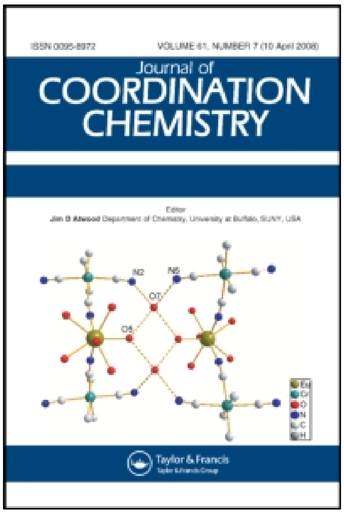

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SINGLET-TRIPLET SPIN TRANSITION IN AN IRON(II) COMPLEX OF 1,10-PHENANTHROLINE-2-CARBOTHIOAMIDE

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SINGLET-TRIPLET SPIN TRANSITION IN AN IRON(II) COMPLEX OF 1,10-PHENANTHROLINE-2-CARBOTHIOAMIDE

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The ^{57}Fe Mössbauer effect for the solid complex $FeLCl_2 \cdot H_2O$ (L = 10-phenanthroline-2-carbothioamide) has been studied between 4.2°K and 298°K. Two overlapping doublets (I and II) are observed, their relative intensity being strongly temperature dependent. The doublets are characterized by $\Delta E_Q(I) = 0.53$ mm sec^{-1}, $\delta^{IS}(I) = +0.22$ mm sec^{-1} and $\Delta E_Q(II) = 1.33$ mm sec^{-1}, $\delta^{IS}(II) = +0.23$ mm sec^{-1} at 4.2°K. In conjunction with magnetic data, the Mössbauer spectra are interpreted in terms of a singlet-triplet spin transition of the central iron(II) ion. In an applied magnetic field at 4.2°K, $H_{int} = 0$, $V_{zz}(I) > 0$, and $V_{zz}(II) > 0$. The results are consistent with optical electronic and infrared vibrational spectra.

INTRODUCTION

Triplet ground states in six-coordinated $3d^6$ complexes were tentatively suggested, for the first time, in a certain series of bis(1,10-phenanthroline) iron(II) complexes by König and Madeja.[2,3] Recently, it was demonstrated by extending Mössbauer effect studies and magnetic measurements to 4.2°K and 1.2°K, respectively,[4] that a slightly spin-mixed $^3A_2(\xi^2\eta^2\epsilon\zeta)$ ground state is indeed involved in $[Fe(phen)_2ox] \cdot 5H_2O$ (ox = oxalate). A more detailed investigation[5] produced evidence for triplet ground states in all compounds of the series previously reported.[2,3] In addition, the conditions required for triplet ground state formation in six-coordinated $3d^6$ ions are now well understood.[6] In the present work, we demonstrate on the basis of Mössbauer effect studies and magnetism, that a temperature induced transition between a spin singlet and a spin triplet ground state has to be assumed in the compound $FeLCl_2 \cdot H_2O$ where L = 1,10-phenanthroline-2-carbothioamide.

EXPERIMENTAL SECTION

Preparation of Dichloro(1,10-phenanthroline-2-carbothioamide iron(II) *monohydrate*

To a solution of 1,10-phenanthroline-2-carbothioamide (0.96 g, 4 mmole; the preparation of the ligand, together with that of other derived iron(II) complexes will be described elswewhere[7]) in hot ethanol (70 ml) was added a solution of iron(II) chloride tetrahydrate (0.8 g, 4 mmole) in ethanol (10 ml). The solution, which immediately became very intense purple, was stirred rapidly and crystals of the complex quickly separated. These were collected after the solution had cooled, washed with ethanol and dried in vacuum. *Anal.* Calcd. for $FeCl_{13}H_9N_3SCl \cdot H_2O$: C, 40.65; H, 2.89; N, 10.94; Fe, 14.54; S, 8.35; Cl, 18.46; O, 4.17. Found: C, 40.6; H, 2.9; N, 10.7; Fe, 14.3; S, 8.4; Cl, 17.3.

