Effect of Metal Dilution on the Thermal and Light-induced Spin Transition in $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ (mtz = 1-methyl-1*H*-tetrazole)

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The thermal and light-induced spin transition in $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ (mtz = 1-methyl-1*H*-tetrazole) was studied by ^{57}Fe Mössbauer spectroscopy and magnetic susceptibility measurements. The pure iron compound possesses two different lattice sites A and B for the complex molecules. At temperatures below 100 K a high spin (h.s.) ⟶ low spin (l.s.) transition of the complexes at site A was observed, whereas the B molecules stay in the h.s. state at all temperatures down to 4.2 K. On isotypic dilution with zinc the spin transition was shifted to lower temperatures and became more gradual with decreasing iron content x of the mixed-metal crystals. At $T \leqslant 40$ K the l.s.(A) state can be converted by green light into the long-lived metastable h.s.(A) state [light-induced excited spin state trapping (LIESST) (l ⟶ h)] and the h.s.(B) state can be converted into a metastable long-lived l.s.(B) state using red light [LIESST (h ⟶ l)]. Reverse LIESST using red and green light, respectively, is possible in both cases.

Thermal and light-induced spin transition is a well established phenomenon in the co-ordination chemistry of iron(II). Many examples are known, particularly for complexes with FeN_6 cores, for which the high spin (h.s.) $\rightleftharpoons$ low spin (l.s.) transition behaviour has been extensively studied employing various techniques.[1-4] In most of the iron(II) complexes exhibiting such conversions the central ion is co-ordinated to bi-poly-dentate ligands. Complexes with tetrazole ligands with different alkyl substituents in the 1 position are one of the few classes of complexes with six monodentate ligands exhibiting h.s. $\rightleftharpoons$ l.s. transitions.

Earlier studies on the complex $[Fe(mtz)_6][BF_4]_2$ (mtz = 1-methyl-1*H*-tetrazole) have revealed the existence of two different lattice sites for the central iron(II) ion.[5,6] Only those at site A were found to undergo thermal h.s. ⟶ l.s. transition between 95 and 65 K, whereas those at site B remain in the h.s. state down to 4.2 K. The A site molecules show the well known LIESST (light-induced excited spin state trapping) effect with green light, which was discovered with the analogous ptz (1-propyl-1*H*-tetrazole) complex in 1984.[7,8] Surprisingly it was also found that the molecules in site B of $[Fe(mtz)_6][BF_4]_2$ could be converted from the stable h.s. state into a long-lived metastable l.s.(B) state by irradiation with red light ($\lambda \geqslant 700$ nm). This light-induced spin-state conversion was called LIESST (h ⟶ l) in order to distinguish it from the original LIESST effect, *viz.* the spin-state conversion from the thermodynamically stable l.s. state to the metastable h.s. state, which we shall now refer to as LIESST (l ⟶ h). The complex $[Fe(mtz)_6][BF_4]_2$ was the first for which the light-induced formation of a long-lived metastable l.s. state in an iron(II) h.s. complex was established. The LIESST (h ⟶ l) effect has also been demonstrated for the complex $[Fe(mtz)_6][CF_3SO_3]_2$.[9]

In continuation of our studies on iron(II) spin-cross-over complexes with tetrazole ligands[7-12] we have also investigated the spin-transition behaviour of the perchlorate $[Fe(mtz)_6][ClO_4]_2$, which is isomorphous to $[Fe(mtz)_6][BF_4]_2$.[6] Some preliminary results for the thermal and light-induced spin transition in this compound have already been published.[13] The interpretation of the earlier LIESST experiments, however, needs some revision. In this report we also present an analysis of the metal dilution effect on the thermal spin transition in the $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ system (x = 1.0, 0.85, 0.65, 0.46 or 0.005) and a careful reinvestigation of the light-induced spin conversion.

Experimental

Sample Preparation.—1-Methyl-1*H*-tetrazole was prepared as described earlier.[14,15] The complexes $[Fe(mtz)_6][ClO_4]_2$ and $[Zn(mtz)_6][ClO_4]_2$ were obtained from equimolar concentrated aqueous solutions of $[Fe(H_2O)_6][ClO_4]_2$ and $[Zn(H_2O)_6][ClO_4]_2$, respectively, and mtz under nitrogen. The volume was carefully reduced at room temperature until the complex crystallized. The crude product was filtered off and dried. It was further purified by dissolving in dry nitromethane and evaporating the solvent with an oxygen-free dry nitrogen stream. Mixed-metal crystals of $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ were obtained by dissolving the theoretical amounts of $[Fe(mtz)_6][ClO_4]_2$ and $[Zn(mtz)_6][ClO_4]_2$ in nitromethane and evaporating the solvent as described above.

