(7) We observed at most a shift of ~+1.5 eV between the chlorine 2p binding energies of chloride ion and chlorine in a terminal M–Cl bond.[3]

(8) B. J. Lindberg, *Int. J. Sulfur Chem., Part C*, **7**, 33 (1972), and references therein.

(9) T. B. Rauchfuss, J. S. Shu, and D. M. Roundhill, *Inorg. Chem.*, **15**, 2096 (1976), and references therein.

(10) R. B. King, Ed., "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 180.

(11) "Handbook of Preparative Inorganic Chemistry", Vol. 2, G. Brauer, Ed., Academic Press, New York, N.Y., 1965, p 1765.

(12) L. M. Volshtein and M. F. Mogilevkina, *Dokl. Akad. Nauk SSSR*, **142**, 1305 (1962).

(13) C. A. McAuliffe, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **5**, 1996 (1966).

(14) Reference 11, p 1764.

(15) J. D. Gilbert, M. C. Baird, and G. Wilkinson, *J. Chem. Soc. A*, 2198 (1968).

(16) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968).

(17) L. Pignolet, R. A. Lewis, and R. H. Holm, *J. Am. Chem. Soc.*, **93**, 360 (1971).

(18) O. A. Ileperuma and R. D. Feltham, *Inorg. Synth.*, **16**, 5 (1975).

(19) D. C. Frost, C. A. McDowell, and R. L. Tapping, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 297 (1975).

(20) B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc. A*, 1668 (1969).

(21) H. Büttner and R. D. Feltham, *Inorg. Chem.*, **11**, 971 (1972).

(22) W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, **11**, 1100 (1974).

(23) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Am. Chem. Soc.*, **88** 4604 (1966).

(24) J. A. McCleverty, N. M. Atherton, J. Locke, E. J. Wharton, and C. L. Winscom, *J. Am. Chem. Soc.*, **89**, 6082 (1967).

(25) A. Davison, N. Edelstein, R. H. Holm, and E. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(26) A. D. Hamer, D. G. Tisley, and R. A. Walton, *J. Inorg. Nucl. Chem.*, **36**, 1771 (1974).

(27) P. Brant and R. D. Feltham, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 77 (1976).

(28) P. Brant and R. D. Feltham, "Proceedings of the Climax Second International Conference on the Chemistry and Uses of Molybdenum," P. C. H. Mitchell, Ed., Climax Molybdenum Co. Ltd., London, 1976.

(29) H. Rupp and U. Weser, *Bioinorg. Chem.*, **5**, 21 (1975).

(30) U. Weser, H. Rupp, F. Donay, F. Linnemann, W. Voelter, W. Voetsch, and G. Jung, *Eur. J. Biochem.*, **39**, 127 (1973).

(31) S. O. Grim, L. J. Matienzo, and W. E. Swartz, Jr., *Inorg. Chem.*, **13**, 447 (1974).

(32) L. N. Kramer and M. P. Klein in "Electron Spectroscopy", D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, pp 731–751.

(33) L. F. Dahl, and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(34) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.*, **11**, 599 (1958).

(35) M. V. Veidis and G. J. Palenik, *Chem. Commun.*, 1277 (1969).

(36) C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta, Rev.*, 103 (1972).

(37) H. C. Freeman and M. L. Golomb, *Chem. Commun.*, 1523 (1970).

(38) M. F. Mogilevkina, M. V. Sekacheva, I. M. Cheremisina, and E. A. Gal'tsova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **21**, 77 (1976).

(39) G. Jung, M. Ottnad, H. J. Hartmann, H. Rupp, and U. Weser, *Z. Anal. Chem.*, **263**, 282 (1973).

(40) G. Sokolowski, W. Pilz, and U. Weser, *FEBS Lett.*, **48**, 222 (1974).

(41) H. Shindo and T. L. Brown, *J. Am. Chem. Soc.*, **87**, 1904 (1965).

(42) H. Rupp and U. Weser, *FEBS Lett.*, **44**, 293 (1974).

(43) D. Leibfritz, *Angew. Chem., Int. Ed. Engl.*, **11**, 232 (1972).

(44) I. B. Baranovskii, M. A. Golubnichaya, G. Ya. Mazo, V. I. Nefedov, Ya. V. Salyn', and R. N. Shchelokov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **21**, 1085 (1976).

(45) G. Battistoni, M. Bossa, C. Furlani and G. Mattogno, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 297 (1975).

(46) This value will of course change with any variation in the binding energy referencing procedure.

(47) G. Jung, M. Ottnad, W. Bohnenkamp, W. Bremser, and U. Weser, *Biochem. Biophys. Acta*, **295**, 77 (1973).

(48) C.-C. Su and J. W. Faller, *Inorg. Chem.*, **13**, 1734 (1974). The S 2p binding energies in this paper have been corrected by +1.0 eV (i.e., to a Au $4f_{7/2}$ value of 84.0 eV rather than 83.0 eV) to make them more compatible with our referencing procedure.

(49) A recent report of the S 2p binding energy spectrum of a cysteine complex of copper(I) describes the presence of peaks at 167.8 and 162.7 eV.[50] The former peak is attributed[50] to sulfate impurity. This result agrees with our conclusions.

(50) H. Rupp and U. Weser, *Biochem. Biophys. Acta*, **446**, 151 (1976).