Physical Measurements

Electronic spectra of solid samples were measured using a Cary 14 spectrophotometer equipped with a type 1411 diffuse reflectance accessory. Infrared spectra were obtained in KBr pellets on a Beckman IR 7 instrument over the range 4000–200 cm^{-1}. Magnetic susceptibilities were measured employing the Gouy method, and effective magnetic moments were calculated according to $\mu_{eff} = 2.828\,(\chi'_m \cdot T)^{1/2}$. Here, χ'_m is the corrected molar susceptibility, the diamagnetic corrections used being Fe^{2+}, −13; Cl^-, −26; H_2O, −13; 2-thioamido-phen, −155 (in 10^{-6} cgs mol^{-1}). ^{57}Fe Mössbauer spectra were measured between 298°K and 4.2°K with a Frieseke and Hoepfner FHT 800A constant-acceleration spectrometer operating in the multiscaler mode. The results were processed by a LGP 21 computer and the normalized spectra plotted by a Calcomp 565 plotter. Cobalt-57 diffused into copper was used as source. The isomer shifts δ^{IS} are measured relative to the midpoint of the spectrum of an iron foil absorber at 295°K. To convert to the nitroprusside scale, add $+0.257$ mm sec^{-1}. Movement of the source toward the absorber corresponds to positive velocities.

RESULTS

Electronic Spectrum

No bands are observed in the region between 5000 and 9000 cm^{-1}. At the latter wavenumber, the absorbance rises steeply, the first intense band being encountered at about 11,500 cm^{-1}. At still larger wavenumbers the absorbance remains high, the spectrum showing little significant structure.

Infrared Spectrum

The spectrum is dominated by the i.r. frequencies of 1,10-phenanthroline-2-carbothioamide, relatively minor changes being observed, in general, as compared to the free ligand. Empirical assignments are possible, *e.g.* by comparison with the spectra of complexes of 1,10-phenanthroline,[8] 1,10-phenanthroline-2-carboxamide[9] and 2-thioamidopyridine.[10] The prominent frequencies are listed in Table 1 along with the most important assignments.

Magnetism

The results of magnetic measurements in the temperature range between 313°K and 83°K are listed in Table 2.

^{57}Fe Mössbauer Effect

Values of the quadrupole splitting ΔE_Q and of the isomer shift δ^{IS} extracted from Mössbauer spectra measured between 298°K and 4.2°K are compiled in Table 3. Typical spectra are displayed in Fig. 1.

TABLE 1

Infrared frequencies of $FeLCl_2 \cdot H_2O$ (L = 1,10-phenanthroline-2-carbothioamide) in cm^{-1}.[a]

~3000 s,br, ν(NH); 1635 vs,br, $\delta_d(NH_2)$ + ring(phen); 1596 m; 1558 m; 1484 s; 1462 vs,br, $\delta_s(NH_2)$; 1436 vs; 1414 m; 1388 m; 1335 m; 1241 w; 1219 w; 1163 m; 1142 m; 1096 s; 1049 w; 929 s, ν(CS); 852 vs; 778 s; 730 m; 682 m,br; 646 w; 534 m; 520 m; 494 m; 451 w; 393 m, ν(FeS); 368 s; 353 s; 313 s.

[a] Unassigned frequencies are due to the phen moiety slightly modified by complex formation.

TABLE 2

Magnetic susceptibility and effective magnetic moment of $FeLCl_2 \cdot H_2O$ between 313°K and 83°K.

T, °K	χ_m, 10^{-6} cgs mol^{-1} [a]	μ_{eff}, BM [b]
313	1240	1.77
303	1255	1.75
273	1268	1.68
233	1347	1.59
203	1408	1.52
183	1469	1.47
163	1529	1.42
143	1621	1.37
113	1834	1.29
98	1987	1.25
83	2170	1.31

[a] Experimental uncertainty ± 50 × 10^{-6} cgs mol^{-1}.
[b] Experimental uncertainty ± 0.02 BM.

