Articles

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Singlets, Triplets, and Exciplexes: Complex, Temperature-Dependent Emissions from $Cu(dmp)(PPh_3)_2^+$ and $Cu(phen)(PPh_3)_2^+$ in Solution

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Factors affecting the speciation of $Cu(dmp)(PPh_3)_2^+$ and $Cu(phen)(PPh_3)_2^+$ in solution are described. (Here phen and dmp denote 1,10-phenanthroline and its 2,9-dimethyl-substituted derivative, respectively.) $Cu(phen)(PPh_3)_2^+$ can be studied in methanol or methylene chloride, but the speciation of the dmp analogue is not well-defined in methylene chloride. In methanol at 25 °C $Cu(dmp)(PPh_3)_2^+$ is a relatively strong emitter ($\Phi = (1.4 \pm 0.2) \times 10^{-3}$, $\tau = 330 \pm 30$ ns) because steric crowding inhibits solvent-induced exciplex quenching. At 25 °C much less intense emission is observed from $Cu(phen)(PPh_3)_2^+$ in methanol ($\Phi = (2.8 \pm 0.3) \times 10^{-5}$) or even in methylene chloride ($\Phi = (6.6 \pm 0.7) \times 10^{-4}$, $\tau = 220 \pm 30$ ns) because of solvent-induced exciplex quenching and/or the energy gap law. In methylene chloride the emission intensity from $Cu(phen)(PPh_3)_2^+$ increases with increasing temperatures due to the thermal population of a singlet state with a favorable radiative rate constant. On the other hand, in methanol the emission intensity of each complex increases with decreasing temperature because of a thermally activated quenching process involving solvent-induced exciplex formation. The relative heights of the thermal barriers to quenching correlate with known steric effects.

Introduction

The luminescence from $Cu(dmp)_2^+$, where dmp denotes 2,9-dimethyl-1,10-phenanthroline, has been shown to exhibit an unusual temperature dependence in that the emission yield *increases* with increasing temperature over a wide temperature range.[1-3] Although the lowest energy excited state is a metal-to-ligand charge-transfer (CT) state with triplet multiplicity, the corresponding singlet state occurs only about 1500 cm^{-1} to higher energy.[1] Thermal population of the singlet state, which has a relatively large radiative rate constant, causes the luminescence intensity to increase at higher temperatures.

Mixed-ligand complexes of the type $Cu(dmp)(PPh_3)_2^+$ or $Cu(phen)(PPh_3)_2^+$, where phen denotes 1,10-phenanthroline, exhibit a similar energy level scheme,[2,4,5] and emission spectra from singlet and triplet CT states have been measured in low-temperature glasses by using time-resolved emission methods.[4,5] However, in the course of our studies of the mixed-ligand systems, we have found that their solution behavior is quite complex. Aside from problems encountered in defining speciation, the temperature dependence of the emission intensity depends strongly upon the nature of the phenanthroline ligand as well as the solvent. As we shall see, these results can be explained in terms of a competing thermally activated process, which we assign as solvent-induced exciplex quenching. The quenching efficiency depends upon the nucleophilicity of the solvent and steric considerations, and in some cases exciplex quenching determines the temperature dependence of the luminescence intensity.

Experimental Section

Materials. The complexes were prepared as described previously[5] from 1 equiv of the phenanthroline and $[Cu(PPh_3)_4]X$ where X denotes the anion. $[Cu(PPh_3)_4]X$ was prepared from a copper(II) solution or from $[Cu(CH_3CN)_4]X$[6] depending on the availability of the anion. For all of the mixed-ligand complexes C, H, and N analyses agreed with the expected formulas. High-purity distilled-in-glass grade methylene chloride and methanol were purchased from Burdick and Jackson and used as solvent for the spectral studies.

Equipment. Luminescence lifetimes were measured with a nitrogen-pumped dye laser system as described previously.[7] Absorption measurements were carried out on a Cary 17D spectrophotometer. The emission spectra were obtained with a Perkin-Elmer MPF-44B fluorescence spectrophotometer or an SLM/Aminco SPF-500C spectrofluorometer. For all experiments, samples were thermostated with a Lauda K-2/RD circulating water bath. Low-temperature measurements were obtained with an Oxford Instruments DN-704 liquid-nitrogen cryostat. Luminescence data were collected from samples that were deoxygenated by at least three freeze–pump–thaw cycles.

