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New Aspects of the High Spin–Low Spin Transition in Tris(2-methyl-1,10-phenanthroline)iron(II) Perchlorate

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The high spin–low spin transition in the polycrystalline complex compound $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ (2-CH$_3$phen = 2-methyl-1,10-phenanthroline) has been reinvestigated by Mössbauer measurements at 21 temperatures between 4.2 and 295 K, magnetic susceptibility measurements down to 2.6 K, and ir and far-ir spectroscopy. The far-ir spectra at 298 and 108 K exhibit distinct absorption lines characteristic of high-spin and low-spin Fe–N vibrations. Two high-spin iron(II) quadrupole doublets are observed in the Mössbauer spectra, which are interpreted as arising from two different lattice sites for high-spin iron(II); apparently both of them convert into one and the same low-spin state appearing as a characteristic quadrupole doublet. From a theoretical analysis of the temperature dependence of the quadrupole splitting, with trigonal field distortion, spin–orbit coupling, and effects of covalency taken into account, it can be shown that the two high-spin iron(II) doublets can be attributed to iron(II) in ^5E and $^5A_1$ ground states respectively, under D_3 symmetry. Anomalous magnetic behavior and a discontinuity in several Mössbauer parameters in the temperature range 70–100 K have been detected; these are believed to originate from a phase transition.

Introduction

The high spin–low spin transition in $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ (2-CH$_3$phen = 2-methyl-1,10-phenanthroline) has been well established by magnetic[1] and Mössbauer[2] measurements. In connection with Mössbauer emission spectroscopy on ^{57}Co-labeled diimine complexes of cobalt(II) performed in our laboratory a more profound knowledge of the magnetic behavior of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ was desirable. As already partly reported in a preliminary publication,[3] Mössbauer effect measurements at 21 temperatures between 4.2 and 295 K confirm the existence of the spin transition, but in contrast to the earlier publication[2] two ferrous high-spin doublets are apparent from the spectra.

Earlier magnetic susceptibility studies by Goodwin et al.[1] had been carried out in the temperature range 300–90 K. To learn more about the low-temperature magnetism we have extended the magnetic measurements down to 2.6 K. Moreover, from far-ir spectra taken at room temperature and 108 K we hoped to gain specific signals on vibrational properties above and below the magnetic crossover.

Experimental Section

The complex $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ was prepared according to the method of Pfeiffer and Christeleit[4] by adding an aqueous solution containing excess sodium perchlorate to a solution of stoichiometric amounts of ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$, and the ligand[5] dissolved in a water–methanol mixture (1:1). The product was recrystallized from water–methanol and dried under vacuum with phosphorus pentoxide.

The magnetic susceptibility data were recorded with a Foner-type magnetometer calibrated with nickel metal. Temperatures between 2 and 300 K at the sample could be obtained by means of a continuous-flow cryostat. The temperature was measured with a gallium arsenide diode (accuracy ≥0.5%). The maximum error of the susceptibility data is estimated to be 1%. Effective magnetic moments, μ_{eff}, were calculated using the formula

$$\mu_{eff} = 2.8273\sqrt{\chi'_m T} \qquad (1)$$

where χ'_m is the molar susceptibility corrected for diamagnetism (505 $\times 10^{-6}$ emu mol^{-1} calculated according to Figgis and Lewis[6]).

Table I. Characteristic Bands in the Far-Ir Spectra of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ at 108 and 298 K and of the Free Ligand at 298 K (in Parentheses)

Wavenumber $\tilde{\nu}$, cm^{-1}		
108 K	298 K	Assignment
419 s	419 s (405 w)	Ligand
348 m	348 w, sh (348 s)	
331 w	330 w	
318 w, sh	310 (305)	Ligand
283 w		ν(Fe–N) (low spin)
270 w, sh		
247 s	247 s (245 m, sh)	Ligand
231 s		δ(N–Fe–N) (low spin)
216 s	213 s	ν(Fe–N) (high spin)
190 m, sh	185 m, sh (190 s, br)	Ligand
73 m	68 m (72 m)	

The far-infrared spectra (50–500 cm^{-1}) were measured at 298 and 108 K, using a Polytec FIR 30 spectrometer (polyethylene pellets).

