Mössbauer Effect Study of the Electronic Ground State of Iron(II) in Tris (2-chlorophenanthroline)iron(II) Perchlorate[1]

J. FLEISCH, P. GÜTLICH, and K. M. HASSELBACH

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-6500 Mainz, Saarstrasse, West Germany

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Mössbauer spectra of [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O have been measured in the temperature range 293 – 5 K. The spectra indicate that the iron atom in this compound possesses a spin quintet ground state throughout the temperature range under study, in contradiction to the suggested high spin–low spin transition, which has been concluded from a magnetic susceptibility study by other authors. From a theoretical analysis of the temperature dependence of the quadrupole splitting, with trigonal distortion, spin–orbit coupling, and effects of covalency taken into account, the ground term of iron (II) in this compound has been elucidated as being $^5A_1(^5T_{2g})$, separated from the $^5E(^5T_{2g})$ term by ca. 165 cm^{-1}. The principal component V_{zz} of the electric field gradient tensor is negative. This result agrees with conclusions from magnetically perturbed Mössbauer spectra from other authors.

Introduction

Considerable interest has recently been devoted to the study of the electronic ground state of iron(II) in a good number of six-coordinate diimine complexes of iron(II). The magnetic behaviour of these complexes depends strongly on the strength of the ligand field. It is well known, *e.g.*, that the diamagnetic complex [Fe(phen)$_3$](ClO$_4$)$_2$ (phen = 1,10-phenanthroline) changes its spin state dramatically if one or both hydrogen atoms in α-positions to the nitrogen atoms of phenanthroline are replaced by other atoms or molecules; *e.g.* [Fe(2-CH$_3$-phen)$_3$](ClO$_4$)$_2$ shows high spin–low spin transition as a function of temperature,[2,3] whereas the compound [Fe(2,9-dimethyl-phen)$_3$](ClO$_4$)$_2$ is strictly high spin in the temperature range 300–80 K.[4]

Recently, Halbert *et al.*[5] have reported on magnetic susceptibility studies of the compound [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O. They have suggested a high spin–low spin transition to occur in this compound as a function of temperature, although μ_{eff} decreases from 5.4 B.M. at 300 K to only 5.0 B.M. at 100 K. In the meantime, Reiff and Long[6] have published results from Mössbauer measurements, which demonstrate the high spin behaviour of [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$ in the temperature range 300–4.2 K. By applying an external magnetic field to the sample they find that the electronic ground state is $^5A_1$ with the $|z^2>$ orbital being lowest.

Independently from Reiff and Long we have measured Mössbauer spectra of [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O in the temperature range 293–5 K and derived the electronic ground state of iron(II) from a theoretical analysis of the quadrupole splitting as a function of temperature taking into account trigonal field distortion, spin–orbit coupling and covalency effects. The results are communicated in the following.

Experimental

The compound [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O was prepared in the following way: a solution of 2-chlorophenanthroline[7] in methanol was added to an aqueous solution of Mohr's salt (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O, keeping the molar ratio of iron/ligand to 1:3. The polycrystalline compound precipitated upon adding a saturated solution of sodium perchlorate. The orange–yellow material was recrystallized from a methanol/water mixture and dried under vacuum over phosphorus pentoxide. All operations were performed in oxygen-free solvents and in nitrogen atmosphere to prevent the iron from being oxidized.

Anal. Found: C, 47.01; H, 2.27; N, 9.35; [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O requires C, 47.17; H, 2.53; N, 9.17%.

For the sake of further identification i.r. spectra of the solid compound (in KBr tablets) were taken with a Perkin–Elmer 325 spectrometer. The assignment of typical frequencies was possible by comparison with i.r. spectra of other phenanthroline complexes of iron(II)[8,9] and with i.r. tables from the literature. The most characteristic lines are listed in Table I.

TABLE I. I.r. and F.i.r. Data (at room temperature) of [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O.

Wave number (cm^{-1}), Intensity and Shape[a]		Assignment[b]
3350–3450	m, br	ν(O–H), ν_{as}(O–H)
3060	m, sh ⎱	ν(C–H)
3075	m, sh ⎰	
1620	w, sp	δ(H–O–H)
1582	m, sp ⎫	
1565	s, sp	
1498	s, sp	δ(C–H) "in plane" and
1490	s, sh	vibrations of the ring system
1412	s	
1140	s ⎭	
1085	s, br	ClO$_4^-$
883	m, sp	ν(C–Cl)
855	s, sp ⎫	
728	s, sh	δ(C–H) "out of plane",
720	s, sh	central ring and heterocyclic
620	s, br ⎭	rings
370	m ⎫	
344	w	
320	w	ligand
236	m, sh ⎭	
222	s, br ⎱	ν(Fe–N), ligand
206	w, sh ⎰	

[a] w = weak, m = medium, s = strong; br = broad, sp = sharp, sh = shoulder. [b] ν = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration; δ = deformation vibration.