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Thermally Induced Spin Transition in Tris(2-methoxy-1,10-phenanthroline)iron(II) Perchlorate. Variable-Temperature Mössbauer, Magnetic Susceptibility, and Far-Infrared Measurements

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Tris(2-methoxy-1,10-phenanthroline)iron(II) perchlorate, $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2{\cdot}H_2O$, has been prepared in polycrystalline form and studied by variable-temperature ^{57}Fe Mössbauer spectroscopy (293–15 K), magnetic susceptibility (300–2 K), and far-IR (298 and 108 K) measurements. The compound shows a temperature-dependent $^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$ transition with $T_c \approx 205$ K (T_c is temperature of 50% conversion). The magnetic crossover is clearly reflected in the Mössbauer spectra as well as in the effective magnetic moment. The far-IR spectra at 298 and 108 K exhibit distinct absorption lines which are characteristic of high-spin and low-spin Fe–N vibrations. The Debye–Waller factors of the different spin states differ in a factor of nearly 2. Two high-spin iron(II) quadrupole doublets are observed in the Mössbauer spectra. From a theoretical analysis of the temperature dependence of the quadrupole splitting in conjunction with a ligand field calculation, with trigonal distortion, spin–orbit coupling, and covalency effects taken into account, these high-spin doublets have been found to be consistent with $^5E(D_3)$ and $^5A_1(D_3)$ ground states. The magnetic properties of this compound and other $[Fe(2\text{-}Xphen)_3](ClO_4)_2$ complexes are discussed in terms of electronic and steric influences of the substituent X.

Introduction

The nature of the substituent X in the 2 position of 1,10-phenanthroline (phen) exerts a marked influence on the magnetic properties of the ferrous complexes $[Fe(2\text{-}Xphen)_3](ClO_4)_2$. For X = H (abbreviated here as phen complex) the compound is diamagnetic with iron being in the $^1A_{1g}(O_h)$ electronic ground state. For X = CH_3 (abbreviated as the 2-CH_3phen complex) it has been shown by magnetic[1,2] and Mössbauer effect measurements[2,3] that a temperature-dependent high-spin $^5T_{2g}(O_h) \rightleftarrows$ low-spin $^1A_{1g}(O_h)$ transition takes place. In the case of X = Cl (abbreviated as the 2-Cl(phen) complex) the iron(II) compound is paramagnetic with the electronic ground state of iron being $^5A_1(^5T_{2g})$ under D_3 symmetry in the temperature range 300–4.2 K;[4,5] the complex does not exhibit thermally induced spin crossover as originally believed by Halbert et al.[6] One methyl group each in the 2 and 9 positions of 1,10-phenanthroline causes the complex $[Fe(2,9\text{-}(CH_3)_2phen)_3](ClO_4)_2{\cdot}2H_2O$ (abbreviated as 2,9-$(CH_3)_2$phen complex) to exhibit high-spin behavior in the temperature range 300–79 K.[7]

A combined steric and electronic effect of the substituent X appears to play a dominating role in the magnetic behavior of these complex compounds. To gain more insight into these effects we have investigated the electronic structure of iron in $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2{\cdot}H_2O$, where the methoxy group next to the nitrogen atom is bigger and therefore likely to be sterically more demanding than the above substituents Cl and CH_3 but falls between the two regarding the inductive effect. We report here on variable-temperature magnetic, Mössbauer, and far-IR measurements. The results indicate a high-spin $\rightleftharpoons$ low-spin transition to take place in this complex; the conversion, however, is shifted to higher temperatures as compared to the spin transition in the 2-CH_3phen complex. A CNDO/2-MO calculation on the ligand with X = H, Cl, CH_3, or OCH_3 has been carried out; the results correlate well with the observations. A ligand field calculation has been performed in conjunction with a theoretical analysis of the temperature dependence of the electric field gradient, from which the nature of the electronic state of the high-spin species may be deduced.

Experimental Section

Preparations. The ligand 2-methoxy-1,10-phenanthroline (abbreviated to 2-CH_3Ophen) was prepared following the method of Claus et al.[8] by reaction of 2-Cl-1,10-phen, which was synthesized following Halcrow et al.,[9] with sodium methanolate. The ligand was recrystallized from a water/ethanol mixture (1:1); mp 74.5–76.5 °C; yield 51%.

The ^1H NMR spectrum of the ligand dissolved in $CDCl_3$ at room temperature shows resonances at δ (ppm) (relative to TMS) = 4.33 for OCH_3; 8.06, 7.06 for H_3, H_4; 7.66 for H_5, H_6; 8.2 for H_7; 7.55 for H_8; 9.18 for H_9; and the coupling constants $J_{34} = 9$, $J_{78} = 8$, $J_{79} = 2$, $J_{89} = 5$ Hz.

$[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2\cdot H_2O$ was prepared as follows. A 18.97-mg (0.339-mmol) amount of iron powder (analytical grade, Merck Darmstadt) was dissolved in concentrated hydrochloric acid. After evaporation to dryness the chloride was dissolved in 5 mL of water. The solution was added to a solution of 250 mg (1.19 mmol) of the ligand in 10 mL of methanol. After cooling of the mixture to 5 °C and addition of a few milliliters of a saturated aqueous sodium perchlorate solution the iron complex precipitated in oily form. A red-brown crystalline product was obtained by recrystallization from a water/methanol mixture (1:1). The material was dried under vacuum at 40 °C. In all operations care was taken to exclude oxygen. Anal. Calcd for $Fe(C_{39}H_{32}N_6O_{12})$: C, 51.84; H, 3.57; N, 9.3. Found: C, 51.15; H, 3.44; N, 9.18.

Magnetic Measurements. The magnetic susceptibility data were recorded using a Foner-type magnetometer calibrated with nickel metal. The sample was thermostated at temperatures 2.6–300 K using a continuous-flow cryostat. The temperature was measured with a gallium arsenide diode; the accuracies are reported to be ±0.02 K (2–5 K), ±0.1 K (5–10 K), ±0.2 K (10–100 K), and ±0.5 K (100–300 K). The maximum errors of the susceptibility data are estimated to be 1%. Effective magnetic moments, μ_{eff}, were calculated using the formula

$$\mu_{eff} = 2.8273(\chi_m{}'T)^{1/2} \tag{1}$$

where $\chi_m{}'$ is the molar susceptibility corrected for diamagnetism (523 × 10^{-6} emu/mol).[10]

Far-infrared spectra in the range 50–600 cm^{-1} were taken at 298 and 108 K with a POLYTEC FIR 30 spectrometer. The samples were pressed into polyethylene.