The complex $[^{57}Fe_{0.005}Zn_{0.995}(mtz)_6][ClO_4]_2$ was prepared by dissolving isotopically enriched iron (99% ^{57}Fe) in 1 mol dm^{-3} perchloric acid (1 cm^3). After complete dissolution the theoretical amount of mtz and a concentrated aqueous solution of $[Zn(mtz)_6][ClO_4]_2$ were added. The product was isolated as described above. The relative iron content of all the samples used in this study was determined by X-ray fluorescence analysis using a Philips PW1400 spectrometer. The purity of the complexes was monitored by routine elemental analysis.

Susceptibility Measurements.—The magnetic susceptibility $\chi(T)$ of the mixed-metal crystals $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ ($0.46 \leqslant x \leqslant 1$) between 20 and 295 K was measured with a Foner-type magnetometer, equipped with a helium-flow cryostat, in an external field of 1 T. The diamagnetic corrections for the iron(II) complex were determined by measuring χ of the diamagnetic $[Zn(mtz)_6][ClO_4]_2$ complex ($\chi = -419 \times 10^{-6}$ cm^3 mol^{-1}) at room temperature. The h.s. fraction as a function of temperature was calculated from the measured susceptibilities assuming Curie–Weiss behaviour for the pure compound in the h.s. state and temperature-independent paramagnetism for the l.s. state.

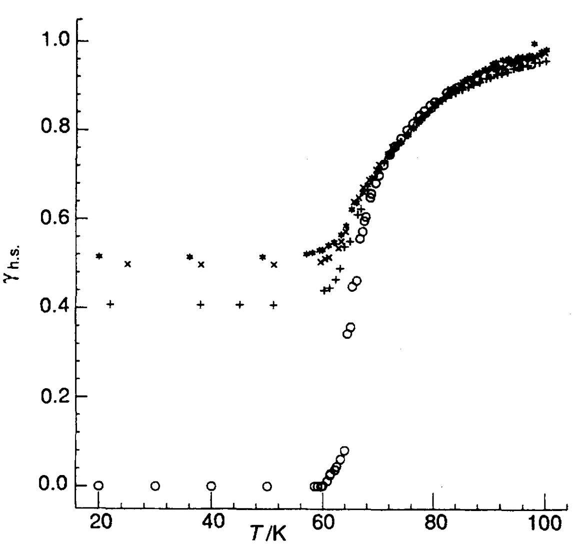

Fig. 1 The fraction $\gamma_{h.s.}$ as a function of temperature in $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ with x = 1 (○), 0.85 (+), 0.65 (×) and 0.46 (✱); $\gamma_{h.s.}$ was evaluated from measurements of the magnetic susceptibility

Mössbauer Spectroscopy.—Mössbauer spectra of $[Fe(mtz)_6][ClO_4]_2$ and $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ ($0.005 \leqslant x \leqslant 1$) were recorded between 5 and 295 K with a conventional Mössbauer spectrometer. The $^{57}Co/Rh$ source was kept at room temperature. The samples were sealed in polished Plexiglass containers (3 cm^2, *ca.* 7 mg Fe cm^{-2}) and mounted in a helium-flow cryostat (CF 506, Oxford Instruments). The cryostat was equipped with windows of transparent mylar foil. The samples were irradiated with an Xe-arc lamp using a water-bath as IR filter. For LIESST ($l \longrightarrow h$) experiments a filter with maximum transmission between 350 and 650 nm and for LIESST ($h \longrightarrow l$) experiments a filter transparent for $\lambda \geqslant 700$ nm was used. A carbon/glass resistance was directly mounted at the sample holder to control the temperature during irradiation. The Mössbauer spectra were fitted by Lorentzians using the program MOSFUN.[16]

Results

Thermal Spin Transition.—Mössbauer spectra of $[Fe(mtz)_6][ClO_4]_2$ recorded at different temperatures were published earlier.[13] The derived high-spin fraction $\gamma_{h.s.}(T)$ yields a spin-state conversion curve which is shifted by approximately 8 K to lower temperatures as compared to that of the isomorphous BF_4^- compound. Similarly to $[Fe(mtz)_6][BF_4]_2$, two different lattice sites A and B exist for the complex molecules in $[Fe(mtz)_6][ClO_4]_2$.[6] The h.s. ⟶ l.s. transition of the complexes at site A is observed between 100 and 55 K, whereas the B site molecules stay in the h.s. state down to 4.2 K.

