The expression $5\sigma - {}^{13}/_2\pi - 5B - 8C$ depends on the ligands in roughly the same way as $10Dq = 3\sigma - 4\pi$. The activation energy for stereomobility increases for larger σ and smaller π parameters, that is approximately for increasing $10Dq$. This is indeed the tendency which seems to summarize the experimental data.[33,37] For instance, for the Co(III) β-diketonates $5\sigma - {}^{13}/_2\pi - 5B - 8C$ is found to be negative, so that the dissociation and the $C_{4v} \rightarrow D_{3h}$ process may proceed in a concerted manner. In the aquation of *trans*-Co(en)$_2$AX complexes, where X is the leaving ligand, the reactions are stereomobile when A is a π donor (Cl⁻, OH⁻, etc.); otherwise the reactions are stereoretentive.[3] This is consistent with the appearance of the negative π coefficient in the above expression. There is no need to invoke the role of metal 4p orbitals, as in the π-bonding theory of Basolo and Pearson.[3,50] A more detailed treatment of the Co(en)$_2$AX complexes, accounting for the differences between the coordinated ligands, as well as for the different stereochemical aspects, will be published subsequently.[51]

Another confirmation of the spin flip hypothesis can be derived from the fact that even those Co(en)$_2$AX complexes that do exhibit stereomobility upon aquation become stereoretentive when the amine ligands are replaced by the stronger diimine ligands.[52]

Conclusion

In racemizations, isomerizations, and stereomobile substitution reactions of strong-field d⁶ complexes, a quintet state (exceptionally perhaps a triplet state) has to be formed somewhere along the reaction coordinate. Within the framework of ligand field theory, this conclusion appears to be inescapable.

In all cases, the reason for the necessity of a spin flip is basically the same: both in the six-coordinated complex of Figure 1 and in the five-coordinated complex of Figure 2, the stereomobility forces one low-lying π orbital to become essentially a high-lying σ orbital. In the thermal reactions of low-spin d⁶ systems, this orbital is doubly occupied, and the resulting destabilization is responsible for a very high energy barrier: in the Woodward–Hoffmann sense, the reactions are strongly forbidden. Apparently, when a reacting transition-metal complex is given the choice between a Woodward–Hoffmann type selection rule and a spin selection rule ($S = 0 \nrightarrow S = 2$), it overcomes the latter one more easily than the former one.

(50) Pearson, R. G.; Basolo, F. *J. Am. Chem. Soc.* **1956**, *78*, 4878.
(51) Vanquickenborne, L. G.; Pierloot, K., to be submitted for publication.
(52) Aprile, F.; Basolo, F.; Illuminati, G.; Maspero, F. *Inorg. Chem.* **1968**, *7*, 519.

The Nature of Proposed Six-Coordinate "Spin-Triplet Iron(II)": Low-Spin Iron(II) Cation/High-Spin Iron(III) Anion Complexes. A Chemical Application of Magnetic Hyperfine Interaction

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The preparation of a number of low-spin iron(II) cation/high-spin iron(III) anion complexes of the type [Fe^{II}(diimine)$_3$]$_m$[Fe^{III}(dianion)$_3$]$_n$ (diimine = 1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, or 2,2'-bipyridyl; dianion = oxalate, malonate; m:n = 1:1, 3:2, 2:1) is reported. The ^{57}Fe Mössbauer effect shows, as the result of superposition of the two individual spectra, a single doublet characterized by $\Delta E_Q \sim 0.28$ mm s⁻¹ and $\delta^{IS} \sim +0.30$ mm s⁻¹. An external magnetic field resolves the doublet into a central Collins-type iron(II) spectrum and a six-line hyperfine spectrum with $564 \leq H_{int} \leq 581$ kG typical for iron(III). The spectra are practically identical with those of a series of red iron compounds reported earlier, such as Fe(phen)$_2$ox·5H$_2$O and Fe(phen)$_2$mal·7H$_2$O. A new formulation for the latter type compounds is proposed in terms of low-spin iron(II) and high-spin iron(III) species. The new formulation is consistent with the known physical properties of the red iron compounds, previously considered to have a spin-triplet ground state. The implications of the present results concerning the proposals for a triplet ground state in six-coordinate iron(II) complexes are considered.

Introduction

Several years ago, one of the present authors reported on the synthesis of a series of red heterocyclic (diimine)iron complexes that were believed to be representatives for the rare case of a spin-triplet ground state in iron(II).[1] Two characteristic species of this series may serve as an example, viz., the phenanthroline complexes described as (oxalato)bis-(1,10-phenanthroline)iron(II) pentahydrate, [Fe(phen)$_2$ox]·5H$_2$O, and (malonato)bis(1,10-phenanthroline)iron(II) heptahydrate, [Fe(phen)$_2$mal]·7H$_2$O. Analogous products had

been obtained with 4,7-dimethyl-1,10-phenanthroline and 2,2'-bipyridyl as ligands. The proposed $S = 1$ electronic ground state was supported by physical measurements such as the magnetism of the solid compounds, subsequently extended to below 1 K;[2] the magnetism in solution; the ^{57}Fe Mössbauer effect including magnetic hyperfine studies, albeit only for small Doppler velocities; the IR vibrational spectra; and the electronic spectra in the UV, vis, and near-IR regions. More recently, the preparation of the two characteristic 1,10-phenanthroline iron complexes was repeated under the rigorous exclusion of oxygen.[3] The resulting compounds are

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(1) König, E.; Madeja, K. *Inorg. Chem.* **1968**, *7*, 1848.
(2) König, E.; Ritter, G.; Kanellakopulos, B. *J. Chem. Phys.* **1973**, *58*, 3001.

a violet [Fe(phen)₂ox]·5H₂O complex, showing a continuous high-spin ($^5T_2$) ⇌ low-spin ($^1A_1$) transition centered at $T_c \sim$ 205.4 K, and a violet [Fe(phen)₂mal]·2H₂O complex, which is a normal paramagnet between 4.2 and 300 K with a high-spin $^5T_2$ ground state. It should be noted that the violet color of these compounds is much more in line with that of other members of the [Fe(phen)₂X₂] series (X = univalent anionic ligand).[4–6]

