Other Applications. The results concerning the numbers and types of atoms and their coordinates may also be useful in understanding the morphology and habits of microcrystallites[38] and the structure (cavities) and properties of zeolites and clays[39] and in investigating the electronic structure[40] of metal clusters and the dynamic simulation[41] of crystal and cluster growth, as well as in many branches of science involving sphere packing.

The results presented in this paper should also be useful in spectroscopic techniques such as extended X-ray absorption fine structure (EXAFS)[42] and low-energy electron diffraction (LEED),[43] where, in addition to the numbers and types of atoms, the site geometry, symmetry, and coordination numbers are important parameters to be applied to, or deduced from, experimental data.

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Systems Exhibiting Spin Equilibrium. Do Different Chromophores Really Coexist in the Lattice?

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Depending upon the strength of the coupling between two different pure spin states, a double or a single minimum can occur on the potential energy surface of the ground state. In the former case two different chromophores can be revealed by suitable fast experiments, while in the latter the whole system behaves as if constituted by chromophores of only one kind in the presence of large anharmonicity. As an example the problem of the singlet–triplet spin equilibrium in iron(II) complexes is considered.

Introduction

The strength of the ligand field (LF) governs the ground-state spin multiplicity in transition-metal complexes having electronic configurations d^2, d^3, ..., d^8. When the LF splitting is comparable with the interelectronic repulsion, high-spin (HS) and low-spin (LS) states are nearly degenerate and an anomalous magnetic behavior has to be expected, with magnetic moments intermediate between those of purely HS and LS complexes.

Since the first examples reported by Cambi and his school in the early 1930s,[1] many compounds with "anomalous" magnetic moment have been described, particularly in the chemistry of iron(II), iron(III), and cobalt(II).[2-5] In spite of the vast amount of experimental data that is now available, a full description of these systems has not yet been reached and several issues are still open. One of these issues concerns the effective coexistence of HS and LS species or, in other words, the possibility of distinguishing the simultaneous presence of HS and LS complexes in the lattice by using suitable experiments.[4-19] When intermolecular mechanisms induce phase transitions, it is obvious that two alternative species can be identified in the two phases. The situation is quite different when no apparent phase transition occurs. With regard to X-ray diffraction studies two extremes have been described: (i) a multiple-temperature analysis has revealed the coexistence of two spin isomers for the methanol solvate of tris(2-picolylamine)iron(II) dichloride;[19] on the contrary, (ii) the crystal structures of the $[Fe(P_4)Br]BPh_4{\cdot}CH_2Cl_2$ complex (P_4 = hexaphenyl-1,4,7,10-tetraphosphadecane) at 298 and 150 K have shown only one species with "normal" thermal ellipsoids in the lattice.[6,11] Moreover, spectroscopic measurements can provide a double or a single signal, and in the latter case, usually it is said that the lifetimes of the coexisting spin isomers are shorter than

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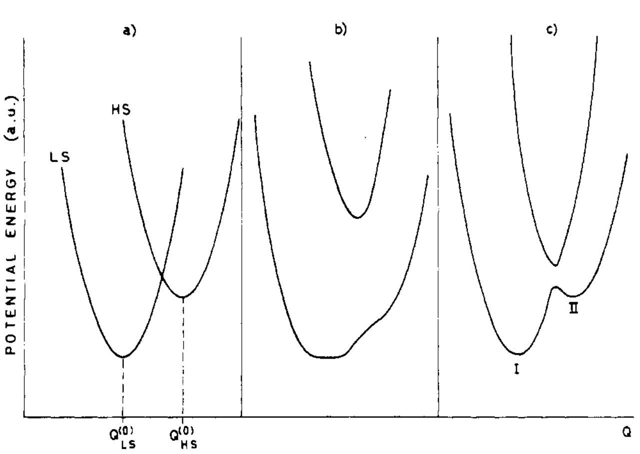

Figure 1. Cross sections along the generic coordinate Q: (a) uncoupled low-spin and high-spin levels; (b) strong coupling; (c) weak coupling.

the characteristic time of the measurement process.

Since, in our opinion, this matter has frequently been treated in a contradictory manner, in this paper we dwell mainly upon the above aspect. Moreover, we will show that some physical systems can exist where the coupling between the two pure states is so strong that the picture by means of two different interconverting complexes is no longer valid.

At this point a consideration is in order.

It is now widely recognized that cooperative effects play a fundamental role in spin equilibrium systems mainly when phase transitions occur.[20-26] Moreover, the very recent experiments by Hendrickson et al.[27] have nicely shown that spin transitions involve the formation and the subsequent growth of single domains, the size of which strongly affects the experimental results. However, it should be remembered that every cooperative effect is built up upon local effects, which are the indispensable primer of the macroscopic modification. Therefore, since we are not interested in those cases where the existence of different species is self-evident (i.e. phase transitions), here we shall limit ourselves to a "molecular" picture of the physical system and will not consider explicitly cooperative effects, which could be triggered off by local electronic and/or nuclear rearrangements.

