The High-Spin($^5T_2$) ⇌ Low-Spin($^1A_1$) Transition in Oxalatobis(1,10-phenanthroline)-iron(II) Pentahydrate and the Significance of Lattice Water

E. KÖNIG*, R. SCHNAKIG, G. RITTER, W. IRLER

Institut für Physikalische und Theoretische Chemie and Physikalisches Institut Abt. II, University of Erlangen-Nürnberg, D-8520 Erlangen, F.R.G.

B. KANELLAKOPULOS and B. POWIETZKA

Institut für Heisse Chemie, Kernforschungszentrum Karlsruhe, D-7500 Karlsruhe, F.R.G.

Received December 19, 1978

The magnetism between 0.99 and 314.6 K and ^{57}Fe Mössbauer effect demonstrate that violet [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O (phen = 1,10-phenanthroline) shows a high-spin($^5T_2$) ⇌ low-spin($^1A_1$) transition centred at T_c ~ 205.4 K. The magnetic moment decreases continuously from μ_{eff} = 5.225 BM at 250.6 K to μ_{eff} = 2.680 BM at 150.15 K, the Mössbauer parameters being $\Delta E_Q(^5T_2)$ = 2.78 mm s^{-1}, $\delta^{IS}(^5T_2)$ = +0.99 mm s^{-1} (at T_c) and $\Delta E_Q(^1A_1)$ = 0.69 mm s^{-1}, $\delta^{IS}(^1A_1)$ = +0.39 mm s^{-1} (at any T). Extensive pumping shows that the only lower hydrate stable under the conditions of experiment is [Fe(phen)$_2$C$_2$O$_4$]·H$_2$O. This compound is a $^5T_2$ paramagnet, μ_{eff} = 5.364 BM at 291.8 K, μ_{eff} = 5.033 BM at 77.63 K and ΔE_Q = 2.50 mm s^{-1}, δ^{IS} = +0.99 mm s^{-1} at 300 K. Magnetism and ^{57}Fe Mössbauer effect of violet [Fe(phen)$_2$mal]·2H$_2$O have been also studied and show a high-spin $^5T_2$ ground state.

Introduction

Recently, numerous investigations have been reported [1] on compounds of iron(II) which show thermally driven transitions between high-spin($^5T_2$) and low-spin($^1A_1$) ground states as solids. In some systems of [Fe^{II}N$_6$] type, e.g. [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] where phen = 1,10-phenanthroline [2], the high-spin($^5T_2$) ⇌ low-spin($^1A_1$) transition is associated with a phase change of first order [3] and, occasionally, pronounced hysteresis effects may be observed [4, 5]. In some other systems, e.g. [Fe(mephen)$_3$]X$_2$ where mephen = 2-methyl-1,10-phenanthroline [6, 7], the high-spin ($^5T_2$) ⇌ low-spin($^1A_1$) transition extends over a considerable range of temperature, the character of the transition being not so clearly evident as in the first case. In the present study we report, on the basis

of detailed magnetic susceptibility and ^{57}Fe Mössbauer effect measurements, the behaviour of a novel system of the second type, oxalatobis(1,10-phenanthroline)iron(II) pentahydrate, [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O. These investigations may provide additional insight into the factors influencing the formation of spin transitions since, in this sytem, the existence of the high-spin($^5T_2$) ⇌ low-spin($^1A_1$) transition may be shown to critically depend on the presence of five molecules of lattice water.

Experimental

Preparations

The oxalatobis(1,10-phenanthroline)iron(II) complex was obtained by precipitation from a solution of the corresponding tris complex as follows. Iron(II) oxalate, FeC$_2$O$_4$·2H$_2$O, and a little in excess of the threefold molar quantity of 1,10-phenanthroline were dissolved in a few ml of degassed water, heated on a steam bath for several hours and filtered. From the resulting concentrated solution of [Fe(phen)$_3$]C$_2$O$_4$, dropwise addition of deaerated acetone precipitated blue-violet crystals which were collected. Purification was effected by repeated recrystallization from water and reprecipitation from a water/acetone mixture by acetone. All operations were performed in a nitrogen atmosphere under strict exclusion of air. All solvents employed were carefully deaerated and saturated with nitrogen.

Oxalatobis(1,10-phenanthroline)iron(II) Pentahydrate

Anal. Found: C, 52.86; H, 4.31; N, 9.47; Fe, 9.99; O, 23.35; H$_2$O, 13.80. Calcd for FeC$_{26}$H$_{16}$N$_4$O$_4$·5H$_2$O: C, 52.54; H, 4.40; N, 9.43; Fe, 9.40; O, 24.23; H$_2$O, 15.15. Calcd for FeC$_{26}$H$_{16}$N$_4$O$_4$·4.5H$_2$O: C, 53.35; H, 4.31; H, 9.57; Fe, 9.54; O, 23.23; H$_2$O, 13.85.

*Author to whom correspondence should be addressed.

Oxalatobis(1,10-phenanthroline)iron(II)   *Monohydrate*

The sample was obtained by extended pumping on the pentahydrate under vacuum within the magnetic balance as described in the results section. Handling of the sample in order to perform analyses apparently resulted in take-up of lattice water. *Anal.* Found: C, 55.66; H, 4.14; N, 10.00; Fe, 10.12; H_2O, 9.71. Calcd for $FeC_{26}H_{16}N_4O_4 \cdot 3H_2O$: C, 55.93; H, 3.97; N, 10.03; Fe, 10.00; H_2O, 9.67.

Malonatobis(1,10-phenanthroline)iron(II) Dihydrate

The same synthetic procedure as above was followed except that the pyridine adduct of iron(II) malonate, $FeCH_2C_2O_4 \cdot py \cdot H_2O$ was employed as the starting iron(II) salt. *Anal.* Found: C, 58.30; H, 4.01; N, 10.07; Fe, 10.29; O, 17.21; H_2O, 6.61. Calcd for $FeC_{27}H_{18}N_4O_4 \cdot 2H_2O$: C, 58.50; H, 4.00; N, 10.11; Fe, 10.07; O, 17.32; H_2O, 6.50.

Microanalyses were performed by Dr. F. Pascher, Bonn, W. Germany

Infrared Spectra

The IR spectra of the compounds show the vibrational frequencies characteristic for coordinated oxalate and malonate ions. The frequencies found for violet $[Fe(phen)_2C_2O_4] \cdot 5H_2O$ and violet $[Fe(phen)_2mal] \cdot 2H_2O$ are listed below. The notation is based for the oxalate complex on a normal coordinate analysis by Fujita *et al.* [8, 9], whereas for the malonate complex the empirical assignments of Schmelz *et al.* [10] are used.

