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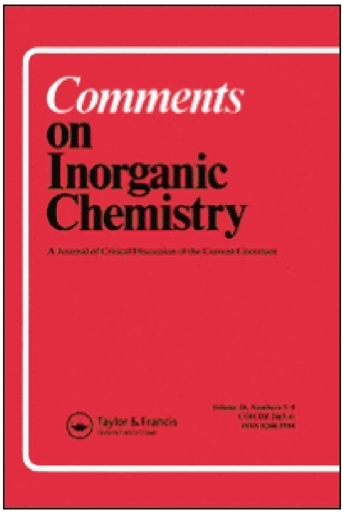

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Spin-State Transformation in Some Iron(III) Complexes with Schiff Base Ligands

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The magnetic properties of spin-crossover iron(III) complexes with N_4O_2 ligands are reviewed and especially the rapid spin-state interexchange is discussed on the basis of absorption, ir, epr and Mössbauer spectra. Results from single crystal X-ray structure determination, kinetics and dilution experiments are also reported.

Key Words: *spin-crossover complexes, rapid spin-state interexchange, iron(III) complexes with Schiff base ligands, intramolecular and intermolecular interaction*

Spin-state transformation properties ($^2T \rightleftharpoons {}^6A$) of some iron(III) complexes with N_4O_2 ligands—transformation temperature, temperature range, and spin-state interexchange rate—are characteristic of each complex. In the solid state the essentially intramolecular phenomenon is strongly coupled with the phonon system, and the properties are sensitive to slight geometrical modifications of the coordination sphere and solid state packing effects. Some of these new complexes exhibit the dynamic spin-state interexchange and open up new aspects in solid state chemistry.

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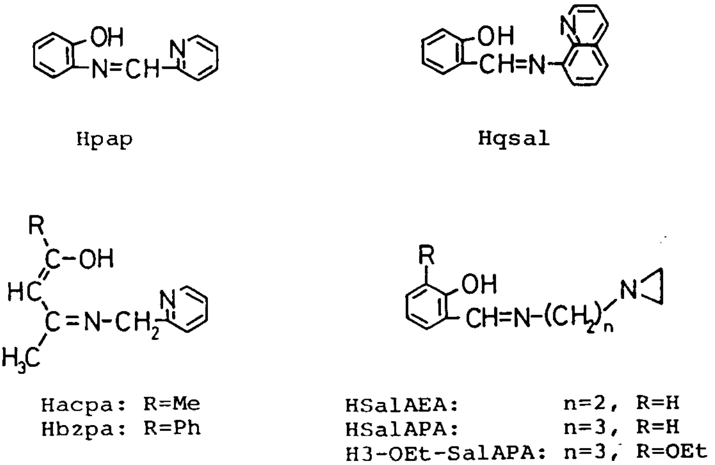
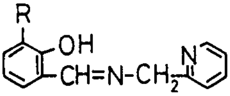
INTRODUCTION

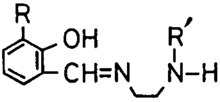
Transition-metal complexes exhibiting "spin crossover" between thermally populated low- and high-spin states have been recognized since Cambi and Szegö first observed "magnetic isomerism" for the tris(dithiocarbamate)iron(III) complexes in 1931.[1] The complexes and their derivatives show rapid spin-state interexchange on the ^{57}Fe Mössbauer time scale (0.98×10^{-7} s). More remarkable is the low-spin (LS) $\rightleftharpoons$ high-spin (HS) crossover process arising from iron(III) in a tetragonally distorted N_4O_2 ligand environment, which is less covalent and has less spin-orbit interaction. Effects of the chelate ring size, substituents, counterions, solvation, metal dilution, and lattice defect on spin crossover for the FeN_4O_2 complexes have recently been vigorously examined. The very latest studies have focused upon understanding the mechanism and dynamics of rapid spin-state interexchange in the solid state and the reason why the rates of spin-state interexchange in the FeN_4O_2 systems are sensitive to solid state packing effects. Ligand observations used here are shown in Scheme 1.



