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# Synthesis of 2,6-Di(pyrazol-1-yl)pyrazine Derivatives and the Spin-State Behavior of Their Iron(II) Complexes

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Chlorination of 2,6-bis(pyrazol-1-yl)pyrazine (bppz) with Na-ClO in acetic acid afforded 2,6-bis(4-chloropyrazol-1-yl)pyrazine ( $L^2$ Cl). 2,6-Bis(4-bromopyrazol-1-yl)pyrazine ( $L^2$ Br), 2,6-bis(4-iodopyrazol-1-yl)pyrazine ( $L^2$ I), 2,6-bis(4-methylpyrazol-1-yl)pyrazine ( $L^2$ Me), and 2,6-bis(4-nitropyrazol-1yl)pyrazine ( $L^2$ NO<sub>2</sub>) were also prepared by reactions of the preformed 4-substituted pyrazoles with 2,6-dichloropyrazine. The reduction of  $L^2$ NO<sub>2</sub> with iron powder gave 2,6-bis(4aminopyrazol-1-yl)pyrazine ( $L^2$ NH<sub>2</sub>) and  $L^2$ I was converted into 2,6-bis[4-(phenylethynyl)pyrazol-1-yl]pyrazine ( $L^2$ CCPh) by a Sonogashira coupling reaction. The salts [Fe( $L^2$ Me)<sub>2</sub>]X<sub>2</sub> (X<sup>-</sup> = BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>) underwent thermal spin-crossover abruptly at around 200 K in one and two steps, respectively. The [Fe( $L^2$ Me)<sub>2</sub>]X<sub>2</sub> salts exhibited dif-

## Introduction

Salts of  $[Fe(bpp)_2]^{2+}$  [bpp = 2,6-di(pyrazol-1-yl)pyridine] and its derivatives commonly undergo thermal spin transitions<sup>[1,2]</sup> at accessible temperatures, often close to room temperature.<sup>[3]</sup> They have been particularly useful for spincrossover research because the bpp ligand framework can be derivatized at any position of its heterocyclic rings.<sup>[3,4]</sup> Substituents at the pyrazole 3-position in  $[Fe(bpp)_2]^{2+}$  have a strong steric and inductive influence on the coordinated metal ion, whereas substituents at the pyrazole 4-position (i.e.,  $L^1R$ ) allow the ligand field to be modulated without any steric consequences. Conversely, substitution of the pyr-

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ferent light-induced excited spin-state trapping (LIESST) behavior; the BF<sub>4</sub><sup>-</sup> salt behaves classically [*T*(LIESST) = 93 K], but the ClO<sub>4</sub><sup>-</sup> salt undergoes a multistep LIESST relaxation. In contrast, solid [Fe( $L^2$ Cl)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> adopts a fixed 2:1 high/low-spin-state population that does not change with temperature below 300 K, whereas [Fe( $L^2$ Br)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> and [Fe( $L^2$ I)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> form low-spin solvated crystals that are transformed into high-spin powders on drying. The pyrazinyl group in the  $L^2$ R ligands slightly stabilizes the low-spin state of the complexes, as determined by solution-phase magnetic measurements. The crystal structure of [Fe( $L^2$ CCPh)(OH<sub>2</sub>)<sub>2</sub>]-[BF<sub>4</sub>]<sub>2</sub> contains a disordered mixture of six- (z = 3) and sevencoordinate (z = 4) iron centers.

idine ring allows a [Fe(bpp)<sub>2</sub>]<sup>2+</sup> center to be functionalized without significantly perturbing the iron center. The good availability of crystallographic data from this series of complexes has allowed structure–function relationships to be elucidated that control their spin-crossover under both thermodynamic<sup>[5]</sup> and kinetic (light-induced excited spin-state trapping, LIESST) conditions.<sup>[6]</sup> In addition, their ease of functionalization has allowed multimetallic complexes,<sup>[7]</sup> coordination polymers,<sup>[8]</sup> multifunctional spin-crossover molecules,<sup>[9]</sup> and surface assemblies<sup>[10]</sup> to be constructed by using [Fe(bpp)<sub>2</sub>]<sup>2+</sup> components.

An alternative way of modifying the bpp ligand is to incorporate additional heteroatoms into its constituent rings.<sup>[11–13]</sup> One such derivative is 2,6-di(pyrazol-1-yl)pyrazine (bppz), which was first prepared by Hossenii and coworkers.<sup>[11]</sup> Several salts of  $[Fe(bppz)_2]^{2+[14,15]}$  and  $[Fe(bppz^*)_2]^{2+[14,16]}$  are spin-crossover active. However, these materials are generally not isostructural with their analogues from the  $[Fe(bpp)_2]^{2+}$  series, and there is no clear relationship between the temperatures of spin-crossover in  $[Fe(bpp)_2]^{2+}$  and  $[Fe(bppz)_2]^{2+}$  derivatives in the solid state.<sup>[3]</sup> With a view to clarifying these observations, we have now extended the number of known  $[Fe(bppz)_2]^{2+}$  derivatives by derivatizing the bppz ligand at the pyrazole 4position, yielding a new series of ligands  $L^2R$ .

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Figure 1. View of the crystal structure of  $L^2$ Cl, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (i) 1 - y, 1 - x,  $\frac{1}{2} - z$ .

#### **Results and Discussion**

The pyrazole rings of bpp can be halogenated in good yield under electrophilic conditions.<sup>[17,18]</sup> Similar reactions with bppz were less successful, however, perhaps because the more electron-deficient pyrazine ring in bppz deactivates its pyrazole groups to electrophilic attack. Chlorination of bppz to give  $L^2$ Cl in moderate yield was achieved by using NaOCl in acetic acid. However, Br<sub>2</sub>/acetic acid and I<sub>2</sub>/[NH<sub>4</sub>]<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>], which readily halogenate bpp,<sup>[17]</sup> yielded only unchanged starting material when reacted with bppz.