The Mössbauer spectra were taken with a constant-acceleration electromagnetic drive operating in the multiscaling mode. The source ^{57}Co–Cu was kept at room temperature. The absorber temperature was varied between 4.2 and 300 K, with a constancy of ±0.1 K. The absorbers contained about 0.15 mg of ^{57}Fe/cm^2.

Results

The far-ir spectra contain a number of bands which are essentially identical with those of the free ligand (in Table I the free ligand vibrations at room temperature are given in parentheses) and are practically not shifted by changing the temperature. The Fe–N vibrations with temperature-dependent intensities occur in the region of ca. 330–213 cm^{-1}. Their assignment is possible by comparison with far-ir spectra of similar iron–diimine complexes from the literature.[7,8] The bands at 213 cm^{-1} (298 K) and 216 cm^{-1} (108 K) can be assigned to the high-spin Fe–N stretching vibration. The absorption lines with the center of gravity at about 300 cm^{-1} in the low-temperature spectrum should contain low-spin Fe–N stretching vibrations, but the assignment is complicated by a ligand absorption occurring in the same region. The band at

Table II. Isomer Shift δ (Relative to $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$), Quadrupole Splitting ΔE_Q, Full Width at Half-Maximum Γ, and Relative Area F of the Doublets A, B, and C in the Mössbauer Spectra of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ at Selected Temperatures

T, K		δ, mm s^{-1}	ΔE_Q, mm s^{-1}	Γ, mm s^{-1}	F, %
4.2	A	0.779 ± 0.007	0.670 ± 0.011	0.409 ± 0.010	81.1 ± 1.8
	B	1.70 ± 0.10	1.44 ± 0.17	0.73 ± 0.27	7.5 ± 3.6
	C	1.411 ± 0.039	2.018 ± 0.085	0.46 ± 0.10	11.4 ± 2.8
56.3	A	0.775 ± 0.006	0.645 ± 0.010	0.380 ± 0.012	78.8 ± 2.4
	B	1.64 ± 0.10	1.51 ± 0.18	0.80 ± 0.28	9.1 ± 3.0
	C	1.395 ± 0.018	2.12 ± 0.036	0.367 ± 0.076	12.2 ± 2.4
77.4	A	0.760 ± 0.010	0.614 ± 0.010	0.390 ± 0.010	79.1 ± 1.8
	B	1.65 ± 0.10	1.28 ± 0.20	0.75 ± 0.10	6.3 ± 2.9
	C	1.364 ± 0.025	2.283 ± 0.039	0.402 ± 0.062	14.6 ± 2.0
97.4	A	0.768 ± 0.015	0.661 ± 0.018	0.424 ± 0.015	77.0 ± 2.0
	B	1.474 ± 0.042	1.06 ± 0.17	0.58 ± 0.23	8.2 ± 4.1
	C	1.414 ± 0.039	2.033 ± 0.068	0.473 ± 0.067	14.8 ± 3.3
133	A	0.753 ± 0.008	0.647 ± 0.016	0.376 ± 0.014	54.8 ± 2.1
	B	1.358 ± 0.013	1.092 ± 0.055	0.502 ± 0.078	24.2 ± 5.4
	C	1.398 ± 0.021	1.837 ± 0.075	0.440 ± 0.058	20.9 ± 4.7
173	A	0.777 ± 0.015	0.535 ± 0.028	0.378 ± 0.040	28.9 ± 3.1
	B	1.221 ± 0.008	1.029 ± 0.039	0.477 ± 0.049	41.2 ± 6.4
	C	1.308 ± 0.016	1.760 ± 0.032	0.441 ± 0.048	29.9 ± 6.4
248	A	0.735 ± 0.048^a	0.518 ± 0.085^a	0.40 ± 0.15	3.3 ± 2.2
	B	1.259 ± 0.015	0.877 ± 0.051		54 ± 12
	C	1.290 ± 0.018	1.350 ± 0.067		42 ± 12
295	A				
	B	1.218 ± 0.016	0.835 ± 0.089	0.361 ± 0.052	44 ± 21
	C	1.230 ± 0.050	1.126 ± 0.085		55 ± 21

[a] Parameter not varied during the fitting procedure.