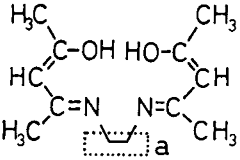
SCHEME 1 Abbreviations for ligands (notice that some of these abbreviations are different from the original ones used) Me=CH_3, Et=CH_2CH_3, Ph=C_6H_5. im: imidazole; Nmim: N-methylimidazole; 2mim:2-methylimidazole; py: pyridine; 3-pic: 3-methylpyridine; 4-pic: 4-methylpyridine; lut: 3,4-dimethylpyridine; dpp: 1,3-di-4-pyridylpropane.



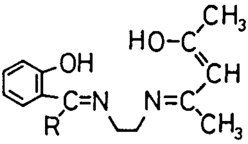
Hsapa: R=H
Hvapa: R=OMe



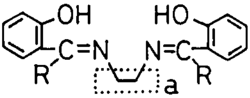
HSalEen: R=H, R'=Et
H3-OMe-SalEen: R=OMe, R'=Et
H3-R-SalBzen: R=OEt or allyl, R'=benzyl



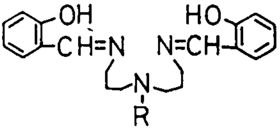
H_2acen: a= 
H_2acac$_2$trien: a= 



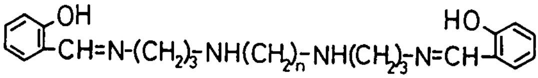
H_2salacen: R=H
H_2hapacen: R=Me



H_2salen: R=H a= 
H_2hapen: R=Me, a= 
H_2salphen: R=H, a= 
H_2Sal$_2$trien: R=H, a= 



H_2salten: R=H



H_2Sal$_2$3,3,3-tet: n=3
H_2Sal$_2$3,2,3-tet: n=2

SCHEME 1 (continued)

MAGNETISM

The effective magnetic moments (μ_{eff}) for LS isomers are larger than the spin-only value 1.73 μ_B because the ^2T ground states usually possess a sizeable orbital contribution. The complexes are classified for convenience into "gradual transformation type" (GTT) or "abrupt transformation type" (ATT) on the basis of temperature dependence of μ_{eff}. For the former type complexes, μ_{eff} values change continuously over a wide temperature range, and the behavior results from the fact that the spin-state transformation in the complexes proceeds gradually with temperature or that the electronic state of an iron ion is in thermal equilibrium between the ^2T ground and ^6A excited states and the equilibrium point is dependent on temperature. For the latter type complexes, electronic states change between HS and LS states within a few degrees at a certain critical temperature and the transformations are connected with a first-order phase transition.

The complexes $[Fe(acpa)_2]X$ (X = ClO_4, PF_6, or Bph_4) and $[Fe(bzpa)_2]PF_6$ undergo gradual and complete spin-state transformations.[2-4] $[Fe(sapa)_2]NO_3$ and $[Fe(bzpa)_2]Bph_4$ exhibit incomplete transformation, and the transformation temperature T_c (formally defined as the temperature at which LS and HS states are equally occupied) for $[Fe(acpa)_2]NO_3$ is situated above 300 K.[3] Both $[Fe(pap)_2]ClO_4$ and $[Fe(qsal)_2]NCS$ exhibit a pronounced hysteresis effect in the spin-state transformation and are anion dependent.[5] $[Fe(pap)_2]PF_6$ is in the LS state and the NO_3 and Bph_4 salts in the HS state. It is unpredictable which spin-state is favored by a counterion. Fresh $[Fe(qsal)_2]NCS$ recrystallized below 280 K is predominantly in the LS state. However, the magnetic moment at room temperature increases with time as shown in Fig. 1, the complexes experiencing spin crossover. Remarkable is the fact that the T_c's and temperature ranges are unchanged. The crystal structure for the time/thermal annealed complexes is different from that for the fresh one.

Spin-crossover behavior of $[Fe(SalAPA)_2]ClO_4$, the CH_2Cl_2 adducts, $[Fe(SalAEA)]ClO_4$, and $[Fe(3\text{-}OEt\text{-}SalAPA)_2]X$ (X = ClO_4 or Bph_4) is classified into GTT.[6,7] More crystalline samples of $[Fe(SalAPA)_2]ClO_4$, $[Fe(3\text{-}OEt\text{-}SalAPA)_2]ClO_4\cdot C_6H_6$ and $[Fe(3\text{-}OEt\text{-}SalBzen)_2]Bph_4\cdot CH_3CN$ experience gradual and nearly com-