$[Fe(phen)_2C_2O_4] \cdot 5H_2O$, violet: 1700 m, $\nu_7 = \nu_{as}(CO)$; 1655 vs,br, $\nu_1 = \nu_{as}(CO)$; ~1388 s,sh, $\nu_2 = \nu_s(CO) + \nu(CC)$; 1279 s,br, $\nu_8 = \nu_s(CO) + \delta(OCO)$; 887 m, $\nu_3 = \nu_s(CO) + \delta(OCO)$; 782 vs, 778 sh, $\nu_9 = \delta(OCO) + \nu(FeO)$; 508 m,br, $\nu_4 = \nu(FeO) + \nu(CC)$; 480 w,br, $\nu_{10} =$ ring def $+ \delta(OCO)$.

$[Fe(phen)_2mal] \cdot 2H_2O$, violet: 1627 vs,br, $\nu_{as}(CO)$; 1400 vs,br, $\nu_s(CO)$; 1311 m,br, CH_2 wag; 949 s, $\nu_s(CC)$; 927 s, CH_2 rock; 776 m, $\delta(OCO)$; 705 s, $\delta(OCO)$; 554 m,br, $\nu(FeO)$.

The IR frequencies of the phenanthroline ligand correspond to those reported previously for the members of the $[Fe(phen)_2X_2]$ series [11].

Instrumentation

Magnetic susceptibilities were measured in the temperature range between 0.99 and 314.6 K by the Faraday method. The equipment employs a 10 in. electromagnet (Bruker-Physik) with Henry-type pole caps, an electrical microbalance (Sartorius type 4102), and the required cryogenic equipment. Temperatures below 4.2 K were achieved by pumping on the helium reservoir with a Roots pump (Leybold-Heraeus type WS-250, suction power 324 m^3/hr), all connecting pipes and flanges being of 65 mm diameter or larger. Temperatures in the cryogenic range

were measured using a gold/iron *vs.* chromel thermocouple and checked *via* the vapor pressure of helium. The thermocouple was calibrated against a Pt or Ge resistor placed in the position of the sample employing the known linear dependence on temperature of the reciprocal magnetic susceptibility of certain substances. More details may be found elsewhere [12]. All measurements were performed at six different field strengths, *viz.* 3.50, 5.55, 8.60, 10.90, 12.00 and 13.10 kG. The diamagnetic corrections applied to χ_m are -359 and -329×10^{-6} cgs mol^{-1} for $[Fe(phen)_2C_2O_4] \cdot 5H_2O$ and $[Fe(phen)_2mal] \cdot 2H_2O$, respectively. The corresponding χ_m^{dia} values for the intermediate products which have a composition approximating that of the tetra- and trihydrate of the oxalato complex were taken as -346 and -333×10^{-6} cgs mol^{-1}, whereas that for $[Fe(phen)_2C_2O_4] \cdot H_2O$ is -307×10^{-6} cgs mol^{-1}. The effective magnetic moment was obtained according to $\mu_{eff} = 2.828\sqrt{\chi_m^{corr} \cdot T}$ where χ_m^{corr} is the molar magnetic susceptibility corrected for the diamagnetism of all constituents.

^{57}Fe Mössbauer spectra were measured employing a spectrometer of the constant-acceleration type (Frieseke and Hoepfner FHT 800A) operating in the multiscaler mode. A 50-mCi source of ^{57}Co in rhodium was used, the calibration being effected with a metallic iron absorber. All velocity scales and isomer shifts are referred to the iron standard at 298 K. To convert to the sodium nitroprusside scale, add +0.257 mm s^{-1}. Movement of the source toward the absorber corresponds to positive velocities. Variable-temperature measurements between 145 and 244 K were obtained by the use of a small heating coil with the sample placed in a superinsulated cryostat. The temperatures were carefully monitored by means of a calibrated copper/constantan thermocouple, a cryogenic temperature controller (Artronix Model 5301-E), and liquid nitrogen as coolant. All measurements were performed with the identical geometrical arrangement for source, absorber, and detector, the resulting data being corrected for nonresonant background of the γ rays. Normalized individual areas $A(^5T_2)$ and $A(^1A_1)$ were extracted from the Mössbauer spectra by decomposition into Lorentzians where

$$A(^5T_2) = S f_S L(\tfrac{1}{2}t_{s_{T_2}})$$
$$A(^1A_1) = S f_S L(\tfrac{1}{2}t_{A_1}) \tag{1}$$

In Eq. (1), S is a scale factor, f_S the Debye–Waller factor of the source, t_i the effective thickness, and $L(t_i)$ the saturation function. It has been verified that t_i is always less than 0.8 in which case $L(t)$ is well approximated by
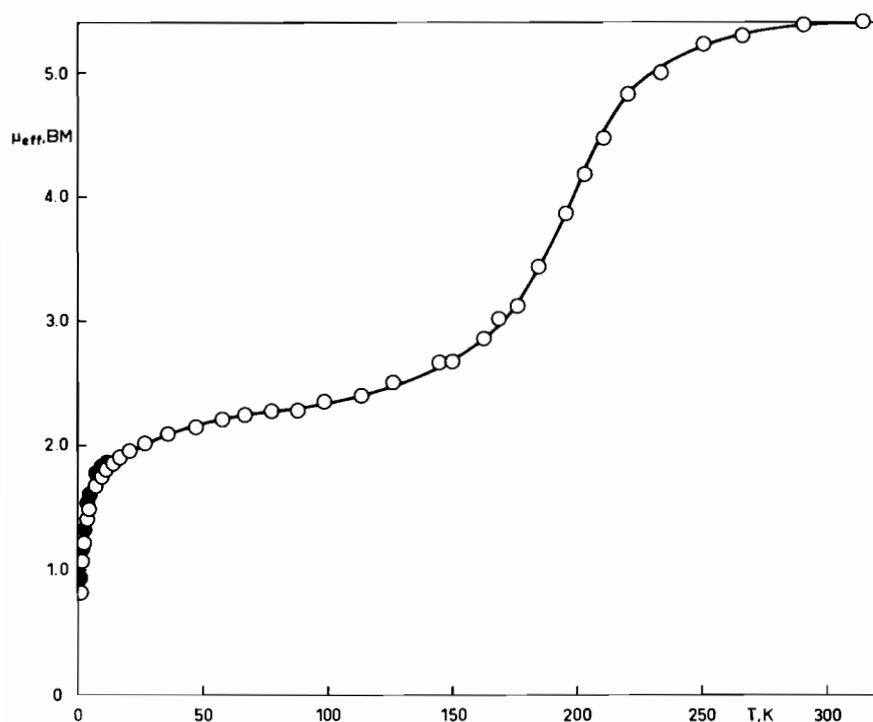
$$L(t) = t/(1 + 0.25 t) \tag{2}$$

Fig. 1. Temperature dependence of the effective magnetic moment, μ_{eff}, for $[Fe(phen)_2C_2O_4]\cdot5H_2O$ between 0.99 and 314.6 K. Experimental data indicated by open circles correspond below 10.88 K to H = 13.10 kG, whereas above 10.88 K average values for six field strengths are displayed. Full circles below 10.88 K correspond to μ_{eff} at H = 3.50 kG.