The ligands  $L^2$ Me,  $L^2$ Br,  $L^2$ I, and  $L^2$ NO<sub>2</sub> were obtained by the alternative approach of treating the appropriate deprotonated 4-substituted pyrazoles with 0.5 equiv. 2,6dichloropyrazine in warm dmf.<sup>[11,12,14]</sup> These products are less soluble than the corresponding  $L^1R$  derivatives,<sup>[6,17]</sup> and only  $L^2$ Me was sufficiently soluble to be purified by column chromatography. The other  $L^2R$  ligands, including  $L^2$ Cl, were purified by washing the yellow crude materials with dmf or ethyl acetate until all the colored impurities had leached out of the white insoluble product. The synthesis of  $L^2NO_2$  is notable because  $L^1NO_2$  could not be prepared by this method, because the more forcing conditions required (3-5 d at 130 °C) led to product decomposition.<sup>[19]</sup> Reduction of  $L^2NO_2$  with iron powder afforded  $L^2NH_2$ with good NMR purity. Finally, coupling of  $L^2$ I with 2 equiv. of phenylacetylene under Sonogashira conditions yielded  $L^2$ CCPh. No Heck reaction took place between  $L^2$ I and styrene with  $Pd(OAc)_2/PPh_3$  or  $[Pd(PPh_3)_4]$  as catalyst, however.

The identity of  $L^2$ Cl was confirmed by a crystal structure determination, which showed it to adopt the expected conformation with near-coplanar and transoid pyrazole and pyrazine rings (Figure 1).<sup>[8,11,17,20,21]</sup> The molecules in the lattice associate into alternating canted sheets parallel to (001) through a combination of electrostatic  $\pi$ - $\pi$  interactions and van der Waals contacts.

Treatment of Fe[BF<sub>4</sub>]<sub>2</sub>·6H<sub>2</sub>O with 2 equiv.  $L^2$ R (R = Me or a halogen) in nitromethane at reflux afforded [FeL<sub>2</sub>]-[BF<sub>4</sub>]<sub>2</sub> (L =  $L^2$ Me,  $L^2$ Cl,  $L^2$ Br, and  $L^2$ I) as orange or brown solids following the usual work-up. The halogenated ligand complexes are moisture-sensitive in solution and could only be crystallized in the presence of the drying agent triethyl orthoformate. If this reagent was omitted, the solutions decolorized over a period of hours and the free  $L^{R}$  ligands precipitated; the single crystals of  $L^2Cl$  described above were obtained by this route. Similarly, the iron complexes of  $L^2NO_2$  and  $L^2NH_2$  could not be purified from uncomplexed ligand, even in the presence of triethyl orthoformate, and reactions of  $Fe[BF_4]_2$  and 2 equiv.  $L^2CCPh$  yielded the 1:1 complex  $[Fe(L^2CCPh)(OH_2)_x][BF_4]_2$  (x = 3 or 4; see below). We previously noted that  $[Fe(bppz)_2]^{2+}$  is more sensitive to protic solvents than  $[Fe(bpp)_2]^{2+,[14]}$  It is likely that the electron-withdrawing substituents in  $L^2$ Cl,  $L^2$ Br,  $L^2$ I,  $L^2$ NO<sub>2</sub>, and  $L^2$ CCPh further reduce the basicity of the pyrazole donors to the extent that they are easily displaced from the iron center. Further evidence for the solution lability of  $[Fe(L^2R)_2]^{2+}$  was provided by their electrospray mass spectra, which only exhibit peaks from the free  $L^2 R$ ligands with no detectable iron-containing fragments. Attempts to prepare the ClO<sub>4</sub><sup>-</sup> salts of these complexes led to only  $[Fe(L^2Me)_2][ClO_4]_2$ ,  $[Fe(L^2Br)_2][ClO_4]_2$ , and  $[Fe(L^2I)_2][ClO_4]_2$  being obtained in analytical purity. This may again reflect the poor stability of the complexes with electron-withdrawing pyrazole substituents in the presence of the more nucleophilic perchlorate anion.<sup>[22]</sup>

Variable-temperature magnetic susceptibility data showed that the  $BF_4^-$  and  $ClO_4^-$  salts of  $[Fe(L^2Me)_2]^{2+}$  are high-spin complexes at room temperature and exhibit spincrossover upon cooling (Figure 2). For  $[Fe(L^2Me)_2][BF_4]_2$ ,



Figure 2. Variable-temperature magnetic susceptibility data for  $[Fe(L^2Me)_2][BF_4]_2$  ( $\bullet$ ) and  $[Fe(L^2Me)_2][ClO_4]_2$  ( $\diamond$ ). The data for both salts were measured in both cooling and warming modes.



the transition occurs abruptly at  $T_{\frac{1}{2}} = 242$  K with a 3 K hysteresis loop. The temperature of the transition was confirmed by a DSC measurement with a warming temperature ramp, which exhibited a first-order endotherm at 245 K with  $\Delta H = 23.0 \text{ kJ mol}^{-1}$  and  $\Delta S = 94 \text{ J mol}^{-1} \text{ K}^{-1}$ . The form of this transition and its thermodynamic parameters are similar to those found for  $[Fe(bppz)_2]X_2$  (X<sup>-</sup> = BF<sub>4</sub><sup>-</sup> and  $ClO_4^{-})^{[14]}$  and several complexes from the  $[Fe(bpp)_2]^{2+}$ series.<sup>[5,17]</sup> The spin transition in  $[Fe(L^2Me)_2][ClO_4]_2$  is more complicated, occurring in two steps with a discontinuity near 50% conversion (Figure 2). The midpoint temperatures of the two steps are  $T_{\frac{1}{2}}$  = 171 and 207 K, with the higher temperature step exhibiting a 3 K hysteresis loop as before. A DSC analysis of this transition was not possible because its lower temperature is outside the range of our instrument.