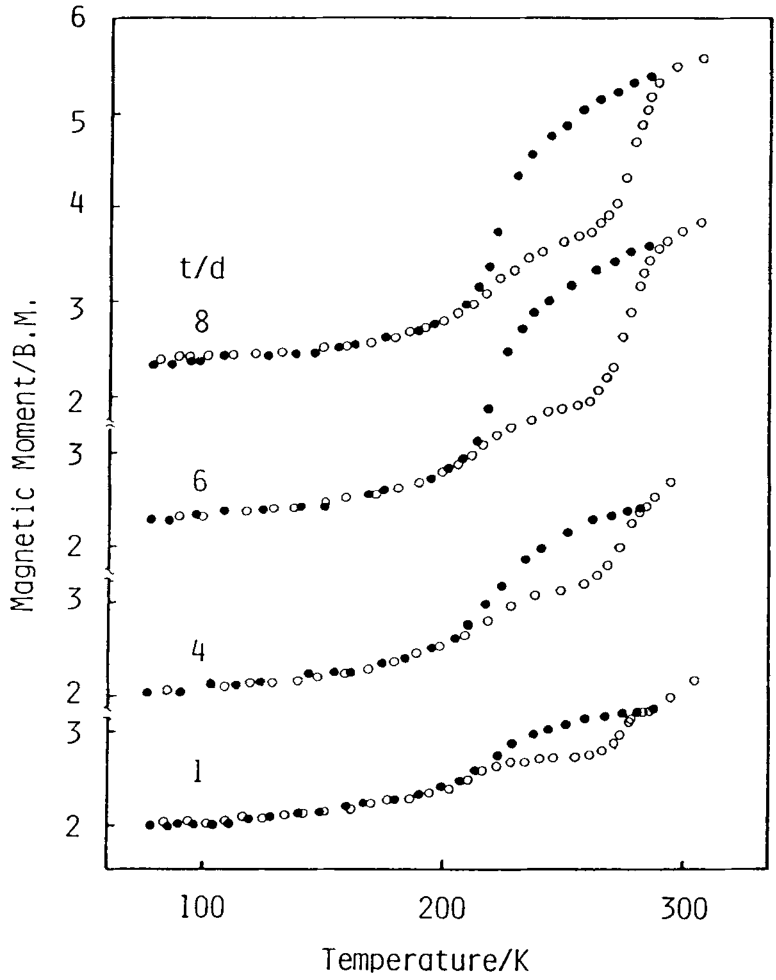


FIGURE 1 Temperature dependence of the magnetic moment for [Fe(qsal)$_2$]NCS after various periods of aging [decreasing temperature (●), increasing temperature (○)]. The time intervals at 286 K after preparation are shown.

plete transformation.[7,8] [Fe(3-Allyl-SalBzen)$_2$]NO$_3$ is mainly in the LS state.[9] [Fe(SalEen)$_2$]PF$_6$ exhibits complete transformation[10,11] and the nitrate exhibits incomplete transformation. [Fe(3-OMe-SalEen)$_2$]PF$_6$ is one of the rare examples which exhibit relatively sharp transformation within ca. 2 K.

$[Fe(acen)L_2]Bph_4$ (L = 1/2 dpp, 4-pic, or lut)[12–14] and [Fe(hapacen) $(Nmim)_2]PF_6$[15,16] with tetradentate ligands undergo gradual and complete transformation. $[Fe(im)_2(salacen)]Bph_4{\cdot}CH_3OH$ and [Fe(hapacen) $(im)_2]Bph_4{\cdot}2CH_3OH$ are almost in the LS state in the solid, although both of the complexes exhibit spin crossover in solution. The fact that $[Fe(hapen)(im)_2]Bph_4$ experiences spin crossover is remarkable, because $[Fe(im)_2(salen)]^+$ is of the HS type. The spin state would depend not only on the strength of the ligand field, but also on the crystal lattice energy and the steric effect, and this fact suggests less flexibility of salen than acen.