TABLE 3

^{57}Fe Mössbauer effect data on $FeLCl_2 \cdot H_2O$ (L = 1,10-phenanthroline-2-carbothioamide).

T	ΔE_Q(I)	δ^{IS}(I)[a]	ΔE_Q(II)	δ^{IS}(II)[a]	Areas	
°K	mm sec^{-1}	mm sec^{-1}	mm sec^{-1}	mm sec^{-1}	I	II
298	0.53 ± 0.03	+0.26 ± 0.04	1.22 ± 0.06	+0.25 ± 0.07	0.77	0.23
77	0.53 ± 0.03	+0.22 ± 0.04	1.28 ± 0.03	+0.23 ± 0.04	0.58	0.42
4.2	0.53 ± 0.03	+0.22 ± 0.04	1.33 ± 0.03	+0.23 ± 0.04	0.53	0.47

[a] Isomer shifts relative to natural iron at 298°K. To convert to the sodium nitroprusside scale, add $+0.257$ mm sec^{-1}.

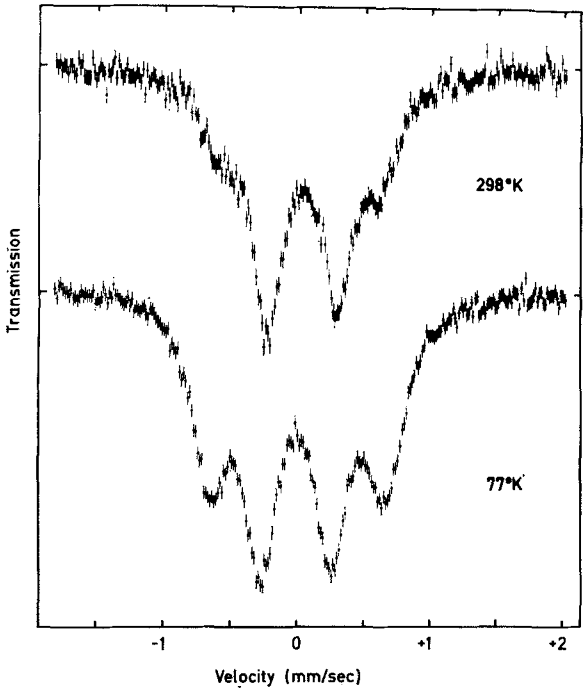

FIGURE 1 Mössbauer spectra of the complex $FeLCl_2 \cdot H_2O$ at 298°K (top spectrum) and 77°K (bottom spectrum).

DISCUSSION OF THE MOLECULAR STRUCTURE

The complex under study is not soluble in any solvent investigated except with decomposition, *e.g.* in water it rearranges to the bis-ligand complex $[FeL_2]^{2+}$. Decomposition is likewise observed on heating above ~70°C. Assignment of the overall molecular structure in the absence of X-ray structural data requires considerable caution since, under the circumstances, the results of physical measurements are liable to erroneous interpretation. On the other hand, the compound is a well defined solid and consists of equally developed small crystals which show identical optical properties in polarized light.