Finally, it should be noted that the title systems are a typical example of systems displaying electronic and/or stereochemical lability:[28] in fact the spin-state change is accompanied by a variation of the equilibrium nuclear configuration. Other examples are found in systems exhibiting mixed valence,[29-34] Jahn-Teller activity,[35-38] and multiwell potential energy surfaces induced by conformational changes.[39] The results and conclusions of this paper could be applied, mutatis mutandis, to all of the above systems, but we have considered only systems exhibiting spin equilibrium, because we feel that particularly on account of these the debate is more lively.

Theoretical Approach

The eigenfunctions describing pure spin states can be expressed as a Born-Oppenheimer product ($\phi_i^{(0)}(r,Q)S_u\chi^{(n)}(Q - Q_i^{(0)})$, where $\phi_i^{(0)}(r,Q)$ are the electronic wave functions, S_u are the spin functions of the appropriate multiplicity, and $\chi^{(n)}(Q - Q_i^{(0)})$ are the vibrational wave functions (n is the vibrational quantum number) centered at the nuclear equilibrium position $Q_i^{(0)}$; here r stands for the electronic coordinates. Although some authors[20-22] have considered the Jahn-Teller effect as a trigger for cooperative spin transitions, we will disregard this effect in our "molecular" picture. Actually, weak Jahn-Teller interactions are expected in iron(III) and iron(II) complexes, which we are mainly concerned with, whereas a much stronger coupling should be present in the spin doublet terms of Co(II) complexes.[40]

The two pure spin states generally have different equilibrium positions $Q_i^{(0)}$ (Figure 1a). If, for the sake of simplicity, only the totally symmetric breathing mode is considered, it is clear that $Q_{HS}^{(0)}$ is longer than $Q_{LS}^{(0)}$ owing to greater occupancy of the antibonding orbitals in the HS form.[5,41] In this framework we expect smaller bond distance changes, when a single electron is involved in the spin transition (singlet $\rightleftharpoons$ triplet in iron(II) or doublet $\rightleftharpoons$ quartet in cobalt(II) complexes).

Depending upon the strength of the coupling between the two different pure spin states and/or the distance between the two minima, two extremes are possible: (a) a single minimum with a large anharmonicity (Figure 1b); (b) an asymmetric double minimum (Figure 1c).

Case a is favored when the minima of the pure spin states are close to each other and the coupling is strong, so that it should be typical of doublet-quartet spin equilibria in Co(II) complexes and of singlet-triplet spin equilibria in Fe(II) and Ni(II) complexes. In fact, in these complexes a direct spin-orbit coupling between the two states is accompanied by a small variation of the bond distances in passing from the LS to the HS state (see above). On the contrary, case b is more probable in complexes of Fe(II) and Fe(III) exhibiting singlet-quintet and doublet-sextet spin equilibria, respectively, since spin-orbit coupling can be effective only at the second order and a much larger displacement of the minima is expected.

The wave functions describing type a systems (Figure 1b) are always a close mixture of the unperturbed HS and LS functions, whereas the eigenfunctions corresponding to the low-lying states in type b systems (Figure 1c) are mainly constituted by the unperturbed LS functions and the HS contribution increases as more excited states are considered.

It is clear that case b (Figure 1c) involves a typical nonadiabatic process, because the electronic part of the wave function changes notably along the trajectory connecting the two spin states, while case a (Figure 1b) can be considered a more adiabatic process (see below).

At this point an important question arises: what can we expect from a measurement of some property f in case a and b? This question is strictly connected to the characteristic time of the measurement and to the possibility of observing nonstationary states.[42]

Because of the uncertainty principle, $(\Delta E)(\Delta t) \geq \hbar/2$, the detection of stationary states requires a slow measurement of f (large Δt) so that the associated uncertainty in energy (ΔE) is much less than the separation among the stationary states. Therefore, for symmetric or nearly symmetric potential wells slow and high-resolution measurements like radio-frequency techniques

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are necessary to detect stationary states, due to the presence of couples of energy levels that are very close to each other. On the contrary, fast spectroscopic techniques have ΔE values, which are large compared to the separation of the stationary states, and as a consequence, a statistical average $\langle f \rangle$ appropriate to a mixture of stationary states is observed. In other words, for systems characterized by a multiwell potential we can "catch" molecules in a given well, if sufficiently short measurements are performed.

Instead, when the energy difference between the potential minima is increased, the stationary states are well separated and they can be revealed also by not too slow measurements (EPR, Mössbauer).

Furthermore, another characteristic time, that is the relaxation time between the levels, should be considered. This relaxation process, which is assisted by the phonon modes of the thermal bath, is usually so fast at high temperature (of the order of ps or less[43-45]) as to be safely disregarded when traditional measurements are performed. However, when the temperature decreases, there is a corresponding increase in relaxation time (and a decrease in uncertainty in energy), which could make it possible to detect different stationary states simultaneously. Of course this is only a qualitative picture, while further details, which are not the purpose of the present article, can be found in literature.[46]

From the above, it is clear that in case a only ultrafast techniques could detect molecules in a pure spin state while, as for other slower physical methods of investigation, the whole system behaves as if constituted by only one kind of molecule with an intermediate spin state. Accordingly, bond angles and distances change gradually with temperature like "normal" molecules due to anharmonicity of the potential, the magnetic moment increases smoothly by increasing temperature, only one Mössbauer doublet is observed, and so on.