TABLE I. Magnetic Susceptibility χ_g and χ_m^{corr} [a] and Effective Magnetic Moment μ_{eff} [b] for $[Fe(phen)_2C_2O_4]\cdot5H_2O$.[c]

H (kG)	T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
3.50	0.99	186.91	111453	0.944
	1.68	173.07	103227	1.178
	2.25	166.14	99107.6	1.335
	3.57	140.24	83713.4	1.546
	4.20	127.29	76016.4	1.598
	6.93	96.470	57697.9	1.788
	9.42	75.107	45000.3	1.841
	10.88	65.653	39381.2	1.851
5.55	0.99	176.66	105360	0.913
	1.70	165.13	98507.3	1.157
	2.27	158.25	94418.1	1.309
	3.58	133.57	79749.0	1.511
	4.20	122.90	73407.1	1.570
	6.93	92.635	55418.5	1.753
	9.42	73.510	44051.1	1.822
	10.88	64.564	38733.9	1.836
8.60	0.99	162.38	96872.8	0.876
	1.72	154.61	92254.5	1.127
	2.29	148.48	88611.1	1.274
	3.59	127.11	75909.4	1.476
	4.20	118.21	70619.5	1.540
	6.93	89.318	53446.9	1.721
	9.42	71.649	42945.0	1.799
	10.88	63.442	38067.0	1.820

TABLE I. *(continued)*

H (kG)	T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
10.90	0.99	151.37	90328.8	0.846
	1.74	145.89	87071.6	1.101
	2.31	140.65	83957.1	1.245
	3.60	122.18	72979.1	1.450
	4.20	114.58	68461.9	1.516
	6.93	87.371	52289.7	1.702
	9.42	70.523	42275.8	1.785
	10.88	62.593	37562.4	1.808
12.00	0.99	144.42	86197.9	0.826
	1.76	139.58	83321.2	1.083
	2.33	135.64	80979.3	1.228
	3.60	118.99	71083.1	1.431
	4.20	112.25	67077.0	1.501
	6.93	86.096	51531.9	1.690
	9.42	69.718	41797.3	1.775
	10.88	62.054	37242.0	1.800
13.10	0.99	139.46	83249.8	0.812
	1.78	135.54	80919.9	1.073
	2.36	131.28	78387.9	1.216
	3.64	116.30	69484.2	1.422
	4.20	110.28	65906.1	1.488
	6.93	84.948	50849.5	1.679
	9.42	68.950	41340.8	1.765
	10.88	61.450	36883.0	1.791

(continued overleaf)

TABLE I. *(continued)*

H (kG)	T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
	13.44	54.042	32479.9	1.868
	16.69	45.259	27259.6	1.908
	20.51	38.551	23272.6	1.954
	26.70	31.336	18984.2	2.013
	35.99	24.875	15144.0	2.088
	46.99	20.086	12297.5	2.150
	57.85	17.184	10572.7	2.212
	66.50	15.397	9510.51	2.249
	77.57	13.514	8391.32	2.282
	87.80	11.994	7487.87	2.293
	98.50	11.237	7037.94	2.355
	113.45	10.019	6313.99	2.394
	126.10	9.901	6243.86	2.509
	145.20	9.762	6161.24	2.675
	150.15	9.459	5981.34	2.680
	163.0	9.978	6289.62	2.863
	169.2	10.837	6800.29	3.033
	176.0	11.123	6970.18	3.132
	184.5	12.933	8046.19	3.446
	195.4	15.552	9602.35	3.874
	203.0	17.584	10810.4	4.189
	210.4	19.492	11944.5	4.483
	220.5	21.672	13240.2	4.832
	233.4	22.456	13706.2	5.058
	250.6	22.315	13622.4	5.225
	266.7	21.511	13144.5	5.295
	290.8	20.387	12476.4	5.387
	314.6	18.953	11624.1	5.408

[a]Molecular weight M = 594.37, diamagnetic correction -359×10^{-6} cgs/mol, experimental uncertainty between 0.2 and 0.9%, dependent on temperature. [b]$\mu_{eff} = 2.828(\chi_m^{corr} \cdot T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c]Between 0.99 and 10.88 K, values for six different field strengths (H = 3.50 to H = 13.10 kG) are listed individually. Above 10.88 K, the average values for the six fields are given. Sample weight is 14.912 mg.

The factor Sf_S in Eq. (1) was determined by measurements on thin absorbers of known Debye–Waller factor, *i.e.* metallic iron and $Na_2[Fe(CN)_5NO] \cdot 2H_2O$. The effective thickness t_i may then be easily determined from the quantity A_i of Eq. (1) by application of the inverse function $t_i(L)$.

Measurements at 4.2 K were performed with a separate spectrometer (Nuclear Data ND 2400) and a suitable helium dewar, the modulation of the pulse height being achieved by the driving waveform. In order to perform magnetic hyperfine measurements, this spectrometer was equipped with a superconducting coil capable of producing 50 kG. The magnetic field was parallel to the direction of the γ-rays.

Results

For the solid complex $[Fe(phen)_2C_2O_4] \cdot 5H_2O$, magnetic measurements were performed on a sample of 14.912 mg between 0.99 and 314.6 K. A representative selection of the data is listed in Table I, the temperature dependence being displayed, in terms of the effective magnetic moment, μ_{eff}, in Fig. 1. In the table, data obtained for six different fields (H = 3.50 to 13.10 kG) are presented individually for temperatures between 0.99 and 10.88 K, whereas above 10.88 K, the average values for the six fields are given. According to these results, the effective magnetic moment is a continuously decreasing function of temperature ($\mu_{eff} = 5.408$ BM at 314.6 K, $\mu_{eff} = 0.812$ BM at 0.99 K for H = 13.10 kG). The lowering of μ_{eff} appears to be particularly prominent in the temperature region between about 250 and 150 K ($\mu_{eff} = 5.225$ BM at 250.6 K, $\mu_{eff} = 2.680$ BM at 150.15 K), *cf.* Fig. 1. Towards lower temperatures, the moment continues to slowly decrease down to about 15 K ($\mu_{eff} = 1.908$ BM at 16.69 K), whereupon a more pronounced lowering again sets in, ultimately arriving at $\mu_{eff} = 0.812$ BM at 0.99 K (for H = 13.10 kG). Obviously, the magnetism of the solid complex $[Fe(phen)_2C_2O_4] \cdot 5H_2O$ resembles in many respects the behaviour found for some iron(II) systems which are involved in high-spin($^5T_2$) $\rightleftharpoons$ low-spin($^1A_1$) transitions [6, 7, 13–15].