In addition to the Mössbauer studies, measurements of the magnetic susceptibility have now been carried out and used to determine the temperature dependence of the h.s. fraction $\gamma_{h.s.}$ for the mixed-metal crystals as shown in Fig. 1; $\gamma_{h.s.}(T)$ was calculated only for the A site molecules, which are the only ones exhibiting thermal spin transition. With decreasing iron content the spin transition becomes more gradual and is shifted to lower temperatures. Below 60 K the rate of the spin-transition process becomes very slow and the metastable h.s. states are frozen in, which is reflected by a levelling off in $\gamma_{h.s.}(T \longrightarrow 0)$ with values up to *ca.* 50%. For this reason we have restricted the analysis of the spin-transition behaviour to temperatures above 60 K.

Light-induced Spin Transition.—The LIESST experiments were carried out with a single crystal of $[Fe(mtz)_6][ClO_4]_2$. The crystal was first slowly cooled to ≈20 K (*cf.* Mössbauer spectra at top of Fig. 2). The spectrum contains two doublets, one arising from the l.s.(A) state (inner two lines with isomer shift $\delta = 0.48$ mm s^{-1} and quadrupole splitting $\Delta E_Q = 0.21$ mm s^{-1}) and one (outer two lines with $\delta = 1.06$ mm s^{-1} and $\Delta E_Q = 2.46$ mm s^{-1}) arising from the h.s.(B) state. If the crystal is irradiated with green light (≈350–650 nm) at 20 K one observes a quantitative conversion of the l.s.(A) into the h.s.(A) state, which is known as the normal LIESST ($l \longrightarrow h$) effect. The Mössbauer spectrum (see Fig. 2, right) now contains the h.s.(A) and h.s.(B) quadrupole doublets, and that of the l.s.(A) state has disappeared. The metastable h.s.(A) state has a practically infinite lifetime below 45 K. It relaxes back to the thermodynamically stable l.s.(A) state if the crystal is warmed to ≈45 K (quantitative relaxation within 7 d at 48 K). The Mössbauer spectrum taken at 50 K (bottom of Fig. 2) is identical to the initial one at 20 K (top of Fig. 2).

In another irradiation experiment we again started with a crystal cooled to 20 K. After irradiating it with red light ($\lambda \geqslant 700$ nm) at 20 K the Mössbauer spectrum shown in Fig. 2 (left) was obtained. A partial conversion from h.s.(B) to l.s.(B) has taken place. The intensity of the h.s.(B) quadrupole doublet is considerably reduced in favour of a newly formed l.s.(B) doublet with a splitting of only ≈0.11 mm s^{-1} (isomer shift, $\delta = 0.47$ mm s^{-1}), which overlaps strongly with the doublet of the l.s.(A) state. Thus, undoubtedly a spin-state conversion from the thermodynamically stable h.s. state at lattice site B to a metastable l.s. state has been effected by light, which we denote as LIESST ($h \longrightarrow l$). This conversion, however, is not quantitative, as can be seen from the Mössbauer spectra. The reason lies in the fact that the crystal was irradiated with a broad-band light source which leads to simultaneous light-induced back conversion l.s.(B) ⟶ h.s.(B) yielding finally a steady-state concentration of h.s.(B) and l.s.(B).

From the Mössbauer spectrum (Fig. 2, left) it can also be seen that simultaneously with the h.s.(B) ⟶ l.s.(B) conversion a partial transformation of l.s.(A) to h.s.(A) has occurred as indicated by the reduced intensity of the l.s.(A) quadrupole doublet and the reappearance of the h.s.(A) quadrupole doublet. This effect was also observed with $[Fe(mtz)_6][BF_4]_2$ and is due to the fact that the $^1A_1 \longrightarrow {}^1T_1$ ligand-field absorption band of the l.s. state overlaps to some extent with the $^5T_2 \longrightarrow {}^5E$ band of the h.s. state.[5] In addition the $^5T_2 \longrightarrow {}^5E$ transition of the h.s. state overlaps with the spin-forbidden $^1A_1 \longrightarrow {}^3T_1$ and $^1A_1 \longrightarrow {}^3T_2$ transitions of the l.s. state.[17] When irradiating with red light the h.s. band so as to cause light-induced h.s. ⟶ l.s. conversion excitation also of the l.s. state is unavoidable (though only to a minor extent) causing partial light-induced l.s. ⟶ h.s. conversion. These light-induced spin-state conversions are expected to be more quantitative if sharp-band laser light is employed rather than Xe-arc lamps with filters as in the present case.