231 cm^{-1} most probably stems from the corresponding low-spin N–Fe–N deformation vibration.

Some selected results of the Mössbauer measurements are presented in Table II; three typical spectra are shown in Figure 1.

It is evident that the 133-K spectrum consists of three doublets A, B, and C. The isomer shifts and quadrupole splittings of B and C are typical of high-spin iron(II) whereas doublet A can unambiguously be assigned to low-spin iron(II). With increasing temperature the intensity of doublet A decreases in favor of the high-spin resonances B and C which overlap more and more and finally coincide at room temperature.

The earlier reported line broadenings[2] can be readily explained by the presence of the high-spin doublets B and C. Below 133 K the intensity of A increases and remains practically constant below 77.4 K.

The Mössbauer parameters presented in Table II are the results of a least-squares fitting procedure in which a modified Lorentzian line shape was assumed, because of the known deviations of the experimental absorption lines from pure Lorentzian line shape, particularly in the line wings. To describe the experimental line shape a convolution of Lorentzian and Gaussian functions has been proposed.[9] We used, however, a simpler empirical function consisting of a linear combination of Lorentzian and Gaussian functions (20–40% Gaussian fraction) which proved to match the experimental line shape much more satisfactorily than a pure Lorentzian. The "goodness of fit" parameter $z = \chi_{\text{exptl}}^2/\chi_{\text{theor}}^2$ ranges from 0.9 to 1.6. With pure Lorentzian lines the results were in most cases the same within the experimental error, but the "goodness of fit" parameter typically was twice as large.

The results of the magnetic susceptibility measurements are shown in Figure 2. The strong temperature dependence of the effective magnetic moment is apparent: μ_{eff} decreases continuously from 5.38 BM at room temperature to 2.11 BM at 70 K, then increases again slightly, and, after passing a flat maximum, decreases sharply below 20 K. No field dependence could be observed.

Theoretical Analysis

The appearence of the two quadrupole doublets B and C assigned to high-spin iron(II) is interpreted in terms of iron(II) occupying two different lattice sites. Both of them show a spin transition to apparently one and the same low-spin species. There is a remarkable difference in size and temperature dependence of the quadrupole splitting of the two high-spin doublets. To attain some knowledge about the electronic structure of the two lattice sites the temperature dependence

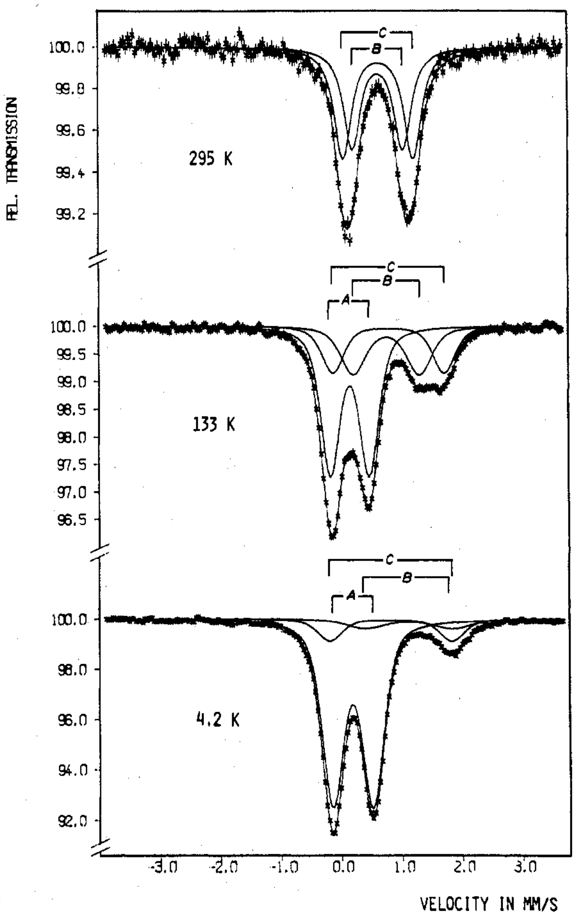

Figure 1. Mössbauer spectra of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ at various temperatures; ^{57}Co–Cu source at 293 K.