Conclusive evidence in support of this assumption is provided by the results of ^{57}Fe Mössbauer effect measurements. The individual data obtained by a decomposition of the spectra into Lorentzians are listed in Table II. At 308 K, the highest temperature studied, the Mössbauer spectrum of $[Fe(phen)_2C_2O_4] \cdot 5H_2O$ consists of a single doublet characterized by the quadrupole splitting $\Delta E_Q = 2.44 \pm 0.01$ mm s^{-1} and the isomer shift $\delta^{IS} = +0.97 \pm 0.02$ mm s^{-1}. On the basis of these data, assignment of the doublet to the high-spin $^5T_2(t_2^4e^2)$ ground state of iron(II) is justified. Term symbols within cubic symmetry are employed for convenience only. Let us consider next the Mössbauer spectra for the temperature region where a peculiar decrease of μ_{eff} was found, *cf.* Fig. 2. Here we observe that the overall spectrum at 244 K is governed by the high-spin($^5T_2$) ground state, $t_{s_{T_2}}/t_{total} = 0.740$, although the asymmetry in the center is indicative of a second contribution which will emerge at lower temperatures. At 204 K, the spectrum consists of approximately equal contributions of the $^5T_2$ and $^1A_1$ ground states, $t_{s_{T_2}}/t_{total} = 0.484$. Indeed, the center two lines may be assigned to the low-spin($^1A_1$) ground state on the basis of Mössbauer effect parameters, *viz.* $\Delta E_Q = 0.69$ mm s^{-1}, $\delta^{IS} = +0.39$ mm s^{-1}. With additional lowering of temperature, the area fraction of the high-spin ($^5T_2$) spectrum decreases further and, at 145 K, the predominant part of the spectrum is due to the low-

TABLE II. ^{57}Fe Mössbauer Effect Data for [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O.

T (K)	ΔE_Q ($^5T_2$)[a] (mm s^{-1})	δ^{IS}($^5T_2$)[b,c] (mm s^{-1})	ΔE_Q($^1A_1$)[a] (mm s^{-1})	δ^{IS}($^1A_1$)[b,c] (mm s^{-1})	$t_{s_{T_2}}/t_{total}$
308	2.44	+0.97	...	...	>0.95
244	2.65	+0.99	0.71 ± 0.02	+0.40 ± 0.03	0.740
230	2.69	+0.99	0.71 ± 0.02	+0.39 ± 0.03	0.689
220	2.72	+0.99	0.69	+0.39	0.639
212	2.75	+0.99	0.70	+0.39	0.576
208	2.76	+0.99	0.69	+0.39	0.523
204	2.77	+0.98	0.69	+0.39	0.484
200	2.78	+0.99	0.69	+0.39	0.419
195	2.79	+0.99	0.69	+0.39	0.351
190	2.80	+0.98	0.69	+0.39	0.264
180	2.81	+0.98	0.69	+0.39	0.175
170	2.84 ± 0.02	+0.98 ± 0.03	0.69	+0.38	0.115
160	2.82 ± 0.03	+0.98 ± 0.04	0.69	+0.38	0.083
150	2.80 ± 0.03	+0.95 ± 0.04	0.69	+0.38	0.074
145	2.79 ± 0.03	+0.95 ± 0.04	0.70	+0.38	0.067
4.2	...	...	0.69	+0.35	0

[a]Experimental uncertainty ±0.01, except where specified.   [b]Isomer shifts δ^{IS} are relative to natural iron at 298 K.   [c]Experimental uncertainty ±0.02, except where specified.
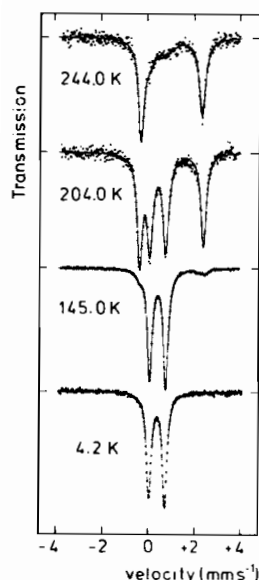

Fig. 2. ^{57}Fe Mössbauer spectra for [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O at the temperatures of 244, 204, 145 and 4.2 K.

spin ($^1A_1$) ground state, $t_{s_{T_2}}/t_{total}$ = 0.067, cf. Fig. 2. The Mössbauer parameters are identical to those 204 K, cf. Table II, as expected. Finally, at 4.2 K, the Mössbauer spectrum consists alone of the low-spin ($^1A_1$) ground state doublet. Figure 3 shows the temperature dependence, over the region 150 to 250 K, of the relative effective thickness $t_{s_{T_2}}/t_{total}$. Since

$$t_{s_{T_2}} = \frac{1}{2} \ w \ \sigma_0 \ f_{s_{T_2}} \ n_{s_{T_2}}$$

$$t_{1_{A_1}} = \frac{1}{2} \ w \ \sigma_0 \ f_{1_{A_1}} \ (1 - n_{s_{T_2}}) \tag{3}$$

an observed variation in $t_{s_{T_2}}/t_{total}$ will not directly reflect the variation of $n_{s_{T_2}}$, the site fraction of molecules on the $^5T_2$ ground state. In eqn. (3), w denotes the number of resonant nuclei per unit area of absorber, σ_0 is the resonant cross section, and $f_{s_{T_2}}$ and $f_{1_{A_1}}$ are the Debye–Waller factors for the corresponding ground state. On a qualitative basis, the temperature function of $t_{s_{T_2}}/t_{total}$, viz. Fig. 3, is equivalent to that of $n_{s_{T_2}}$ which may be determined from the temperature dependence of μ_{eff}, cf. Fig. 1. However, all differences between these two results have to be attributed to the possible difference [14, 16, 17] between the Debye–Waller factors for the ground states involved, $f_{s_{T_2}}$ and $f_{1_{A_1}}$.

The decrease of μ_{eff} below ~15 K, cf. Fig. 1, is similar to the corresponding behaviour encountered for some iron(II) complexes in the cryogenic temperature range [13, 14, 18]. It is suggested that this change is due to the depopulation of all paramagnetic states which contribute to the overall magnetic moment. The small field dependence of the magnetic susceptibility below ~10 K is attributed to paramagnetic saturation, although a small amount if a ferromagnetic impurity is difficult to exclude.