Now let us consider in more detail the problem of the spin equilibrium ${}^1A_1 \rightleftarrows {}^3E$ in iron(II) complexes, although the same or similar considerations are still valid for triplet–quintet and doublet–quartet spin equilibria in iron(II) and cobalt(II) complexes, respectively.

Actually, singlet–triplet spin equilibria in iron(II) complexes have seldom been recorded,[5,6,11,12,47,48] but interest in these systems has recently grown since an analogous equilibrium was found in oxygenated hemoglobin.[49]

Let us take as a model a five- or six-coordinated Fe(II) complex in C_{4v} symmetry with two low-lying pure spin states (${}^1A_1$, ${}^3E$) separated by an energy Δ, the singlet being the ground state in a zeroth-order approximation. Moreover, let us assume that the electronic doublet ${}^3E$ derives directly from the ${}^3T_{1g}$ state in O_h symmetry, thus disregarding the mixing with the triplet terms at higher energy. This assumption is not too drastic because the next triplet terms are well separated. In the strong-field configuration the two levels can be described as

$$|{}^1A_1a_10\rangle\text{:}\quad (\xi^2\eta^2\zeta^2)$$

$$|{}^3Ex1\rangle\text{:}\quad -3^{1/2}/2\xi^+\eta^2\zeta^2\theta^+ - (1/2)\xi^+\eta^2\zeta^2\epsilon^+$$

$$|{}^3Ey1\rangle\text{:}\quad 3^{1/2}/2\xi^2\eta^+\zeta^2\theta^+ - (1/2)\xi^2\eta^+\zeta^2\epsilon^+$$

where ξ, η, ζ, θ, and ϵ stand for the one-electron d levels d_{yz}, d_{xz}, d_{xy}, d_{z^2}, and $d_{x^2-y^2}$, respectively; the spin components $M_s = 0$ and $M_s = -1$ for the level ${}^3E$ are easily derived from symmetry considerations.[50]

Although both bond angles and distances are affected by temperature,[6] for the sake of simplicity we will consider the two electronic states ${}^1A_1$ and ${}^3E$ displaced only along a totally symmetric coordinate $Q_\alpha = Q$ (let us say the one describing the breathing mode, that is the lengthening or shortening of the bond distances).

Since spin–orbit interaction is the most important term, which couples the states ${}^1A_1$ and ${}^3E$, we shall disregard any weaker interaction in our analysis.

In C_{4v} symmetry the spin–orbit state ${}^1A_1$ transforms as Γ_1, while the triplet ${}^3E$ spans the following irreducible representations:

$$\begin{aligned} &\Gamma_1\text{:}\ (1/2^{1/2})(E_xS_x + E_yS_y) \\ &\Gamma_2\text{:}\ (1/2^{1/2})(E_xS_y - E_yS_x) \\ &\Gamma_3\text{:}\ (1/2^{1/2})(E_xS_x - E_yS_y) \end{aligned} \tag{1a}$$

$$\Gamma_4\text{:}\ (1/2^{1/2})(E_xS_y + E_yS_x) \qquad \Gamma_5\text{:}\ \text{(a) } E_yS_z\text{; (b) } -E_xS_z$$

where

$$\begin{aligned} S_z = -(i/2^{1/2})(\alpha\beta + \beta\alpha) \qquad S_x = (i/2^{1/2})(\alpha\alpha - \beta\beta) \\ S_y = (1/2^{1/2})(\alpha\alpha + \beta\beta) \end{aligned} \tag{1b}$$

and α and β stand for the up and down spins, respectively.

The Hamiltonian $H_{SO} = -4\lambda\sum_{i=1}^{6}\mathbf{l}_i\cdot\mathbf{s}_i$ has nonvanishing matrix elements between the two Γ_1 spin–orbit levels

$$\langle\Gamma_1({}^1A_1)|H_{SO}|\Gamma_1({}^3E)\rangle = 8\lambda \tag{2}$$

Here λ is the spin–orbit constant of the ferrous ion in the molecule, and it is related to the value of free Fe^{2+} by $\lambda = \alpha^2\lambda_0$ ($\lambda_0 = -103$ cm^{-1}), where α^2 is a reduction factor, due for example to covalency. Instead, the levels Γ_2–Γ_5 are not coupled by the Hamiltonian H_{SO} because of symmetry rules. If one assumes that the singlet ${}^1A_1$ is centered at $Q = 0$ and the minimum of the triplet ${}^3E$ is displaced at $Q = Q^{(0)}$, the energies of the different spin–orbit levels as a function of the coordinate Q are given by

