	1.316	52.3	0.39	13.41	0.08				
110	1.959	1.304	52.0	0.50	13.70	0.12	<i>P cnb</i>		febpyc02	44
175	1.962	1.305	52.1	0.47	13.88	0.11			febpyc03	
295	2.133	1.212	45.0	1.49	10.96	0.30			febpyc04	
293	2.156	1.233	45.8	1.41	10.79	0.26	<i>P bcn</i>	5.2	kekvi01	45
130	1.992	1.309	51.7	0.45	13.22	0.09		2.2	kekvi02	
293 <sup>c</sup>	1.978	1.320	52.0	0.42	13.15	0.09			pasgof	
295	2.136	1.213	47.8	1.20	12.56	0.27	<i>P bcn</i>	5.2	pasgof01	46
130	1.963	1.286	51.9	0.57	14.13	0.14		2.4	pasgof02	46
295 <sup>c</sup>	1.962	1.290	50.9	0.60	13.53	0.16		—	pasgof02	42
295	2.215	1.223	50.8	1.02	13.56	0.13	<i>P-1</i>		pohlon	47
135	1.985	1.324	55.8	0.25	14.88	0.04			pohlon01	
295	2.173	1.209	49.7	1.60	13.18	0.31	<i>P ccn</i>	5.4	ronpit	48
295	2.173	1.209	49.7	1.60	13.18	0.31		5.4	ronpit01	49
140	1.956	1.296	54.9	0.45	15.05	0.16		1.0	ronpit02	
140	2.120	1.230	49.7	1.14	13.22	0.29	<i>P ccn</i>	4.3	xecmib	50
295	2.173	1.205	48.3	1.41	12.71	0.37		5.1	xecmib01	
11	2.022	1.269	52.5	0.65	14.36	0.17		3.2	xecmib02	
110	1.967	1.293	55.2	0.44	14.57	0.12	<i>P2<sub>1</sub>/c</i>	0.0	xecnau	50
295	2.161	1.207	50.5	1.25	13.32	0.30		5.2	xecnau01	

<sup>a</sup> The values of magnetic moment given are only approximate, because in most cases these have been reported only in graphical form. <sup>b</sup> High spin through LIESST effect. <sup>c</sup> Applied pressure of 1 GPa.

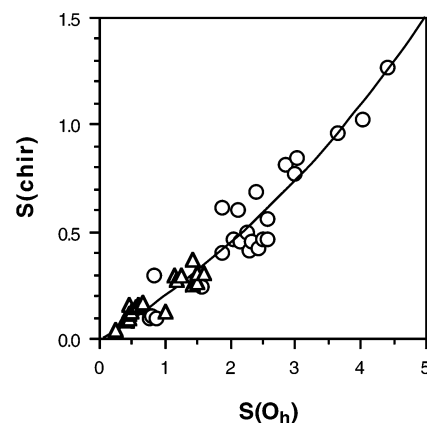


**Figure 6.** Dependence of the octahedral symmetry measure of the FeN<sub>6</sub> core of two [Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>] complexes<sup>42,45,46</sup> on the pressure at room temperature (above) and on the temperature at ambient pressure (below).

structural data under pressure are available for spin crossover systems. An intriguing aspect of the crystal structure of these compounds is that none of them crystallizes in an enantiomorphic space group and, even if the molecules themselves are chiral, the corresponding crystals are thus racemic.

### Chirality and Magnetism

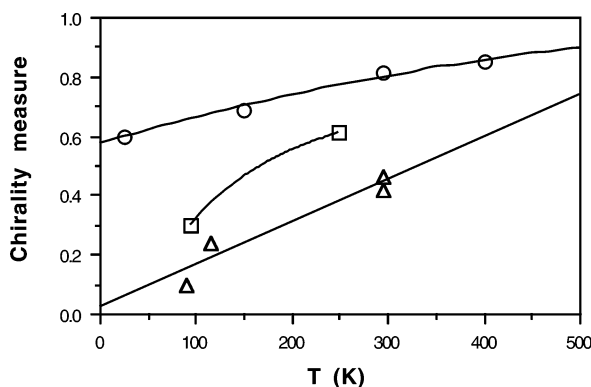
We have seen that bis- or trischelate complexes undergo trigonal twists associated with the spin transition. Because the octahedron is achiral but the twisted *D*<sub>3</sub> metaprismatic structures are chiral, we should expect the chirality measure of the metal coordination sphere to increase as the Bailar<sup>51</sup> trigonal distortion