As a consequence of these results, the original red "spin-triplet iron(II)" compounds were carefully reexamined. Essentially all data described previously were confirmed. However, an important new observation was made. We have reported earlier[2] that, if the ^{57}Fe Mössbauer effect of the red compounds is studied at 4.2 K in an external magnetic field of, e.g., 40 kG, apart from two weak outer lines, a hyperfine spectrum normally typical for low-spin iron(II) is found. It should be observed that this simple result is obtained only for small Doppler velocity, e.g., ±4.0 mm s⁻¹. If a considerably higher Doppler velocity, e.g., ±15.0 mm s⁻¹, is employed, a hyperfine spectrum characteristic of iron(III) is observed in addition. The important fact is that the fractional intensity of the iron(III) hyperfine component spectrum appears to be almost the same for all the red compounds investigated. Moreover it is found that even different, i.e., independently prepared, samples of the same red compound similarly produce the same fractional intensity of the iron(III) hyperfine spectrum. This finding precludes the possibility that the additional hyperfine spectrum could be attributed to some iron(III) impurity, since differing amounts of impurity would be expected for different compounds as well as for different samples of the same compound. It thus became clear that iron(III) forms an integral constituent of the reported red iron complexes. Unfortunately, all subsequent attempts at an elucidation of the problem by means of various physical measurements were not successful. We have therefore resorted to the synthesis of compounds that were expected to show chemical properties and to produce physical data similar to those of the red iron compounds.

In this paper, we report the preparation of a series of low-spin iron(II) cation/high-spin iron(III) anion complexes and the study of some of their physical properties. The nature of the red "spin-triplet iron(II)" complexes is investigated, particularly on the basis of ^{57}Fe Mössbauer-effect magnetic hyperfine spectra. The most likely formulation of the red iron compounds is then deduced by analogy with the results on the new low-spin iron(II)/high-spin iron(III) complexes.

Experimental Section

Preparations. A solution containing [FeL₃]Cl₂ (L = phen, 4,7-(CH₃)₂-phen, or bpy) was prepared as follows: Freshly prepared iron(II) chloride tetrahydrate (0.6 g; 3 mmol) was added to a suspension of L (9 mmol) in hot water (100 mL when L = phen or 4,7-(CH₃)₂-phen; 15 mL when L = bpy). The mixture was kept hot for 10 min and then filtered.

To the deep red filtrate of [FeL₃]Cl₂ was slowly added a solution of potassium tris(oxalato)ferrate(III) (1 g) in water (50 mL) (when L = phen or 4,7-(CH₃)₂-phen) or sodium tris(oxalato)ferrate(III) (1 g) in water (15 mL) (when L = bpy) or potassium tris(malonato)-ferrate(III) (1 g) in water (50 mL when L = phen or 4,7-(CH₃)₂-phen; 15 mL when L = bpy). When the mixture was cooled bright red crystals of the product separated. These were washed with ice-cold water and air-dried.

(1) Tris(1,10-phenanthroline)iron(II) Tris(oxalato)ferrate(III) Pentadecahydrate, [Fe(phen)₃]₂[Fe(ox)₃]₂·15H₂O. Anal. Calcd for Fe₅C₁₂₀H₁₀₂N₁₈O₃₉: C, 53.37; H, 3.81; N, 9.34; O, 23.13; Fe, 10.38;

H₂O, 10.01. Found: C, 53.17; H, 3.90; N, 9.33; O, 23.03; Fe, 10.40; H₂O, 10.18.

(2) Tris(1,10-phenanthroline)iron(II) Tris(malonato)ferrate(III) Dotriacontahydrate, [Fe(phen)₃]₃[Fe(mal)₃]₂·32H₂O. Anal. Calcd for Fe₅C₁₂₆H₁₄₈N₁₈O₅₆: C, 48.96; H, 4.83; N, 8.16; O, 29.02; Fe, 9.07; H₂O, 18.65. Found: C, 49.05; H, 4.91; N, 8.43; O, 28.60; Fe, 8.81; H₂O, 18.52.

(3) Tris(4,7-dimethyl-1,10-phenanthroline)iron(II) Tris(oxalato)-ferrate(III) Pentacosahydrate, [Fe(4,7-(CH₃)₂-phen)₃]₃[Fe(ox)₃]₂·25H₂O. Anal. Calcd for Fe₅C₁₃₈H₁₅₈N₁₈O₄₉: C, 52.92; H, 5.08; N, 8.05; O, 25.03; Fe, 8.92; H₂O, 14.38. Found: C, 52.83; H, 5.02; N, 8.10; O, 24.60; Fe, 9.03.

(4) Tris(4,7-dimethyl-1,10-phenanthroline)iron(II) Tris(malonato)ferrate(III) Pentacosahydrate, [Fe(4,7-(CH₃)₂-phen)₃]₃[Fe-(mal)₃]₂·25H₂O. Anal. Calcd for Fe₅C₁₄₄H₁₇₀N₁₈O₄₉: C, 53.77; H, 5.33; N, 7.84; O, 24.38; Fe, 8.68; H₂O, 14.00. Found: C, 53.20; H, 5.30; N, 7.78; O, 24.40; Fe, 8.65.

(5) Sodium Tris(2,2'-bipyridyl)iron(II) Tris(oxalato)ferrate(III), [Fe(bpy)₃]Na[Fe(ox)₃]. Anal. Calcd for Fe₂NaC₃₆H₂₄N₆O₁₂: C, 49.85; H, 2.79; N, 9.69; O, 22.14; Na, 2.65; Fe, 12.88. Found: C, 49.08; H, 2.95; N, 9.73; O, 23.00; Na, 2.22; Fe, 12.90.