A sample dried in vacuum over P$_2$O$_5$ for 14 days still showed strong absorption bands around 3500 cm^{-1} indicating the presence of crystal water. The results from the elemental analysis call for the formula [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O, in contrast to ref. 5 and 6, where the compound is named without crystal water.

The frequencies of the free ligand 2-Cl-phenanthroline are slightly shifted in the iron complex due to coordination.

Further vibrational data, also included in Table I, could be extracted from f.i.r. spectra, which were recorded in the range 500–30 cm^{-1} using a Beckman Fourier Spectrometer model IR 720. The strong band at 222 cm^{-1} should be assigned to the Fe–N(phen) stretching vibration by comparison with room temperature f.i.r. spectra of Fe(phen)$_2$(NCS)$_2$ (ν(Fe–N) at 220 cm^{-1} [10]) and Fe(phen)$_2$(NCSe)$_2$ (ν(Fe–N) at 218 cm^{-1} [11]). The N–Fe–N deformation vibration should be expected around 80 cm^{-1}, but could not be revealed here.

A u.v./visible absorption spectrum of the complex dissolved in acetone was taken with a Zeiss spectrometer model DMR 22. A broad absorption band occurs in the d–d transition region at 800 nm (ε = 16.1 l mol^{-1} cm^{-1}) in good agreement with observation by Halbert *et al.*[5] (790 nm); this absorption band most

probably arises from the spin-allowed transition $^5T_{2g}$ → ^5E_g corresponding to *ca.* 12500 wave numbers for the octahedral splitting parameter 10 Dq. A very weak shoulder occurs at 950 nm (1020 nm in Halbert's paper[5]), which, in our opinion, should rather be attributed to a spin-forbidden transition from the $^5T_{2g}$ state to the excited spin triplet states $^3T_{1g}$ and $^3T_{2g}$ (which are near the magnetic cross-over point lower in energy than the ^5E_g term) and should not – for intensity reasons – be thought of as being caused by Jahn–Teller distortion as has been suggested by Halbert *et al.*[5]

The Mössbauer spectra were measured in transmission geometry using a conventional Kankeleit drive in constant-acceleration mode (CAM). The ^{57}Co/Cu source (The Radiochemical Centre, Amersham) was kept at 293 K, whereas the absorber temperature was varied between 293 and 5.0 K. The absorber thickness
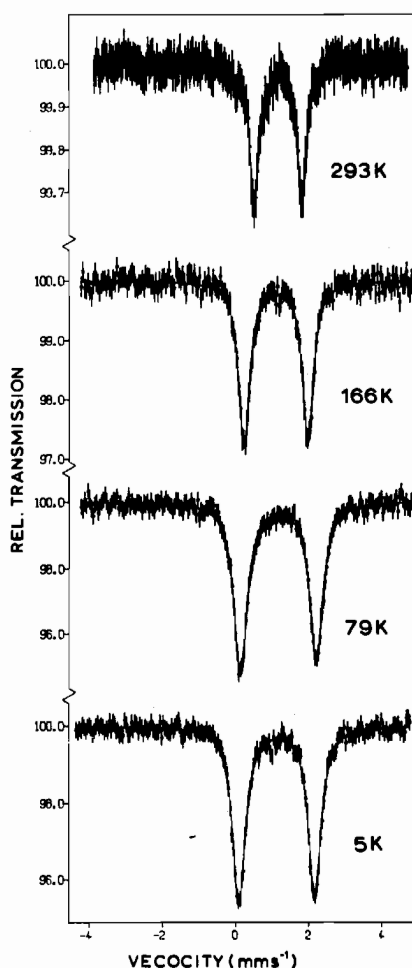

Figure 1. Mössbauer spectra of [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2$·H$_2$O at various temperatures; ^{57}Co/Cu source at 293 K (spectra relative to metallic iron).