The ligand is tridentate, coordination to the iron atom being effected almost certainly by the two nitrogen atoms of the phenanthroline moiety and the sulphur atom, evidence for the latter being the shift of a band at 815 cm^{-1} in the spectrum of the free ligand to 778 cm^{-1} in that of the complex. This band, absent from the spectrum of 1,10-phenanthroline-2-carboxamide, probably arises from a composite vibration with a contribution from the C = S stretch, as in the spectrum of 2-thioamido-pyridine and its complexes.[10] In addition, there is a band at approximately 1400 cm^{-1} common to the spectra of 1,10-phenanthroline-2-carbothioamide, 2-thioamido-pyridine, 1,10-phenanthroline-2-carboxamide and pyridine-2-carboxamide. It is suggested that this band arises in all instances from the CN stretch of the amido groups, as has been demonstrated[11] for pyridine-2-carboxamide. The shift of this band to 1436 cm^{-1} in the spectrum of $FeLCl_2 \cdot H_2O$ further indicates that the ligand is sulphur-bonded. Finally, the band at 393 cm^{-1} is assigned to the Fe-S stretch since there are no bands in this region in the spectrum of the ligand, of 1,10-phenanthroline-2-carboxamide or of comparable complexes of the latter ligand.[12] Although the Fe-Cl stretches were not definitely located, due to various ligand-based frequencies, the two chlorine atoms are assumed to be coordinated. On the other hand, there is no indication of the $\nu_s(OH)$ and $\nu_{as}(OH)$ vibrations in the 3200–3550 cm^{-1} region, and the H-O-H bending at 1600 cm^{-1} is masked by the degenerate deformation vibration of the NH_2 group. Presumably then, the water molecule is involved in hydrogen bridging, *e.g.* with the free NH_2 group, and thus not bonded to the metal atom.

The spin multiplicity of the electronic ground state *at high temperature* may be ascertained from a collective consideration of several physical measurements. Thus a quintet (S = 2) ground state is incompatible with both the magnetism and Mössbauer effect at 313° K and 298° K, respectively, since $\mu_{eff} > 5.0$ BM and ΔE_Q between 1.0 and 4.0 mm sec^{-1} as well as $\delta^{IS} \sim 1.0$ mm sec^{-1} would be expected. In addition, high-spin iron (II) complexes which are not six-coordinate show d-d bands in the elecronic spectral region not masked in the spectrum of the present complex, *i.e.* bands at ~5000 cm^{-1} and ~10,000 cm^{-1} if five-coordinate and a single band at ~6000 cm^{-1} if four-coordinate.[12a, b] A singlet (S = 0) ground state would be in conflict with the magnetism, in particular since magnetic moments higher than ~1.0 BM are not expected.[13] We are thus left with the assumption of a triplet (S = 1) ground state, a situation for which only limited experience seems to be available.[2-5] Indeed, all data are consistent with this assumption: (i) the magnetism at 313° K ($\mu_{eff} = 1.77$ BM) corresponds to an S = 1 / S = 0 mixture; (ii) the parameters of the prominent Mössbauer spectrum (*cf.* doublet I) at 298° K, *viz.* $\Delta E_Q = 0.53$ mm sec^{-1}, $\delta^{IS} = +0.26$ mm sec^{-1} are consistent with $S = 1$; (iii) the absence of absorption between 5000 and 9000 cm^{-1} in the electronic spectrum is consistent with the behavior of the previously studied $S = 1$ complexes, for which no d-d bands were observed in this region.[2,3]

Bridged structures are difficult to exclude completely. However, the only ligands which could reasonably be involved in bridging are the two chlorine atoms. If such Cl-bridges were present, close approach of two iron atoms would inevitably lead to antiferromagnetic exchange coupling. No evidence for this is apparent from the magnetism and/or Mössbauer spectra. Thus the magnetism is independent of field strength throughout the temperature range studied. Also, as evident from the last section, no antiferromagnetic interaction is indicated in applied magnetic fields up to 40 kGauss.

Summing up, the present complex may be considered best, in the limit of high temperature, as consisting of discrete penta-coordinated spin triplet ground state molecules, $FeLCl_2 \cdot H_2O$, the H_2O not being coordinated to the iron.

THE QUADRUPOLE SPLITTING AND THE ISOMER SHIFT OF THE MÖSSBAUER SPECTRA

The Mössbauer spectrum of $FeLCl_2 \cdot H_2O$ consists of the superposition of two simple quadrupole split doublets, their intensity ratio being strongly temperature dependent (*cf.* Fig. 1 and Table 3). The two doublets (I and II) show essentially the same isomer shift, *viz.* $\delta^{IS} \sim 0.23$ mm sec^{-1}, although their quadrupole splitting is characteristically different, $\Delta E_Q = 0.53$ mm sec^{-1} for I and $\Delta E_Q = 1.22$ mm sec^{-1} for II at 298° K. The intensity ratios were determined by decomposition into Lorentzians and are included in Table 3, the total intensity being normalized to unity.