A single-crystal X-ray analysis of  $[Fe(L^2Me)_2][BF_4]_2$  was achieved at 300 K in its high-spin state (Figure 3, Table 1). The compound adopts the space group  $P\overline{42}_1c$  and is isostructural with high-spin  $[Fe(L^1Me)_2][ClO_4]_2$ ,<sup>[6]</sup>  $[Fe(L^1Br)_2]$ - $[BF_4]_2$ , and one polymorph of  $[Fe(L^1Cl)_2][BF_4]_2$ ,<sup>[17]</sup> but not



Figure 3. View of the dication complex in the crystal structure of  $[Fe(L^2Me)_2][BF_4]_2$  at 300 K showing the atom numbering scheme employed. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Symmetry codes: (ii) -1 + y, 1 - x, -z; (iii) -x, 2 - y, z; (iv) 1 - y, 1 + x, -z.

with  $[Fe(L^1Me)_2][BF_4]_2$ .<sup>[6]</sup> The cations in the crystal pack into four-fold layers through interdigitation of the pyrazolyl substituents (see the Supporting Information).<sup>[23]</sup> Although this crystal packing can afford intermolecular  $\pi$ – $\pi$  interactions between these groups,<sup>[23]</sup> that is not the case in  $[Fe(L^2Me)_2][BF_4]_2$ , whose overlapping pyrazolyl groups are separated by 3.80(1) Å. This reflects the steric influence of the  $L^2Me$  methyl substituents. The adoption of this mode of crystal packing by  $[Fe(L^2Me)_2][BF_4]_2$  is consistent with the abrupt form of its spin transition in the susceptibility data (Figure 2).<sup>[5]</sup> At 150 K, the same crystal had undergone a crystallographic phase change and diffracted more weakly, so the resultant dataset could not be solved.

Powder X-ray diffraction analysis of a bulk sample of  $[Fe(L^2Me)_2][BF_4]_2$  showed it to be phase pure and isostructural with the single-crystal phase of the compound (Figure 4). Variable-temperature measurements showed some changes in peak intensity between 250 and 220 K, most notably the disappearance of a moderate intensity diffraction peak near  $2\theta = 22.5^{\circ}$ . This is consistent with the spin transition at 242 K in the susceptibility data (Figure 2). These changes were fully reversed upon rewarming to room temperature. The powder pattern of  $[Fe(L^2Me)_2][BF_4]_2$  resembles those of  $\alpha$ -[Fe( $L^1$ Cl)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> and [Fe( $L^1$ Br)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> in the high-spin state, when they are all isostructural with the  $P\bar{4}2_1c$  space group, but not those of the low-spin-state complexes.<sup>[17]</sup> Hence, the phase change undergone by  $[Fe(L^2Me)_2][BF_4]_2$  during spin-crossover must be different to those of the  $[Fe(L^1R)_2][BF_4]_2$  compounds, which adopt the  $P2_1$  space group when in the low-spin state.

Powder X-ray diffraction analysis of  $[Fe(L^2Me)_2][ClO_4]_2$ showed that the chlorate salt is less crystalline, but isostructural with the  $BF_4^-$  salt at 290 K (Figure 4 and the Supporting Information). The powder pattern was unchanged at 220 K, but showed progressive changes on further cooling to 200, 190, and 140 K (Figure 4). The changes in the powder pattern are similar to those observed for the  $BF_4^-$  salt, but occur over a wider temperature range. This is again consistent with the spin-crossover shown by these two compounds (Figure 2). Therefore the different forms of the spin transitions in the salts of  $[Fe(L^2Me)_2]^{2+}$  do not reflect large differences in their structural chemistry.

The behavior of  $[Fe(L^2Me)_2][ClO_4]_2$  is reminiscent of  $[Fe(bppz^*)_2]X_2$  (X<sup>-</sup> = BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>).<sup>[14]</sup> These adopt a

Table 1. Selected bond lengths [Å] and angles [°] for the crystal structures of  $[Fe(L^2R)_2][BF_4]_2$  in this work. *a*,  $\Sigma$ , and  $\Theta$  are indices showing the spin state of the complex,<sup>[3,24]</sup> and  $\theta$  and  $\phi$  are measures of the angular Jahn–Teller distortion sometimes shown by these iron centers in their high-spin state (see the text for details).<sup>[25,26]</sup> Typical values for these parameters in  $[Fe(bpp)_2]^{2+}$  and  $[Fe(bpp2_2)_2]^{2+}$  derivatives are given in ref.<sup>[3]</sup>

	$L^2 \mathbf{R} = L^2 \mathbf{M} \mathbf{e}$ (high-spin)	$L^{2}R = L^{2}Cl$ (Molecule 1)	$L^2$ R = $L^2$ Cl (Half-molecule 2)	$L^2$ R = $L^2$ Br	$L^2 \mathbf{R} = L^2 \mathbf{I}$
Fe-N(pyrazinyl)	2.150(3)	2.148(2), 2.165(2)	1.913(2)	1.900(3), 1.903(3)	1.922(3), 1.922(3)
Fe-N(pyrazolyl)	2.218(2)	2.210(2)-2.226(3)	2.000(3), 2.000(3)	1.981(3)-1.987(3)	1.998(3)-2.012(3)
a	73.19(6)	73.0(2)	80.0(1)	80.0(3)	79.8(2)
Σ	153.7(2)	156.0(3)	86.7(4)	87.0(4)	88.9(4)
Θ	475	483	285	285	291
$\phi$	180	171.98(9)	178.48(15)	178.19(11)	176.85(11)
$\dot{\theta}$	90	89.23(2)	89.56(2)	88.33(4)	88.34(3)





