

Mössbauer Effect Study of the Electronic Ground State of Iron(II) in $[^{57}\text{Fe}_x\text{M}_{1-x}(\text{bipy})_3](\text{ClO}_4)_2$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Zn}$) and $[^{57}\text{Fe}_x\text{M}_{1-x}(\text{phen})_3](\text{ClO}_4)_2$ ($\text{M} = \text{Ni}, \text{Zn}$) at Very Low Iron Concentrations ($x \leq 0.005$)

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Earlier work in our laboratory on the effect of metal dilution on the ${}^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$ equilibrium in polycrystalline spin crossover systems of iron(II) has shown that the relative stability of the high spin state, ${}^5T_2(O_h)$, at a given temperature, increases markedly with decreasing iron concentration. These results have initiated the present work. Using ${}^{57}\text{Fe}$ Mössbauer spectroscopy, we have investigated the electronic ground state of iron(II) in the highly diluted solid solutions $[\text{Fe}_x\text{M}_{1-x}\text{L}_3]$ with $\text{L} = \text{bipy}$, $\text{M} = \text{Mn}, \text{Ni}, \text{Zn}$, $x \leq 0.005$ and $\text{L} = \text{phen}$, $\text{M} = \text{Ni}, \text{Zn}$, $x \leq 0.005$. Although the critical field potential (V_c) of the pure iron complexes, which are known to be low spin, is reported to be not far from the crossover point $V_c = \bar{P}$ (\bar{P} , the mean spin pairing energy), the effect of metal dilution does not reduce the difference $|V_c - \bar{P}|$ sufficiently as to thermally populate the ${}^5T_2(O_h)$ state at room temperature to any noticeable extent. $|V_c - \bar{P}|$ has been estimated to be $\geq 1200 \text{ cm}^{-1}$.

The quadrupole splitting and the resonance line width are nearly the same in the pure compounds and the solid solutions. The isomer shift, however, is found to increase slightly in the order $\text{M} = \text{Fe} < \text{Ni} < \text{Zn} < \text{Mn}$, and parallels the increase in the ionic radii of the M^{2+} host ions.

Introduction

First-row transition metal complexes of 1,10-phenanthroline (phen), α, α' -dipyridyl (bipy) and related ligands have attracted much interest in modern inorganic chemistry [1–3]. One of the reasons is that the electronic ground state of the central metal ion – and thus the magnetism of the complex molecule – feature interesting properties. Depending on the ligand field strength 10 Dq (for simplicity we consider the approximation of O_h -symmetry) as compared to the mean spin pairing energy \bar{P} , transition metal complexes with d^4 , d^5 , d^6 , and d^7 electron configuration may have either high spin ($10 \text{ Dq} < \bar{P}$) or low spin ($10 \text{ Dq} > \bar{P}$) elec-

tronic ground states. A good number of complexes have even been found to exhibit temperature dependent spin state equilibria high spin (HS) \rightleftharpoons low spin (LS). This phenomenon, called *magnetic crossover* or *spin crossover* [2–6], occurs if the difference $|10 \text{ Dq} - \bar{P}|$ is on the order of kT .

A relatively large variety of ${}^5T_2(O_h) \rightleftharpoons {}^1A_1(O_h)$ spin crossover systems have been found in the class of six-coordinate iron(II) complexes with nitrogen donor atoms [7]. It has been observed, mostly by magnetic susceptibility and ${}^{57}\text{Fe}$ Mössbauer effect measurements, that the spin crossover characteristics may be influenced in various ways. One of these is intra-ligand substitution, for which the group of $[\text{Fe}(\text{X-phen})_3]^{2+}$ complexes provides simple but instructive examples demonstrating the combined action of steric hindrance and electronic effects exerted by the X substituents [7–10]. Another drastic influence is ligand replacement to form a heterogeneous coordination sphere; an example is the replacement of one phen ligand in $[\text{Fe}(\text{phen})_3]^{2+}$, which is low spin, by two NCS-groups to form the spin crossover system $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, the first one of iron(II) reported in the literature [11]. The nature of the non-coordinated anion [12–14] and of the crystallizing solvent molecules [15, 16] have also been reported to play a significant rôle for the magnetic properties. The spin crossover behaviour may also depend on the way of preparing the sample [17–19], due to differences in crystal size distribution and eventually in the crystal structure, and due to lattice defects.