On the basis of the isomer shift, both I and II are consistent with either $S = 0$ or $S = 1$ ground states. The former assertion is supported by the Mössbauer parameters of bis complexes with the same ligand, *e.g.* $\Delta E_Q = 0.40$ mm sec^{-1}, $\delta^{IS} = +0.22$ mm sec^{-1} for $[FeL_2]Cl_2 \cdot H_2O$[7] for which the $S = 0$ ground state has been established by magnetic studies. However, the decrease of the magnetic moment and the concurrent increase in the intensity of doublet II relative to I with decreasing temperature suggest assignment of I and II to $S = 1$ and $S = 0$ ground states, respectively. This then corresponds to a triplet-singlet spin transition between different electronic ground states in the complex, $FeLCl_2 \cdot H_2O$. At the lowest temperature studied, *i.e.* 4.2° K, the area ratio of the Mössbauer spectra is approximately 1 : 1, and at 77° K it is only slightly changed, *viz.* $I(^3A_2) : I(^1A_1) = 0.58 : 0.42$. Since the magnetism (at 83° K) amounts to only 1.21 BM, this demonstrates that *the Debye-Waller factors of the ground states $^3A_2$ and $^1A_1$ are considerably different.*

The quadrupole splitting values observed in I and II are by themselves no evidence for $S = 1$ or $S = 0$ ground states. Triplet states originating in the $^3T_{1g}(t_{2g}^5 e_g)$ term of O_h symmetry which might form an $S = 1$ ground state in the penta-coordinated geometry of the iron(II) site are[6]

$$\left.\begin{aligned} |^3A_2 1a_2\rangle &= |\xi^2\eta^2\epsilon^+\zeta^+\rangle \\ |^3E 1e_a(e_b)\rangle &= -\frac{1}{2}|\zeta^2\xi^2(\eta^2)\epsilon^+\eta^+(\xi^+)\rangle \\ &\quad \pm\frac{\sqrt{3}}{2}|\zeta^2\xi^2(\eta^2)\theta^+\eta^+(\xi^+)\rangle \end{aligned}\right\} \tag{1}$$

if based on the idealized C_{4v} symmetry or

$$\left.\begin{aligned} |^3A_2 1a_2\rangle &= \frac{i}{\sqrt{2}}\{|x_+^2 x_0^2\, x^{\pm}u^{\pm}\rangle \\ &\qquad - |x_-^2 x_0^2\, x^{\mp}u^{\mp}\rangle\} \\ |^3E(^3T_1)1u_\pm\rangle_\pm &= \mp\frac{i}{\sqrt{2}}\{|x_+^2 x_-^2\, u^{\pm}x_0^{+}\rangle \\ &\qquad \mp |x_\mp^2 x_0^2\, u^{\mp}x^{\mp}\rangle\} \end{aligned}\right\} \tag{2}$$

if based on the idealized symmetry C_{3v}. In Eq (2), x_+, x_-, x_0, u_+, u_- are trigonally oriented one-electron d functions.[14] The quadrupole splitting ΔE_Q of a given state may be calculated by application of the nuclear quadrupole-interaction Hamiltonian[15]

$$\mathscr{H}_Q = \frac{e^2Q\langle r^{-3}\rangle}{7I(2I-1)}\sum_i\{(\mathbf{l}_i \cdot \mathbf{I})^2 + \tfrac{1}{2}(\mathbf{l}_i \cdot \mathbf{I}) - 2I(I+1)\} \tag{3}$$

where all quantities have the usual meaning. In this approach, the lattice contribution to ΔE_Q is assumed to be small and is therefore neglected. Denoting the operator in Eq (3) by $\mathscr{H}'$ the basic matrix elements corresponding to Eq (1) are

$$\left.\begin{aligned}\langle \xi M_I|\mathscr{H}'|\xi M_I\rangle &= \langle \eta M_I|\mathscr{H}'|\eta M_I\rangle \\ &= -\tfrac{1}{2}\{3M_I^2 - I(I+1)\} \\ \langle \epsilon M_I|\mathscr{H}'|\epsilon M_I\rangle &= \langle \zeta M_I|\mathscr{H}'|\zeta M_I\rangle \\ &= \{3M_I^2 - I(I+1)\} \\ \langle \theta M_I|\mathscr{H}'|\theta M_I\rangle &= -\{3M_I^2 - I(I+1)\}\end{aligned}\right\} \quad (4)$$