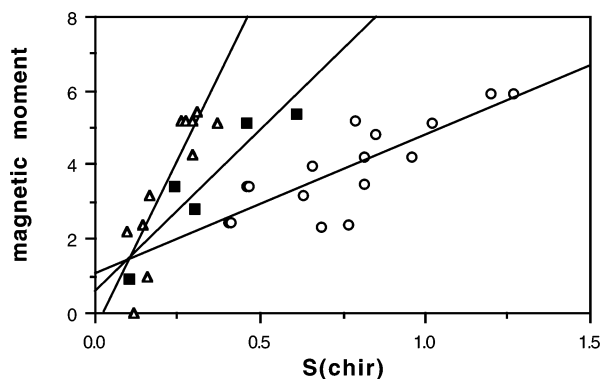
**Figure 7.** Scatterplot of the octahedral symmetry and the chirality measures of the FeN<sub>6</sub> core of complexes of the [Fe<sup>II</sup>(*N*-chelate)<sub>3</sub>] (○) and [Fe<sup>II</sup>(*N*-chelate)<sub>2</sub>(NCS)<sub>2</sub>] (△) families.

from the octahedron increases, reaching a maximum<sup>52</sup> at a twist angle of 23°. Indeed, a nice correlation between octahedrality and chirality can be found for the bis- and trischelate complexes studied here (Figure 7), which present twist angles larger than 23°. A further consequence of this variation in chirality is that trischelate spin crossover complexes should exhibit an interesting temperature dependence of their chirality, as found in the variable temperature structural data of three different trischelate complexes<sup>18–20,22,25,26</sup> (Figure 8). Consequently, the temperature dependence of chirality should be reflected in the changes of the optical activity and circular dichroism spectra of enantiomerically pure trischelate complexes with temperature. Although there are no reports of enantiomerically resolved spin crossover systems, many of the complexes studied here crystallize in

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**Figure 8.** Temperature dependence of the chirality measure of the first atomic shell of [Fe(Me<sub>2</sub>dtc)<sub>3</sub>] (○), [Fe(3-pyridin-2-yl)-1,2,4-triazole-*N,N'*]<sub>3</sub> (□), and [Fe(2-pic)<sub>3</sub>] (△). Continuous lines are given as guides to the eye.



**Figure 9.** Relationship between the effective magnetic moment and chirality measure of the first coordination shell for trischelate complexes with Fe<sup>II</sup>N<sub>6</sub> (■) and Fe<sup>III</sup>S<sub>6</sub> (○) cores and for [Fe(bidentate)<sub>2</sub>(NCS)<sub>2</sub>] complexes (△).

enantiomorphic<sup>53</sup> space groups (Tables 2–4), a fact that indicates the presence of only one enantiomer in the crystal structure, and these are good candidates for circular dichroism studies.

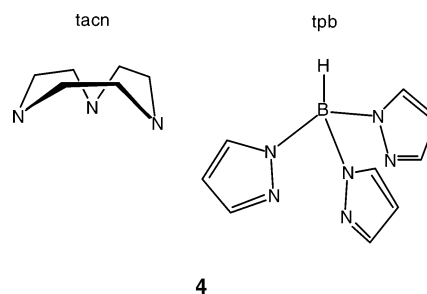
Still another consequence of the correlation between octahedrity and chirality is that the decreased chirality associated with decreasing temperature and transition to the low-spin state should be expected to correlate with the magnetic moment. The reader will thus not be surprised to see that, for a given family of complexes, magnetic moment and chirality present a positive correlation: the larger the chirality is, the larger the magnetic moment is (Figure 9). Even if these families include compounds with quite different ligands, the qualitative behavior is the same in the three families included in the figure.