Results

Room-Temperature Absorption Spectrum of $Cu(dmp)(PPh_3)_2^+$ in Solution. The near-UV spectrum of $Cu(dmp)(PPh_3)_2^+$ is dominated by a broad, featureless absorption centered at 365 nm, which has previously been assigned as a metal-to-ligand charge-transfer transition.[5,8] Although the complex is subject to ligand redistribution reactions, a 10-fold excess of PPh_3 has been shown to suppress phosphine dissociation in methanol[5] at a total copper concentration of ca. 0.4 mM, which is convenient for spectroscopic studies.

In the present work, we have attempted to characterize the complex in methylene chloride solution, but we have been unable to find conditions where copper is uniquely bound as $Cu(dmp)(PPh_3)_2^+$, regardless of the counterion. When the pure mixed-ligand complex is dissolved in CH_2Cl_2, the spectrum is time-dependent. Over a period of minutes, the exact rate depends on the anion present, the characteristic absorbance at 365 nm decreases, and a new band appears at 454 nm, presumably due to the formation of $Cu(dmp)_2^+$.[9] The addition of excess PPh_3 tends to suppress the 454-nm band, but before the 454-nm band

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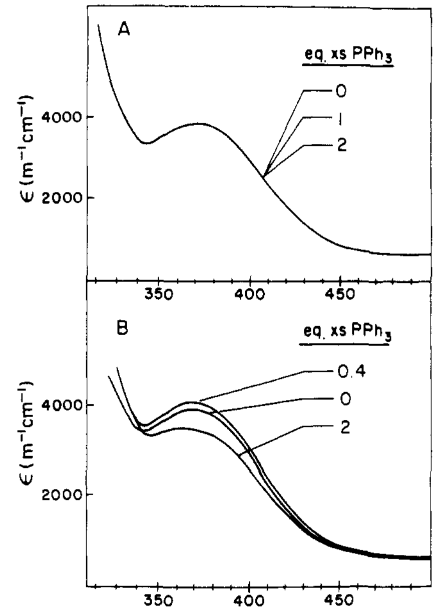

Figure 1. Absorption spectra of (A) $[Cu(phen)(PPh_3)_2]BF_4$ and (B) $[Cu(phen)(PPh_3)_2]ClO_4$ in methylene chloride at 35 °C. The spectra have been measured with varying amounts excess PPh_3 added.

Table I. Anion Dependence of Emission from $Cu(phen)(PPh_3)_2^+$ in CH_2Cl_2 at 25 °C

anion	Φ^a	τ,^{b} ns	equiv of excess PPh_3^{c}
PF_6^-	1.0	220	0.4
BF_4^-	1.0	220	
ClO_4^-	0.8	*d*	0.4
NO_3^-	0.6	*d*	

[a] Relative to BF_4^- sample. [b] Estimated uncertainty 10%. [c] Equivalents of excess PPh_3 added. [d] Non-single-exponential decay.

is completely eliminated, the absorbance at 365 nm begins to bleach as well.

Absorption Spectrum of $Cu(phen)(PPh_3)_2^+$ in Solution. In contrast, absorption studies indicate that, at similar concentrations of the complex in methanol, excess PPh_3 is not required to control the speciation of $Cu(phen)(PPh_3)_2^+$.[5] Consistent with this finding, the luminescence intensity of the complex in methanol is not affected by the presence of excess PPh_3. However, speciation is more problematic in solvents with a lower dielectric constant, unless the BF_4^- salt is used. In methylene chloride the charge-transfer absorption maximum of $Cu(phen)(PPh_3)_2^+$ also occurs at about 365 nm, but the absorption intensity varies with the temperature, total phosphine concentration, and anion (Figure 1). Thus, at 37 °C the absorbance of a 73 μM solution of $[Cu(phen)(PPh_3)_2]BF_4$ remains constant when as much as 2 equiv of excess PPh_3 is added. In contrast, there is no significant range of total phosphine concentration over which the absorbance of a solution of the ClO_4^- or PF_6^- salt is independent of phosphine. In both cases the addition of excess PPh_3 initially gives rise to a small increase in absorbance at 365 nm, but at around a 0.5 molar excess of PPh_3 the absorbance begins to decrease. The nitrate salt exhibits still different behavior. Here, the absorption spectrum is unaffected by the addition of small amounts of excess phosphine, but as discussed below, the decay of the CT emission is biphasic. This indicates at least two species are present.