(6) Tris(2,2'-bipyridyl)iron(II) Tris(malonato)ferrate(III) Chloride Heptadecahydrate, [Fe(bpy)₃]₂[Fe(mal)₃]Cl·17H₂O. Anal. Calcd for Fe₃C₆₉H₈₈N₁₂O₂₉Cl: C, 47.29; H, 5.06; N, 9.59; O, 26.48; Fe, 9.56; Cl, 2.02; H₂O, 17.48. Found: C, 47.15; H, 5.05; N, 9.69; O, 26.0; Fe, 9.43; Cl, 2.11; H₂O, 17.11.

Magnetic Measurements. The magnetism between 90 and 303 K was measured with a Newport Instruments variable-temperature balance according to the Gouy method. HgCo(NCS)₄ was used as the calibrant. The molar magnetic susceptibilities were corrected for diamagnetism of the constituents. The effective magnetic moment, μ_{eff}, was determined according to $\mu_{eff} = 2.828(\chi_m^{cor}T)^{1/2}$, χ_m^{cor} being the corrected molar susceptibility in emu mol⁻¹ and T the temperature in K. In the following, susceptibilities and μ_{eff} values are always given per Fe atom.

^{57}Fe Mössbauer Effect. Mössbauer-effect measurements were performed with a spectrometer of the constant-acceleration type (Elscint AME-30A) operating in the multiscalar mode. The source was 20-mCi ^{57}Co in copper, giving a minimum observable line width of 0.23 mm s⁻¹. The system was calibrated with a metallic iron absorber. All velocity scales and isomer shifts refer 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. Measurements at 4.2 K were obtained by a separate spectrometer (Nuclear Data ND 2400, modulation of the pulse height achieved by the driving wave form) and a suitable helium Dewar. In order to perform magnetic hyperfine measurements, this spectrometer was equipped with a superconducting coil capable of producing 55 kG. The magnetic field was parallel to the direction of the γ rays.

Results and Discussion

Physical Measurements of Low-Spin Iron(II)/High-Spin Iron(III) Complexes. The iron(II)/iron(III) complexes reported in this study have been chosen such as to duplicate, as closely as possible, the ^{57}Fe Mössbauer spectra of the red "spin-triplet iron(II)" complexes reported earlier.[1,2] Indeed, the Mössbauer spectra of the present compounds show, between 4.2 and 300 K, a single closely spaced doublet with a quadrupole splitting, ΔE_Q, between 0.25 and 0.35 mm s⁻¹ (at 308 K) and an isomer shift $\delta^{IS} \sim 0.33$ mm s⁻¹ at 308 K which slightly decreases to $\delta^{IS} \sim 0.27$ mm s⁻¹ at 4.2 K. The detailed values of the Mössbauer-effect parameters have been collected in Table I. Comparison with Table V of our earlier report[1] reveals that the values for the new compounds are practically identical, within the experimental uncertainty, to the results for the corresponding "spin-triplet iron(II)" compounds. Thus, e.g., $\Delta E_Q = 0.24$ mm s⁻¹ and $\delta^{IS} = +0.35$ mm s⁻¹ for [Fe-(phen)₃]₃[Fe(mal)₃]₂·32H₂O at 308 K closely approach the values $\Delta E_Q = 0.23$ mm s⁻¹ and $\delta^{IS} = +0.33$ mm s⁻¹ for red "Fe(phen)₂mal·7H₂O" at 298 K with similar agreement at 4.2 K. In all compounds studied here, the single observed doublet apparently is formed by a superposition of the Mössbauer spectra of the low-spin iron(II) cation and the high-spin

(3) König, E.; Schnakig, R.; Ritter, G.; Irler, W.; Kanellakopulos, B.; Powietzka, B. *Inorg. Chim. Acta* **1979**, *35*, 239.

(4) Madeja, K.; König, E. *J. Inorg. Nucl. Chem.* **1963**, *25*, 377.

(5) König, E.; Madeja, K. *Inorg. Chem.* **1967**, *6*, 48.

(6) König, E.; Ritter, G.; Madeja, K.; Böhmer, W. H. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 390.

Table I. ^{57}Fe Mössbauer-Effect Parameters for Low-Spin Iron(II) Cation/High-Spin Iron(III) Anion Complexes

compd	T, K	$\Delta E_Q,^a$ mm s^{-1}	$\delta^{IS},^b$ mm s^{-1}
[Fe(phen)$_3$]$_3$[Fe(ox)$_3$]$_2$·15H$_2$O	308	0.25	+0.33
	4.2	0.27	+0.29
[Fe(phen)$_3$]$_3$[Fe(mal)$_3$]$_2$·32H$_2$O	308	0.24	+0.35
	80	0.26	+0.31
	4.2	0.27	+0.28
[Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_3$[Fe(ox)$_3$]$_2$·25H$_2$O	308	0.26	+0.33
	80	0.26	+0.29
	4.2	0.27	+0.27
[Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_3$[Fe(mal)$_3$]$_2$·25H$_2$O	308	0.26	+0.34
	80	0.27	+0.29
	4.2	0.27	+0.27
[Fe(bpy)$_3$]Na[Fe(ox)$_3$]	308	0.32	+0.31
	4.2	0.34	+0.25
[Fe(bpy)$_3$]$_2$[Fe(mal)$_3$]Cl·17H$_2$O	308	0.35	+0.33
	80	0.37	+0.29
	4.2	0.37	+0.27

^{a} Experimental uncertainty ±0.01 mm s^{-1}. ^{b} Experimental uncertainty ±0.02 mm s^{-1}.

iron(III) anion. The Mössbauer parameters for these are so closely similar that an experimental separation of the two spectra would not be expected. Thus, e.g., $\Delta E_Q = 0.15$ mm s^{-1} and $\delta^{IS} = +0.31$ mm s^{-1} have been reported for [Fe(phen)$_3$]$^{2+}$ [7,8] and $\Delta E_Q = 0.32$ mm s^{-1} and $\delta^{IS} = +0.25$ mm s^{-1} for [Fe(ox)$_3$]$^{3-}$; [9,10] on the other hand, for [Fe(phen)$_3$]$_3$[Fe(ox)$_3$]$_2$·15H$_2$O, we have obtained $\Delta E_Q = 0.25$ mm s^{-1} and $\delta^{IS} = +0.33$ mm s^{-1} at 308 K (cf. Table I). The decreasing values of the isomer shift with lowering of temperature (viz., Table I) are unusual, although the differences are generally small. We assume that this is the result of a superposition of two spectra which have somewhat different temperature dependences of the quadrupole splitting.