Figure 4. Variable-temperature powder X-ray diffraction patterns for  $[Fe(L^2Me)_2]X_2$  [X<sup>-</sup> = BF<sub>4</sub><sup>-</sup> (left), ClO<sub>4</sub><sup>-</sup> (right)].

closely related crystal lattice type, in a different space group, but also with expanded intermolecular distances within the four-fold layers. Two-step spin transitions also occur in these compounds, with the discontinuity corresponding to a change in X<sup>-</sup> anion disorder at 50% conversion.<sup>[16]</sup> Notably, the discontinuity in  $[Fe(bppz^*)_2]X_2$  is more pronounced in the salt containing the larger perchlorate anion, as in  $[Fe(L^2Me)_2][ClO_4]_2$  (Figure 2).

The photomagnetic properties of  $[Fe(L^2Me)_2][BF_4]_2$  and  $[Fe(L^2Me)_2][ClO_4]_2$  were investigated by using thin layers of polycrystalline samples. For both compounds, the most efficient wavelength to induce the LIESST effect<sup>[27]</sup> was found to be 514 nm, which leads to a strong increase in the magnetic signal at 10 K (Figure 5, a and Figure 6). The *T*(LIESST) curves were then recorded for each compound (Figure 5, a and Figure 6) to determine the stability of the photoinduced HS states.<sup>[28]</sup> In this procedure, the irradiation was maintained until the signal was saturated, then the light was switched off and the temperature was slowly increased at 0.3 K min<sup>-1</sup>.<sup>[29]</sup> The increase in  $\chi_M T$  from 10 to 30 K is a typical signature for zero-field splitting of the



Figure 5. (a) Temperature dependence of  $\chi_{\rm M}T$  for  $[{\rm Fe}(L^2{\rm Me})_2]$ - $[{\rm BF}_4]_2$ . (O) Data recorded in the cooling and warming modes without irradiation, ( $\Delta$ ) data recorded with irradiation at 514 nm at 10 K, and ( $\blacksquare$ ) *T*(LIESST) measurement, data recorded in the warming mode with the laser turned off after irradiation for 1 h. The inset shows the derivative of the  $d\chi_{\rm M}T/dT$  vs. *T* curve, the minimum of which corresponds to the *T*(LIESST) value. (b) Relaxation kinetics at various temperatures from 77.5 to 90 K. The solid lines are simulations, see the text.

iron(II) HS state.<sup>[30]</sup> The maximum  $\chi_{\rm M}T$  values for the two compounds, reached at around 30 K, correspond to a photoconversion efficiency of almost 90%.

For  $[Fe(L^2Me)_2][BF_4]_2$ , the HS $\rightarrow$ LS relaxation becomes efficient above 50 K, and  $\chi_M T$  decreases rapidly above 80 K. The limiting temperature T(LIESST), above which the light-induced magnetic high-spin information is erased, was determined to be 93 K from the minimum point of the  $d\chi_M T/dT$  vs. T plot (Figure 5, a, inset).<sup>[29]</sup> The curve is a classical shape for mononuclear complexes with only one crystallographic site. The LIESST relaxation kinetics were systematically investigated at temperatures between 75 K and the highest temperatures accessible with our SQUID apparatus, which are close to the T(LIESST) value (Figure 5, b). The relaxation curves strongly deviate from a single exponential and can be modeled by using a sigmoidal law describing the self-accelerating behavior predicted for strong cooperative systems. This cooperativity arises from



Figure 6. Temperature dependence of  $\chi_M T$  for  $[Fe(L^2Me)_2]$ - $[ClO_4]_2$ . ( $\bigcirc$ ) Data recorded in the cooling and warming modes without irradiation, ( $\Delta$ ) data recorded with irradiation at 514 nm at 10 K, and ( $\blacksquare$ ) *T*(LIESST) measurement, data recorded in the warming mode with the laser turned off after irradiation for 1 h. The inset shows the derivative of the  $d\chi_M T/dT$  vs. *T* curve, the minimum of which corresponds to the *T*(LIESST) value. The full pale- and dark-gray lines are simulations, see the text.

the propagation of the large difference in metal–ligand bond lengths between the HS and LS states through the crystal lattice, resulting in elastic interactions caused by the change in internal pressure inside the solid as the spin transition proceeds.<sup>[31]</sup> Thus, the height of the activation barrier to LIESST relaxation changes as a function of  $\gamma_{\rm HS}$  (the fraction of spin centers in the sample that are high spin at a given temperature), and the relaxation rate  $k^*_{\rm HL}(T, \gamma_{\rm HS})$ depends exponentially on both  $\gamma_{\rm HS}$  and T [Equations (1) and (2) in which a(T) (=  $E_a^*/k_{\rm B}T$ ) is the acceleration factor at a given temperature].

$$\frac{\partial \gamma_{\rm HS}}{\partial t} = -k^*_{\rm HL} \gamma_{\rm HS} \tag{1}$$

$$k^*_{\rm HL}(T, \gamma_{\rm HS}) = k_{\rm HL}(T) \exp[a(T)(1 - \gamma_{\rm HS})]$$
<sup>(2)</sup>

The curves fitted with  $E_a^* = 245 \text{ cm}^{-1}$  are shown as solid lines in Figure 5 (b). The apparent activation energy,  $E_a$ (1670 cm<sup>-1</sup>), and the apparent pre-exponential factor,  $k_{\infty}$ ( $4.9 \times 10^7 \text{ s}^{-1}$ ), of the activated region were calculated from the straight-line fit given by the Arrhenius plot,  $\ln k_{\text{HL}}(T)$ vs. 1/*T*.