Room-Temperature Emission. The emission intensities from solutions of $Cu(phen)(PPh_3)_2^+$ in methylene chloride also vary with the anion. The relative emission yields are listed in Table I, where the total copper concentration is about 75 μM in each case. In the case of the PF_6^- or ClO_4^- derivative, 0.4 equiv of excess PPh_3 has been added to maximize the $Cu(phen)(PPh_3)_2^+$ concentration. The emission yields are the same within experimental error for the PF_6^- and BF_4^- derivatives, and in both cases the emission decays in single-exponential fashion with a lifetime of 220 ± 30 ns in deoxygenated methylene chloride. In contrast, the emission decay is complex for both the ClO_4^- and NO_3^- derivatives, and we have been unable to fit the data to a single-exponential decay.

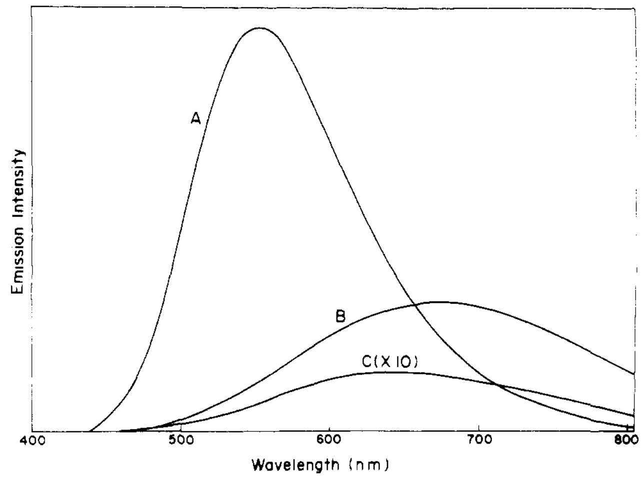

Figure 2. Corrected emission spectra at 20 °C: (A) $[Cu(dmp)(PPh_3)_2]BF_4$ in methanol with 10 equiv of excess PPh_3; (B) $[Cu(phen)(PPh_3)_2]BF_4$ in methylene chloride; (C) $[Cu(phen)(PPh_3)_2]BF_4$ in methanol at 10 times the gain. The emissions have been excited at 390 nm with the excitation slits set at 4 nm and the emission slits at 10 nm.

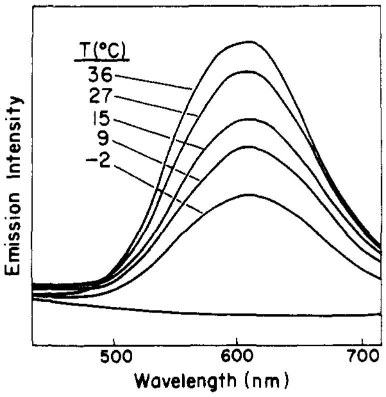

Figure 3. Uncorrected emission spectra of $[Cu(phen)(PPh_3)_2]BF_4$ in methylene chloride as a function of temperature. No excess PPh_3 has been added. The wavelength of excitation is 365 nm, and the excitation and emission slits are set at 4 nm.

Table II. Quantum Yields and Lifetimes at 25 °C

compd	solvent	λ_{max},^{a} nm	Φ^{b-d}	τ,^{d} ns
$[Cu(dmp)(PPh_3)_2]BF_4$^{e}	methanol	560	1.4×10^{-3}	330^f
$[Cu(phen)(PPh_3)_2]BF_4$	methanol	650	2.8×10^{-5}	*g*
$[Cu(phen)(PPh_3)_2]BF_4$	methylene chloride	680	6.6×10^{-4}	220

[a] From corrected spectra. [b] 390-nm excitation. [c] Measured relative to $[Cu(dmp)(PPh_3)_2]BF_4$ in methanol.[5] [d] Estimated uncertainty 10%; 337-nm excitation. [e] 10 equiv of excess PPh_3 added. [f] Reference 5. [g] Signal too weak to measure.

Quite different results are obtained in methanol where the emission intensity is dramatically reduced and independent of the anion. The contrast between the emission intensities of $Cu(dmp)(PPh_3)_2^+$ and $Cu(phen)(PPh_3)_2^+$ in methanol is also striking. Whereas the emission from the phen complex is extremely weak, the dmp complex has one of the largest emission yields obtained from a CT excited state of a copper chelate in solution.[5] The emission spectra are drawn to scale in Figure 2, and the emission quantum yields are presented in Table II.