The situation is drastically changed if the ^{57}Fe Mössbauer effect is measured within an applied magnetic field at 4.2 K. As an example, let us consider the results for [Fe(phen)$_3$]$_3$[Fe(mal)$_3$]$_2$·32H$_2$O; cf. Figure 1. As a consequence of the magnetic hyperfine interaction, the unique quadrupole doublet is resolved into a multiple-line spectrum of somewhat complicated nature. The center consists of a Collins-type spectrum [11] characteristic for nonmagnetic iron and thus originates from the low-spin [Fe(phen)$_3$]$^{2+}$ component of the substance. This part of the spectrum (including the two central lines of the additional spectrum, which are in close proximity) is virtually identical with the low-velocity hyperfine spectrum of the corresponding red "spin-triplet iron(II)" compound, i.e., Fe(phen)$_2$mal·7H$_2$O reported earlier. [2] The splitting of the additional six-line spectrum is essentially complete at 20 kG. The effective field may be estimated as $H_{eff} = 555$ kG, this value being characteristic for iron(III). Consequently, this section of the hyperfine spectrum is originating from the high-spin [Fe(mal)$_3$]$^{3-}$ component of the substance. It should be noted that the hyperfine lines attributed to iron(III) are also apparent as very weak humps in the $H = 0$ spectrum of the compound, viz., Figure 1. These lines show the complete splitting, i.e., the same H$_{int}$ as the iron(III) hyperfine spectrum at 20 or 40 kG. This observation indicates slow relaxation for a small fraction of the involved iron(III) ions, a result which
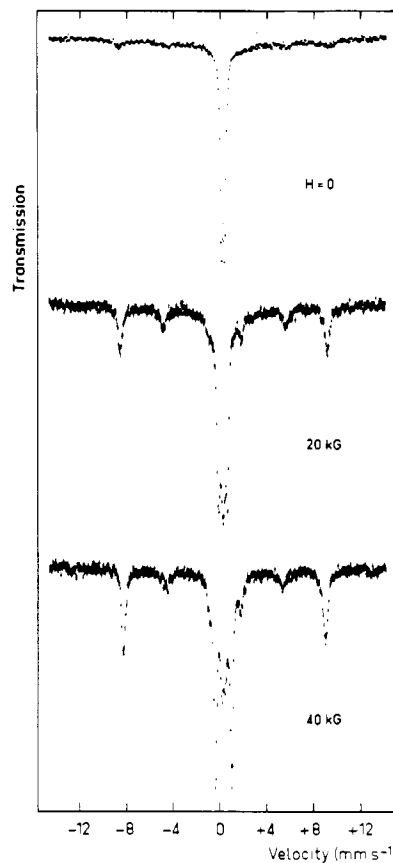

Figure 1. ^{57}Fe Mössbauer-effect spectra of [Fe(phen)$_3$]$_3$[Fe(mal)$_3$]$_2$·32H$_2$O at 4.2 K for magnetic field strengths $H = 0$, 20, and 40 kG.
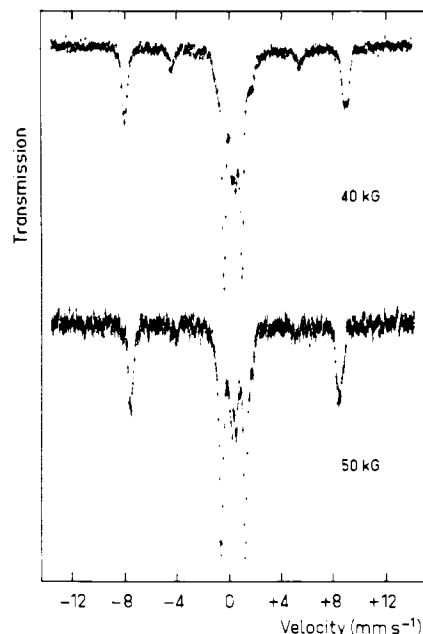

Figure 2. ^{57}Fe Mössbauer-effect spectra of [Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_3$[Fe(ox)$_3$]$_2$·25H$_2$O (upper spectrum, $H = 40$ kG) and so-called Fe-(4,7-(CH$_3$)$_2$-phen)$_2$ox·4H$_2$O (reformulated as [Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_2$[Fe(ox)$_3$](ox)$_{1/2}$·14H$_2$O) (lower spectrum, $H = 50$ kG) at 4.2 K for the indicated strength of the magnetic field.

is difficult to rationalize as long as the detailed structure of the compound is unknown. A small amount of an iron(III) impurity cannot be excluded. The results for the other iron-(II)/iron(III) complexes studied here are very similar to those discussed above for [Fe(phen)$_3$]$_3$[Fe(mal)$_3$]$_2$·32H$_2$O. In every

(7) Berrett, R. R.; Fitzsimmons, B. W.; Owusu, A. *J. Chem. Soc. A* **1968**, 1575.
(8) Collins, R. L.; Pettit, R.; Baker, W. A. *J. Inorg. Nucl. Chem.* **1966**, *28*, 1001.
(9) Gallagher, P. K.; Kurkjian, C. R. *Inorg. Chem.* **1966**, *5*, 214.
(10) Greenwood, N. N.; Gibb, T. C. "Mössbauer Spectroscopy"; Chapman and Hall: London, 1971.
(11) Collins, R. L.; Travis, J. C. *Moessbauer Eff. Methodol.* **1967**, *3*, 123.