TABLE II. Isomer Shift δ (relative to metallic iron) and Quadrupole Splitting ΔE_Q of $[Fe(2\text{-}Cl\text{-}phen)_3](ClO_4)_2 \cdot H_2O$ as a Function of Temperature (the experimental line width varies between 0.35 and 0.43 mm s^{-1}).

Temperature T/K	Isomer Shift δ/mm s^{-1}	Quadrupole Splitting ΔE_Q/mm s^{-1}
293.0 ± 0.1	$0.97_7 \pm 0.01_3$	$1.32_5 \pm 0.02_5$
166.0 ± 0.1	$1.05_5 \pm 0.01$	$1.75_1 \pm 0.01_7$
79.0 ± 0.1	$1.12_0 \pm 0.01$	$2.08_2 \pm 0.01_9$
27.0 ± 0.5	$1.06_0 \pm 0.02$	1.95 ± 0.03
5.0 ± 0.5	$1.15_1 \pm 0.01_2$	$2.07_9 \pm 0.01_7$

was 0.15 mg ^{57}Fe/cm^2. The Mössbauer spectra were computer fitted to Lorentzian lines by least squares iterations. The data for the isomer shift and quadrupole splitting derived from the Mössbauer spectra taken at five different temperatures are listed in Table II. The experimental line width varies between 0.35 and 0.43 mm s^{-1}. Four spectra taken at various temperatures are shown in Figure 1.

Theoretical Analysis

The spectra as well as the data in Table II are typical of high spin ferrous compounds and clearly indicate that the complex compound $[Fe(2\text{-}Cl\text{-}phen)_3](ClO_4)_2 \cdot H_2O$ exhibits high spin behaviour throughout the temperature range 293–5.0 K, in full agreement with the findings by Reiff and Long.[6] This is substantial evidence for ruling out a magnetic cross-over in this compound, which had been suggested by Halbert *et al.*[5]

The local symmetry at the iron atom in $[Fe(2\text{-}Cl\text{-}phen)_3](ClO_4)_2 \cdot H_2O$ may be regarded as being approximately D_3, corresponding to a trigonally distorted octahedron. Accordingly, the electronic term of iron-(II) is expected to be either $^5A_1(^5T_{2g})$ or $^5E(^5T_{2g})$ depending on the direction of the trigonal distortion.

To determine the nature of the electronic ground state we have calculated the quadrupole splitting as a function of temperature employing the expression

$$\Delta E_Q = \frac{1}{2} e^2 Q (1-R) <r^{-3}>_{3d}^{\circ} \cdot \alpha^2 \cdot F(T)$$
$$(1 + \frac{\eta^2(T)}{3})^{1/2} + \Delta E_Q^{const} \quad (1)$$

in which e, Q, R, $<r^{-3}>_{3d}^{\circ}$, and η represent well-known quantities of electric quadrupole interaction[16]. α^2, generally ranging from about 0.6 to 0.9, is the so-called covalency factor, which describes the reduction of the free-ion spin–orbit coupling constant,[17] $\lambda = \alpha^2 \lambda_o$ (*cf.* Eq. 2) as well as the radial expansion,[18] $<r^{-3}>_{3d} = \alpha^2 <r^{-3}>_{3d}^{\circ}$, upon complex formation. The function F(T) reflects the temperature dependence of the electric field gradient (EFG) and may take on values

between $-4/7$ and $2/7$.[18] The term ΔE_Q^{const} represents the temperature independent part of the quadrupole splitting and comprises mainly contributions from non-cubic charge distributions in the ligand sphere around the iron atom and anisotropic electronic populations of molecular orbitals, predominantly of $\sigma(e_g)$ type. The factor $e^2 Q(1-R)<r^{-3}>_{3d}^{\circ}$ was taken to be 17.5 mm s^{-1} [19] corresponding to a maximum value of 5 mm s^{-1} for the quadrupole splitting (a quadrupole splitting as large as 4.5 mm s^{-1} has in fact been observed in a ferrous compound by König *et al.*[20]). The asymmetry parameter η is zero under D_3 symmetry, reducing the factor $(1 + \eta^2(T)/3)^{1/2}$ to unity.