$$E[\Gamma_1({}^1A_1)] = (1/2)KQ^2 + \Delta/2 + (1/4)KQ^{(0)2} - (1/2)KQ^{(0)}Q - \lambda/2 - 1/2[(\Delta + (1/2)KQ^{(0)2} - KQ^{(0)}Q - \lambda)^2 + 256\lambda^2]^{1/2} \tag{3a}$$

$$E[\Gamma_1({}^3E)] = (1/2)KQ^2 + \Delta/2 + (1/4)KQ^{(0)2} - (1/2)KQ^{(0)}Q - \lambda/2 + 1/2[(\Delta + (1/2)KQ^{(0)2} - KQ^{(0)}Q - \lambda)^2 + 256\lambda^2]^{1/2} \tag{3b}$$

$$E(\Gamma_2) = \Delta + (1/2)K(Q - Q^{(0)})^2 - \lambda \tag{3c}$$

$$E(\Gamma_3) = \Delta + (1/2)K(Q - Q^{(0)})^2 + \lambda \tag{3d}$$

$$E(\Gamma_4) = \Delta + (1/2)K(Q - Q^{(0)})^2 + \lambda \tag{3e}$$

$$E(\Gamma_5) = \Delta + (1/2)K(Q - Q^{(0)})^2 \tag{3f}$$

where K is the harmonic force constant, which was assumed to be the same for both spin states.

The eigenvalues and eigenfunctions of the Hamiltonian $\mathcal{H} = H_O + H_{SO}$, where H_O is the unperturbed Hamiltonian including the kinetic and potential energy operators, can be easily calculated if the following vibronic functions are assumed as a basis set:

$$\Gamma_1({}^1A_1)\chi^{(n)}(Q) \tag{4a}$$

$$\Gamma_1({}^3E)\chi^{(n)}(Q - Q^{(0)}) \tag{4b}$$

In such a case the matrix elements of the secular equations are given by

$$\langle\Gamma_1({}^1A_1)\chi^{(n)}(Q)|\mathcal{H}|\Gamma_1({}^1A_1)\chi^{(n)}(Q)\rangle = \hbar\omega_0(n + 1/2) \tag{5a}$$

$$\langle\Gamma_1({}^3E)\chi^{(n)}(Q - Q^{(0)})|\mathcal{H}|\Gamma_1({}^3E)\chi^{(n)}(Q - Q^{(0)})\rangle = \Delta + \hbar\omega_0(n + 1/2) - \lambda \tag{5b}$$

$$\langle\Gamma_1({}^1A_1)\chi^{(n)}(Q)|\mathcal{H}|\Gamma_1({}^3E)\chi^{(m)}(Q - Q^{(0)})\rangle = 8\lambda S_{nm} \tag{5c}$$

Here S_{nm} is the overlap integral between two displaced harmonic

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oscillators and can be expressed as[51]

$$S_{nm} = (n!m!)^{1/2}\gamma^{(m-n)} \exp\left(-\frac{\gamma^2}{2}\right)\sum_{p=0}^{n}\frac{(-1)^p\gamma^{2p}}{(n-p)!(m-n+p)!p!} \tag{6}$$

with

$$\gamma = \left(\frac{K}{2\hbar\omega_0}\right)^{1/2} Q^{(0)}$$

If the first N vibrational levels are considered for each spin state, the vibronic eigenfunctions of Γ_1 type corresponding to the ith eigenvalue are given by

$$\phi_i(\Gamma_1) = \Gamma_1(^1\mathrm{A}_1)\sum_{j=1}^{N} c_{ij}\chi^{(j-1)}(Q) + \Gamma_1(^3\mathrm{E})\sum_{j=N+1}^{2N} c_{ij}\chi^{(j-N-1)}(Q - Q^{(0)}) \tag{7}$$

where the coefficients c_{ij} are obtained by diagonalizing the Hamiltonian matrix (5).

Now we are able to obtain the expectation value of the coordinate Q for the ith level using the relationship $\bar{Q}_i = \int \phi_i^* Q \phi_i \mathrm{d}\tau$:

$$\bar{Q}_i = 2\left(\frac{\hbar\omega_0}{K}\right)^{1/2}\left[\sum_{j=2}^{N} c_{ij}c_{i,j-1}\left(\frac{j-1}{2}\right)^{1/2} + \sum_{j=N+2}^{2N} c_{ij}c_{i,j-1}\left(\frac{j-N-1}{2}\right)^{1/2}\right] \tag{8}$$

The mean value $\langle Q\rangle$ for a statistical ensemble is then obtained by assuming a Boltzmann distribution and recalling that also the uncoupled levels Γ_2–Γ_5, centered at $Q^{(0)}$, must be included. In the same way, we can proceed to evaluate the mean values of other physical properties. In particular, the mean value of the magnetic moment $\langle\mu_{\mathrm{eff}}\rangle$ is (in axial symmetry)

$$\langle\mu_{\mathrm{eff}}\rangle = [(1/3)\langle\mu_{\parallel}\rangle^2 + (2/3)\langle\mu_{\perp}\rangle^2]^{1/2} \tag{9}$$

where $\langle\mu_{\parallel}\rangle$ and $\langle\mu_{\perp}\rangle$ are calculated by Van Vleck's procedure[52]

$$\langle\mu\rangle = \left[\frac{3}{Z}\sum_i(\epsilon_i^{(1)2} - 2kT\epsilon_i^{(2)}) \exp\left(\frac{-\epsilon_i^{(0)}}{kT}\right)\right]^{1/2} \tag{10}$$