Recently, we have performed a systematic ${}^{57}\text{Fe}$ Mössbauer effect study of the effect of metal dilution on the spin crossover characteristics in the solid solutions of $[\text{Fe}_x\text{Zn}_{1-x}(2\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ ($0.0009 \leq x \leq 1.0$; 2-pic = 2-picolyamine) [20, 21]. The Mössbauer spectra clearly show that, at a given temperature, the HS state ${}^5T_2(O_h)$ becomes more and more favoured over the LS state ${}^1A_1(O_h)$ upon lowering the iron concentration. The observations can be interpreted on the basis of a phenomenological thermodynamic model [22], and support the idea of the spin

transition taking place in a cooperative manner [20, 23].

A very pronounced effect of metal dilution has also been demonstrated for the spin crossover characteristics in $[\text{Fe}_x\text{Me}_{1-x}(\text{phen})_2(\text{NCS})_2]$ (Me = Co, Mn, Ni) by ^{57}Fe Mössbauer spectroscopy [24]. As in the case of the 2-pic system mentioned above, the $^5\text{T}_2(\text{O}_h)$ becomes increasingly favoured over the $^1\text{A}_1(\text{O}_h)$ state with decreasing iron concentration. Even at very low temperatures (≥ 5 K), where the pure $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ compound is almost exclusively found in the LS ground state, except for some 10–15% of what is called residual paramagnetism which is created only in a particular way of preparing the compound [19], the LS ground state may be almost completely quenched if the iron concentration is sufficiently low. These results show unambiguously that the effect of metal dilution in the crossover systems studied so far [19–22, 24] is to vary the relative stabilities of the two spin states involved, shifting the transition temperature T_c to lower values. The stimulus to the present investigation emerged from what we have learned from the metal dilution studies on real spin crossover systems. The idea has been that the LS ground state of iron(II) compounds like $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$ and $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$, which are known to have ligand field strengths not very far from the critical crossover point $10 Dq = P$ [25], but apparently far enough as to cause $|10 Dq - P| > kT$, so that the HS state is not thermally accessible to any noticeable extent at room temperature, is eventually forced to turn gradually over to the HS state, if the $[\text{FeL}_3]^{++}$ complex molecules are sufficiently diluted in a $[\text{ML}_3]^{++}$ matrix (M = Mn, Ni, Zn). In the following we report the results of Mössbauer effect measurements on the solid solutions $[\text{Fe}_x\text{M}_{1-x}(\text{bipy})_3](\text{ClO}_4)_2$ (M = Mn, Ni, Zn) and $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_3](\text{ClO}_4)_2$ (M = Ni, Zn) with $x \leq 0.005$.

Experimental

Preparations

The mixed crystals $[\text{Fe}_x\text{M}_{1-x}\text{L}_3](\text{ClO}_4)_2$ (L = phen, bipy) were obtained by dissolving stoichiometric amounts of the two respective pure complexes $[\text{FeL}_3](\text{ClO}_4)_2$ and $[\text{ML}_3](\text{ClO}_4)_2$ in hot water separately, combining the two solutions and allowing the mixed crystals to crystallize slowly. As the iron concentration should be as low as possible in order to increase the chance of the LS state of iron(II) to change to the HS state at room temperature, we had to prepare the mixed crystals with enriched ^{57}Fe . We have chosen x to be ≤ 0.005 .

The pure complexes $[\text{M}(\text{bipy})_3](\text{ClO}_4)_2$ (M = Mn, Zn) and $[\text{M}(\text{phen})_3](\text{ClO}_4)_2$ (M = ^{57}Fe , Zn, Ni) were prepared according to the method of Schilt and

Taylor [26]. The compounds $[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$ and $[\text{Ni}(\text{bipy})_3](\text{ClO}_4)_2$ were prepared after Burstall and Nyholm [27] and Morgan and Burstall [28], respectively.

A ^{57}Fe foil (enriched to $> 90\%$) was purchased from Rohstoff-Einfuhr GmbH (Düsseldorf, Germany) and converted into Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a starting material.

Elemental analysis was carried out for the pure compounds as well as for the mixed crystals. The metal content of the pure complexes was determined by titration with Titriplex III (Merck, Darmstadt), after the ClO_4^- anions have been converted into Cl^- following a method given in the literature [29] and the organic material destroyed by fuming nitric acid and concentrated sulphuric acid. Very good agreement between the experimental and the calculated data was found for the pure compounds as well as for the mixed crystals. For the determination of the small iron content in the mixed crystals, atomic absorption spectroscopy using a Perkin-Elmer 373 spectrometer proved to be most useful. The iron content (x) determined this way is given in the first column of the Table.