We have determined the function F(T) in a ligand field calculation making allowance for trigonal distortion, spin–orbit coupling and the effects of orbital reduction. The perturbation is represented by the Hamiltonian

$$\hat{H} = \hat{V}_{cub} + \hat{V}_{trig} + \alpha^2 \cdot \lambda_o \cdot \hat{L} \cdot \hat{S} \quad (2)$$

$\hat{V}_{cub}$ is the cubic term of the ligand field operator; $\hat{V}_{trig}$, described by the operator $\delta_{trig} \cdot \hat{L}_z^2$ [21], expresses the trigonal distortion; $\alpha^2 \lambda_o \cdot \hat{L} \cdot \hat{S}$ is the spin–orbit coupling operator. The free-ion value of $\lambda_o = 104$ cm^{-1} for iron was taken from ref. 22.

The perturbation calculation was carried out with two different sets of basis functions. In one calculation we made use of the ^5P–$^5T_2$ isomorphism[23]; the 15 functions $|M_L M_S>$ were employed and the operator $\hat{V}_{trig}$ was in this case chosen to be $\hat{V}_{trig} = -\delta_{trig} \cdot (\hat{L}_z^2 - 2/3)$. In the second calculation the $^5E(^5D)$ term was included; all 25 functions quantized along the trigonal axis were employed.[24] In this case the trigonal distortion operator was chosen to be $\hat{V}_{trig} = -\delta_{trig}/3[(\hat{L}_z^2 - 2)]$. The effective trigonal potential $\hat{V}_{trig}$ was in the two cases modified such as to conserve the center of gravity after the splitting of the $^5T_{2g}$ term into ^5E and $^5A_1$ terms with an energy separation $\delta_{trig} = E(^5A_1) - E(^5E)$.

The valence contribution to the EFG for any temperature of interest was obtained from a Boltzmann distribution over all energy levels involved using the population numbers, which were derived from the coefficients of the eigenfunctions after diagonalization of the perturbation matrix, and the well known[18] contributions of the individual 3d orbitals. In similar calculations on tetragonally distorted octahedral systems other authors[18,25] have found valence contributions to the EFG close to ours but opposite in sign.

δ_{trig}, ΔE_Q^{const}, and α^2 are the quantities to be determined by curve fitting to the experimental data of the quadrupole splitting. The "best fit" values derived from the calculated curve, which is shown together with the experimental points in Figure 2, are:

$$\delta_{trig} = -165 \pm 5 \text{ cm}^{-1}$$
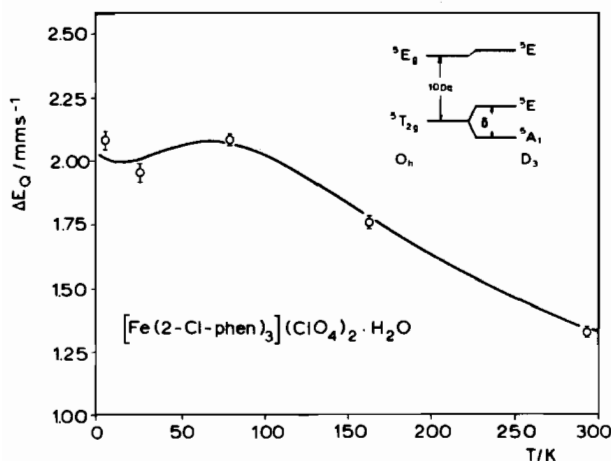$$\Delta E_Q^{const} = -0.53 \pm 0.05 \text{ mm s}^{-1}$$
$$\alpha^2 = 0.57 \pm 0.03$$

Figure 2. Quadrupole splitting ΔE_Q as a function of temperature. O experimental data; —— theoretical curve calculated with the parameters $\delta_{trig} = -165 \pm 5$ cm^{-1}, $\Delta E_Q = -0.53 \pm 0.05$ mm s^{-1} and $\alpha^2 = 0.57 \pm 0.03$. The energy level diagram inserted in the figure shows schematically the influence of trigonal distortion.

The two calculations with the different sets of basis functions yielded, within the errors, the same results for the three fitting parameters. This means that the ^5E_g term, separated from the $^5T_{2g}$ term by approximately 12500 cm^{-1}, has no noticeable influence on the splitting of the $^5T_{2g}$ ground term by trigonal distortion.

The sign of δ_{trig} has been found to be negative; this indicates that the iron atom in [Fe(2-Cl-phen)$_3$](ClO$_4$)$_2 \cdot$ H$_2$O possesses an orbitally non-degenerate ground term, $^5A_1$ under the assumption of D$_3$ symmetry. This result fully agrees with the observations by Reiff and Long[6] from Zeeman-split Mössbauer spectra.

Acknowledgments

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