Mössbauer spectra were measured in transmission geometry with a constant-acceleration electromagnetic drive system operating in the multiscaling mode. The source, $^{57}Co/Cu$ (The Radiochemical Center, Amersham, England), was kept at 298 K and moved relative to the absorber, which was kept stationary at controlled temperatures between 273 and 15 K with a constancy of ±0.1 K. The absorbers contained 0.15–0.20 mg of $^{57}Fe/cm^2$.

All Mössbauer spectra were fitted to Lorentzian line shape by a least-squares iteration method.

Results and Discussion

The results of the magnetic susceptibility measurements are shown in Figure 1. μ_{eff} changes gradually from 5.31 μ_B at 300.0 K to ca. 1.51 μ_B at 80.0 K, decreases thereafter very slowly upon further lowering the temperature, and finally falls off rapidly below ~10 K to 0.87 μ_B at 2.6 K. A very small field dependence was observed, which is believed to be due to a ferromagnetic impurity. The data of Figure 1 refer to measurements in an applied field of 10 kOe. The observed dependence of μ_{eff} on the temperature clearly indicates a thermally induced conversion between the high-spin $^5T_{2g}(O_h)$ and low-spin $^1A_{1g}(O_h)$ states.

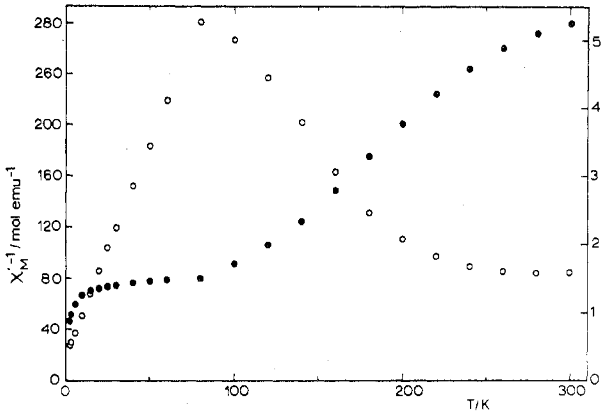

Figure 1. Reciprocal molar magnetic susceptibility (○) and effective magnetic moment (●) of $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2\cdot H_2O$ as a function of temperature.

Table I. Characteristic Vibrational Bands in the Far-IR Spectra of $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2\cdot H_2O$ at 298 and 108 K and of the Free Ligand at 298 K (Given in Parentheses in Last Column)

Wavenumber, ν/cm^{-1}		
298 K	108 K	Assignment
534 w	537 w, sh	(537 w, sh)
458 w	457 m	(460 w)
395 w	396 w	(397 s)
	352 w 341 w	$\}$ ν(Fe–N) low spin
323 m	325 m	(320 s)
234 s, br	237 m, sh 227 w, sh	$\}$ ν(Fe–N) high spin
182 w, sh	185 m	δ (N–Fe–N) low spin
160 m	163 m	(167 s)
135 w, br	138 w 123 w	(127 m; 115 w, sh)

The most characteristic vibrational bands in the far-IR spectra at 298 and 108 K are listed in Table I. There are a number of bands which can be assigned to ligand vibrations (the free ligand vibrations are given in parentheses in Table I) and which are practically independent of temperature. As expected, in analogy to variable-temperature far-IR studies on similar compounds showing temperature-dependent spin crossover,[2,11] the Fe–N stretching vibrations for the high-spin and low-spin species are distinguishable from each other in the variable-temperature spectra. The bands at 234 cm^{-1} (298 K) and 237, 227 cm^{-1} (108 K) are assigned to Fe–N stretching vibrations in the iron(II) high-spin state, and the bands at 352 cm^{-1} (108 K) and 341 cm^{-1} (108 K) to the Fe–N stretching vibration in the iron(II) low-spin state.[11,12] The band at 185 cm^{-1}, particularly well resolved at 108 K, most likely originates from the N–Fe–N deformation vibration in the iron(II) low-spin state.

Some selected results of the Mössbauer effect measurements are collected in Table II. A few representative Mössbauer spectra at various temperatures are shown in Figure 2. The measured spectra were fitted to three quadrupole doublets A, B, and C, which are distinguishable particularly well in the approximate temperature region 130–200 K. The "goodness-of-fit" parameter, $Z = \sum_{i=1}^{N}(N-P)^{-1}(Y^i_{exptl} - Y^i_{theor})^2/(Y^i_{exptl})$, where N is the number of data points and P the number of free parameters, is in most cases slightly larger than unity (cf. Table II). On the basis of the isomer shift and quadrupole splitting data and the temperature behavior of ΔE_Q, the doublets B and C are assigned to high-spin iron(II)

Table II. Isomer Shift δ (Relative to the ^{57}Co/Cu Source at 298 K), Quadrupole Splitting ΔE_Q, Experimental Line Width Γ, and Fractional Area F under the Resonance Lines of the Doublets A, B, and C of $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2 \cdot H_2O$