The pure compounds were further characterized by Debye–Scherrer radiographs, FIR spectroscopy (Bruker IFS 113) and UV–VIS spectroscopy (Cary 219 spectrophotometer) and the spectra compared with the literature. The Debye–Scherrer pattern shows that only $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$ and $[\text{Ni}(\text{phen})_3](\text{ClO}_4)_2$ are isomorphous. However, we did not expect any difficulty in preparing the mixed crystals in other cases because of the very small amount of iron, which should be easily accommodated in normal lattice sites of the hosts.

Mössbauer Effect Measurements

The Mössbauer spectra were recorded in transmission geometry, using a $^{57}\text{Co}/\text{Rh}$ source (The Radiochemical Centre, Amersham; ca. 10 mCi). Wherever sufficient absorber material was available, the sample weight was optimized with respect to the ratio of resonance effect and electronic absorption. Both the source and the absorber were kept at room temperature in all the measurements [30]. The spectra were computer-fitted to Lorentzian lines employing a least squares iteration program.

Results and Discussion

The Mössbauer spectra recorded at room temperature of all the systems listed in Table I show a single quadrupole doublet, which is, on the basis of the data for IS and QS, unambiguously assigned to iron(II) in the LS state, $^1\text{A}_1(\text{O}_h)$. Four representative spectra of the tris-bipy systems are shown in Fig. 1. The data of the Mössbauer parameters evalu-

TABLE I. Isomer Shift (IS) with respect to the $^{57}\text{Co/Rh}$ source), Quadrupole Splitting (QS), Line Width ($\Gamma/2$), and Goodness-of-fit Parameter χ^2 from the Room Temperature Mössbauer Spectra of the Mixed Crystals $[\text{Fe}_x\text{M}_{1-x}\text{L}_3](\text{ClO}_4)_2$ (L = bipy, phen) and of the Corresponding Pure Iron Compounds.

System	IS mm s^{-1}	QS mm s^{-1}	$\Gamma/2$ mm s^{-1}	χ^2
$[\text{Fe}(\text{bipy})_3](\text{ClO}_4)_2$	0.188(3) ^a	0.414(3)	0.103(4)	1.62
$[\text{Fe}_x\text{Ni}_{1-x}(\text{bipy})_3](\text{ClO}_4)_2$ ($x = 0.0054$)	0.188(2)	0.396(3)	0.103(3)	0.97
$[\text{Fe}_x\text{Zn}_{1-x}(\text{bipy})_3](\text{ClO}_4)_2$ ($x = 0.0020$)	0.205(2)	0.412(2)	0.113(2)	0.97
$[\text{Fe}_x\text{Mn}_{1-x}(\text{bipy})_3](\text{ClO}_4)_2$ ($x = 0.0026$)	0.208(6)	0.265(5)	0.115(9)	1.00
$[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$	0.203(3)	0.265(3)	0.117(4)	1.17
$[\text{Fe}_x\text{Ni}_{1-x}(\text{phen})_3](\text{ClO}_4)_2$ ($x = 0.0048$)	0.218(5)	0.255(3)	0.117(4)	1.17
$[\text{Fe}_x\text{Zn}_{1-x}(\text{phen})_3](\text{ClO}_4)_2$ ($x = 0.0054$)	0.237(5)	0.248(4)	0.110(6)	0.97

^aQuotation of error reads 0.188 ± 0.003 .

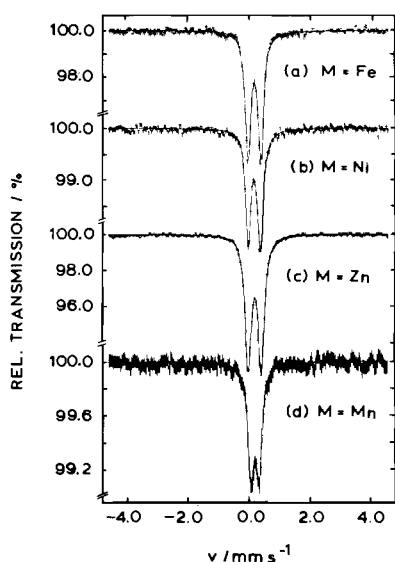


Fig. 1. Mössbauer spectra of the solid solutions $[\text{}^{57}\text{Fe}_x\text{M}_{1-x}(\text{bipy})_3](\text{ClO}_4)_2$, M = Ni, Zn, Mn, $x \lesssim 0.005$, recorded at room temperature using a $^{57}\text{Co/Rh}$ source. Spectrum (a) refers to the pure iron complex for comparison.

ated from the spectra, as well as those of the χ^2 criterion for the quality of the computer fits, are listed in the Table.