Table II. Magnetic Data for $[Fe(phen)_3]_3[Fe(ox)_3]_2 \cdot 15H_2O$ (A) and $[Fe(phen)_3]_3[Fe(mal)_3]_2 \cdot 32H_2O$ (B)

	A		B	
T, K	$10^6 \times$ $\chi_m^{cor,a,b}$ emu mol⁻¹	μ_{eff},^{c} μ_B	$10^6 \times$ $\chi_m^{cor,a,d}$ emu mol⁻¹	μ_{eff},^{c} μ_B
98	17 580	3.73	17 120	3.66
127	13 660	3.72	13 230	3.67
156	11 080	3.72	10 770	3.67
185	9330	3.72	9050	3.66
215	8010	3.71	7810	3.66
245	7020	3.71	6810	3.65
275	6250	3.71	6100	3.66
303	5670	3.71	5530	3.66

^{a} Per Fe atom. Experimental uncertainty $\pm 100 \times 10^{-6}$ emu mol⁻¹. ^{b} Diamagnetic correction $\chi^{dia} = -355 \times 10^{-6}$ emu mol⁻¹. ^{c} Per Fe atom. Experimental uncertainty $\pm 0.02 \mu_B$. ^{d} Diamagnetic correction $\chi^{dia} = -404 \times 10^{-6}$ emu mol⁻¹.

Table III. Magnetic Data for $[Fe(4,7-(CH_3)_2-phen)_3]_3[Fe(ox)_3]_2 \cdot 25H_2O$ (A) and $[Fe(4,7-(CH_3)_2-phen)_3]_3[Fe(mal)_3]_2 \cdot 25H_2O$ (B)

	A		B	
T, K	$10^6 \times$ $\chi_m^{cor,a,b}$ emu mol⁻¹	μ_{eff},^{c} μ_B	$10^6 \times$ $\chi_m^{cor,a,d}$ emu mol⁻¹	μ_{eff},^{c} μ_B
98	17 590	3.71	17 340	3.69
127	13 760	3.74	13 450	3.70
156	11 220	3.74	10 970	3.70
185	9430	3.73	9140	3.68
215	8200	3.76	7870	3.68
245	7240	3.77	6920	3.68
275	6500	3.78	6280	3.72
303	5940	3.79	5650	3.70

^{a} Per Fe atom. Experimental uncertainty $\pm 100 \times 10^{-6}$ emu mol⁻¹. ^{b} Diamagnetic correction $\chi^{dia} = -340 \times 10^{-6}$ emu mol⁻¹. ^{c} Per Fe atom. Experimental uncertainty $\pm 0.02 \mu_B$. ^{d} Diamagnetic correction $\chi^{dia} = -351 \times 10^{-6}$ emu mol⁻¹.

Table IV. Magnetic Data for $[Fe(bpy)_3]Na[Fe(ox)_3]$ (A) and $[Fe(bpy)_3]_2[Fe(mal)_3]Cl \cdot 17H_2O$ (B)

	A			B	
T, K	$10^6 \times$ $\chi_m^{cor,a,b}$ emu mol⁻¹	μ_{eff},^{c} μ_B	T, K	$10^6 \times$ $\chi_m^{cor,a,d}$ emu mol⁻¹	μ_{eff},^{c} μ_B
92	23 136	4.13	90	16 160	3.41
118	18 200	4.14	118	12 460	3.43
146	14 710	4.14	146	10 000	3.42
176	12 230	4.15	175	8270	3.40
205	10 520	4.15	205	7060	3.40
225	9620	4.16	235	6210	3.42
245	8770	4.14	265	5580	3.44
275	7800	4.14	294	4990	3.42
303	7148	4.16			

^{a} Per Fe atom. Experimental uncertainty $\pm 100 \times 10^{-6}$ emu mol⁻¹. ^{b} Diamagnetic correction $\chi^{dia} = -211 \times 10^{-6}$ emu mol⁻¹. ^{c} Per Fe atom. Experimental uncertainty $\pm 0.02 \mu_B$. ^{d} Diamagnetic correction $\chi^{dia} = -339 \times 10^{-6}$ emu mol⁻¹.

Table V. Values of the Molar Extinction Coefficient ϵ for Low-Spin Iron(II) Cation/High-Spin Iron(III) Anion Complexes

compd	ϵ, L mol⁻¹ cm⁻¹	rel iron(II) content
$[Fe(phen)_3](ClO_4)_2$	10 200	1
$[Fe(phen)_3]_3[Fe(ox)_3]_2 \cdot 15H_2O$	30 290	2.97
$[Fe(phen)_3]_3[Fe(mal)_3]_2 \cdot 32H_2O$	31 650	3.10
$[Fe(4,7-(CH_3)_2-phen)_3](ClO_4)_2$	13 740	1
$[Fe(4,7-(CH_3)_2-phen)_3]_3[Fe(ox)_3]_2 \cdot 25H_2O$	40 740	2.97
$[Fe(4,7-(CH_3)_2-phen)_3]_3[Fe(mal)_3]_2 \cdot 25H_2O$	40 470	2.95
$[Fe(bpy)_3](ClO_4)_2$	8 440	1
$[Fe(bpy)_3]Na[Fe(ox)_3]$	8 150	0.97
$[Fe(bpy)_3]_2[Fe(mal)_3]Cl \cdot 17H_2O$	16 960	2.01

case, the hyperfine pattern consists of an iron(II) and an iron(III) component spectrum, the internal field of the latter being characterized by $564 \le H_{int} \le 581$ kG. A further example is illustrated in Figure 2, which shows the ^{57}Fe Mössbauer-effect hyperfine spectrum of $[Fe(4,7-(CH_3)_2-phen)_3]_3[Fe(ox)_3]_2 \cdot 25H_2O$ compared with that of the red so-called $Fe(4,7-(CH_3)_2-phen)_2ox \cdot 4H_2O$.