Resonance doublet	T/K	δ/(mm s^{-1})	ΔE_Q/(mm s^{-1})	Γ/(mm s^{-1})	F/%	Z[a]
A	273	0.20 ± 0.04	0.37 ± 0.09	0.39 ± 0.02	18.2 ± 2.0	2.6
B		0.76 ± 0.02	1.18 ± 0.02		56.1 ± 3.7	
C		0.67 ± 0.02[b]	0.80 ± 0.08		26.2 ± 3.3	
A	237.5	0.21 ± 0.02	0.51 ± 0.03	0.33 ± 0.02	34.5 ± 1.8	1.1
B		0.80 ± 0.01	1.39 ± 0.04		44.5 ± 5.0	
C		0.74 ± 0.02	0.99 ± 0.06		21.1 ± 4.0	
A	221	0.21 ± 0.01	0.50 ± 0.02	0.31 ± 0.01	41.2 ± 0.7	1.01
B		0.82 ± 0.01	1.55 ± 0.03		29.2 ± 1.3	
C		0.80 ± 0.01	1.10 ± 0.03		29.6 ± 1.3	
A	193.5	0.22 ± 0.01	0.50 ± 0.02	0.28 ± 0.02	59.5 ± 2.0	1.2
B		0.83 ± 0.02	1.59 ± 0.04		25.0 ± 1.8	
C		0.80 ± 0.02	1.14 ± 0.05		15.7 ± 1.9	
A	171.5	0.23 ± 0.01	0.52 ± 0.01	0.31 ± 0.03	62.6 ± 2.2	1.0
B		0.83 ± 0.02	1.56 ± 0.05	0.31 ± 0.15	33.7 ± 3.1	
C		0.77 ± 0.03	1.05 ± 0.06	0.43 ± 0.08	3.7 ± 1.9	
A	144.5	0.26 ± 0.01	0.49 ± 0.01	0.32 ± 0.01	75.5 ± 1.2	1.4
B		0.80 ± 0.02	1.81 ± 0.04		18.2 ± 1.3	
C		0.80 ± 0.05	1.11 ± 0.11		6.3 ± 1.3	
A	138.5	0.25 ± 0.01	0.48 ± 0.01	0.27 ± 0.02	77.7 ± 3.2	2.1
B		0.83 ± 0.03	1.80 ± 0.07	0.36 ± 0.15	15.4 ± 5.4	
C		0.86 ± 0.06	1.08 ± 0.17	0.35 ± 0.34	7.0 ± 5.6	
A	119.5	0.26 ± 0.00	0.54 ± 0.01	0.36 ± 0.01	85.5 ± 1.2	1.1
B		0.93 ± 0.03	1.87 ± 0.06		13.9 ± 1.3	
C		0.83 ± 0.1[b]	1.17 ± 0.2[b]		1.0 ± 3.0	
A	78.5	0.28 ± 0.01	0.53 ± 0.01	0.37 ± 0.01	94.0 ± 1.0	1.1
B		0.93 ± 0.07	1.97 ± 0.15		5.0 ± 3.0	
C		...	...		...	
A	15	0.27 ± 0.01	0.53 ± 0.01	0.27 ± 0.01	96.3 ± 1.0	1.1
B		0.85 ± 0.08	1.93 ± 0.10		≤4	
C		...	...		...	

[a] Z is explained in the text. [b] Parameter not varied.

species and doublet A is assigned to iron(II) in the low-spin state. The area fractions of their resonance lines, F (%), are listed in Table II and show that the intensity of the low-spin state, which is already present at 273 K to 18%, increases steadily with decreasing temperature, while the sum of the intensities of the high-spin resonances continuously decreases in the same direction of temperature change. Virtually the same Mössbauer spectral behavior has been observed with samples prepared independently and measured at some selected temperatures. Measurements were also repeated of the same sample sealed in the Plexiglas holder and stored at room temperature for several months; no changes could be detected as compared to the case of freshly prepared samples. The observations are similar to those made in a study on the polycrystalline compound $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$,[2] except that in the present case the spin conversion from high spin ($S = 2$) to low spin ($S = 0$) is shifted to higher temperatures, whereas in the 2-CH$_3$phen complex no spin singlet state is observable at room temperature.[1-3] Similarly to the findings in the 2-CH$_3$phen complex we again observe two high-spin iron(II) resonance doublets besides the $^1A_{1g}(O_h)$ ground state in the Mössbauer spectra. Their electronic nature may be derived from the temperature dependence of the quadrupole splitting by a calculational method originally proposed by Ingalls,[13] employing the general expression

$$\Delta E_Q(T) = \frac{1}{2}e^2Q(1-R)\langle r^{-3}\rangle^0{}_{3d}\alpha_c^2[F(\delta_t, \alpha_\lambda^2\lambda_0, T)]\left(1 + \frac{\eta^2(T)}{3}\right)^{1/2} + \Delta E_Q{}^c \qquad (2)$$

in which e, Q, R, and η have the usual meaning,[14] $\langle r^{-3}\rangle^0{}_{3d}\alpha_c^2$ describes the free-ion radial expansion for 3d electrons upon complex formation (α_c^2 is the covalency factor), and $\Delta E_Q{}^c$ is the temperature-independent contribution to the quadrupole splitting. The function F(δ_t, $\alpha_\lambda^2\lambda_0$, T) describes the temperature dependence of the electric field gradient (EFG) and may take on values between $-{}^4/_7$ and $+{}^2/_7$.[13] To determine this reduction function we have performed a perturbation calculation on the $^5T_{2g}(O_h)$ subspace assuming D_3 symmetry (for which the asymmetry parameter η becomes zero) and making allowance for trigonal distortion (parameter δ_t), spin–orbit coupling, and covalency effects by multiplying the free-ion spin–orbit coupling coefficient λ_0 (=104 cm^{-1}) with the orbital reduction factor α_λ^2: $\lambda = \alpha_\lambda^2\lambda_0$. We have taken the reduction factors α_c^2 and α_λ^2 to be equal: $\alpha^2 = \alpha_\lambda^2 = \alpha_c^2$. The effective Hamiltonian

$$\hat{H}_{eff} = \hat{V}_t + \hat{H}_{so} = -\frac{\delta_t}{3}(\hat{L}_z^2 - 2) - \alpha^2\lambda_0\hat{L}\cdot\hat{S} \qquad (3)$$

was applied to the $15|M_LM_S\rangle$ basis functions of the $^5T_{2g}(O_h)$ state, quantized along the trigonal axis.[15,16] The interaction between the $^5T_{2g}(O_h)$ and the $^5E_g(O_h)$ states was neglected, because the energy separation $E(^5T_{2g}) - E(^5E_g) \equiv 10Dq$ has been found in similar iron(II) diimine complexes to be very much larger than the energy separation $E(^5A_1) - E(^5E) \equiv \delta_t$ due to trigonal distortion.[5] The valence contributions to the EFG at any temperature was obtained from a Boltzmann distribution over all energy levels of the $^5A_1(^5T_{2g})$ and $^5E(^5T_{2g})$ states using the population numbers, derived from the coefficients of the eigenfunctions of the diagonalized perturbation matrix, and the well-known[13] contributions to the EFG of the