The trigonal twist has been proposed as a pathway for the racemization reaction of trischelate complexes.<sup>54</sup> In such a mechanism, the pseudo-octahedral coordination sphere of a given handedness is converted to its mirror image by rotating two parallel faces of the coordination octahedron relative to each other around a trigonal axis, reaching a trigonal prismatic transition state and continuing rotation to the alternative enantiomer. Because in the high-spin state the geometry of the complexes is closer to the trigonal prism than that in the low-spin state, whatever factor favors the high-spin configuration (e.g., high temperature, low pressure, photoexcitation at low temperature)

should lower the barrier for the corresponding racemization reactions. Conversely, whatever favors the low-spin state should increase the racemization barrier and could be of help in the resolution of the two enantiomers. A further consequence is that the rates of racemization reactions for bis- and trischelate spin crossover complexes should be much more temperature dependent than those of analogous compounds without spin crossover behavior.

### Complexes with Tridentate Ligands

Two types of tridentate ligands can be considered, those that span three *fac* positions (4), such as triazacyclononane (tacn) or tris(pyrazolyl)borate (tpb), and those spanning three *mer* positions (5), topologically analogous to terpyridine (terpy). An Fe<sup>II</sup> complex with a tridentate ligand that presents spin crossover is [Fe(Me<sub>3</sub>tacn)(NCMe)<sub>3</sub>](BPh<sub>4</sub>)<sub>2</sub>, whose structure has been solved at 243 and 368 K.<sup>55</sup> In such a compound, the metal–ligand bond shortening characteristic of the high- to low-spin transition is appreciated both for the macrocyclic tridentate (average Fe–N = 2.145 and 2.054 Å, respectively) and for the monodentate ligands (average Fe–N = 2.110 and 1.976 Å, respectively). Given the rigidity of the tacn ligand, the changes in Fe–N bond distances are reflected in changes in the corresponding N–Fe–N bond angles, which we calibrate by the sum of these three angles (Σ), which should be 270° in a perfect octahedron. The spin transition affects the two ligands in a quite different way: whereas the angles subtended by tacn slightly increase upon cooling (Σ = 248.2° and 254.3° for the high- and low-temperature phases, respectively), those corresponding to monodentate ligands are practically unaffected (Σ = 268.7° and 268.4° at high and low temperatures, respectively). As a consequence, the octahedral symmetry measure *S*(O<sub>h</sub>) is only slightly affected by the spin transition (0.31 at high temperature and 0.17 at low temperature), in contrast with changes in excess of 1.0 units observed above for the tris-(bidentate) complexes.



4

A different family of complexes has the general topology shown in 5, with two tridentate ligands spanning perpendicular *mer* positions of the coordination octahedron. Depending on the rings present in the ligand and on its substituents, the corresponding Fe compounds may present spin crossover, although in most cases either structural or magnetic data at different temperatures are not available. The bis(2,6-bis(pyrazol-1-yl)pyridine) complex of Fe<sup>II</sup> has been studied at four temperatures<sup>56</sup> between 150 and 375 K. In that case, the small bite angle imposed by the ligand results in a distortion from the

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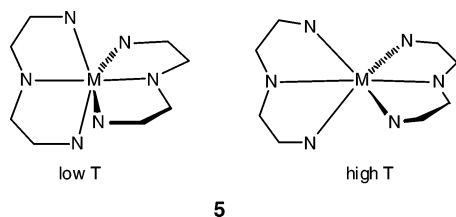


**Table 5.** Structural, Continuous Symmetry, and Magnetic Data for Bis(2,6-bis(pyrazol-1-yl)pyridine)iron(II)<sup>54 a</sup>

refcode	T (K)	Fe–N <sub>c</sub>	Fe–N <sub>t</sub>	α	b	S(O <sub>h</sub> )	S(tp)	S(chir)	μ (μ <sub>B</sub> )
xenbex03	150	1.902	1.978	80.0	1.28	2.078	12.29	0.01	0.89
xenbex02	240	1.899	1.976	80.0	1.28	2.071	12.32	0.01	1.26
xenbex	295	2.126	2.184	73.5	1.19	5.604	10.53	0.03	5.51
xenbex01	375	2.129	2.191	73.2	1.19	5.741	10.62	0.02	5.58