Since it is required that $M_I = M_I'$ and $M_S = M_S'$, the summation of Eq (3) produces

$$\begin{aligned}&\langle {}^3A_2 M_S M_I|\mathscr{H}_Q|{}^3A_2 M_S M_I\rangle \\ &\quad = \langle {}^3E\ M_S M_I|\mathscr{H}_Q|{}^3E\ M_S M_I\rangle = 0 \quad (5)\end{aligned}$$

and thus $\Delta E_Q = 0$ for the $^3A_2$ and ^3E states of C_{4v} symmetry. It may be shown that for the $^3A_2$ and ^3E states in C_{3v} symmetry Eq (5) is likewise valid and again $\Delta E_Q = 0$. Finally, for the $^1A_1(\xi^2\eta^2\zeta^2)$ ground state it follows, irrespective of symmetry,

$$\langle {}^1A_1 M_S M_I|\mathscr{H}_Q|{}^1A_1 M_S M_I\rangle = 0 \quad (6)$$

and therefore $\Delta E_Q = 0$. These results are in good agreement with experience. Thus extremely small values for the quadrupole splitting are encountered in triplet ground states of *six-coordinated* iron(II), *e.g.* $\Delta E_Q = 0.23$ mm sec^{-1} in $[Fe(phen)_2ox]\cdot 5H_2O$ between 4.2° K and 298° K.[4,5] The somewhat larger value of ΔE_Q in doublet I of $FeLCl_2\cdot H_2O$ (*cf.* Table 3) may be due to mixing with higher levels of significantly larger ΔE_Q initiated by the low symmetry ligand field. On the other hand, the quadrupole splitting of the $^1A_1$ ground states is much more susceptible to the effect of low symmetry, this being particularly evident with tridentate ligands. Thus in $[Fe(pythiaz)_2]\ (ClO_4)_2$ at 77° K where pythiaz = 2,4-bis(2-pyridyl)thiazole, the $^1A_1$ ground state component spectrum shows $\Delta E_Q = 1.58$ mm sec^{-1} [16], despite the requirements of Eq (6). The ΔE_Q value of doublet II in $FeLCl_2\cdot H_2O$ (*cf.* Table 3) is therefore well in accord with results on related systems.

Conformational changes giving rise to the two different spectra in conjunction with the assumption of $^1A_1$ ground state for both I and II cannot be ruled out on the basis of Mössbauer effect alone. However, such changes are unlikely to cause the observed variation of the magnetic moment.

The assignment of one or both of the Mössbauer spectra to the $^2T_2$ ground state in iron(III) may be ruled out, since, in this case, an appreciable thermal population of close-lying excited levels would arise. Consequently, a strong temperature dependence of the quadrupole splitting would be expected,[15] contrary to the experimental findings, *viz.* Table 3 and Fig. 1. Of course, this conclusion is in complete agreement with results from chemical studies.