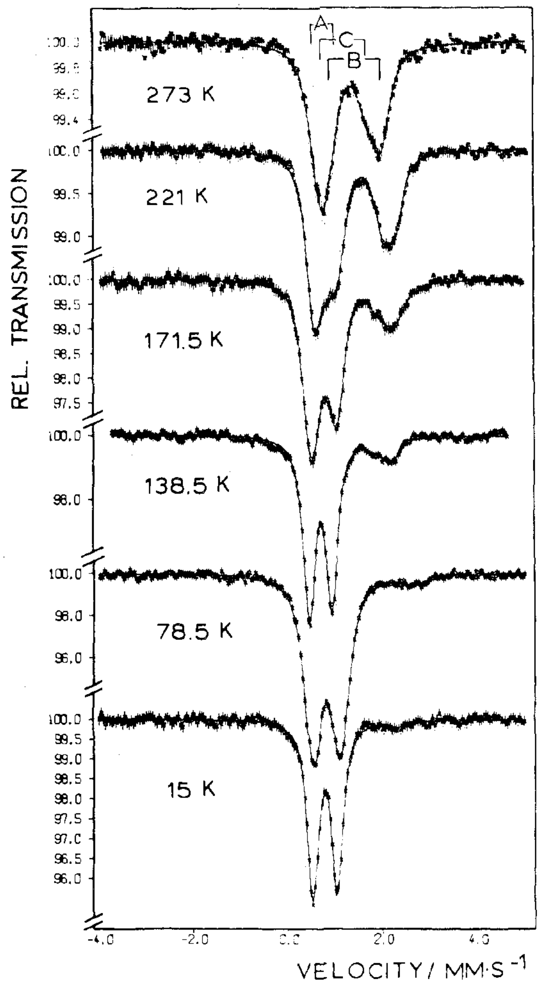

Figure 2. Some representative Mössbauer spectra of $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2{\cdot}H_2O$ at various temperatures; the zero point of the velocity scale refers to the isomer shift of $Na_2[Fe(CN)_5NO]{\cdot}2H_2O$ relative to the $^{57}Co/Cu$ source at 298 K.

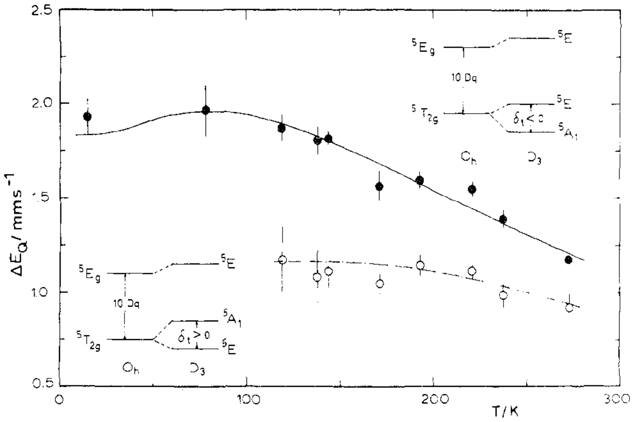

Figure 3. Temperature dependence of the quadrupole splitting ΔE_Q of the two high-spin iron(II) species B (●) and C (○) in $[Fe(2\text{-}CH_3Ophen)_3](ClO_4)_2{\cdot}H_2O$. The solid and broken lines are calculated functions. The inserted energy level diagrams show the splitting of the $^5T_{2g}(O_h)$ term under the influence of negative ($\delta_t < 0$) and positive ($\delta_t > 0$) trigonal distortion (D_3 symmetry).

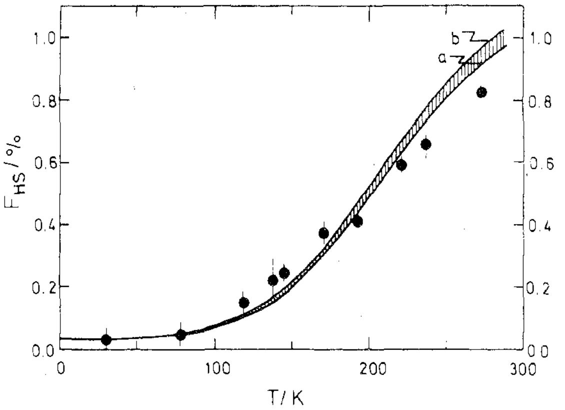

Figure 4. Temperature dependence of the relative area F of the sum of the high-spin resonances (B, C) from the Mössbauer spectra (●) and molar fraction γ_{HS} of the high-spin states evaluated from magnetic measurements using the parameters $\delta_t/\lambda = 3.0$, $\alpha_\lambda^2 = 0.7$ (a) and $\delta_t/\lambda = 3.0$, $\alpha_\lambda^2 = 0.5$ (b).

individual 3d orbitals. The parameters δ_t, α^2, and $\Delta E_Q^{\,c}$ were determined by curve fitting to the experimental data of the quadrupole splitting, where the quantity $e^2Q(1 - R)\langle r^{-3}\rangle^0_{3d}$ was taken to be 17.5 mm s^{-1} as an upper limit for a ferrous compound with $\Delta E_Q \approx 4.5$ mm s^{-1}.[17]

The following "best-fit values" were obtained for the quadrupole doublet B

$$\delta_t = -184 \pm 4\ \text{cm}^{-1}$$

$$\alpha^2 = 0.70 \pm 0.05$$

$$\Delta E_Q^{\,c} = -0.69 \pm 0.02\ \text{mm s}^{-1}$$

The theoretical function $\Delta E_Q(T)$, calculated with these values, is drawn as a solid line in Figure 3; it covers the experimental data very satisfactorily. $\delta_t < 0$ (EFG < 0) indicates that the iron(II) atom of species B possesses an orbitally nondegenerate ground term $^5A_1$ under D_3 symmetry (cf. Figure 3). The results agree well with those of similar studies on $[Fe(2\text{-}Cl\text{-}(phen))_3](ClO_4)_2{\cdot}H_2O$[5] and $[Fe(2\text{-}CH_3phen)_3](ClO_4)_2$.[2]