In order to investigate the specific effect, on the observed high-spin($5T_2$) ⇌ low-spin($^1A_1$) transition, of the solvent molecules included in the lattice, a separate sample of [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O (sample weight 62.351 mg) was evacuated for a prolonged period of time within the Faraday balance. The weight change of the sample was followed by application of the electric balance and the resulting weight was adjusted such as to approximate thy stoichiometry of possible tetra, tri, and monohydrates, cf.
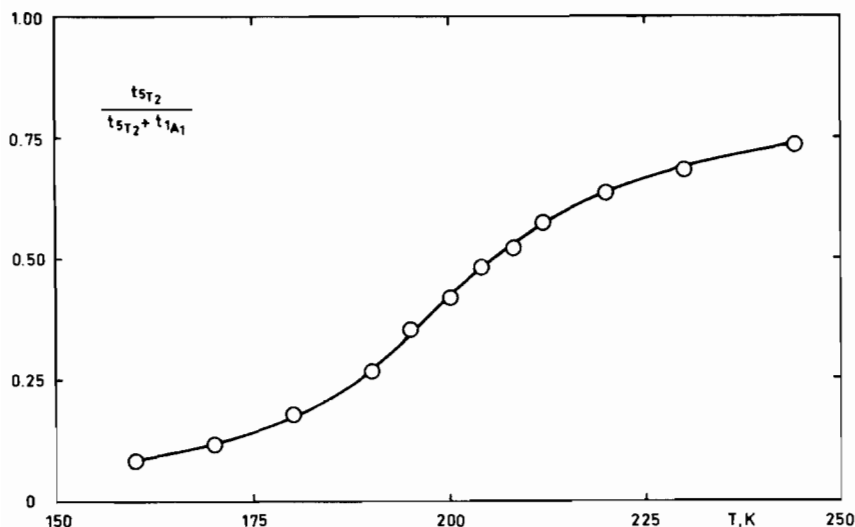
Fig. 3. Temperature dependence of the relative effective thickness t_{5T_2}/t_{total} for $[Fe(phen)_2C_2O_4] \cdot 5H_2O$ between 150 and 250 K.

TABLE III. Data Characterizing Pumping Experiment on $[Fe(phen)_2C_2O_4] \cdot 5H_2O$.

Time for Evacuation	Weight Loss (mg)	Assumed Chemical Composition	Calcd. Weight Loss (mg)	Calcd. Sample Weight (mg)
. . .	. . .	$[Fe(phen)_2C_2O_4] \cdot 5H_2O$	. . .	62.351
50 min	2.005	$[Fe(phen)_2C_2O_4] \cdot 4H_2O$	1.890	60.346
1 hr	3.960	$[Fe(phen)_2C_2O_4] \cdot 3H_2O$	3.779	58.572
20 to 64 hr	7.497	$[Fe(phen)_2C_2O_4] \cdot H_2O$	7.559	54.854

Table III. After the composition has arrived at that of $[Fe(phen)_2C_2O_4] \cdot H_2O$, no additional loss of hydrate water was accomplished, at least at 300 K, even if the pumping period was extended to 64 hours. At each intermediate composition specified in Table III, the evacuation process was interrupted, helium was admitted to the system, and the magnetic susceptibility was measured over the temperature range 77 to 300 K. The detailed magnetic data listed in Table IV are average values of the data collected for six different fields (H = 3.50 to 13.10 kG), no significant field dependence having been found. The results are illustrated in Fig. 4 and Fig. 5 in terms of the effective magnetic moment, μ_{eff}, and the reciprocal molar magnetic susceptibility, $1/\chi_m^{corr}$, respectively. It is evident that a completely continuous change of magnetism over the temperature range is found for any of the four systems studied. In particular, the magnetism of the final product, $[Fe(phen)_2C_2O_4] \cdot H_2O$, approximates to that of a pure high-spin $^5T_2$ ground state (μ_{eff} = 5.364 BM at 291.8 K, μ_{eff} = 5.033 BM at 77.63 K).

Since it is thus of interest to perform a more detailed study of the monohydrate $[Fe(phen)_2C_2-$ $O_4] \cdot H_2O$, a larger sample was produced by a longterm evacuation of the pentahydrate. The magnetism of the solid product was studied between 1.09 and 295.0 K, the detailed data being collected in Table V. Again, data obtained for field strengths between H = 3.50 and 13.10 kG are listed individually up to 6.03 K, whereas above this temperature, average values are given. According to these results, the magnetic moment shows a slight decrease with lowering of temperature (μ_{eff} = 5.294 BM at 295.0 K, μ_{eff} = 4.505 BM at 15.48 K), consistent with a high-spin $^5T_2$ ground state. A detailed comparison shows that the μ_{eff} values of Table 5 are somewhat lower than those obtained for the sample directly evacuated within the Faraday balance, viz. Table IV(d). If it is assumed that the difference is due to partially increased hydration (caused by handling of the substance), and thus to some contribution by the pentahydrate which involves the $^5T_2 \rightleftharpoons {}^1A_1$ transition, the actual composition of the sample investigated in Table V follows as $[Fe(phen)_2C_2O_4] \cdot 1.12H_2O$.

The results are further substantiated by a ^{57}Fe Mössbauer effect study of the above product which shows, at 300 K, a slightly asymmetric doublet with

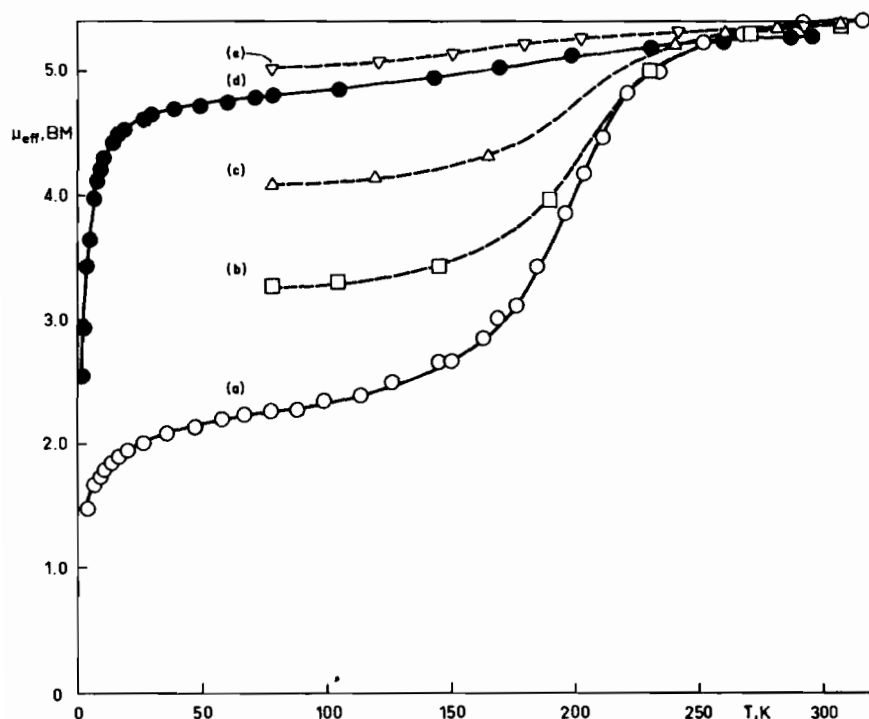Fig. 4. Temperature dependence of the effective magnetic moment, μ_{eff}, for the pumping experiment: (a) [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O (open circles); (b) approximate composition [Fe(phen)$_2$C$_2$O$_4$]·4H$_2$O (open squares); (c) approximate composition [Fe(phen)$_2$C$_2$O$_4$]·3H$_2$O (open triangles); (d) separately produced [Fe(phen)$_2$C$_2$O$_4$]·1.12H$_2$O (full circles); (e) end product [Fe(phen)$_2$C$_2$H$_4$]·H$_2$O (reversed open triangles). For details refer to Table III.