The Mössbauer spectra of the mixed crystals are very similar to those of the corresponding pure iron compounds. An eventual change in the spin state from LS to HS, *i.e.* from $^1\text{A}_1(\text{O}_h)$ to $^5\text{T}_2(\text{O}_h)$, would have been reflected in the appearance of a new quadrupole doublet with the parameters of IS $\sim 1.0 \text{ mm s}^{-1}$ and QS $\sim 3.0 \text{ mm s}^{-1}$. The difference in the free energies of the HS and the LS states,

$\Delta F = F(\text{HS}) - F(\text{LS})$, may have been decreased by the metal dilution effect, similarly to observations in the *a priori* spin crossover systems $[\text{Fe}_x\text{M}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$, with M being Zn [20, 21] and Co [30], and $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$ (M = Co, Mn, Ni, Zn) [24]. The decrease in ΔF , however, is not strong enough to thermally populate the HS state to any noticeable extent. Assuming the lowest possible admixture of the HS state detectable in the Mössbauer spectra with the present counting statistics to be on the order of 3%, the energy gap between the HS and the LS states is at least *ca.* 1200 cm^{-1} . With this figure taken into account the absorber temperature must be raised to about 400 K, in order to convert about 20% of the LS molecules into the HS state. We have not done this experiment for two reasons: (i) the compounds do not withstand temperatures close to 400 K [31]; (ii) the resonance effect decreases markedly above room temperature, the time for recording a spectrum, which is at room temperature already about a week, due to the low iron concentration, would therefore be unpractically long.

The width of the resonance lines (the natural width is broadened by only 10–20%) and the quadrupole splitting, with the exception of the Fe/Mn/bipy system, where QS is somewhat smaller than in the other systems, stay nearly the same on going from the pure iron compounds to the highly diluted systems. Thus the quadrupole interaction in the individual $[\text{FeL}_3]^{2+}$ complex molecules is practically the same in the pure and the diluted lattice. This is not surprising because of the effective shielding of the metal ion by the voluminous organic molecules. Similar observations have been made on the metal-diluted spin crossover systems $[\text{Fe}_x\text{M}_{1-x}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ [20, 21, 30] and $[\text{Fe}_x\text{M}_{1-x}(\text{phen})_2(\text{NCS})_2]$ [24].

The isomer shifts (IS) observed in the present studies appears to become more positive in the order of $M = \text{Fe} < \text{Ni} < \text{Zn} < \text{Mn}$ in the Fe/M/bipy systems and of $M = \text{Fe} < \text{Ni} < \text{Zn}$ in the Fe/M/phen systems (see Table I). The effect is very weak in the former series, but distinctly outside the error limits in the latter one. It is interesting that the increasing IS tendency parallels the increase in the ionic radius of the divalent central metal ions in the same order, viz. Fe (0.61 Å in the LS state) < Ni (0.70) < Zn (0.745) < Mn (0.82) [32]. It is quite likely that the relatively small $[\text{Fe}(\text{phen})_3]^{2+}$ complex molecule, when accommodated in a normal lattice site of the $[\text{M}(\text{phen})_3](\text{ClO}_4)_2$ host, tends to expand somewhat isotropically (without affecting the quadrupole interaction) due to the difference in the ionic radii of Fe on the one hand and the bigger Ni and Zn ions on the other. An increase in the Fe–L bond length is accompanied by a reduction in the $d_{\pi}p_{\pi}$ back-donation; i.e. the electron density in the t_{2g} space increases and, due to a reduction of the effective shielding, causes the electron density at the nucleus to decrease and thus the isomer shift to become more positive.

Finally, we should like to refer to similar investigations by Drickamer *et al.* [33] on solid solutions of $\text{Fe}_x\text{Mn}_{1-x}\text{S}_2$. It is found that the low spin electron configuration of FeS_2 , if sufficiently diluted into the isomorphous MnS_2 host, turns to high spin: the system with 2% ^{57}Fe yields ca. 10% of the diamagnetic FeS_2 species, which decreases to 5–6% if the system contains only 0.5% ^{57}Fe . The authors explain this in terms of a negative pressure acting on the Fe ions accommodated in normal lattice sites of the bigger Mn ions.

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