Impurity effects do not seem to be of any significance. Three different samples were measured between 298 and 4.2° K and practically identical Mössbauer spectra were obtained. On the other hand, the magnetic moments of these samples varied by about ±0.20 BM ($\mu_{eff} = 1.56$ or 1.96 BM at 303° K), although $\mu_{eff} = 1.75$ BM seems to be more normal since it has been obtained in three additional samples as well. Similar dependence of magnetism on solid state effects has been encountered in various complexes exhibiting $^5T_2$–$^1A_1$ transitions.[17,18]

The possibility that the observed spectra could be due to a strongly temperature-dependent Debye-Waller factor in a mixture of two different complexes has been considered. This, however, we regard as extremely unlikely given the optical behavior of the material and the fact that identical intensity ratios of the doublets I and II were encountered in three different samples. In addition, possible contaminants were studied and considerably different Mössbauer spectra were obtained for these. Mössbauer parameters for $[FeL_2]Cl_2\cdot H_2O$ were given above, and for the complex of the deprotonated ligand, $[Fe(L\text{–}H)_2]\cdot H_2O$, $\Delta E_Q = 0.76$ mm sec^{-1} and $\delta^{IS} = +0.19$ mm sec^{-1} (S = 0).

Recently, triplet-singlet "spin equilibria" were claimed[19] in $[Fe(R_1R_2(dtc))_2(tfd)]$ where $R_1R_2(dtc)$ and tfd denote an N,N-disubstituted dithiocarbamate and bis(perfluoromethyl)-1,2-dithietene, respectively. However, in this complex an electron redistribution has taken place such that electron density has been transferred from iron to the tfd ligand, the electronic structure at the central ion thus corresponding to Fe^{3+} rather than to Fe^{2+}. Therefore, the complex $FeLCl_2\cdot H_2O$ may be considered, to the authors' knowledge, as the *first authentic example of a triplet-singlet spin transition* in the $3d^6$ configuration of an iron(II) complex.

MAGNETIC HYPERFINE INTERACTIONS

Magnetic hyperfine interactions were observed by studying the Mössbauer transitions within a longitudinal magnetic field of 40 kGauss at 4.2° K. Two overlapping asymmetric triplets were obtained which correspond to the zero-field spectra of S = 1 and $S = 0$ ground states. Each of the triplets is of the same type as found previously[20,21] in $[Fe(mephen)_3]^{2+}$ complexes where mephen = 2-methyl-1,10-phenanthroline. The complete spectrum was accurately fitted by a program similar to that of Collins and Travis.[22] The result which is shown in Fig. 2 demonstrates that the internal field $H_{int} = 0$, and for the electric field gradients of the zero-field doublets I and II it follows that $V_{zz}(I) > 0$ and $V_{zz}(II) > 0$.

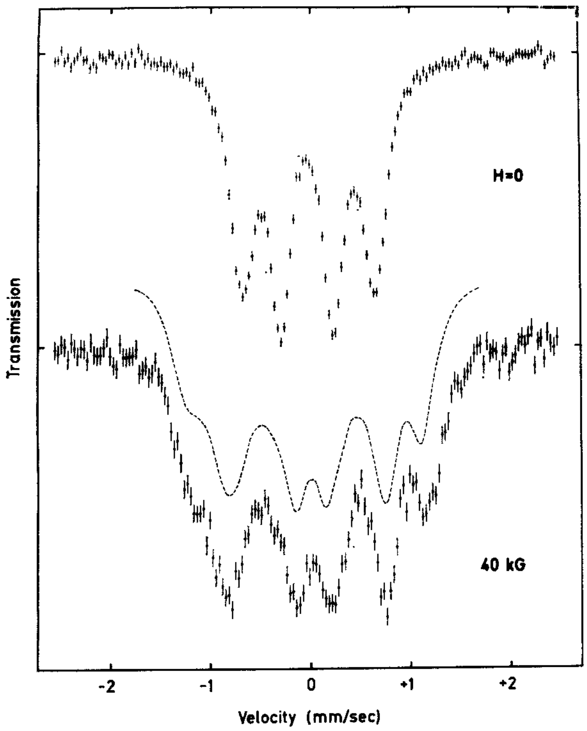

FIGURE 2 Mössbauer spectrum of $FeLCl_2.H_2O$ without (top spectrum) and in an applied magnetic field of 40 kGauss (bottom spectrum) at 4.2°K. Calculated spectrum shown by the broken line ($H_{int} = 0$, $V_{zz}(I) > 0$, $V_{zz})II) > 0$).

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