TABLE IV. Magnetic Susceptibility χ_g and χ_m^{corr} [a] and Effective Magnetic Moment μ_{eff} [b] for Sample of [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O in Pumping Experiment.

T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
(a) [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O			
77.60	11.454	7166.91	2.109
118.15	8.172	5216.19	2.220
198.3	13.781	8550.01	3.682
239.8	21.847	13344.2	5.059
286.4	20.180	12353.4	5.319
305.5	19.258	11805.4	5.371
(b) Assumed composition [Fe(phen)$_2$C$_2$O$_4$]·4H$_2$O			
77.70	29.229	17192.1	3.269
103.8	22.204	13143.3	3.303
144.0	17.183	10249.4	3.436
189.5	17.304	10319.2	3.955
229.7	23.123	13672.9	5.012
270.2	22.057	13058.6	5.312
306.6	19.905	11818.2	5.383
(c) Assumed composition [Fe(phen)$_2$C$_2$O$_4$]·3H$_2$O			
77.68	47.381	26787.7	4.079
119.3	31.579	17964.8	4.140
165.0	24.727	14139.1	4.319
240.0	24.906	14239.0	5.228

TABLE IV. *(continued)*

T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
260.0	23.756	13596.9	5.317
280.7	22.287	12776.7	5.356
306.5	20.653	11864.4	5.393
(d) Assumed composition [Fe(phen)$_2$C$_2$O$_4$]·H$_2$O (time of evacuation 20 hr)			
77.63	77.520	40796.5	5.033
120.5	50.820	26850.8	5.087
149.9	41.747	22111.9	5.149
179.5	35.648	18926.3	5.212
201.4	32.387	17223.1	5.267
241.0	27.598	14721.7	5.327
291.8	23.021	12331.1	5.364

[a] Molecular weight for [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O M = 594.37, for the tetrahydrate 576.35, for the trihydrate 558.34 and for the monohydrate 522.31. Diamagnetic correction for [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O χ^{dia} = −359 × 10^{-6} cgs/mol, for the tetrahydrate −346, for the trihydrate −333 and for the monohydrate −307 × 10^{-6} cgs/mol. Experimental uncertainty between 0.2 and 0.9% dependent on temperature. [b] μ_{eff} = 2.828 $(\chi_m^{corr} \cdot T)^{1/2}$, experimental uncertainty approximately ±0.005BM.
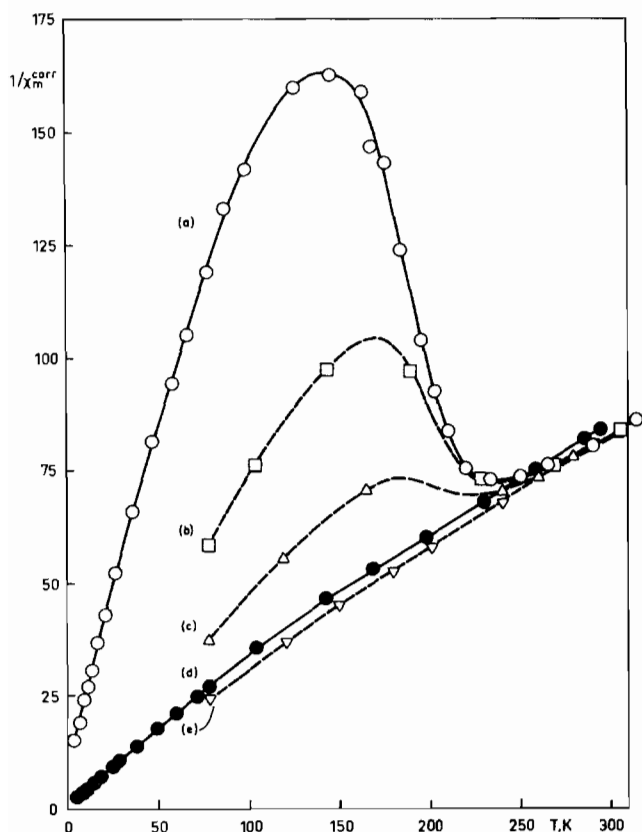(Listed above are average values for the six fields employed (H = 3.50 to 13.10 kG).

Fig. 5. Temperature dependence of the reciprocal molar magnetic susceptibility, $1/\chi_m^{corr}$, for the pumping experiment: (a) $[Fe(phen)_2C_2O_4] \cdot 5H_2O$ (open circles); (b) approximate composition $[Fe(phen)_2C_2O_4] \cdot 4H_2O$ (open squares); (c) approximate composition $[Fe(phen)_2C_2O_4] \cdot 3H_2O$ (open triangles); (d) separately produced $[Fe(phen)_2C_2O_4] \cdot 1.12H_2O$ (full circles); (e) end product $[Fe(phen)_2C_2O_4] \cdot H_2O$ (reversed open triangles). For details refer to Table III.

TABLE V. Magnetic Susceptibility χ_g and χ_m^{corr} [a] and Effective Magnetic Moment μ_{eff} [b] for $[Fe(phen)_2C_2O_4] \cdot H_2O$.[c,d]

H (kg)	T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
3.50	1.09	1172.6	612767	2.311
	1.57	1161.2	606813	2.760
	2.26	1110.0	580071	3.238
	3.27	971.10	507522	3.643
	4.20	779.70	407552	3.700
	6.03	705.80	368953	4.218
5.55	1.09	1134.7	592972	2.274
	1.60	1106.4	578191	2.720
	2.27	1047.4	547374	3.152
	3.29	955.40	499322	3.625
	4.20	770.90	402956	3.679
	6.03	681.90	356366	4.146
8.60	1.09	1054.2	550926	2.191
	1.63	1033.8	540271	2.654
	2.28	1003.2	524288	3.092

TABLE V. (continued)