$[Fe(salten)L]Bph_4$ (L = py, 3-pic, 4-pic, lut, or 2mim) with a quinquedentate ligand exhibits gradual spin-state transformation, the 2mim complexes experiencing complete transformation.[17]

$[Fe(Y\text{-}Sal_2trien)]X$ ($X = PF_6$ or Bph_4) containing a hexadentate ligand exhibits incomplete transformation in the solid, the magnetic moments being anion dependent.[18] $[Fe(acac_2trien)]PF_6$ is of the HS type, and the BPh_4 salts and $[Fe(Sal_2trien)]NO_3{\cdot}H_2O$ are nearly in the LS state.[18] These complexes exhibit spin crossover in solution, in which the spin states are dependent on the electron-withdrawing capability of the chelate ring substituents. Spin crossover of $[Fe(acac_2trien)]X$ is strongly solvent dependent in solution.

$[Fe(Sal_23,3,3\text{-}tet)]NO_3$ and $[Fe(Sal_23,2,3\text{-}tet)]NO_3$ are in HS and LS states in the solid, respectively, but the former complexes show spin crossover in methanol.[19]

[Fe(salen)NO][20] and [Fe(salphen)NO][21] exhibit spin crossover between S = 3/2 and S = 1/2 states. [Fe(salen)NO] is of ATT (T_c = 175 ± 3 K) and the transformation of [Fe(salphen)NO] is gradual and the rates are greater than the inverse of the Mössbauer lifetime.

ABSORPTION AND EPR SPECTRA

The reversible thermochromism accompanying spin transformation is observed for FeN_4O_2 complexes. The color of the LS complexes (generally green) differs from that of the HS complexes (blue, dark red, brown, violet, or black). The higher energy bands at 500–550 nm decrease steadily in intensity and the lower energy bands at 600–700 nm increase in intensity with decreasing temperature and moment. Generally these bands with extinction coefficients of 500–3500 $dm^3mol^{-1}cm^{-1}$ may be attributed to the charge transfer transitions between metal and ligands in origin, which would be important in the spin-transformation process.

EPR is useful in the study of the electronic state of the spin-crossover compounds. In the EPR spectra of some iron(III) complexes, broad peaks are observed at $g \approx 2$ and in the range of $g = 4.1–4.3$, indicating that the molecular symmetry is low.[22] As the temperature is lowered, new sharp peaks split into two (axial symmetry) or three (rhombic symmetry) bands, for example g = 2.389, 2.130, 1.901 for $[Fe(acen)(lut)_2]Bph_4$, or $g_{\parallel} = 1.954$, $g_{\perp} =$ 2.220 for $[Fe(acpa)_2]PF_6$, at the expense of the broad $g \approx 2$ signal. $[Fe(SalAPA)_2]ClO_4$ with *trans* geometry for the two oxygen atoms exhibits rhombic signals (g = 2.349, 2.109, 1.951).

These complexes are tetragonally distorted so that the actual S = 1/2 electronic ground state is either a ^2E or a ^2A state arising from the octahedral ^2T state. From the g values for LS iron(III) complexes an unpaired electron is determined to be occupied in the d_{xy} orbital for $[Fe(im)_2L]^+$ (L = acen, hapacen, or salacen), $[Fe(acpa)_2]^+$, $[Fe(SalAPA)_2]^+$, and $[Fe(SalEen)_2]^+$ series. All the complexes with the "time averaged" Mössbauer spectra exhibit the individual EPR signals (10^{-10} s for X-band frequency) at the intermediate temperature in accordance with the absorption experiment (10^{-15} s) and this fact implies that the rates of spin-state interexchange are slower than 10^{-10} s.

IR SPECTRA

Bands for ν_{N-H} are observed at 3100–3420 cm^{-1} and there is no systematic correlation between the degree of multiplicity in the N–H stretching pattern.[18] Spin-crossover behavior of $[Fe(Y\text{-}Sal_2trien)]X$ is correlated to the hydrogen bonding of the N–H group with the anion and/or water.[18] The C=N stretching vibrations appear to be insensitive to the change in the spin states for FeN_4O_2 complexes. The six normal mode frequencies of ν_{Fe-L} for the LS isomers of $[Fe(acpa)_2]PF_6$ are 17 ~ 163 cm^{-1} greater than the corresponding frequencies of the HS isomers,[23] respectively, and then geometrical modification in the coordination sphere is deemed to be important.