Above 40 K the l.s.(B) as well as the h.s.(A) state relax back to the thermodynamically stable h.s.(B) and l.s.(A) states, respectively, with roughly equal rate constants. It was not possible to find a temperature at which these processes could be observed separately. At 47 K it took 8 d for the excited metastable states l.s.(B) and h.s.(A) to decay completely to the respective ground states.

Discussion

For a theoretical consideration of the thermal h.s. ⟶ l.s. transition in $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ we assume that the mixed metal crystals form solid solutions with a random distribution of h.s., l.s. and zinc molecules. According to previous work[18,19] the condition for thermal equilibrium is given by equation (1) where g is the Gibbs free enthalpy per

$$\left(\frac{\partial g}{\partial \gamma_{h.s.}}\right)_T = g_{h.s.} - g_{l.s.} - k_B T \ln\left[\frac{1-\gamma_{h.s.}(T,x)}{\gamma_{h.s.}(T,x)}\right] + \left(\frac{\partial g_I}{\partial \gamma_{h.s.}}\right)_T = 0 \quad (1)$$

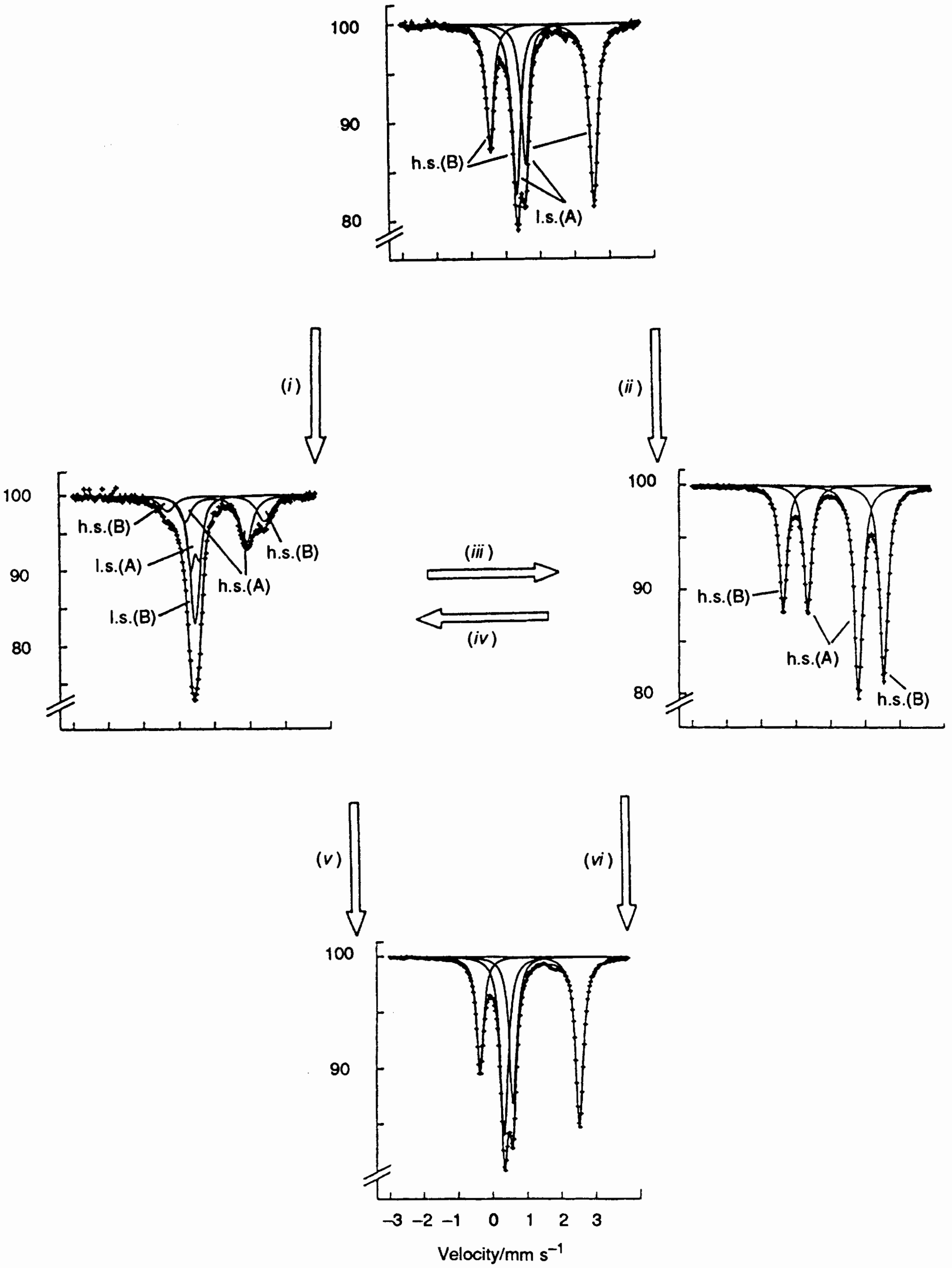

Fig. 2 The ^{57}Fe Mössbauer spectra of $[Fe(mtz)_6][ClO_4]_2$ after various irradiation experiments (see text). The spectrum at 20 K (top) was obtained after slowly cooling from 295 K. (*i*) 20 K, irradiation $\lambda > 700$ nm, h.s.(B) ⟶ l.s.(B) and l.s.(A) ⟶ h.s.