Here Z is the partition function, $\epsilon_i^{(1)}$ and $\epsilon_i^{(2)}$ are the first- and second-order Zeeman coefficients, $\epsilon_i^{(0)}$ is the eigenvalue of the vibronic level at zero magnetic field, and the sum is extended to all the vibronic levels. Since the magnetic field mixes the levels Γ_1 with the levels $\Gamma_2(H_{\parallel})$ and $\Gamma_5(H_{\perp})$ but it does not act upon the vibrational part of the wave function, the corresponding second-order Zeeman coefficients will be reduced. Indeed, the following relationship is easily verified, if one recalls the orthonormality of the harmonic oscillator wave functions:

$$\langle\phi_i^{(0)}(\Gamma_1)|\mu_{\parallel(\perp)}|\phi_k^{(0)}(\Gamma_{2(5)})\rangle = \sum_{j=N+1}^{2N} c_{ij}\chi^{(j-N-1)}(Q - Q^{(0)})\langle\Gamma_1(^3\mathrm{E})|\mu_{\parallel(\perp)}|\chi^{(k-1)}(Q - Q^{(0)})\Gamma_{2(5)}(^3\mathrm{E})\rangle = c_{i,N+k}\langle\Gamma_1(^3\mathrm{E})|\mu_{\parallel(\perp)}|\Gamma_{2(5)}(^3\mathrm{E})\rangle \tag{11}$$

μ being the magnetic field Hamiltonian, $\mu = \beta(L + 2.0023S)$.

The previously described functions ϕ_i correspond to stationary states; however, we are interested also in "catching" the system in a pure spin state that is in a nonstationary state. An initial pure spin state can be described by means of a function $\psi(Q)$, which is expanded in terms of a complete set of stationary states

$$\psi(Q) = \sum_i c_i\phi_i(Q) \tag{12}$$

The behavior as a function of time is given by

$$\psi(Q,t) = \sum_i c_i\phi_i(Q) \exp(-(i/\hbar)\epsilon_i t) \tag{13}$$

with the coefficients $c_i = \langle\phi_i|\psi\rangle$.

The probability of finding the system in the other well at time t could be obtained by the relation

$$P(t) = \int_{Q_{\mathrm{crossing}}}^{\infty} |\psi(Q,t)|^2 \mathrm{d}Q \tag{14}$$

However, here we attempt to evaluate the singlet–triplet conversion rate by following a simpler approach,[53] which is able, with some restrictions, to take into account the nuclear motion of the medium where the chromophore is situated and therefore the temperature effect. This approach describes spin conversion processes in terms of a radiationless nonadiabatic multiphonon process, occurring between the two pure spin states, which are characterized by different nuclear configurations.[53] In fact, from Fermi's golden rule, the rate constant can be expressed as

$$k = \frac{2\pi}{\hbar} g_{\mathrm{f}}|V|^2 G \tag{15}$$

where g_{f} is the total degeneracy (spin + orbit) of the final electronic state, V is the matrix element that couples the two electronic states and in our example is given by $V = \langle ^1\mathrm{A}_1|H_{\mathrm{SO}}|^3\mathrm{E}\rangle = 4(2)^{1/2}\lambda$, and G is the thermally averaged nuclear Franck–Condon vibrational overlap factor, which can be expressed as

$$G = \frac{1}{\hbar\omega_0} \exp[-S \coth x - px] I_p\left(\frac{S}{\sinh x}\right) \tag{16}$$

when the vibrational modes of the medium have a very low frequency in comparison with the thermal energy and only one internal mode is considered. Here $x = \hbar\omega_0/2kT$; $p = \Delta/\hbar\omega_0$; $S = [K(\Delta Q)_2/2\hbar\omega_0]$, Δq being the distance along the coordinate Q between the minima of the two pure spin states and I_p being the modified Bessel function of order p.

Results and Discussion

In our calculations we have selected parameter values that are acceptable for iron(II) complexes displaying singlet–triplet equilibrium without any attempt at fitting the experimental data concerning a given complex.

With information obtained from experiments, the pure triplet state has been put at higher energy and its equilibrium position in the totally symmetric coordinate has been considered up to 0.2 Å larger than that of the singlet state.[6,54] Moreover, we have chosen a spin–orbit constant value ($\lambda = -80$ cm^{-1}) slightly reduced in comparison with that of the free ion[52] and a force constant of 2.4×10^5 cm^{-1} Å^2, which corresponds to a vibrational quantum of 300 cm^{-1} for an effective mass of 90 au. If all the other parameters are kept constant, the potential energy cross section along the totally symmetric coordinate Q is strongly affected by the distance between the two minima ΔQ (Figure 2).