H (kG)	T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
	3.31	917.40	479474	3.563
	4.20	759.80	397158	3.652
	6.03	651.10	340383	4.052
10.90	1.09	986.40	515514	2.120
	1.66	976.50	510343	2.603
	2.29	952.40	497755	3.019
	3.33	879.30	459574	3.498
	4.20	766.70	400762	3.669
	6.03	649.80	339704	4.048
12.00	1.09	942.90	492793	2.073
	1.69	934.80	488562	2.570
	2.30	916.40	478952	2.968
	3.35	851.80	445211	3.454
	4.20	762.10	398359	3.658
	6.03	640.80	335003	4.019
13.10	1.09	913.80	477594	2.040
	1.71	906.20	473624	2.545
	2.31	892.30	466364	2.935
	3.37	834.20	436018	3.428
	4.20	757.00	395696	3.646
	6.03	630.40	329571	3.987
	7.33	552.70	288988	4.116
	8.71	485.88	254089	4.207
	10.24	432.77	226345	4.305
	13.59	345.42	180722	4.432
	15.48	313.23	163912	4.505
	18.00	271.68	142210	4.525
	25.93	195.64	102492	4.610
	28.83	178.66	93623.8	4.646
	38.54	136.38	71537.9	4.696
	49.27	107.67	56545.9	4.720
	60.20	89.266	46931.7	4.753
	70.77	76.884	40464.4	4.786
	77.43	70.856	37315.5	4.807
	104.40	53.256	28123.1	4.846
	142.75	40.462	21440.7	4.948
	169.0	35.386	18789.6	5.039
	198.3	31.183	16594.1	5.130
	229.8	27.560	14722.5	5.202
	258.7	24.905	13315.0	5.249
	286.0	22.762	12195.9	5.282
	295.0	22.159	11880.7	5.294

[a]Molecular weight M = 522.31; diamagnetic correction -307×10^{-6} cgs/mol, experimental uncertainty between 0.2 and 0.9%, dependent on temerature. [b]$\mu_{eff} = 2.828(\chi_m^{corr} \cdot T)^{1/2}$, experimental uncertainty ±0.005 BM. [c]Assumed composition. [d]Between 1.09 and 6.03 K, values for six different field strengths (H = 3.50 to H = 13.10 kG) are listed individually (sample weight 0.195 mg). [d]Above 6.03 K, the average values for the six fields are given (sample weight 27.247 mg).

$\Delta E_Q = 2.50 \pm 0.02$ mm s^{-1}, $\delta^{IS} = +0.99 \pm 0.03$ mm s^{-1}. These data are typical for a high-spin $^5T_2$ ground state, and, since the 4.2 K spectrum is governed by

TABLE VI. Magnetic Susceptibility χ_g and χ_m^{corr} [a] and Effective Magnetic Moment μ_{eff}[b] for [Fe(phen)$_2$mal]·2H$_2$O.[c]

T (K)	$10^6 \chi_g$ (cgs/g)	$10^6 \chi_m^{corr}$ (cgs/mol)	μ_{eff} (BM)
4.20	779.60	432498	3.812
11.10	458.84	254685	4.755
28.97	196.39	109196	5.030
48.26	119.05	66326.2	5.060
77.63	76.856	42934.2	5.163
143.1	42.004	23613.9	5.199
206.3	29.262	16550.6	5.226
284.6	21.242	12104.6	5.249

[a]Molecular weight M = 554.35, diamagnetic correction -329×10^{-6} cgs/mol, experimental uncertainty between 0.2 and 0.9%, dependent on temperature. [b]$\mu_{eff} = 2.828(\chi_m^{corr} \cdot T)^{1/2}$, experimental uncertainty approximately ±0.005 BM. [c]The values listed are average values for the six field strengths H = 3.50 to H = 13.10 kG.

the same doublet where now $\Delta E_Q(^5T_2) = 2.86 \pm 0.01$ mm s^{-1}, $\delta^{IS}(^5T_2) = +0.99 \pm 0.02$ mm s^{-1}, no spin transition is involved. However, the asymmetry in the 300 K spectrum is resolved at 4.2 K into a separate spectrum producing a small contribution by the low-spin $^1A_1$ ground state, $\Delta E_Q(^1A_1) = 0.67 \pm 0.02$ mm s^{-1}, $\delta^{IS}(^1A_1) = +0.35 \pm 0.03$ mm s^{-1}, $t_{^5T_2}/t_{total} = 0.772$. Spectra intermediate in appearance were obtained at 200 and 100 K. A second sample of [Fe(phen)$_2$C$_2$O$_4$]·H$_2$O has been transfered into the Mössbauer spectrometer with particular speed and care. This sample produced Mössbauer parameters identical to the above and, at 4.2 K, $t_{^5T_2}/t_{total} = 0.820$. The $^1A_1$ contribution thus apparent is again attributed to partial hydration of the sample. It is evident, from the values of $t_{^5T_2}/t_{total}$, that it may be minimized by protection of the sample. It should be also noted that the obtained values of $t_{^5T_2}/t_{total}$ may be affected by a difference in the Debye–Waller factors, $f_{^5T_2}$ and $f_{^1A_1}$ [14, 16, 17]. The excess hydration is smaller in magnetism studies, since there the sample is little exposed in handling.

The Mössbauer effect data obtained for [Fe(phen)$_2$C$_2$O$_4$]·H$_2$O are little different from those of [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O (*cf.* Table II), and thus provide evidence that no changes beyond the loss of lattice water are involved. In particular, since no additional spectrum apart of the two reported above has been observed in the partly hydrated 'monohydrate', the intermediate products with four and three molecules of lattice water are most likely nothing but mixtures between the high-spin complex [Fe(phen)$_2$C$_2$O$_4$]·H$_2$O and the compound [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O which shows a high-spin($^5T_2$) $\rightleftharpoons$ low-spin($^1A_1$) transition.

A sample of [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O was investigated for hysteresis effects, using the Mössbauer effect technique, with negative result. In particular, at 204 K where the effect of any hysteresis would be expected to be largest (*cf.* Fig. 3), $t_{^5T_2}/t_{total} = 0.484$ has been obtained both in a rising and in a lowering temperature cycle.

Magnetic data on the complex [Fe(phen)$_2$mal]·2H$_2$O which has been produced in the course of the present investigation are listed in Table VI. Mössbauer effect studies produced at 300 K $\Delta E_Q = 2.46 \pm 0.01$ mm s^{-1}, $\delta^{IS} = +1.01 \pm 0.02$ mm s^{-1}, whereas at 4.2 K $\Delta E_Q = 2.60 \pm 0.01$ mm s^{-1}, $\delta^{IS} = +1.00 \pm 0.02$ mm s^{-1}. Evidently, this complex shows a high-spin $^5T_2$ ground state behaviour over the temperature range investigated.

In an external magnetic field, [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O shows, at 4.2 K, a Collins type spectrum [19], no contribution from iron(III) impurities having been detected. Whereas at 40 kG a symmetric and thus uninformative pattern due to the overlap of hyperfine lines was obtained, at 20 kG apparently $V_{zz} > 0$ where V_{zz} is the z component of the electric field gradient tensor. A sample of [Fe(phen)$_2$mal]·2H$_2$O produced, at 4.2 K, a 40 kG spectrum characterized by $V_{zz} < 0$ and $H_{eff} \sim 85$ kG indicating an internal magnetic field at the iron nucleus.