Variable-Temperature Emission. As the temperature is increased from −2 to +36 °C, the emission intensity from $Cu(phen)(PPh_3)_2^+$ *increases* in methylene chloride as shown in Figure 3. Analogous behavior has previously been seen in the solid state,[2]

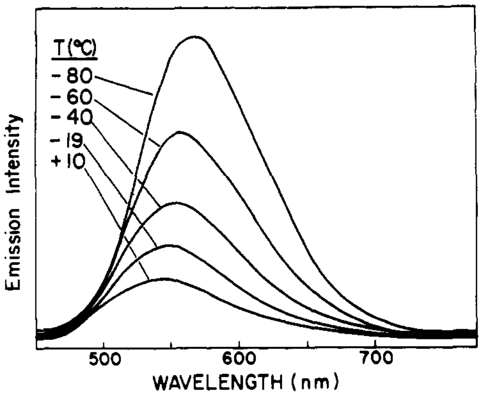

Figure 4. Uncorrected emission spectra of $[Cu(dmp)(PPh_3)_2]BF_4$ in methanol as a function of temperature. 10 equiv of excess PPh_3 has been added. The wavelength of excitation is 400 nm, and the excitation and emission slits are set at 8 nm.

and the emission of $Cu(dmp)_2^+$ also shows the same temperature dependence in methylene chloride.[1]

In contrast, the emission is much less temperature-dependent for the same complex in methanol and the temperature coefficient has the opposite sign. Thus, in methanol the emission intensity is slightly higher at 6 °C than it is at 24 °C. The same type of behavior is observed from $Cu(dmp)(PPh_3)_2^+$ in methanol, but the effect is much more pronounced (Figure 4). Here, the spectra also reveal that the emission maximum undergoes a distinct red shift with decreasing temperature. Note that for the dmp complex the measurements have been made in the presence of 10 equiv of excess PPh_3, which is enough to suppress dissociation at the highest temperature investigated.

Discussion

Speciation. Since copper(I) forms labile complexes, competing equilibria determine the speciation. In the present systems the synergic effect associated with a good σ-donor like PPh_3 in concert with a π-acid ligand like phen or dmp strongly favors the formation of the mixed-ligand complex.[9,10] However, steric effects are also important. In the solid state[9] the P–Cu–P angle is 122.7° in $Cu(dmp)(PPh_3)_2^+$ and 115.5° in $Cu(phen)(PPh_3)_2^+$, while the cone anlge for PPh_3 is 145°.[11] The relatively small P–Cu–P angle is possible because the phenyl groups of the respective phosphines "mesh" with each other in the complex. Although this tends to minimize steric interactions between the bulky phosphines, steric interactions with the other ligands occur. As has been shown previously,[9] there are several unfavorable contacts between the phenyl groups from the PPh_3 ligands and the methyl substituents on the dmp ligand in $Cu(dmp)(PPh_3)_2^+$. Hence, $Cu(dmp)(PPh_3)_2^+$ is prone to the dissociation of phosphine.

Yet another competing effect is indicated by our studies of $Cu(phen)(PPh_3)_2^+$. Here the ligand–ligand steric interactions are much less severe, and the complex survives dissolution in methanol. However, the speciation is complex in methylene chloride. In this case, the speciation depends upon the anion presumably because of the formation of quaternary complexes of the type $Cu(phen)(PPh_3)X$.[12] Consistent with this hypothesis, anion binding would be expected to be a more competitive process in low-dielectric media like methylene chloride, where charge separation is more difficult.[13] The presence of $Cu(phen)(PPh_3)_2^+$ and $Cu(phen)(PPh_3)X$ in solution could also explain the biphasic decay curves that are observed for the NO_3^- and ClO_4^- systems. Finally, competitive anion binding in conjunction with the inherent steric strain in the $Cu(dmp)(PPh_3)_2^+$ complex could also account for the fact that we have been unable to prepare methylene chloride solutions in which $Cu(dmp)(PPh_3)_2^+$ is the only copper-containing species present.