The calculation for the quadrupole doublet C, which also arises from a high-spin iron(II) species, did not proceed as successfully, because experimental data for $\Delta E_Q(T)$ are only available for the region $119.5 \leq T \leq 273$ K, with relatively large errors for ΔE_Q at ≤150 K. Regarding the magnitude and temperature dependence of ΔE_Q, however, this resonance doublet C resembles very much one of the two quadrupole doublets observed in the 2-CH_3phen complex,[2] which was assigned to a $^5E(D_3)$ ($V_{zz} \approx$ EFG > 0) ground state. We therefore conclude that doublet C of the present study also arises from a $^5E(D_3)$ electronic ground state. At present we are not able to give a definite explanation for the coexistence of two high-spin iron(II) lattice sites with opposite sign of the EFG. There may be a temperature-dependent equilibrium (i) between trigonally compressed ($\delta_t < 0$, EFG < 0, $|xy\rangle$ lowest) and trigonally elongated ($\delta_t > 0$, EFG > 0, $|yz\rangle$ and $|xz\rangle$ lowest) complex molecules or (ii) between two geometric isomers, facial and meridional.

In Figure 4 we have plotted the fractional area F of the Mössbauer resonance lines of the sum of the high-spin species B and C as a function of temperature. These data have been compared with the relative amount of high-spin molecules as a function of temperature, evaluated from the results of the magnetic susceptibility measurements using the expression

$$\mu_{\text{eff}}^{\,2} = (1 - \gamma_{\text{HS}})(\mu_{\text{eff}}^{\,\text{LS}})^2 + \gamma_{\text{HS}}(\mu_{\text{eff}}^{\,\text{HS}})^2 \qquad (4)$$

The abbreviations HS and LS stand for *high spin* and *low spin*, respectively. $\gamma_{\text{HS}} = n_{\text{HS}}/(n_{\text{HS}} + n_{\text{LS}})$ is the mole fraction of the high-spin molecules. μ_{eff} is the effective magnetic moment derived from the measured susceptibility data. In analogy to similar iron(II) complexes with low-spin behavior $\mu_{\text{eff}}^{\,\text{LS}}$ has been taken to be 1.0 μ_B and practically independent of temperature. $\mu_{\text{eff}}^{\,\text{HS}}$ has been evaluated as a function of kT/λ and the trigonal distortion parameter δ_t, using the results of the treatment of d^6 high-spin ions by König et al.[18] No distinction between the $^5E(D_3)$ and $^5A_1(D_3)$ states has been made here, because the two electronic states have very similar magnetic properties. The calculated results of the molar fraction γ_{HS} as a function of temperature and for different values of the parameters δ_t/λ and α_λ are shown in Figure 4. The curves for $\delta_t/\lambda = 3.0$, $\alpha_\lambda^2 = 0.7$ and for $\delta_t/\lambda = 3.0$, $\alpha_\lambda^2 = 0.5$ refer to calculations using the upper and lower limits of the δ_t and α_λ^2 values from the ligand field calculations above. In any case, we notice that at higher temperatures ($T \gtrsim 200$ K) the relative amount of high-spin molecules as evaluated from the magnetic measurements exceeds considerably the relative intensity (fractional area F) of the high-spin resonances from the Mössbauer spectra, most probably due to the fact that the relative intensities (areas) of the high-spin and low-spin states do *not* reflect the relative amounts of these spin states because of unequal recoil-free fractions,[14] $f_{HS} \neq f_{LS}$. It is expected that the iron atom in the high-spin state is more loosely bound to the ligands than in the low-spin state, mostly due to weaker π-back-bonding effects; experimental support may be taken from the far-IR spectra, which show that the Fe–N stretching vibrations for the low-spin state appear at considerably higher wavenumbers (352, 341 cm^{-1}) than those for the high-spin state (237, 227 cm^{-1}). Accordingly, we should expect $f_{HS} < f_{LS}$. In a separate calculation in the framework of Debye's model of a solid we have evaluated at $T = 185$ K (transition temperature T_c from magnetic susceptibility measurements) $f_{HS} = 0.06$ and $f_{LS} = 0.11$. Although these values appear to be somewhat low, the expected tendency of $f_{LS} > f_{HS}$ comes out correct. The factor of nearly 2 for f_{LS}/f_{HS} at $T \approx 210$ K has also been found by König et al. in a similar recoil-free fraction study of $Fe(papt)_2$ (papt = 2-(2-pyridylamino)-4-(2-pyridyl)thiazolate), which shows a similar spin transition behavior as the present complex.[19] The gradual change from high spin to low spin, reflected, e.g., by the function $\mu_{eff} = f(T)$, is similar to the one observed in the $2\text{-}CH_3$phen complex[2] except that in the present case the conversion is shifted to higher temperatures by ca. 60 K. The temperature of 50% conversion (taken from the relative area of the Mössbauer resonance lines) is $T_c \approx 205$ K in this study but only ca. 145 K in case of the $2\text{-}CH_3$phen complex. Obviously, the ligand field potential in the $2\text{-}CH_3O$phen complex appears to be somewhat stronger than in the $2\text{-}CH_3$phen complex. Comparing the ligand field strength in the compounds $[Fe(2\text{-}Xphen)_3](ClO_4)_2$, with X = H, CH_3, CH_3O, or Cl, we find at a given temperature that the ligand field potential decreases in the order of substituents X = H > CH_3O > CH_3 > Cl. This ordering suggests that both steric and electronic effects exert decisive influences on the magnetic properties of the central ion. A methyl group in the 2 position of 1,10-phenanthroline requires more space than the H atom. It is believed that the resulting steric hindrance in the $2\text{-}CH_3$phen complex causes the Fe–N bond to elongate somewhat, which in turn reduces the crystal field splitting parameter by a reduced electrostatic interaction according to $10Dq \approx R^{-5}$ and by less effective σ and π interactions between the ligands and the central ion. The steric hindrance becomes even more effective in the $2,9\text{-}(CH_3)_2$phen complex, which may be the dominating effect for this complex to display strictly high-spin behavior even at low temperatures. A steric effect of this kind has been demonstrated by other authors in variable-temperature x-ray crystallographic studies on other iron(II) spin crossover systems.[20,21] The methoxy group seems to demand even more space than the methyl group and one would therefore expect for the same reasons the paramagnetic behavior in the $2\text{-}CH_3O$phen complex to be more pronounced than in the $2\text{-}CH_3$phen complex. The reverse is true. The stronger tendency toward low-spin behavior in the $2\text{-}CH_3O$phen complex as compared to the $2\text{-}CH_3$phen complex may be rationalized by a considerable influence on the Fe–N bonds arising from the electronic properties of the substituent X, which dominates over the steric effect.