The validity of these kinetic parameters was tested by using them to reproduce the experimental T(LIESST) curve. The procedure models both the time and temperature dependence of the relaxation, and combines the quantum mechanical tunneling and the thermally activated regions, in accord with Equation (3).<sup>[28,32]</sup>

$$k_{\rm HL}(T) = k_0 + k_{\infty} \exp(-E_a/k_{\rm B}T)$$
(3)

The rate constant,  $k_0$ , characterizes the relaxation in the quantum tunneling region and is estimated to be an upper limit from the last complete kinetic data recorded at low temperature. The agreement between the calculated and experimental *T*(LIESST) curves is excellent (Figure 5, a),

which confirms that the experimental kinetic parameters used in this simulation and the fitting procedures themselves are appropriate.

In contrast, the T(LIESST) curve of  $[\text{Fe}(L^2\text{Me})_2][\text{ClO}_4]_2$ is clearly nonclassical because at least two steps are observed (Figure 6). The shape of this T(LIESST) curve reflects the two-step character of the thermal spin-crossover curve (Figure 6). The  $d\chi_M T/dT$  vs. T plot reveals a first minimum at 47 K and two minima, close together, at 92 and 98 K. The minimum at 47 K is a broad "peak" and suggests a noncooperative relaxation, whereas the double "peak" at 92-98 K is sharper, which indicates the presence of cooperative interactions in the relaxation process. The large temperature range between the two processes means that their relaxation regimes can be treated separately. We confirmed this by recording the relaxation kinetics at 60 K, that is, in the plateau region separating the two processes (Figure 7). As expected, the magnetic signal remains constant for up to 8 h at 60 K, which confirms that the lowtemperature relaxation step is complete and the high-temperature relaxation step has not commenced at this temperature. This temperature was therefore used to delimit the T(LIESST) curve into two areas, one relating to the lowtemperature process (Step 1) and the other to the high-temperature process (Step 2; Figure 7). From the kinetic data at 60 K, the baseline relating to Step 1 was recorded by decreasing the temperature to 10 K (Figure 7) and was used as a reference to convert the  $\chi_M T$  values into fractions of HS centers,  $\gamma_{\text{HS}}$ . The relaxation kinetics from Steps 1 and 2 are reported in Figure 8a and b, respectively.



Figure 7. (**I**) T(LIESST) measurement for compound [Fe- $(L^2\text{Me})_2$ ][ClO<sub>4</sub>]<sub>2</sub> with various kinetics ( $\nabla$ ) recorded for Steps 1 and 2. (**I**) T(LIESST) measurement for Step 1 only and the related baseline.

The relaxation kinetics for Step 1 are clearly of exponential shape. The data were fitted by using a stretched exponential model that introduces a distribution,  $\sigma$ , of the activation energy,  $E_a$ . The curves fitted with  $\sigma = 30 \text{ cm}^{-1}$  are shown as solid lines in Figure 8 (a). The apparent activation energy,  $E_a$  (550 cm<sup>-1</sup>), and the apparent pre-exponential factor,  $k_{\infty}$  (2.3 × 10<sup>4</sup> s<sup>-1</sup>), were calculated from the straight-line fit given by the Arrhenius plot,  $\ln k_{\text{HI}}(T)$  vs. 1/*T*.

The situation with Step 2 is more complicated because two relaxation processes occur simultaneously. One of these



Figure 8. Relaxation kinetics at various temperatures: (a) Step 1 from 42.5 to 49 K and (b) Step 2 from 60 to 97.5 K. The solid lines are simulations, see the text.

is cooperative and can be described by a sigmoidal law, whereas the other is noncooperative and follows an exponential shape, probably stretched. The simultaneous nature of the relaxations leads to very difficult simulations with many parameters. Hence we were only able to describe the global relaxation rate of Step 2, which we performed by using two approaches. First, the relaxation curves were simulated by a stretched exponential law. This does not provide information on the cooperative character of the kinetics, but usually gives quite relevant values for the relaxation rates because a stretched exponential equates to a simultaneous multiple-relaxation law. The simulations are presented in Figure 8 (b) and the dynamic parameters extracted from the  $\ln k_{\rm HL}(T)$  vs. 1/T plot are  $E_{\rm a} = 1640$  cm<sup>-1</sup>,  $k_{\infty} = 7.5 \times 10^7 \text{ s}^{-1}$ , and  $\sigma = 25 \text{ cm}^{-1}$ . The second approach consisted of trying to simulate the cooperative character of the curve by using a sigmoidal law (see the Supporting Information). The sample behavior is not reproduced on long timescales by this method, but nonetheless, the dynamic parameters obtained are close to those obtained from the stretched exponential simulation ( $E_a = 1600 \text{ cm}^{-1}$ ,  $k_{\infty} =$  $2.0 \times 10^7$  s<sup>-1</sup>, and  $E_a^* = 180$  cm<sup>-1</sup>). They are also comparable to the values obtained for  $[Fe(L^2Me)_2][BF_4]_2$  (see above), which lends them additional credit.