(A); (*ii*) 20 K, $\lambda \approx 350$–650 nm, l.s.(A) ⟶ h.s.(A); (*iii*) 20 K, $\lambda \approx 350$–650 nm, l.s.(A) ⟶ h.s.(A), l.s.(B) ⟶ h.s.(B); (*iv*) 20 K, $\lambda > 700$ nm, h.s.(B) ⟶ l.s.(B), h.s.(A) ⟶ l.s.(A); (*v*) 47 K, thermal relaxation, h.s.(B) ⟶ l.s.(B), l.s.(A) ⟶ h.s.(A); (*vi*) 48 K, thermal relaxation, h.s.(A) ⟶ l.s.(A)

molecule of the system. The difference $g_{h.s.} - g_{l.s.}$ refers to the difference in the free enthalpies of the h.s. and l.s. molecules, and g_I describes the interaction between these molecules in the lattice. At very low iron concentrations the term g_I can be neglected and $\Delta g(T) = g_{h.s.} - g_{l.s.}$ can be obtained from the h.s. ⟶ l.s. transition curve according to equation (2). Thus the

$$\Delta g_{hl} = g_{h.s.} - g_{l.s.} = k_B T \ln\left[\frac{1 - \gamma_{h.s.}(T,x \longrightarrow 0)}{\gamma_{h.s.}(T,x \longrightarrow 0)}\right] \quad (2)$$

term $(\partial g_I/\partial \gamma_{h.s.})_T$ can be determined from the measurements of $\gamma_{h.s.}(T,x \longrightarrow 0)$ and $\gamma_{h.s.}(T,x)$ without further assumptions. The

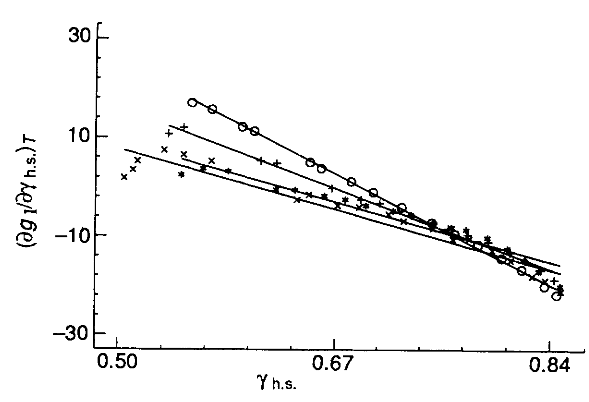

Fig. 3 Plots of $(\partial g_I/\partial\gamma_{h.s.})_T$ as a function of $\gamma_{h.s.}$ for different iron concentrations x in the system $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$; x = 1 (○), 0.85 (+), 0.65 (×) and 0.46 (✱)