Discussion

The compounds described in this study appear to be well characterized although, for the oxalato complex, the analytical data (which were repeatedly obtained) are not sufficient to decide whether the violet substance should be formulated with 4.5H$_2$O or 5H$_2$O. For convenience of presentation we have used above the formulation as [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O. Nonetheless, the indeterminacy here outlined should be kept in mind. Except this minor point, the compounds conform, on the basis of their stoichiometry, physical properties and likely molecular structure, to the series of neutral [Fe(phen)$_2$X$_2$] complexes studied in detail some time ago [20, 21]. It may be assumed, in particular, that violet [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O, [Fe(phen)$_2$C$_2$O$_4$]·H$_2$O, and [Fe(phen)$_2$mal]·2H$_2$O form a molecular lattice composed of isolated molecules similar to the known structure of [Fe(bipy)$_2$(NCS)$_2$] [22].

The molecular structure and the nature of the red compounds of similar stoichiometry, such as that of red [Fe(phen)$_2$C$_2$O$_4$]·5H$_2$O [23, 24], is again under active investigation in this laboratory.

It has been demonstrated in some detail above that the availability of five water molecules which are included in the lattice seems to be required in order to produce a high-spin($^5T_2$) $\rightleftharpoons$ low-spin($^1A_1$) transition in [Fe(phen)$_2$C$_2$O$_4$]. The effect of solvent mole-

cules on the structure and magnetism of spin equilibrium systems was recently studied [25–27] with particular emphasis on tris(dithiocarbamato)iron(III) complexes. According to this investigation, solvents capable of hydrogen bonding, such as $CHCl_3$, CH_2Cl_2, and H_2O, shift the high-spin($^6A_1$) $\rightleftharpoons$ low-spin ($^2T_2$) transition toward the high-spin side. It is assumed that hydrogen bonds between solvent molecules and S donor atoms of the ligands lengthen the Fe–S bonds. In $[Fe(phen)_2C_2O_4] \cdot xH_2O$ (x = 1 or 5), such interactions would be only conceivable with the $C_2O_4^{2-}$ ligand and, indeed, the addition of H_2O molecules into the lattice of $[Fe(phen)_2C_2O_4] \cdot H_2O$ shows the different effect in that the ground state is shifted to the opposite, i.e. the low-spin, side.

A recent example of the stabilization of a low-spin iron(III) complex by lattice water is provided by the crystal structure of bis[N-(2-aminoethyl)salicylaldiminato]iron(III) chloride monohydrate, [Fe(saen)_2]Cl·H_2O [28]. Unfortunately, the role played by the H_2O molecule in stabilizing the $^2T_2$ ground state has not been clarified.

There is sufficient evidence, however, that the spin state in both iron(II) and iron(III) complexes is extremely sensitive to minor variations in the ligand as well as to the solvation of the complex [1, 16, 25–31]. It is thus perhaps not surprising that, in the example of $[Fe(phen)_2C_2O_4]$, the interaction between several molecules of lattice water and the complex is sufficient to shift the ground state markedly to the low-spin side by inducing a high-spin($^5T_2$) $\rightleftharpoons$ low-spin($^1A_1$) transition.

Acknowledgements

References

1 H. A. Goodwin, Coord. Chem. Rev., 18, 293 (1976).
2 E. König and K. Madeja, Inorg. Chem., 6, 48 (1967).
3 M. Sorai and S. Seki, J. Phys. Chem. Solids, 35, 555 (1974).
4 E. König and G. Ritter, Solid State Commun., 18, 279 (1976).
5 E. König, G. Ritter, W. Irler and S. M. Nelson, to be published.
6 E. König, G. Ritter, B. Braunecker, K. Madeja, H. A. Goodwin and F. E. Smith, Ber. Bunsenges. Phys. Chem., 76, 393 (1972).
7 E. König, G. Ritter, H. Spiering, S, Kremer, K. Madeja and A. Rosenkranz, J. Chem. Phys., 56, 3139 (1972).
8 J. Fujita, A. E. Martell and K. Nakamoto, J. Chem. Phys., 36, 324 (1962); ibid., 36, 331 (1962).
9 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York (1963).
10 M. I. Schmelz, I. Nakagawa, S. I. Mizushima and J. V. Quagliano, J. Am. Chem. Soc., 81, 287 (1959).
11 E. König and K. Madeja, Spectrochim. Acta, 23A, 45 (1967).
12 C. Aderhold, F. Baumgärtner, E. Dornberger and B. Kanellakopulos, Z. Naturforsch., 33A, 1268 (1978).
13 E. König, G. Ritter, W. Irler and B. Kanellakopulos, J. Phys. C., 10, 603 (1977).
14 E. König, G. Ritter, W. Irler, H. A. Goodwin and B. Kanellakopulos, J. Phys. Chem. Solids, 39, 521 (1978).
15 G. Ritter, E. König, W. Irler and H. A. Goodwin, Inorg. Chem., 17, 224 (1978).
16 E. König, G. Ritter and H. A. Goodwin, Chem. Phys., 1, 17 (1973).
17 E. König, G. Ritter and H. A. Goodwin, Chem. Phys., 5, 211 (1974).
18 E. König, G. Ritter and B. Kanellakopulos, J. Phys. C., 7, 2681 (1974).
19 R. L. Collins and J. C. Travis, "Mössbauer Effect Methodology", Vol, 3, 123 (1967), Plenum Press (New York).
20 K. Madeja and E. König, J. Inorg. Nucl. Chem., 25, 377 (1963).
21 E. König, Coord. Chem. Rev., 3, 471 (1968).
22 E. König and K. J. Watson, Chem. Phys. Lett., 6, 457 (1970).
23 E. König and K. Madeja, Inorg. Chem., 7, 1848 (1968).
24 E. König, G. Ritter and B. Kanellakopulos, J. Chem. Phys., 58, 3001 (1973).
25 R. J. Butcher, J. R. Ferraro and E. Sinn, Chem. Commun. 910 (1976).
26 E. J. Cukauskas, B. S. Deaver and E. Sinn, Inorg. Nucl. Chem. Lett., 13, 283 (1977).
27 E. J. Cukauskas, B. S. Deaver and E. Sinn, J. Chem. Phys., 67, 1257 (1977).
28 A. P. Summerton, A. A. Diamantis and M. R. Snow, Inorg. Chim. Acta, 27, 123 (1978).
29 E. König, G. Ritter and H. A. Goodwin, J. Inorg. Nucl. Chem., 39, 1131 (1977).
30 E. König, G. Ritter and H. A. Goodwin, J. Inorg. Nucl. Chem., 39, 1773 (1977).
31 G. Ritter, E. König and H. A. Goodwin, J. Inorg. Nucl. Chem., in the press.