The cross section of the low-lying Γ_1 level shows two well-defined potential minima, when the two pure spin states are placed sufficiently far from each other (Figure 2a). From a dynamical standpoint the low-lying vibronic levels are essentially singlet states. It is only from the seventh vibronic level, situated at 820 cm^{-1} above ground level, that there is a 60% contribution from the triplet state, when a distance $\Delta Q = 0.2$ Å is considered. This means that for low or moderate temperatures, the physical properties of the system, which we were able to measure, should correspond mainly to a LS system. *However*, the situation is complicated by the presence of the excited uncoupled components of the triplet spin–orbit level: by increasing temperature not only Γ_1 vibronic levels with high triplet percentage are populated but also a significant population of the uncoupled triplet components is possible such as to induce sharp variations of the physical properties within a narrow range of temperature. On the contrary, when the separation between the minima is reduced (let us say $\Delta Q = 0.1$ Å),

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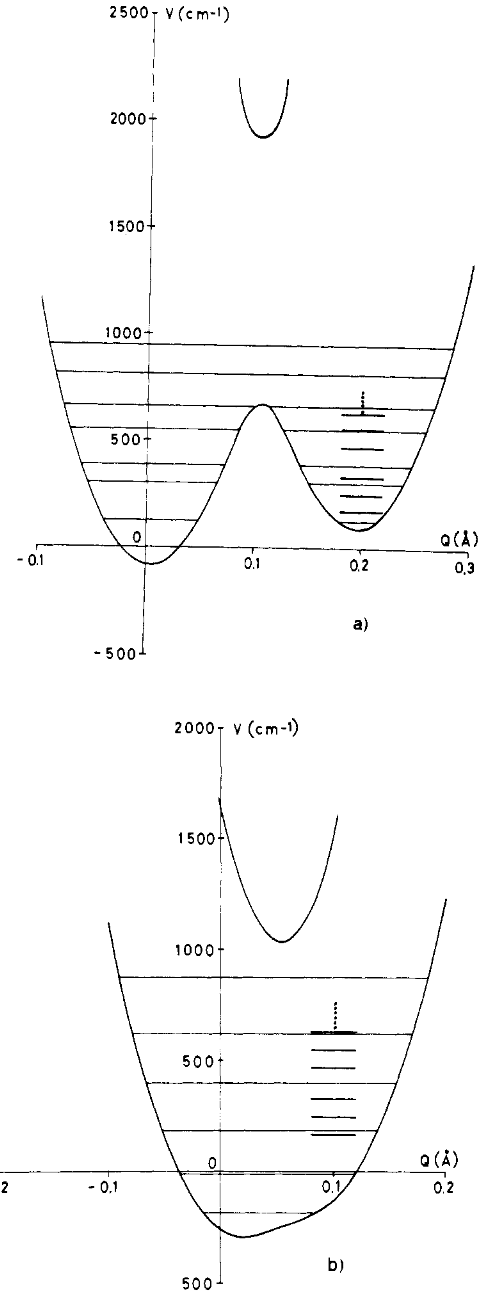

Figure 2. Cross sections along the totally symmetric coordinate Q for the equilibrium $^1A_1 \rightleftarrows {}^3E$ (C_{4v} symmetry) in iron(II) complexes. The curves were calculated for $\Delta = 100\ \mathrm{cm}^{-1}$, $K = 2.4 \times 10^5\ \mathrm{cm}^{-1}/\text{Å}^2$, $\lambda = -80\ \mathrm{cm}^{-1}$, and $Q^{(0)} = 0.2$ Å (a) or $Q^{(0)} = 0.1$ Å (b). The first vibronic levels of Γ_1 type are also indicated, while heavy lines stand for the uncoupled Γ_2–Γ_5 levels.

the cross section of the low-lying Γ_1 level displays a single minimum and an appreciable anharmonicity (Figure 2b). Moreover, in this case even the ground vibronic level contains a nonnegligible percentage of the triplet state (3–4%) so that smoother variations of the physical properties are expected.

At this point it is important to note that the relaxation between the uncoupled triplet levels and the Γ_1 levels corresponds to an intersystem crossing so that the characteristic time is longer than that expected for the relaxation within the set of the Γ_1 levels.[43] Therefore, small couplings between the potential wells and quasi-energetic minima do favor the detection of different species.

Similar results would be obtained for the $^2E \rightleftarrows {}^4T_1$ equilibrium in octahedral Co(II) complexes, where the ground level $\Gamma_8(^2E)$ is to be coupled with the two excited Γ_8 levels arising from the $^4T_1$ state, while the spin–orbit levels Γ_6 and Γ_7 remain uncoupled.