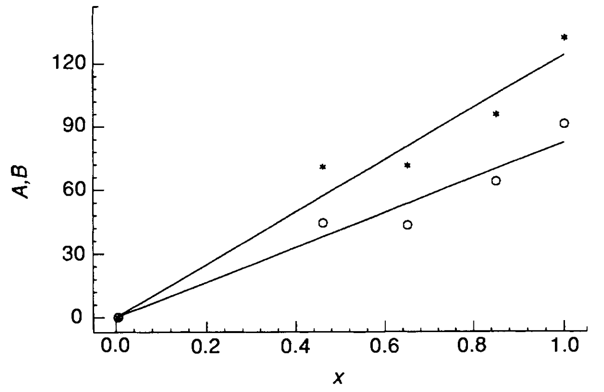

Fig. 4 Concentration dependence of the slopes B (✱) and intercepts A (○) of the plots in Fig. 3 for $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$

term Δg_{hl} was obtained from Mössbauer measurements of the relative h.s. fraction for the compound $[Fe_{0.005}Zn_{0.995}(mtz)_6][ClO_4]_2$ using an expression proposed by Jakobi *et al.*[19]

Fig. 3 shows how $(\partial g_I/\partial\gamma_{h.s.})_T$ varies with $\gamma_{h.s.}$. The curves can be approximated as straight lines according to equation (3). In

$$\left(\frac{\partial g_I}{\partial\gamma_{h.s.}}\right)_T = A(x) - B(x)\gamma_{h.s.} \qquad (3)$$

Fig. 4 the slopes B and intercepts A of the plots in Fig. 3 are represented as a function of the iron content x of the mixed-metal crystals. From a linear regression we find $A = 82\ cm^{-1}$ and $B = 124\ cm^{-1}$. With decreasing iron content of the mixed-metal crystals the transition curves become more gradual which is caused by the reduction of the interaction term g_I due to the dilution by zinc.

An essential quantity for the analysis of the thermal spin transition is the term Δg_{hl} which can be derived from the highly diluted mixed-metal crystals. In the present system, however, it can be obtained only for a small $\gamma_{h.s.}$ interval owing to the incomplete spin transition in $[Fe_{0.005}Zn_{0.995}(mtz)_6][ClO_4]_2$. In addition, the analysis of the spin-transition curves is restricted to $\gamma_{h.s.}$ of 0.5–1 again owing to the incomplete spin transition. Nevertheless, using the values obtained from the linear regression of the plots of $(\partial g_I/\partial\gamma_{h.s.})_T$ *vs.* $\gamma_{h.s.}$ and the Δg_{hl} values from the highly diluted mixed-metal crystals, the calculated spin-transition curves for $[Fe_xZn_{1-x}(mtz)_6][ClO_4]_2$ are in good agreement with the experimental data.

In the framework of the lattice-expansion model of Spiering and co-workers.[19–22] the term g_I is explained on the basis of an elastic interaction of the complexes, which is different in the h.s. and l.s. state as a result of the drastic volume change accompanying the transition from l.s. to h.s. Within this model the parameter B derived in the present metal dilution study represents an interaction constant Γ ($B = 2\,\Gamma$). For the present system we estimate Γ to be 62 cm^{-1}. This is somewhat smaller than the interaction constants found for the metal-diluted spin-cross-over systems $[Fe_xZn_{1-x}(ampy)_3]Cl_2{\cdot}MeOH$ (ampy = 2-aminomethylpyridine, Γ = 98 cm^{-1}), $[Fe_xCo_{1-x}(ampy)_3]Cl_2{\cdot}MeOH$ (Γ = 103 cm^{-1}) and the $[Fe_xZn_{1-x}(dampy)_3]Cl_2{\cdot}EtOD$ (dampy = 2-dideuterioaminomethylpyridine, Γ = 152 cm^{-1}). Nevertheless, the spin-transition curve for the non-diluted $[Fe(mtz)_6][ClO_4]_2$ crystal is comparatively steep.

The light-induced spin transition in $[Fe(mtz)_6][ClO_4]_2$ is very similar to that of the isomorphous compound $[Fe(mtz)_6][BF_4]_2$. The A site molecules show the well known LIESST ($l \longrightarrow h$) and reverse LIESST effect. From a careful reinvestigation of the irradiation experiment with red light it is confirmed that the B-site h.s. ground state is converted into a metastable l.s. state [LIESST ($h \longrightarrow l$)]. Only the resonance lines of the h.s. and l.s. states of the A and B site molecules are observed in the Mössbauer spectrum recorded after irradiation of the sample with red light; there is no evidence for the existence of an additional h.s.(C) state which was postulated previously.[13]

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