Room-Temperature Emission. In the solid state both $Cu(phen)(PPh_3)_2^+$ and $Cu(dmp)(PPh_3)_2^+$ are strong emitters at room temperature, although the phen complex exhibits a slightly higher quantum yield.[2] However, the emission is severely quenched in solution largely because of solvent-induced exciplex quenching.[5,9] This quenching mechanism, which involves a transient increase in the coordination number of the copper center, is widely found for CT excited states of copper(I) complexes.[3,14,15] Steric crowding in the coordination sphere of copper hinders the addition of the fifth ligand,[14] and this explains why the emission from $Cu(dmp)(PPh_3)_2^+$ is much stronger than that from $Cu(phen)(PPh_3)_2^+$ in methanol.[9] The efficacy of exciplex quenching also depends on the nucleophilicity of the quencher;[15] hence, the emission yield of $Cu(phen)(PPh_3)_2^+$ is higher in methylene chloride than in methanol.

If solvent-induced quenching is of reduced importance for $Cu(dmp)(PPh_3)_2^+$ in methanol and for $Cu(phen)(PPh_3)_2^+$ in methylene chloride, albeit for different reasons, there must be another explanation as to why the emission yield and the lifetime are smaller for the phen complex. No such differences are observed in the solid state;[2] hence, vibrational effects involving differences in ligand modes can be discounted. Static, anion-induced quenching from ion pairs in methylene chloride could explain part of the difference in the emission yields,[16] but the lifetime is decreased, too. The difference in lifetime may be explained by the energy gap law since the CT emission of $Cu(phen)(PPh_3)_2^+$ is significantly red-shifted compared to that of $Cu(dmp)(PPh_3)_2^+$ in solution (Figure 2). Apparently, the less sterically demanding phen ligand permits more extensive geometric relaxation in the excited state. In turn, this reduces the energy gap separating the ground and excited states and facilitates relaxation.[17] In the solid state, where geometrical relaxation is restricted, the complexes emit at almost the same wavelength.[2]

Temperature Dependence of Emission. As noted above, part of the emission that is observed from CT excited states of Cu(I) systems is thermally activated.[1-3] In addition to a small singlet–triplet splitting, the phenomenon depends upon the fact that the singlet CT state (^1CT) has a radiative rate constant that is ca. 10^4 times larger than that of the lower energy ^3CT state.[1] Evidence of this phenomenon is presented in Figure 3, where the luminescence from $Cu(phen)(PPh_3)_2^+$ is depicted as a function of temperature in methylene chloride. We have also investigated the temperature dependence of the lifetime over the range 5–25 °C. Consistent with increased participation of the ^1CT state, the lifetime appears to decrease with increasing temperature, but the changes are small compared with the experimental error. Similar behavior has been observed from $Cu(dmp)_2^+$ over a comparable temperature range.[1] The shift in the emission maximum toward higher energy at higher temperatures is also in accord with the model; however, solvation effects also influence the emission maximum. In favorable cases the solvent effect can be interpreted in terms of the relative magnitudes and orientations of the ground- and excited-state dipole moments,[18] but the mixed-ligand complexes are ionic, and the extent of ion pairing as well as solvent ordering is likely to change with temperature. This precludes a quantitative interpretation of the temperature dependence of the emission maximum.

The emission maximum undergoes a similar temperature shift for $Cu(dmp)(PPh_3)_2^+$ (Figure 4); however, the temperature coefficient of the emission intensity has the opposite sign. To explain this behavior, we must invoke a thermally activated quenching process, presumably solvent-induced exciplex quenching

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since it is expected to be a dominant quenching pathway in donor media. This effect is intriguing because, in the case of Cu(dmp)$_2^+$, exciplex quenching proceeds with a negative activation energy due to the bond making that attends exciplex formation.[15] In other words, the quenching is *less* efficient at higher temperature. The data in Figure 4 clearly require that the activation energy for solvent-induced quenching be positive. The difference in the activation requirement can be understood in terms of the ligand–ligand repulsion forces that come into play when the already crowded coordination sphere of Cu(dmp)(PPh$_3$)$_2^+$ has to expand to accept another ligand. Unfortunately, we have been unable to measure activation barriers for Cu(dmp)(PPh$_3$)$_2^+$ directly. Although various Lewis bases quench the emission, they also compete with PPh$_3$ for coordination to the copper center in the ground state, confusing speciation.