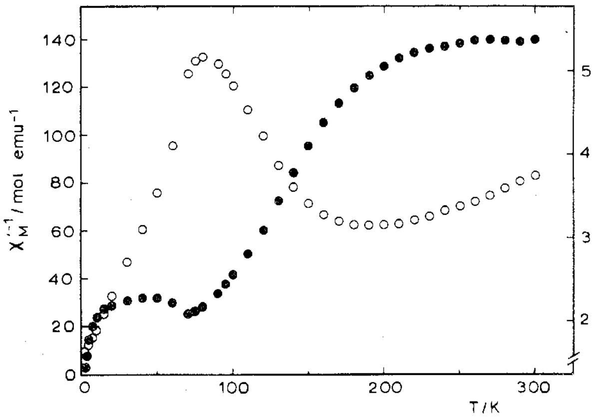

Figure 2. Reciprocal molar magnetic susceptibility (○) and effective magnetic moment (●) of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ as a function of temperature.

of the quadrupole splitting was calculated and least-squares fitted to the experimental data.

In an axially distorted ligand field (D_3 symmetry is assumed) the quadrupole splitting can be expressed as

$$\Delta E_Q = \frac{1}{2}e^2qQ + \Delta E_Q{}^c \tag{2}$$

$\Delta E_Q{}^c$ represents the temperature-independent part, which contains a contribution from noncubic charge distributions in the coordination sphere and a contribution due to anisotropic charge densities in the molecular orbitals, mainly of $\sigma(e_g)$ type.

In the first term of eq 2 $V_{zz} = eq$ is the principal component of the electric field gradient tensor. It represents the temperature-dependent part of the quadrupole splitting

$$\Delta E_Q(T) = \frac{1}{2}e^2Q(1 - R)\langle r^{-3}\rangle\alpha_c{}^2(F(T)) \tag{3}$$

It can be expressed as a maximum value $e^2Q(1 - R)\langle r^{-3}\rangle$[10] reduced by the orbital reduction factor $\alpha_c{}^2$, which takes effects of covalency into account, and multiplied by the reduction function $F(T)$[11] taking on values of $-4/7 \leq F(T) \leq 2/7$.

To determine the reduction function $F(T)$ a perturbation calculation on the ^5D level of the d^6 system was performed making allowance for an octahedral ligand field potential, trigonal distortion, and spin–orbit coupling. The Hamiltonian

$$\hat{H} = \hat{V}_0 - \alpha_\lambda{}^2\lambda_0\hat{L}\hat{S} - (\delta_t/3)(\hat{L}_z{}^2 - 2) \tag{4}$$

was applied to basis functions quantized along the trigonal axis.[10,12] $\hat{V}_0$ is the well-known octahedral ligand field operator, λ_0 is the free-ion spin–orbit coupling constant (λ_0 = 104 cm^{-1} [13]) which is reduced for covalency effects by the factor $\alpha_\lambda{}^2$, and the trigonal distortion parameter δ_t represents the energy difference between the $^5A_1$ ($^5T_{2g}$) and the ^5E ($^5T_{2g}$) terms under D_3 symmetry. The two covalency factors $\alpha_c{}^2$ and $\alpha_\lambda{}^2$ have been introduced in order to allow them to take on different values, a possibility which cannot be excluded a priori although it has been suggested that the effects of covalency upon radial expansion and spin–orbit coupling should parallel each other.[11] The resulting 25 × 25 perturbation matrix has been diagonalized to give eigenvalues and eigenfunctions, from which net populations[14] of the d orbitals are calculated.

The function $F(T)$ was obtained by weighting the net populations of the 25 levels involved with the well-known contributions from the individual 3d electrons[11] and performing a Boltzmann distribution over all levels.