MÖSSBAUER SPECTRA

For the HS FeN_4O_2 complexes, isomer shifts relative to the center of the absorption of metallic iron are in the range of 0.25–0.37 mm/s at r.t. and quadrupole splittings (ΔE) are less than 1.3 mm/s. The isomer shifts for LS isomers are 0.05–0.20 mm/s less than those for the HS isomers, and large ΔE of 1.9–3.0 mm/s are observed. Complex $[Fe(3\text{-}OEt\text{-}SalAPA)_2]ClO_4 \cdot C_6H_6$ having the *trans* geometry for the two oxygen atoms exhibits large ΔE of 2.389 mm/s and the plot of the ΔE vs. T shows the existence of a minimum value in contrast to that for *cis* geometry complex $[Fe(acpa)_2]PF_6$.

Mössbauer spectroscopy is an extremely powerful tool for studying the dynamic electron state over a period of time of the order of 10^{-6}–10^{-8} s. The "time-averaged" Mössbauer spectra are observed for $[Fe(acpa)_2]X$ (X = Bph_4, NO_3, or ClO_4) and $[Fe(bzpa)_2]PF_6$, and slower relaxation of $\tau = 4.4 \times 10^{-7}$ s at 207 K is observed for the anion displaced $[Fe(acpa)_2]PF_6$. The τ values for $[Fe(acpa)_2]PF_6$ are temperature dependent, and so the spin interexchange process can be discussed by the classical activated-complex theory.[24] Here the relaxation time τ is defined as $\tau = \tau_l\tau_h/(\tau_l + \tau_h)$, where τ_l and τ_h are the lifetimes calculated for the LS and HS isomers, respectively.

The "time-averaged" spectra are observed for $[Fe(2mim)(salten)]Bph_4$ and $[Fe(acen)L_2]Bph_4$ (L = 1/2 dpp or 4-pic), but not for axial ligand displaced $[Fe(acen)(lut)_2]Bph_4$. $[Fe(hapacen)(Nmim)_2]PF_6$ exhibits the spin-state interexchange of $\tau = 2.3 \times 10^{-7}$ s at 275 K.

The more crystalline sample $[Fe(SalAPA)_2]ClO_4$, the CH_2Cl_2 adduct, $[Fe(3\text{-}OEt\text{-}SalAPA)_2]ClO_4$, the benzene adduct, and Bph_4 salts experience rapid spin-state interexchange. The less crystalline $[Fe(SalAPA)_2]ClO_4$ shows a superposition of the quadrupole doublets of two spin states in the intermediate temperature range. But both samples have nearly identical ir and X-ray powder diffraction data. Rapid spin-state interexchange is observed for

[Fe(acac$_2$trien)]X and [Fe(Sal$_2$trien)]X in solution, but in the solid state the rates become slower.

The spin-state interexchange rates are anion, substituent, solvent, and crystalinity dependent. We have observed the rate on the basis of the Mössbauer time scale, but it is likely that spin-state interexchanges commonly occur at a slower rate in some FeN$_4$O$_2$ complexes.

SINGLE CRYSTAL X-RAY STRUCTURES

The metal ion environments in [Fe(acpa)$_2$]X (X = PF$_6$ or Bph$_4$) and [Fe(acen)(lut)$_2$]Bph$_4$ are pseudo-octahedral with *cis* geometry on oxygen atoms, and no phase transitions are detected for these complexes.[25] On the other hand, [Fe(3-OEt-SalAPA)$_2$]ClO$_4$ and [FeL]NO$_3$ (L = Sal$_2$3,3,3-tet or Sal$_2$3,2,3-tet) favor *trans* geometry.

The average metal–donor atom distances decrease by 0.10 Å upon transformation, but these differences are not uniform: 0.15 Å for Fe–N(amine or pyridine) bonds and 0.04 Å for Fe–O bonds. König and co-workers[26] have reported that for GTT complexes the HS/LS molar ratios derived crystallographically from the average Fe–donor atom lengths are in good agreement with those derived from the magnetic moments, and that the gradual transformation occurs in a single lattice. In fact, only faint local rearrangements around the metal ion are observed in [Fe(acpa)$_2$]X (X = PF$_6$ or Bph$_4$), etc. Although ΔV values (ΔV = specific volume difference between HS and LS isomers) are in the range from 3.4% to 6.2% for four complexes[8,25,27] of which structures have been determined heretofore and seem to be in the same range as that reported for ATT iron(II) complexes, further examples are needed to discuss the correlation between ΔV and the rate.