The validity of these results was strengthened by simulation of the multistep T(LIESST) curve of  $[\text{Fe}(L^2\text{Me})_2]$ -  $[ClO_4]_2$ . The simulation includes 15% of the stretched exponential for Step 1 and 85% for Step 2, which corresponds to the proportions determined from the T(LIESST) curve (Figure 6). The first calculation (Figure 6, pale-gray line) was performed by using the dynamic parameters deduced for Step 1 (stretched exponential) and the mean values from the two approaches for Step 2 described above ( $E_a$  =  $1620 \text{ cm}^{-1}, k_{\infty} = 5.0 \times 10^7 \text{ s}^{-1}, \text{ and } E_a^* = 90 \text{ cm}^{-1}$ ). The agreement with experiment is relatively good in that the two-step character is well reproduced and the positions of the two T(LIESST) values are also well simulated. The main divergence occurs in fact from the description of the two steps occurring in the 90-100 K region. For this, we performed a second calculation taking into account three contributions. Step 1 was treated as before by using the derived kinetic parameters and a 15% weighting on the T(LIESST) curve. Step 2 [representing 85% of the T(LIESST) curve] was subdivided into two independent contributions of equal weight; 42.5% with the parameters extracted from the stretched exponential approach and 42.5% using the parameters obtained from the sigmoidal law. The result of the simulation is presented as the darkgray curve in Figure 6. This gave a much better agreement with the description of the steps in the experimental T(LIESST) curve because the three-step character is well reproduced.

Be that as it may, however, whatever the aesthetics of the T(LIESST) simulations, the only relevant conclusion from this study is that the two simultaneous relaxation processes in Step 2 have similar dynamic parameters with  $E_a \approx 1600 \text{ cm}^{-1}$  and  $k_{\infty} \approx 5.0 \times 10^7 \text{ s}^{-1}$ . They are distinguished by the presence of cooperativity in one relaxation ( $E_a^* \approx 180 \text{ cm}^{-1}$ ) and a distribution of activation energies in the other ( $\sigma = 25 \text{ cm}^{-1}$ ).

Single-crystal structures were achieved from solvated crystals of the  $BF_4^-$  salts of all the halogenated ligand complexes. The formation of solvates by these compounds contrasts with  $[Fe(L^1R)_2][BF_4]_2$  (R = Cl and Br), which adopt solvent-free phases under the same crystallization conditions (see above).<sup>[5,17]</sup> Crystals of  $[Fe(L^2Cl)_2][BF_4]_2$ . 3.33CH<sub>3</sub>NO<sub>2</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O contain substantial anion and solvent disorder, including channels of disordered solvent, but a good refinement of this material was achieved at 100 K. Its asymmetric unit contains 1.5 formula units with a half-molecule of the complex spanning a crystallographic  $C_2$  axis. From its metric parameters, the whole molecule is clearly high spin at this temperature, whereas the half-molecule is low spin (Table 1).

The magnetic susceptibility measurements on dried, solvent-free [Fe( $L^2$ Cl)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> are consistent with the crystal structure in showing an almost constant value of  $\chi_M T = 2.4-2.6 \text{ cm}^3 \text{ K mol}^{-1}$  between 50–300 K (plotted in the Supporting Information;  $\chi_M T$  decreases upon further cooling owing to zero-field splitting of the high-spin iron center<sup>[27]</sup>). This is close to the predicted value for a sample comprising two-thirds high-spin and one-third low-spin iron(II) centers (ca. 2.3 cm<sup>3</sup> K mol<sup>-1</sup>),<sup>[33]</sup> which shows that the spin-state population of the compound does not change significantly



upon drying. Moreover, little or none of the high-spin content of the sample undergoes spin-crossover upon cooling.

High-spin complexes of this type can exhibit an angular Jahn-Teller distortion, which inhibits spin-crossover in the solid state.<sup>[3,25,26,34]</sup> This is manifested through a reduction in the *trans*-N(pyridyl)–Fe–N(pyridyl) angle ( $\phi$ ) from its ideal value of 180° and/or a twisting of the two tridentate ligands away from the perpendicular ( $\theta < 90^\circ$ ,  $\theta$  is the dihedral angle between the least-squares planes of the two ligands; Figure 9). The angle  $\phi$  in molecule 1 of  $[Fe(L^2Cl)_2]$ -[BF<sub>4</sub>]<sub>2</sub> [171.98(9)°, Table 1] implies a weak distortion of this type, being close to the threshold value below which spincrossover is not observed (Figure 9).<sup>[3]</sup> An alternative explanation, that spin-crossover is prevented by intermolecular steric contacts in the crystal lattice,<sup>[34,35]</sup> seems less likely. The only noteworthy intermolecular interactions involving molecule 1 are C-H···F contacts of 2.3-2.5 Å between the C-H of the pyrazolyl 3-position and disordered anions in the lattice. Comparable cation---anion contacts are also present in  $[Fe(L^2Me)_2][BF_4]_2$  and do not prevent spin-crossover in that material.



Figure 9. Plot of the Jahn–Teller distortion indices  $\theta$  vs.  $\phi$  for published complexes of the  $[Fe(bpp)_2]^{2+}$  and  $[Fe(bppz)_2]^{2+}$  series<sup>[3]</sup> showing compounds that remain high spin on cooling ( $\bullet$ ), spincrossover complexes in their high-spin state ( $\diamond$ ), and low-spin complexes ( $\blacktriangle$ ). The gray arrow indicates the high-spin molecule in the solvate crystal structure of  $[Fe(L^2Cl)_2][BF_4]_2$ .