δ_t, $\alpha_c{}^2$, $\alpha_\lambda{}^2$, and $\Delta E_Q{}^c$ are the quantities to be determined by fitting the calculated quadrupole splittings to the experimental data as a function of temperature. Departing from the largest quadrupole splitting, 4.5 mm s^{-1}, ever observed for a ferrous compound,[15] we have estimated the constant $e^2Q(1 - R)\langle r^{-3}\rangle$[10] to be 17.5 mm s^{-1}. The octahedral ligand field parameter Dq was taken to be 1250 cm^{-1} in analogy to Dq values measured for similar diimine complexes of iron(II).[16] Because $10Dq \gg \delta_t$, the influence of the excited ^5E term is negligible.

Table III. Values of the Trigonal Distortion Parameter δ_t, the Covalency Factors $\alpha_\lambda{}^2$ and $\alpha_c{}^2$, and the Temperature-Independent Part of the Quadrupole Splitting $\Delta E_Q{}^c$ Derived from the Temperature Dependence of the Quadrupole Splitting for the Two High-Spin Doublets in $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$

Parameter	≤117 K	117–295 K
(a) Quadrupole Doublet C ($^5A_1$ Ground State)		
δ_t/cm^{-1}	−300 ± 20	−277 ± 4
$\alpha_\lambda{}^2$	0.55 ± 0.05	0.57 ± 0.03
$\alpha_c{}^2$	0.62 ± 0.05	0.62 ± 0.03
$\Delta E_Q{}^c$/(mm s^{-1})	0.23 ± 0.06	0.25 ± 0.04
(b) Quadrupole Doublet B (^5E Ground State)		
δ_t/cm^{-1}	650 ± 250	297 ± 10
$\alpha_\lambda{}^2$	0.63	0.63 ± 0.03
$\alpha_c{}^2$	0.62	0.62 ± 0.03
$\Delta E_Q{}^c$/(mm s^{-1})	−0.15	−0.15 ± 0.06

In trying to fit the calculated temperature dependence of the quadrupole splitting of both high-spin doublets of $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ to the experimental data no parameter set could be found giving satisfactory congruency over the whole temperature range under study. This and a marked discontinuity detected in the temperature dependence of the isomer shift of doublet B (see below) between 70 and 100 K led us to the assumption that a change of the term diagram in this temperature region seems very likely. In the first step we have therefore restricted the fitting procedure to the temperature range 117–295 K, which is where most of the spin transition takes place. The resulting parameter sets for both doublets B and C are given in Table III. The data are given together with estimated upper and lower limits within which χ^2 was of similar magnitude.

Below 117 K a reasonable fit for the quadrupole doublet C was obtained by starting out with the parameter set of the "high-temperature fit" and otherwise proceeding as above. In case of doublet B this procedure was not appropriate because of the large experimental errors. A plausible fit was obtained by taking the parameters $\alpha_\lambda{}^2$, $\alpha_c{}^2$, and $\Delta E_Q{}^c$ from the "high-temperature fit" to be constant. Comparing the values for the trigonal distortion parameter δ_t from the two temperature regions one finds δ_t to be considerably larger below 117 K for doublet B and only slightly larger for doublet C.

The experimental values and the theoretical curves (calculated with the parameter sets of Table III) are shown in Figure 3. The results from the theoretical analysis (cf. Table III) are consistent with opposite signs of the electric field gradient corresponding to a ^5E groundstate for doublet B ($\delta_t > 0$, $V_{zz} > 0$) and a $^5A_1$ ground state for doublet C ($\delta_t < 0$, $V_{zz} < 0$) under D_3 symmetry.