The ligand field parameter $10Dq \equiv \Delta$ is known to be composed of several terms according to

$$\Delta \propto \Delta_{el} + \Delta_\sigma + \Delta_\pi(M\rightarrow L) - \Delta_\pi'(L\rightarrow M) \tag{5}$$

where the individual terms have the usual meaning.[22] Δ refers to the energy difference between the antibonding $e_g(\sigma^*)$ molecular orbitals and the bonding $t_{2g}(\pi)$ molecular orbitals (cf. Figure 7 of ref 23). 1,10-Phenanthroline as a ligand has relatively strong σ-donor and π-acceptor properties causing a large energy separation between the antibonding $e_g(\sigma^*)$ orbitals and the $t_{2g}(\pi)$ orbitals and thus favoring the $^1A_{1g}$ ground state of the $[Fe(phen)_3](ClO_4)_2$ complex. The positive inductive effect of the methyl group in $2\text{-}CH_3$phen reinforces the basicity of the neighboring nitrogen atom. This is supported by the results which we have obtained from a CNDO/2-MO calculation using a computer program similar to the one of Pople and Beveridge.[24,25] The bond lengths and angles were taken from the literature.[26-29] The results show that in going from phen to $2\text{-}CH_3$phen the electron density at the nitrogen atom in the 1 position, preferentially in the p_z orbital, increases and a simultaneous destabilization of the highest occupied π orbital of the ligand takes place: $E(\pi) = -10.87$ eV in phen and -10.69 eV in $2\text{-}CH_3$phen. As a consequence, $\Delta_\pi'(L\rightarrow M)$ becomes larger and reduces the ligand field splitting parameter Δ in the $2\text{-}CH_3$phen complex with respect to the phen complex. No significant difference occurs in the Δ_σ term between phen and $2\text{-}CH_3$phen. In case of 2-Cl(phen) we have found a considerable stabilization of the highest occupied σ orbital as compared to phen, viz., -11.54 eV for 2-Cl(phen) and -10.97 eV for phen, as well as a decrease of the electron density in the sp^2-hybrid orbital of the nitrogen. This weakens markedly the donation to the metal ion and thus decreases Δ. The smaller steric hindrance caused by the chlorine atom as compared to the methyl group is overbalanced by a significantly weaker σ interaction. As a result, Δ is smaller in the paramagnetic 2-Cl(phen) complex than in the spin crossover complex $2\text{-}CH_3$phen. The difference in the strength of σ interaction also seems to be reflected by a small difference in the Mössbauer isomer shift and thus in the electron density at the nucleus: $\delta_{Cu}(293) = 0.75_1 \pm 0.01_3$ mm s^{-1} for $[Fe(2\text{-}Cl(phen))_3](ClO_4)_2\cdot H_2O$;[5] $\delta_{Cu}(293) = 0.70_6 \pm 0.01_2$ mm s^{-1} for $[Fe(2\text{-}CH_3(phen))_3](ClO_4)_2$.

The CNDO/2-MO calculation for $2\text{-}CH_3O$phen shows that the highest occupied σ^b orbital is destabilized as compared to $2\text{-}CH_3$phen, whereas the energy level of the π^b orbital is practically unaffected as compared to the unsubstituted 1,10-phenanthroline. This apparently causes the ligand field potential in the $2\text{-}CH_3O$phen complex to be stronger than in the $2\text{-}CH_3$phen complex and weaker than in the phen complex.

Although the size and the electronic properties of the substituent X in the ligand 2-Xphen appear to influence the magnetic properties of the perchlorates of $(2\text{-}Xphen)_3Fe^{II}$, it is likely that some additional influence comes from the variable amounts of crystallization water: one water molecule per unit formula each in the solid $2\text{-}CH_3O$phen and 2-Cl(phen) compounds; none in the $2\text{-}CH_3$phen and phen compounds. Such an effect has been observed in similar systems.[30,31]

Since it has been shown that, for example, the spin conversion in the crystalline $2\text{-}CH_3$phen complex is strongly anion dependent,[1,31] it is possible that a different anion may give a different substituent ordering. To test this we plan to extend the present studies into the solution state where other authors recently have shown for a $^2T \rightleftharpoons {}^6A$ transition that anion dependences may largely be diminished.[32]