The magnetic susceptibility of solid samples of the low-spin iron(II) cation/high-spin iron(III) anion complexes was studied between 98 and 303 K. In all instances, an essentially temperature-independent value of the effective magnetic moment per Fe atom was obtained. Thus, e.g., $\mu_{eff} = 3.66$ μ_B for $[Fe(phen)_3]_3[Fe(mal)_3]_2 \cdot 32H_2O$ (cf. Table II) corresponds to $\mu_{eff} = 3.85$ μ_B, a value obtained from that found earlier[1] for the red "spin-triplet iron(II)" compound $Fe(phen)_2mal \cdot 7H_2O$ by adjusting it to the proposed composition $[Fe(phen)_3]_2$-$[Fe(mal)_3](mal)_{1/2} \cdot 20H_2O$; cf. Table VII. On the other hand, $\mu_{eff} = 3.71$ μ_B at 98 K and $\mu_{eff} = 3.79$ μ_B at 303 K have been obtained, e.g., for the compound $[Fe(4,7-(CH_3)_2-phen)_3]_3$-$[Fe(ox)_3]_2 \cdot 25H_2O$ (cf. Table III), the corresponding values for red $Fe(4,7-(CH_3)_2-phen)_2ox \cdot 4H_2O^1$ reformulated as $[Fe-(4,7-(CH_3)_2-phen)_3]_2[Fe(ox)_3](ox)_{1/2} \cdot 14H_2O$ varying between $\mu_{eff} = 3.77$ μ_B at 77 K and $\mu_{eff} = 4.18$ μ_B at 293 K (cf. Table VII). The difference for this and some other substances is not significant but rather reflects the different proposed composition of the compounds being compared. The detailed results for the iron(II)/iron(III) complexes studied at present have been collected in Tables II–IV.

The molar extinction coefficients (which were calculated on the basis of the proposed formulas) were determined at the absorbance maximum of the aqueous solution of the particular species, e.g., at 19 570 cm⁻¹ for the phenanthroline complexes. The resulting values of ϵ are very close to the integral multiples of the ϵ values for the simple iron(II) complexes $[FeL_3]X_2$ (L = phen, 4,7-$(CH_3)_2$-phen, or bpy), which are expected for the respective iron(II):iron(III) ratios; cf. Table V.

The Hyperfine Interaction in "Spin-Triplet Iron(II)" Compounds. ^{57}Mössbauer-effect studies in external magnetic fields of up to 55 kG at 4.2 K of the red compounds, previously believed to contain spin-triplet iron(II), produce magnetic hyperfine spectra that are closely similar to those of the iron(II)/iron(III) complexes discussed above. The spectra of the red compounds so-called $Fe(phen)_2ox \cdot 5H_2O$, Fe-$(phen)_2mal \cdot 7H_2O$, and $Fe(phen)_2F_2 \cdot 4H_2O$ reported earlier[2] form the centers of the complete hyperfine spectra of these substances. As an example, Figure 3 shows the hyperfine spectrum of red $Fe(phen)_2mal \cdot 7H_2O$ for a magnetic field strength of 40 kG. It can be readily seen that the spectrum is virtually identical with the hyperfine spectrum of $[Fe-(phen)_3]_3[Fe(mal)_3]_2 \cdot 32H_2O$; cf. Figure 1. Similarly, the hyperfine spectrum of the red compound $Fe(4,7-(CH_3)_2-$phen)_2ox \cdot 4H_2O$ closely resembles that of $[Fe(4,7-(CH_3)_2-$phen)_3]_3[Fe(ox)_3]_2 \cdot 25H_2O$; cf. Figure 2. The results for the remaining "spin-triplet iron(II)" compounds are similar. These results indicate that the red iron compounds described earlier are in fact low-spin iron(II) cation/high-spin iron(III) anion complexes similar to those which form the subject matter of the present study.

Conclusions. The Correct Formulation of the Red Iron Compounds. The new low-spin iron(II) cation/high-spin iron(III) anion complexes were all prepared under more or less the same experimental conditions. Despite this a variety of different formulas are proposed involving different iron-(II):iron(III) stoichiometries. The proposed formulas are based primarily on the complete elemental analyses obtained, as

Table VI. Analytical Data and Formulas for the Red Iron Compounds

compd		% C	% H	% N	% O	% Fe	% H$_2$O
[Fe(phen)$_3$]$_2$[Fe(ox)$_3$](ox)$_{1/2}$·14H$_2$O^a	calcd	52.45	4.23	9.29	24.76	9.26	13.94
	found	52.68	4.28	9.42		9.55	15.29
[Fe(phen)$_3$]$_2$[Fe(mal)$_3$](mal)$_{1/2}$·20H$_2$O^b	calcd	50.39	4.87	8.55	27.67	8.52	18.33
	found	50.66	4.97	8.58		8.76	19.33
[Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_2$[Fe(ox)$_3$](ox)$_{1/2}$·14H$_2$O^c	calcd	55.27	5.10	8.50	22.66	8.47	12.76
	found	55.25	4.96	8.96	20.15	8.94	11.50
[Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_2$[Fe(mal)$_3$](mal)$_{1/2}$·20H$_2$O^d	calcd	53.17	5.62	7.88	25.49	7.85	16.88
	found	52.76	5.16	8.17	24.74	7.77	17.67
[Fe(bpy)$_3$]$_2$[Fe(ox)$_3$](ox)$_{1/2}$·8H$_2$O^e	calcd	51.67	4.15	10.80	22.62	10.80	9.25
	found	51.82	4.38	10.82		11.12	10.31
[Fe(bpy)$_3$]$_2$[Fe(mal)$_3$](mal)$_{1/2}$·8H$_2$O^f	calcd	52.72	4.46	10.47	21.92	10.43	8.97
	found	52.65	4.49	10.54		10.60	10.20