Discussion

The exsistence of two high-spin species with different signs of V_{zz} might originate from an order–disorder phenomenon in the perchlorate anion, which has been suggested to be responsible for the $^5A_1 \rightleftharpoons {}^5E$ transition in the complexes $[(Fe(N,N'\text{-}(c\text{-}C_6H_{11})_2tu)_6](ClO_4)_2$[17] and $[Fe(H_2O)_6](ClO_4)_2$.[18] Such a transition cannot be excluded a priori in the complex under study, but the interpretation that a somewhat different high-spin to low-spin transition of the high-spin species causes the temperature dependence of the observed intensity ratio is preferred for simplicity. In the complexes of ref 17 and 18 the presence of perchlorate anions apparently gives rise to two different lattice sites of the iron ions; a similar

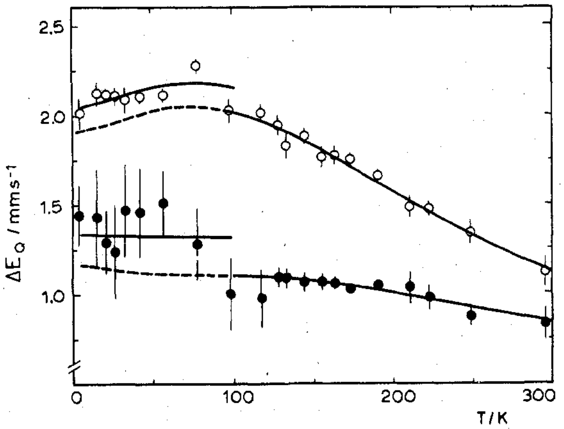

Figure 3. Temperature dependence of the quadrupole splitting of the high-spin doublets B (●) and C (○) (arising from ^5E and $^5A_1$ ground states, respectively) in $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$. The theoretical curves (solid lines) have been calculated with the parameters given in Table IV.

phenomenon may be encountered here. It is interesting that two high-spin species have been observed in the Mössbauer emission spectra of $[^{57}Co(phen)_3](ClO_4)_2 \cdot 2H_2O$[19] and $[^{57}Co(\alpha,\alpha'\text{-bpy})_3](ClO_4)_2 \cdot 2H_2O$,[20] which probably can be assigned in analogy to the present case.

As already stated above the temperature dependence of the isomer shift of the high-spin doublet B shows a marked discontinuity in the temperature region 70–100 K (cf. Figure 4) which coincides with discontinuities in the temperature dependence of the quadrupole splittings of both high-spin doublets. There is also a small but noticeable discontinuity in the reciprocal molar susceptibility (cf. Figure 2) corresponding to an increase in the magnetic moment, which can only be interpreted in terms of an increase of the high-spin portion with decreasing temperature. From the areas under the Mössbauer lines this increase could not be revealed because of the relatively large errors. We believe that a phase transition occurs in the temperature range 70–100 K; however to prove this, more data from other techniques (e.g., heat capacity measurements) are necessary.

Among the various mechanisms for the spin transition discussed by several authors[21,22] we are inclined to adopt the suggestion by Sorai et al.[22] as a working model. From heat capacity and infrared studies (4000–30 cm^{-1}) as a function of temperature on $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$ Sorai et al. concluded that the entropy, taken to be composed of an electronic ($\Delta S_{el} \simeq R \ln 5$) and a vibrational contribution, plays an important role. They suggested that there is a significant coupling between the electronic state and the phonon system acting as a transmitter in the cooperative transition. Although the compound of the present paper shows a gradual spin transition whereas in the compounds $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$[23] the spin state changes abruptly, we believe that the above model applies also to our case. Because of the complicated magnetic behavior and the complex Mössbauer spectra we are not able to test the validity of the model on the basis of the results presented here. Further investigations on simpler systems are in progress.

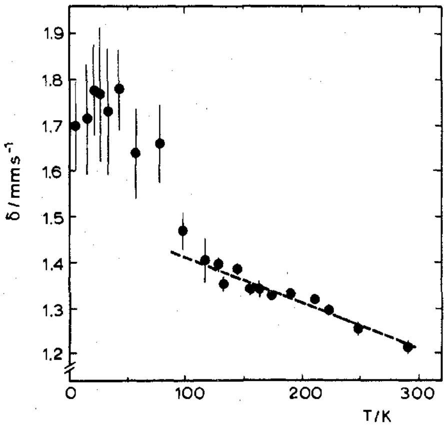

Figure 4. Isomer shift δ (relative to $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$) of doublet B in $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$ as a function of temperature.

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Registry No. $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$, 18433-45-9.

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