Concerning the mechanism of the spin transition in the 2-CH_3Ophen complex and the 2-CH_3phen complex, we believe that of all of the models which have been suggested for spin crossover systems[33-35] the one based on a cooperative coupling between the electronic state of the iron ion involved and the phonon system (including both intramolecular and lattice vibrations)[34] comes closest to reality. We have discussed this model at length in conjunction with systematic experimental investigations on the spin crossover system $[Fe(2\text{-pic})_3]Cl_2\cdot Sol$ (2-pic = α-picolylamine; Sol = C_2H_5OH, CH_3OH, H_2O, $2H_2O$).[35,37] One of the most essential points in this model is that the driving force of the spin transition at a given temperature is the entropy difference ΔS between the two spin states, which in turn governs the free energy difference $\Delta G = \Delta H - T\Delta S$. There are (at least) two main sources contributing to the entropy of the spin states. One of them is the electronic part $R \ln (2S + 1)$, which is $R \ln 5$ for the high-spin state ($S = 2$) and approximately zero for the low-spin state ($S = 0$). The other important contribution arises from the normal modes of intramolecular vibrations, particularly the Fe–N stretching vibrations and the N–Fe–N deformation vibration. The differences in the stretching vibrations observed in the far-IR spectra (cf. Table I), which are due to a larger π-back-bonding effect in the low-spin state as compared to the high-spin state, result in a large difference of the vibrational entropies between the two spin states ($S_{HS} > S_{LS}$).[34] At any temperature the entropy term TS of the high-spin state is larger than that of the low-spin state. This initiates the spin conversion from ${}^1A_{1g}(O_h)$ to ${}^5T_{2g}(O_h)$ in a group of molecules by increasing the temperature. The spin excitation in turn causes a modulation of the normal modes of intramolecular vibrations; this modulation communicates the information of the spin conversion via coupling with lattice vibrations to other low-spin molecules within a "cooperative region". Their normal vibrations will be damped this way which causes the central ion to change spin from $S = 0$ to $S = 2$. This model, which is described in more detail in ref 34, 35, and 37, receives support by experimental results from Mössbauer effect measurements on the diluted system $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$,[35] investigation of the deuterium isotope effect in $[Fe(2\text{-pic})_3]Cl_2\cdot CD_3OD$,[36] and variable-temperature far-IR studies in the present work and other studies.[34] In addition, the difference in the recoil-free fractions for the two spin states of the 2-CH_3Ophen complex, which have been evaluated in a separate calculation in the framework of Debye's model to be $f_{HS} = 0.06$ (185 K) and $f_{LS} = 0.11$ (185 K), strongly supports the spin–flip mechanism based on a cooperative coupling between the electronic state and the phonon system.

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References and Notes

(1) H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, **21**, 81 (1968).
(2) J. Fleisch, P. Gütlich, K. M. Hasselbach, and W. Müller, *Inorg. Chem.*, **15**, 958 (1976).
(3) E. König, G. Ritter, H. Spiering, S. Kremer, K. Madeja, and A. Rosenkranz, *J. Chem. Phys.*, **56**, 3139 (1972).
(4) W. M. Reiff and G. Long, *Inorg. Chem.*, **13**, 2150 (1974).
(5) J. Fleisch, P. Gütlich, and K. M. Hasselbach, *Inorg. Chim. Acta*, **17**, 51 (1976).
(6) E. J. Halbert, C. M. Harris, E. Sinn, and G. J. Sutton, *Aust. J. Chem.*, **26**, 951 (1973).
(7) J. Fleisch, Dissertation, Technische Hochschule Darmstadt, D-6100 Darmstadt, Germany, 1976.
(8) K. G. Claus and J. V. Rund, *Inorg. Chem.*, **8**, 59 (1969).
(9) B. E. Halcrow and W. O. Kermack, *J. Chem. Soc.*, **8**, 155 (1946).
(10) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Compounds", Chapman and Hall, London, 1973.
(11) J. H. Takemoto and B. Hutchinson, *Inorg. Nucl. Chem. Lett.*, **8**, 769 (1972).
(12) B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Am. Chem. Soc.*, **92**, 3335 (1970).
(13) R. Ingalls, *Phys. Rev.*, **133**, 787 (1964).
(14) G. K. Wertheim, "Mössbauer Effect: Principles and Applications", Academic Press, New York, N.Y., 1964.
(15) R. M. Golding, "Applied Wave Mechanics", Van Nostrand, New York, N.Y., 1969, p 442.
(16) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, London, 1962, p 68.
(17) E. König, G. Ritter, E. Lindner, and I. P. Lorenz, *Chem. Phys. Lett.*, **13**, 70 (1972).
(18) E. König, A. S. Chakravarty, and K. Madeja, *Theor. Chim. Acta*, **9**, 171 (1967).
(19) E. König and G. Ritter, *Mössbauer Eff. Methodol.*, **9**, 3 (1974).
(20) M. A. Hoselton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1722 (1975).
(21) L. J. Wilson, D. Georges, and M.-A. Hoselton, *Inorg. Chem.*, **14**, 2968 (1975).
(22) H. L. Schläfer and G. Gliemann, "Einführung in die Ligandenfeldtheorie", Akademische Verlagsanstalt, Frankfurt/Main, 1967, p 115.
(23) H. B. Gray, *J. Chem. Educ.*, **41**, 2 (1964).
(24) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, 129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, 136 (1965); **44**, 3289 (1965).
(25) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970, p 163.
(26) H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. A*, 1956, 2955 (1969).
(27) G. P. Khare and R. Eisenberg, *Inorg. Chem.*, **9**, 2211 (1970).
(28) J. T. Veal, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B*, **29**, 12 (1973).
(29) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, **11**, 1109 (1972).
(30) R. N. Sylva and H. A. Goodwin, *Aust. J. Chem.*, **20**, 479 (1967).
(31) W. Müller, Diplomarbeit, Technische Hochschule Darmstadt, 1974.
(32) M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, **98**, 4824 (1976).
(33) E. König, G. Ritter, B. Braunecker, K. Madeja, H. A. Goodwin, and F. E. Smith, *Ber. Bunsenges. Phys. Chem.*, **76**, 393 (1972).
(34) M. Sorai and S. Seki, *J. Phys. Chem. Solids*, **35**, 555 (1974).
(35) M. Sorai, J. Ensling, and P. Gütlich, *Chem. Phys.*, **18**, 199 (1976).
(36) G. Sudheimer, Diplomarbeit, Technische Hochschule Darmstadt, 1976.
(37) M. Sorai, J. Ensling, K. M. Hasselbach, and P. Gütlich, *Chem. Phys.*, **20**, 197 (1977).