^{a} Previous formulation as Fe(phen)$_2$ox·5H$_2$O. ^{b} Previous formulation as Fe(phen)$_2$mal·7H$_2$O. ^{c} Previous formulation as Fe(4,7-(CH$_3$)$_2$-phen)$_2$ox·4H$_2$O. ^{d} Previous formulation as Fe(4,7-(CH$_3$)$_2$-phen)$_2$mal·7H$_2$O. ^{e} Previous formulation as Fe(bpy)$_2$ox·3H$_2$O. ^{f} Previous formulation as Fe(bpy)$_2$mal·3H$_2$O.
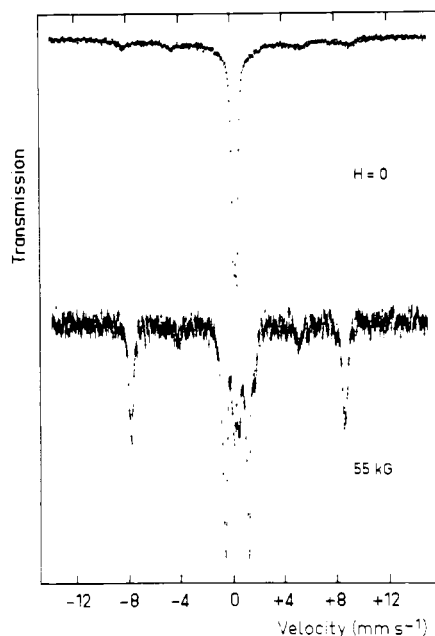
Figure 3. ^{57}Fe Mössbauer-effect spectra of so-called Fe-(phen)$_2$mal·7H$_2$O (reformulated as [Fe(phen)$_3$]$_2$[Fe(mal)$_3$]-(mal)$_{1/2}$·20H$_2$O) at 4.2 K for magnetic field strengths H = 0 and 55 kG.

detailed in the Experimental Section. It should be pointed out, however, that possible alternative formulas cannot readily be distinguished on the basis of analytical data alone. Such alternative formulas will involve different iron(II):iron(III) ratios and perhaps the presence of different extraneous ions. We have not been able to devise any formulas which fit all the analytical data better than those presented. Additional support for the proposed formulations is provided by the magnetic data and by the values of the molar extinction coefficients which are, in general, consistent with the indicated iron(II):iron(III) ratios.

Attempts at a separate determination of iron(III) were not successful, except for the case of phenanthroline complexes. Anal. Calcd for [Fe(phen)$_3$]$_3$[Fe(ox)$_3$]$_2$·15H$_2$O: Fe(III), 4.15. Found: Fe(III), 4.56. Calcd for [Fe(phen)$_3$]$_3$[Fe(mal)$_3$]$_2$·32H$_2$O: Fe(III), 3.63. Found: Fe(III), 3.85.

The attempted determination of separate iron(II) and iron(III) areas from magnetic hyperfine ^{57}Fe Mössbauer spectra did not provide consistent results. The possible reason for this failure is the significant overlap of the spectra and the relaxation broadening of the lines.

The occurrence of different stoichiometries in these compounds can only be ascribed to lattice forces. The mismatch in the charges of the iron(II) and iron(III) complex species necessitates ratios of these other than 1:1 or the presence of extraneous ions leading to double salts. In those instances where double salts were obtained, variations in the preparative procedure were introduced, but the same products were always obtained. It will be noted that most of the complexes are extensively hydrated. In a lattice containing cations and anions of considerably differing dimensions, in which the possibilities for hydrogen bonding to the complex anions are high, this is not surprising. At least some of this lattice water is not firmly bound. Consistent values for the extent of hydration could only be obtained when the samples were allowed to dry in the atmosphere. Loss of water of hydration occurred on desiccation, but the loss was not reproducible.

It can be seen from Table VI that the reported analytical data for the so-called "spin-triplet iron(II)" species are generally consitent with formulas similar to those of the new compounds, containing low-spin iron(II) cations and high-spin iron(III) anions. Because of the method of preparation utilized[1] the only possible extraneous ions are either oxalate or malonate. Hence the variation in formulas noted above for the new compounds is not expected for the old species and indeed the formula [FeL$_3$]$_2$[Fe(anion)$_3$](anion)$_{1/2}$·xH$_2$O is generally applicable for the latter. The differences for the hydrate water values are not considered as serious, particularly since the precision of these data, which were obtained by drying of the substances at 40 °C in vacuo, may not be high. The new formulation of the red compounds appears the more correct, since it resolves a number of inconsistencies associated with these substances. Thus, the characteristic red color of these compounds has been somewhat puzzling, particularly since all members of the Fe(phen)$_2$X$_2$ series of complexes are known to be dark violet.[4–6] The bright red color is in fact typical of the low-spin iron(II) cations, e.g., [Fe(phen)$_3$]$^{2+}$, which form an essential consistuent of the mixed iron(II)/iron(III) compounds. Obviously, the resulting color of these complexes will not be affected to any significant extent by the lightly colored iron(III) anion, e.g., [Fe(ox)$_3$]$^{3-}$. Therefore, the electronic spectra which are governed by the intense charge-transfer band of the iron(II) diimine moiety are almost identical with the spectrum of the corresponding low-spin tris iron(II) complex, e.g., [Fe(phen)$_3$]$^{2+}$, a fact known for some time. Another unusual finding has been the fact that magnetic susceptibilities of the red compounds could be determined in solution, the resulting values being practically identical with those of the solid substances.[1] This result is, of course, to be expected on the basis of the new formulation since, in solution, dissociation into the stable iron(II) cation and the iron(III) anion will take place. It should be noted that immediate decomposition results for any of the violet Fe(phen)$_2$X$_2$ complexes in all the solvents investigated.[4–6]