The temperature dependence of the emission from Cu(phen)(PPh$_3$)$_2^+$ in methanol does, however, provide additional support for the above interpretation. The fact that the luminescence intensity of Cu(phen)(PPh$_3$)$_2^+$ is nearly independent of temperature in methanol suggests that the barrier to quenching is significantly smaller in this case, although still positive. According to our model, a smaller barrier would be expected because the steric forces are reduced in the less crowded phen complex.[9]

Conclusions

The speciation of mixed-ligand copper(I) systems is found to be sensitive to steric and electronic effects associated with the ligands as well as the nature of the counterion and the dielectric constant of the solvent. Conditions have been found such that the absorption and the emission spectra of Cu(dmp)(PPh$_3$)$_2^+$ and Cu(phen)(PPh$_3$)$_2^+$ can be studied in solution. In methanol, Cu(dmp)(PPh$_3$)$_2^+$ is a relatively strong emitter because steric crowding inhibits solvent-induced exciplex quenching. Under these circumstances exciplex quenching is a thermally activated process, which dominates the temperature dependence of the emission yield. A lower barrier to quenching occurs in the less crowded Cu(phen)(PPh$_3$)$_2^+$ complex. As a result, the quantum yield of emission is sharply reduced and only weakly temperature-dependent in methanol. Cu(phen)(PPh$_3$)$_2^+$ can also be studied in the less nucleophilic solvent methylene chloride, wherein solvent-induced quenching is less of a problem. Under these conditions the luminescence intensity increases with increasing temperature, as it does in the solid state. This is explained by thermal population of a singlet CT state with a favorable radiative rate constant.

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Investigation of the ${}^1A_1 \rightleftharpoons {}^5T_2$ Intersystem Crossing Dynamics of an Iron(II) Spin-Crossover Complex in the Solid State by Mössbauer Spectroscopy

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A very gradual thermal high-spin (HS) $\rightleftharpoons$ low-spin (LS) transition of the ferrous ion in [Fe(2-pic)$_3$](PF$_6$)$_2$ (2-pic = 2-(aminomethyl)pyridine) has been observed by Mössbauer and susceptibility measurements. Above 200 K the ${}^1A_1 \rightleftharpoons {}^5T_2$ intersystem crossing rates are comparable to the hyperfine frequencies leading to typical Mössbauer relaxation spectra. The rate constants are derived from a line shape analysis employing the stochastic theory of line shape. Their temperature dependence is described by an Arrhenius equation with the activation energies $\Delta E_{LH} = 20.6$ (6) kJ mol^{-1} and $\Delta E_{HL} = 12.5$ (8) kJ mol^{-1} for the LS $\rightarrow$ HS and HS $\rightarrow$ LS conversions, respectively. The frequency factors are $A_{LH} \sim 3 \times 10^{11}$ s^{-1} and $A_{HL} \sim 1 \times 10^9$ s^{-1}. The activation parameters are compared with the existing liquid-solution data.

Introduction

Studies of various d^5 and d^6 spin-crossover complexes revealed that the temperature interval and the shape of the high-spin (HS) $\rightleftharpoons$ low-spin (LS) transition curves in the solid state are determined to a large extent by the influence of the lattice.[1-3] Also, the question as to what extent the dynamics of the HS $\rightleftharpoons$ LS equilibrium is affected by the lattice has found interest.[4,5] From the molecular point of view the HS $\rightleftharpoons$ LS conversion is an intersystem crossing (ISC) with $\Delta S = 2$ for iron(II) complexes and iron(III) complexes, and $\Delta S = 1$ for Co(II) complexes. Therefore, the study of the dynamics of the HS $\rightleftharpoons$ LS equilibrium may be useful to gain a deeper insight in the factors governing ISC processes that occur in photophysics, photochemistry, and also in some electron-transfer reactions of biological systems. The dynamical nature of the spin equilibrium has been well established for iron(II), iron(III), and cobalt(II) complexes in solution by using different techniques[6-14] and for a number of solid iron(III) complexes with Mössbauer spectroscopy.[4,5,15-21] Whereas quantitative data about the ISC rates and their temperature dependence are available for a variety of complexes in solution,[6-14] such data are rather scarce for the solid state. The order of magnitude of the ISC rates k in the solid state can be estimated from the line shape of the Mössbauer spectra. If k is small, relative to the hyperfine fre-

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[†] In partial fulfillment of the Ph.D. thesis.

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