In contrast,  $[Fe(L^2Br)_2]^{2+}$  and  $[Fe(L^2I)_2]^{2+}$  form tris-nitromethane solvate crystals that are isostructural with each other but not with the  $[Fe(L^2Cl)_2][BF_4]_2$  solvate. Although there are small differences in their Fe–N distances, both compounds are clearly in a low-spin state at the temperature of measurement, 150 K (Table 1). The molecules show only minor deviations from their ideal  $D_{2d}$  symmetry and associate into layers in the crystal that are related to the terpyridine embrace lattice structure.<sup>[23]</sup>

Drying these dark-brown crystalline materials in vacuo resulted in their decomposition into yellow powders. These powders are mostly solvent-free, although solid  $[Fe(L^2Br)_2]$ - $[BF_4]_2$  may contain some residual nitromethane by elemental microanalysis. Variable-temperature magnetic measurements showed that  $[Fe(L^2Br)_2][BF_4]_2$  is fully high spin at 330 K and below (plotted in the Supporting Information). Although  $[Fe(L^2I)_2][BF_4]_2$  is also predominantly high spin at 330 K, a steady decrease in  $\chi_M T$  from 3.0 cm<sup>3</sup> K mol<sup>-1</sup> at

330 K to 2.3 cm<sup>3</sup> K mol<sup>-1</sup> at 30 K indicates a very gradual partial spin-crossover in approximately 20% of the iron centers in the sample over this temperature range. Thus,  $[Fe(L^2Br)_2][BF_4]_2 \cdot nCH_3NO_2$  transforms fully from a lowspin crystalline solvate (n = 3) into a high-spin powder (n = 1), but this change in spin state is incomplete upon drying  $[Fe(L^2I)_2][BF_4]_2 \cdot nCH_3NO_2$ . Solid  $[Fe(L^2Br)_2][CIO_4]_2$  and  $[Fe(L^2I)_2][CIO_4]_2$  are also high spin at room temperature and exhibit very gradual, partial spin-crossover on cooling, but single crystals of these salts were not obtained.

The influence of ligand substituents on spin-crossover in the absence of lattice effects can be probed by solutionphase measurements.<sup>[36,37]</sup> The variable-temperature Evans method was used to study the spin-state behavior of  $[Fe(L^2R)_2][BF_4]_2$  (R = Me, Cl, and Br) and  $[Fe(bppz)_2]$ -[BF<sub>4</sub>]<sub>2</sub> (Figure 10).<sup>[38]</sup> Data for [Fe(bppz)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> were obtained in (CD<sub>3</sub>)<sub>2</sub>CO to maximize the temperature range of the study, but the other compounds were measured in CD<sub>3</sub>NO<sub>2</sub> for reasons of solubility. The use of these different, weakly interacting solvents is unlikely to influence the results of the study.<sup>[37]</sup> Solutions of [Fe(bppz)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> and  $[Fe(L^2Me)_2][BF_4]_2$  exhibited the expected gradual spinstate equilibria; their  $T_{\frac{1}{2}}$  values were estimated to be 268 and 291 K, respectively (Figure 10). These values are both around 20 K higher than those of the corresponding complexes of the  $[Fe(L^1R)]^{2+}$  series,<sup>[25,39]</sup> and the higher  $T_{\frac{1}{2}}$ value for  $[Fe(L^2Me)_2][BF_4]_2$  reflects the electron-donating character of its methyl substituents. The enthalpies of the spin-crossover derived from these analyses are 20.2 kJ mol<sup>-1</sup> for  $[Fe(bppz)_2][BF_4]_2$  and 25.3 kJ mol<sup>-1</sup> for  $[Fe(L^2Me)_2]$ -[BF<sub>4</sub>]<sub>2</sub>. These are typical values for this class of complex and show that the compounds do not undergo significant solvolysis under these conditions.<sup>[40]</sup>



Figure 10. Solution-phase magnetic susceptibility data for  $[Fe(bppz)_2][BF_4]_2$  in  $(CD_3)_2CO$  ( $\bigcirc$ ) and  $[Fe(L^2Me)_2][BF_4]_2$  in  $CD_3NO_2$  ( $\bigcirc$ ).

In contrast, data derived from the Evans method for  $[Fe(L^2Cl)_2][BF_4]_2$  and  $[Fe(L^2Br)_2][BF_4]_2$  in CD<sub>3</sub>NO<sub>2</sub> show  $\chi_M T$  values that are almost constant between 253–323 K, and that lie between the values expected for a high-spin and low-spin complex. In the latter case, <sup>1</sup>H NMR peaks from the free  $L^2Br$  ligand also became resolved at higher temperatures. This indicates substantial decomposition of the



complexes in this weakly associating solvent to the extent that insufficient intact  $[Fe(L^2R)_2]^{2+}$  centers are present for their spin transitions to be measured. This is consistent with the above observations regarding the solution stability of these complexes, but contrasts with  $[Fe(L^1R)_2]^{2+}$  (R = Cl and Br), which are stable in solution under the same conditions.<sup>[17]</sup> The electron-withdrawing halide substituents on the  $L^2$ Cl and  $L^2$ Br ligands reduce the basicity of the pyrazole groups,<sup>[41]</sup> which makes their complexes more reactive in solution for two reasons. First, the resultant weaker ligand field increases the high-spin population of the complexes at a particular temperature. Secondly, the Fe–N bonds in the complex are more kinetically labile, and so more reactive towards solvent.