Table VII. Recalculated Magnetic Data for the Red Iron Compounds

compd	T, K	$10^6 \times \chi_m^{cor}$, emu mol^{-1}	μ_{eff}, μ_B
[Fe(phen)$_3$]$_2$[Fe(ox)$_3$](ox)$_{1/2}$·14H$_2$O	399.4	5863	4.33
	294.2	6847	4.01
	189.5	9568	3.91
	76.8	22258	3.70
[Fe(phen)$_3$]$_2$[Fe(mal)$_3$](mal)$_{1/2}$·20H$_2$O	359.7	5528	3.99
	293.3	6329	3.85
	190.2	9157	3.73
	75.7	22048	3.65
[Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_2$[Fe(ox)$_3$]-(ox)$_{1/2}$·14H$_2$O	293	7452	4.18
	195	10308	4.01
	77	23106	3.77
[Fe(4,7-(CH$_3$)$_2$-phen)$_3$]$_2$[Fe(mal)$_3$]-(mal)$_{1/2}$·20H$_2$O	293	7513	4.20
	195	10732	4.09
	77	25267	3.94
[Fe(bpy)$_3$]$_2$[Fe(ox)$_3$](ox)$_{1/2}$·8H$_2$O	293	7440	4.18
	195	10380	4.02
	77	23671	3.98
[Fe(bpy)$_3$]$_2$[Fe(mal)$_3$](mal)$_{1/2}$·8H$_2$O	293	6566	3.92
	195	9599	3.87
	77	23372	3.79

The results of magnetic measurements reported previously for solid samples of the red complexes have been converted to the new molecular weights. A number of characteristic values, always referring to a single Fe atom, are listed in Table VII. It is evident that the values of μ_{eff} are consistent with the proposed stoichiometry of the complexes. Let us assume that a high-spin iron(III) complex such as [Fe(ox)$_3$]$^{3-}$ is characterized by μ_{eff} = 5.90 μ_B and a low-spin iron(II) complex such as [Fe(phen)$_3$]$^{2+}$, by μ_{eff} = 0.60 μ_B. For a Fe(II):Fe(III) = 2:1 complex, we obtain then μ_{eff} = 3.44 μ_B, a value somewhat lower than the measured values. Again, the difference is not significant and may be caused, among others, by a difference in hydration of the complexes.

The nature of the red iron compounds has thus been clarified by the present results, and these results will have consequences for all those studies where the formation of an S = 1 ground state of iron(II) has been inferred on the basis of magnetic and similar nonspecific data. As typical examples we refer to a number of bis(thiocyanato)bis(substituted 1,10-phenanthroline)iron complexes,[12] to bis((cyano-C)trihydroborato)bis(1,10-phenanthroline)iron,[13] and to the thermolysis of (oxalato)bis(1,10-phenanthroline)iron(III) hydrogen oxalate.[14] Additional complexes for which a reinvestigation is desirable may be found from tabulated results of magnetic measurements.[15]

(12) Cunningham, A. J.; Ferguson, J. E.; Powell, H. K. J.; Sinn, E.; Wong, H. *J. Chem. Soc. Dalton Trans.* **1972**, 2155.
(13) Purcell, K. F.; Yeh, S. M.; Eck, J. S. *Inorg. Chem.* **1977**, *16*, 1708.
(14) Thomas, P.; Benedix, M.; Rehorek, D.; Hennig, H. *Z. Chem.* **1978**, *18*, 264.
(15) König, E.; König, G. "Magnetic Properties of Coordination and Organometallic Transition Metal Compounds". Landolt-Börnstein, New Series; Springer: Berlin, New York; 1976, Vol. II/8; 1979, Vol. II/10; 1981, Vol. II/11.

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Proton NMR Study of the High-Spin–Low-Spin Transition in Fe(phen)₂(NCS)₂ and Fe(pic)₃Cl₂·(EtOH or MeOH)

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The proton NMR spectra of spin-crossover complexes [Fe^{II}(phen)$_2$(NCS)$_2$] (phen = 1,10-phenanthroline) and [Fe^{II}(pic)$_3$]Cl$_2$·X (X = CH$_3$OH or C$_2$H$_5$OH) (pic = 2-(aminomethyl)pyridine) and their Zn(II) analogues have been determined for temperatures that span the crossover region. The line widths of all Fe(II) complexes are constant in the diamagnetic temperature region but increase markedly in the spin-transition region. At higher temperatures the line width follows a T^{-1} dependence. Second-moment measurements in the diamagnetic region reveal a close contact (~0.18 nm) between hydrogen atoms on neighboring complexes in the case of Fe(phen)$_2$(NCS)$_2$. The asymmetric broad lines in the paramagnetic region are quantitatively accounted for by using a point-dipole model of the paramagnetic shift. T_1 vs. temperature studies were made for Fe(phen)$_2$(NCS)$_2$, and the results are shown to be in conflict with predictions of a "cluster" or domain theory for the spin crossover. The results are in complete agreement with an Ising-type theory of the transition, and it is shown that the T_1 measurements readily yield several of the thermodynamic parameters in the theory.

I. Introduction

We recently completed an ESR[1] study of Mn(II) doped into [Fe^{II}(phen)$_2$(NCS)$_2$] (phen = 1,10-phenanthroline) and [Fe^{II}(pic)$_3$]Cl$_2$·EtOH (pic = 2-(aminomethyl)pyridine). These systems undergo a spin transition over a small temperature interval from a diamagnetic (S = 0) system at low temperatures to a paramagnetic (S = 2) system at higher temperatures. Our ESR studies confirmed that no phase transition of the crystal lattice accompanies this spin transition. We undertook a proton NMR study of these systems to see if additional information on the mechanism of this spin transition could be gained from this physical technique.

The spin crossover is very abrupt or discontinuous for Fe(phen)$_2$(NCS)$_2$, but the sharpness and even the crossover temperature vary with preparation. In many instances there is found a residual paramagnetism at low temperatures

(1) Rao, P. S.; Reuveni, A.; McGarvey, B. R.; Ganguli, P.; Gütlich, P. *Inorg. Chem.* **1981**, *20*, 204.