Now, on the basis of the above results, let us consider what observations on our system we may expect. In Figure 3 the variation of the mean value of the totally symmetric coordinate as a function of temperature is reported for two typical cases. In the case of a single minimum potential well the mean value $\langle Q \rangle$ slowly increases with temperature (Figure 3b) in a quite analogous fashion like "normal" molecules or atomic clusters with large anharmonicity. Actually, in such a case temperature-dependent X-ray crystal structures should provide a continuous variation of the bond distances and angles as was observed in some compounds.[6,14] On the other hand, in the case of a double-minimum potential, we get a strong variation of the mean position of equilibrium within few tens of degrees: such a large and abrupt change could induce cooperative effects leading to phase transitions. Accordingly, for this latter example, the magnetic moment μ_{eff} abruptly changes (Figure 4a) from zero up to values not too far from that of spin only ($\mu_{\mathrm{eff}} = 2.83\ \mu_B$). Instead, in the former case (Figure 4b), a residual paramagnetism is observed even at very low temperature, but it increases so gradually as to reach just μ_{eff} values, which can mask a single unpaired electron at room temperature.

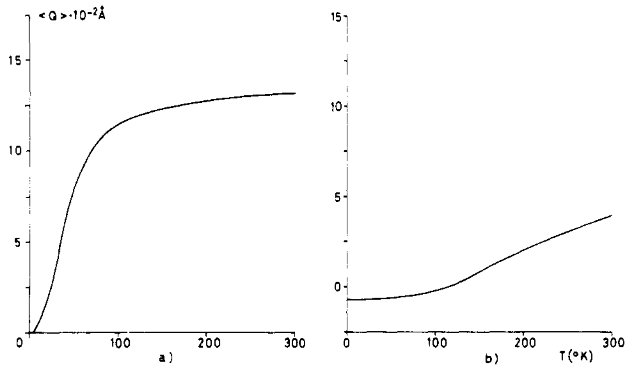

Figure 3. Mean value of the totally symmetric coordinate $\langle Q \rangle$ as a function of temperature. The parameters values are the same as in Figure 2, and $\hbar\omega_0 = 300\ \mathrm{cm}^{-1}$: (a) $Q^{(0)} = 0.2$ Å; (b) $Q^{(0)} = 0.1$ Å. The coordinate of the minimum of the pure singlet state is assumed as zero.

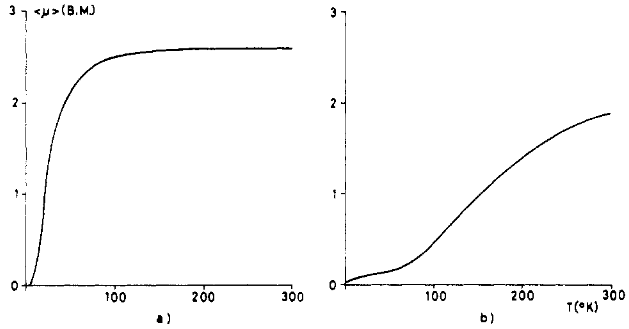

Figure 4. Mean value of the magnetic moment $\langle \mu \rangle$ as a function of temperature. The parameters values are the same as in Figure 3.

Table I. Singlet–Triplet ($^1A_1 \rightarrow {}^3E$) Spin Conversion Rates k (s^{-1}) Computed with Eq 15[53]

ΔQ, Å (S)	T = 300 K	T = 80 K
0.1 (4)	1.7×10^{14}	2.6×10^{13}
0.2 (16)	1.5×10^{12}	4.6×10^{8}

Finally, let us consider the singlet–triplet conversion rate, using the procedure of Buhks et al.,[53] which allows us to take into account also the modes of the environment.

In the examples reported in ref 53 the parameter $p = \Delta/\hbar\omega_0$ was assumed to be zero, thus allowing a simpler evaluation of expression 16. However, although in the limit of high temperature this shortcoming to a large extent does not alter the conversion rate, the value of p greatly affects the rate at low temperature.[53] Therefore, we preferred to avoid this approximation, considering also that the parameter values we had chosen as plausible ones for the system we were interested in ($\Delta = 100\ \mathrm{cm}^{-1}$; $\hbar\omega_0 = 300\ \mathrm{cm}^{-1}$) provided an easy calculation of the overlap factor G (eq 16), by expressing the modified Bessel function $I_{1/3}$ in terms of

Airy functions.[55] The results we have obtained are reported in Table I: of course these figures are significant only with regard to their order of magnitude because of the inherent approximations.[53] However, we note that the conversion rate for $\Delta Q = 0.1$ Å is very high at any temperature and faster or of the order of nuclear motion (10^{12}–10^{13} s^{-1}) so that only electronic and, perhaps, vibrational spectroscopies could "catch" molecules in a pure spin state. Instead, the conversion rates are strongly reduced at low temperature when $\Delta Q = 0.2$ Å, and consequently, even "slower" spectroscopies, like Mössbauer spectroscopy (precession time of the ^{57}Fe nucleus in the range 10^{-7}–10^{-9} s), are suitable to detect spin isomers simultaneously.