EFFECTS OF LATTICE DEFECTS AND METAL DILUTION

Spin-crossover complexes are often sensitive to preparative methods and crystallization conditions. Grinding[11] or ^{60}Co γ-ray irradiation influences the transition behavior because these operations modify the crystal quality. A careful study was done with the GTT complexes $[Fe(im)_2(vanen)]Bph_4$ and $[Fe(SalEen)_2]PF_6$, and with ATT complex $[Fe(VanEen)_2]PF_6$.[28] In the irradiated GTT complexes the fraction of LS isomer decreases with increasing exposure dose at a given temperature, but in ATT complexes no irradiation effect was observed. ATT complexes may possess a relatively large domain size in which the spin transformation takes place cooperatively. These results are interpreted using models proposed by Sorai and Seki,[29] and Gütlich *et al.*[30] Even if a hit of gamma-rays produces a "defective" area in which a structure is distorted, it is likely that the spin-state interexchanges of iron atoms in these areas progressed according to the demand of "cooperativity" from the areas having the normal structure in a domain. On the other hand, in GTT complexes the molecule is no longer able to change its spin-state depending on temperature since there is no such interaction as the defective areas are recovered.

One can distinguish between intramolecular and intermolecular interactions by diluting the iron complexes with other metal complexes. Spin-state transformations for doped $[Fe_xCo_{1-x}(3\text{-OMe-SalEen})_2]PF_6$ or grinding samples are nicely interpreted using a model involving the nucleation and growth mechanism proposed by Hendrickson *et al.*[11] Gütlich *et al.* have proposed the newly developed lattice expansion model for $[Fe_xM_{1-x}(2\text{-pic})_3]Cl_2 \cdot S$ (S = solvent).[31] The effect of grinding causes a slight increase in the HS fraction for $[Fe(3\text{-OEt-SalBzen})_2]Bph_4$ and $[Fe(SalEen)_2]PF_6$. Grinding $[Fe(SalAPA)_2]ClO_4$ with a mortar slows down the rate of the dynamic spin-state interexchange and increases the HS fraction. Slight grinding of fresh LS $[Fe(qsal)_2]NCS$ leads to HS complexes (this complex shows spin crossover).[5]

The spin-state interexchange rates for $[Fe(acpa)_2]Bph_4$ and $[Fe(bzpa)_2]Bph_4$ adsorbed on SiO_2 are slow compared to those for the corresponding pure complexes, whereas Mössbauer spectra for $[Fe(acpa)_2]PF_6$ adsorbed on SiO_2 exhibit no detectable difference in the rate.[32] These observations lead to suggestions that the packing state and intermolecular interactions play a significant role in determining spin-state interexchange rates in the solid state.

KINETICS

Although equilibrium constants (K = (HS)/(LS)) can be calculated as a function of temperature and it is possible to estimate enthalpy changes ΔH and entropy changes ΔS accompanying spin-state transformations from the plots of ln K vs. $1/T$, a linear ln K vs. $1/T$ curve is observed in a limited temperature range for solid complexes. Therefore, $\Delta S = 36.2\ \mathrm{JK^{-1}mol^{-1}}$ for $[\mathrm{Fe(acpa)_2}]\mathrm{PF_6}$ is directly obtained using an adiabatic calorimeter.[23] "Electronic entropy" changes are $R\ln(6/4) = 3.35\ \mathrm{JK^{-1}mol^{-1}}$ for $^2\mathrm{E} \rightleftharpoons {}^6\mathrm{A}$ or $R\ln(6/2) = 9.13\ \mathrm{JK^{-1}mol^{-1}}$ for $^2\mathrm{A} \rightleftharpoons {}^6\mathrm{A}$. The contributions from each part of the phonon system (stretching and deformation vibrations of metal–donor atom and other intramolecular vibrations) of the complexes were estimated. Significant amounts of this could be accounted for by the changes in the Fe–N stretching frequencies and deformation vibrations around an iron, which is close to the main entropy change ($27.1\ \mathrm{JK^{-1}mol^{-1}}$). Therefore, the spin transformation not only in ATT complexes but also in GTT complexes is coupled with the phonon system around the iron atom. Major contributions to ΔH would arise from the changing Fe–donor atom bond distances and energies accompanying the spin-transformation process.

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