<sup>a</sup> α is the average bite angle N<sub>t</sub>–Fe–N<sub>c</sub>, b is the normalized bite (N<sup>⋯</sup>N/Fe–N<sub>av</sub>), and μ is the magnetic moment.

octahedral symmetry even in the low-spin temperature range (Table 5). At higher temperature, the longer Fe–N distances compatible with the high-spin state result in a smaller bite angle, and hence in an additional deviation from ideal octahedricity (see S(O<sub>h</sub>) values in Table 5), schematically represented in 5. Although the trigonal prismatic measures decrease for the high-spin state, indicating that the coordination sphere of Fe approaches the trigonal prism, the actual values of the two symmetry measures correspond to the behavior expected for the bite angle distortion only, keeping a D<sub>2d</sub> symmetry.<sup>4</sup> A scatterplot of the two symmetry measures for the Fe spin crossover compounds of this family<sup>40,53</sup> shows that they are nicely aligned with the D<sub>2d</sub> distortion path previously reported by us<sup>4</sup> (Figure 10, continuous line) rather than with the trigonal twist (Figure 10, dashed line).

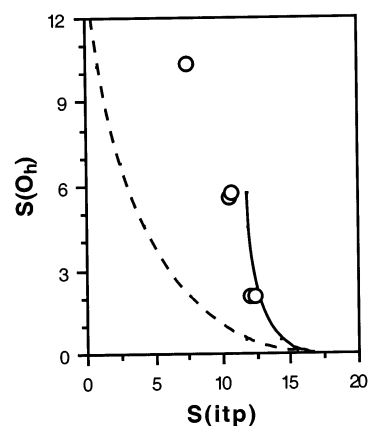


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## Main Conclusions

A reexamination of several transition metal spin crossover systems from the point of view of the continuous symmetry measures has allowed us to widen the number of properties that are affected by the spin transition. Thus, good correlations have been found between a variety of parameters: temperature, magnetic moment, octahedricity, trigonal prismicity, chirality, Fe–X average bond distance, normalized bite of the bidentate ligand, rotation angle θ along the Bailar twist, pressure, size of the cavity of a host lattice, density, and, presumably, optical activity.

The distortion that accompanies the spin transition is associated to changes in the normalized bite of bidentate ligands; hence the extent of the distortion has to do with the rigidity of those ligands. Relationships between octahedricity, trigonal prismicity, and magnetic moment within a family of related complexes hold independently of the nature of the external perturbations applied



**Figure 10.** Symmetry map for hexacoordination, showing the behavior of spin crossover systems with *mer* tridentate ligands (O). The Bailar pathway for the interconversion between the octahedron and trigonal prism<sup>4</sup> 3 is indicated by a dashed line; the pathway for a D<sub>2d</sub> double axial distortion 5 is indicated by a continuous line.

(temperature, light, pressure, host lattice). On the other hand, the spin transition affects the bond distances but scarcely the bond angles subtended by monodentate ligands.

For tris(bidentate) complexes and (to a lesser extent) for bis(bidentate) complexes, the changes in bite angles induce a Bailar trigonal twist and, consequently, enhanced chirality of the first coordination sphere. However, it must be said that such conclusions seem to apply only to chelate systems with rigid bidentate ligands. In contrast, complexes with one facial tridentate ligand or two meridional tridentate ligands preserve their C<sub>3v</sub> and D<sub>2d</sub> symmetries, respectively, and their first coordination spheres remain essentially achiral regardless of the spin state.

The synthesis and structural characterization of enantiopure spin crossover systems, as well as the study of the temperature dependence of their chiroptical properties or the kinetics of their racemization reactions, remain mostly unexplored fields that deserve further research.

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**Supporting Information Available:** Scatterplots showing the relationship between crystal density and octahedral symmetry measures for Fe<sup>III</sup> dithiocarbamates and Fe<sup>II</sup> bis(chelates) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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