At this point it is important to remember that the previous conversion rates were obtained by considering the overall process $^1A_1 \rightarrow {}^3E$, as it was shown in ref 53. A more accurate treatment should take into account two different conversion processes: (i) $\Gamma_1(^1A_1) \rightarrow \Gamma_1(^3E)$, for which rates very similar to those reported in Table I are evaluated; (ii) $\Gamma_1(^1A_1) \rightarrow \Gamma_{2-5}(^3E)$, which is at least 2 orders of magnitude slower than the previous one, because only small perturbing terms, like low-symmetry fields or strain, can couple $\Gamma_1(^1A_1)$ with the other components of the triplet.

To conclude, when the coupling between the potential wells of the pure spin states and the energy difference between the minima are sufficiently small, solid-state effects can stabilize one or both species in the lattice.[19] Instead, in the presence of a strong coupling, it does not make sense to discuss the simultaneous presence of different chromophores in the lattice, because spin–orbit coupling washes out the two wells.

The important point is what we can "see" by means of our experiments or, in other words, whether the characteristic time of our measurements is short enough to individuate pure spin states. Actually, some singlet–triplet spin equilibria in iron(II) complexes appear to be typical examples of type a systems. In these compounds, a strong coupling should be effective and a situation like that depicted in Figure 1b or 2b should occur. Consequently, with the experiments that have been performed so far[6,11,12,49] (except, perhaps, electronic spectroscopy[11]), their fast conversion rate prevents the identifying of pure spin states.

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Thermodynamics of Complexation of Lanthanide Ions by *N*-Methylethylenediamine-*N*,*N'*,*N'*-triacetic Acid

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The thermodynamic parameters of complexation of lanthanide cations with *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetate ion (MEDTA) were determined by potentiometric and calorimetric techniques. The measurements were conducted at 25 °C and ionic strength of 0.10 and 0.50 M ($NaClO_4$). The observed decrease in stability as well as in enthalpy values of Ln–MEDTA chelates compared to EDTA species is attributed to a weaker Ln–N interaction due to the presence of a single acetate arm associated with one of the nitrogens.

Introduction

Amino polycarboxylic acids form strong chelates with the trivalent lanthanide metals. Several of these ligands have been used as reagents for the analytical assay of the lanthanides and for their separation by ion exchange. The thermodynamics and kinetics of chelation of many of these lanthanide–ligand systems have been measured. Of interest in this paper are the complexes of the lanthanides with *N*-methylethylenediamine-*N*,*N'*,*N'*-triacetic acid (MEDTA). Powell et al.[1] reported the stability constants for LnMEDTA complexation. The dissociation kinetics of these chelates were also described recently.[2] Qualitative information on the structure of LnMEDTA in solution was obtained by ^1H NMR studies, which confirmed pentadentate chelation.[3]

MEDTA is interesting as a ligand of intermediate chelation between, for example, iminodiacetic acid (IDA) and ethylenediaminetetraacetic acid (EDTA). To allow comparisons with such ligands, we have determined the thermodynamic parameters of complexation of lanthanides by MEDTA.

Experimental Section

Reagents. Lanthanide perchlorate solutions were prepared and standardized as described previously.[4] A pure, recrystallized sample of MEDTA in the acid form was prepared as reported elsewhere.[2,5]

Potentiometry. The protonation constants of MEDTA and the stability constants of the LnMEDTA complexes were determined in a solution of 0.50 M ($NaClO_4$) ionic strength. The potentiometric measurements were made with a pH-meter (Corning 130) fitted with a combination glass–calomel electrode. The electrode was calibrated with standard "BuffAR" of pH 4.01 and 7.00. In basic media, borax solution (0.01 M) served as a standard buffer of pH 9.17. Corrections for the hydrogen ion activity in solutions of 0.10 and 0.50 M ionic strength were obtained by using the activity coefficients 0.782 and 1.585, respectively.[6,7] The p*K* values for the free ligand were calculated by minimizing the residuals in $\bar{n}_H$ for a series of measurements in the appropriate buffer region. The values of the stability constants were obtained by titrating volumes of equimolar amounts of metal and ligand with standard 0.10 M (CO_2-free) sodium hydroxide solution. In all measurements, the ligand concentration was kept at 0.001 M, the temperature was maintained at 25 °C, and the ionic strength of the reaction medium was maintained constant by the addition of the appropriate amount of sodium perchlorate solution.

The data were processed by using the BETA program based on the SIMPLEX algorithm and written in this laboratory by Dr. William Cacheris. The uncertainties in these constants were estimated from the curvature of the sum square residuals with respect to each parameter. Different models were used in the potentiometric data analysis, i.e. formation of LnMEDTA only and formation of LnMEDTA plus $LnHMEDTA^+$. The value of β_{111} ($\beta_{111} = [LnHMEDTA^+]/[Ln^{3+}][H^+][MEDTA^{3-}]$) for the second model was unrealistic ($\beta_{111} = 2 \pm 57\,000$) and the $\bar{n}_H$ values for this model were also unacceptable ($<10^{-6}$). The conclusion was that formation of $LnHMEDTA^+$ was not significant under these concentrations and pH conditions.

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