Attempts to crystallize  $[Fe(L^2CCPh)_2][BF_4]_2$  from undried MeNO<sub>2</sub>/Et<sub>2</sub>O yielded yellow prisms. The asymmetric unit contains half a  $[Fe(L^2CCPh)(OH_2)_2][BF_4]_2 \cdot (C_2H_5)_2O$  moiety spanning a crystallographic  $C_2$  axis together with three closely spaced Fourier peaks 2.1–2.2 Å from the iron atom that refined reasonably as partial oxygen sites (Figure 11). Therefore this complex was interpreted as being a random co-crystal of seven-coordinate  $[Fe(L^2CCPh)(OH_2)_4]^{2+}$  and six-coordinate  $[Fe(L^2CCPh)(OH_2)_3]^{2+}$  in a 2:3 occupancy ratio, which is consistent with the microanalysis of the dried material (see the Supporting Information



Figure 11. View of the crystal structure of the complex molecule of  $[Fe(L^2CCPh)(OH_2)_4]_x[Fe(L^2CCPh)(OH_2)_3]_{1-x}[BF_4]_2 \cdot (C_2H_5)_2O (x \approx 0.4)$ . Thermal ellipsoids are drawn at the 50% probability level, and carbon-bound H atoms have been omitted for clarity. The complex is seven-coordinate when O(20A) and O(20A<sup>vi</sup>) are both occupied, and six-coordinate with either O(20B), O(20C), or O(20C<sup>vi</sup>) occupied. Symmetry code: (vi) -x, y, 3/2 - z.

for more details). The apparent loss of a  $L^2$ CCPh ligand during the crystallization process again emphasizes the solution lability of the  $[Fe(L^2R)_2]^{2+}$  complexes.

### Conclusions

Several bppz derivatives substituted at the pyrazolyl C-4 positions ( $L^2R$ ) have been prepared. A wider range of derivatives could be accessed than for the corresponding 2,6-di(pyrazol-1-yl)pyridine ligand series ( $L^1R$ ) because the standard  $L^2R$  synthesis employs milder conditions. However, the  $[Fe(L^2R)_2]^{2+}$  complexes were harder to isolate than  $[Fe(L^1R)_2]^{2+}$  because the  $L^2R$  ligands dissociate more easily from the iron center in solution and are less soluble. This led to hydrolysis of the complexes and ligand precipitation to the extent that  $[Fe(L^2NO_2)_2]^{2+}$ ,  $[Fe(L^2NH_2)_2]^{2+}$ , and  $[Fe(L^2CPh)_2]^{2+}$  could not be obtained in pure form. The solution lability of  $[Fe(L^2R)_2]^{2+}$  was also evident from their NMR behavior when R is an electron-withdrawing halo substituent.

Comparison of the  $[Fe(L^1R)_2]X_2$  and  $[Fe(L^2R)_2]X_2$  salts in the solid state is difficult because these pairs of complexes are rarely isostructural for the same "R" group and anion. Thus, for example,  $[Fe(L^2Cl)_2][BF_4]_2$  and  $[Fe(L^2Br)_2]$ -[BF<sub>4</sub>]<sub>2</sub> form solvated crystals that are not spin-crossover active, which contrasts with the spin transitions undergone by solvent-free, crystalline  $[Fe(L^1Cl)_2][BF_4]_2$  and [Fe- $(L^{1}Br)_{2}$ [[BF<sub>4</sub>]<sub>2</sub>.<sup>[5,17]</sup> However, solution data imply that the pyrazinyl groups in  $[Fe(L^2R)_2]^{2+}$  (R = H or Me) thermodynamically stabilize the low-spin state of the complex to a small extent compared with the pyridyl donors in [Fe- $(L^1 R)_2$ <sup>2+</sup>. This is consistent with other studies of spincrossover in pyrazine-containing complexes.<sup>[42]</sup> This result is counter-intuitive because the lower basicity of the pyrazine ring should lead to weaker N→Fe dative bonds. Presumably, therefore, stronger  $Fe \rightarrow L^2R$  back-bonding to the more electron-deficient pyrazine ring has a more significant effect on the d-orbital splitting of the iron center.

Although they are isostructural in both spin states, as determined by powder X-ray diffraction analysis, the salts of  $[Fe(L^2Me)_2][BF_4]_2$  and  $[Fe(L^2Me)_2][ClO_4]_2$  show very different thermal and light-induced spin-transition behavior. Thermal spin-crossover in  $[Fe(L^2Me)_2][BF_4]_2$  occurs in one step at  $T_{\frac{1}{2}} = 242$  K, which is associated with a *T*(LIESST) value of 93 K. This is broadly consistent with the previously reported relationship between  $T_{\frac{1}{2}}$  and T(LIESST) for  $[Fe(L^1R)_2]^{2+}$  and  $[Fe(L^2R)_2]^{2+}$  complexes [Equation (4),  $T_0 = 150$  K].<sup>[6,17,43]</sup>

$$T(\text{LIESST}) = T_0 - 0.3T_{\frac{1}{2}}$$
(4)

In contrast, thermal spin-crossover in  $[Fe(L^2Me)_2]$ -[ClO<sub>4</sub>]<sub>2</sub> occurs in two steps at 171 and 207 K, which is largely reflected by the stepped T(LIESST) curve. The relaxation behavior of the photoinduced phase was found to be even more complicated and was tentatively simulated. A first attempt to relate these data to Equation (4) is to correlate the highest thermal  $T_{\frac{1}{2}}$  (207 K) with the lowest



T(LIESST) value (47 K), and the second step of the thermal spin transition at 171 K with the T(LIESST) value near 95 K. Notably, the abrupt nature of the first step of the spin transition does not match the gradual shape of the lowtemperature step of the T(LIESST) curve. Nonetheless, structural rearrangements occurring during the cooling and/or photoexcitation processes can give rise to such observations. For example, this has been observed in  $[FeL_2]$ - $(ClO_4)_2$  {L = 2-[3-(2'-pyridyl)pyrazol-1-ylmethyl]pyridine}, in which competition between cooperative interactions and structural disorder leads to an abrupt thermal spin-crossover and a gradual T(LIESST) curve.<sup>[44]</sup> As described above, the two-step thermal spin-crossover in  $[Fe(L^2Me)_2]$ -[ClO<sub>4</sub>]<sub>2</sub> could be controlled by changes to perchlorate anion disorder during the transition,<sup>[14,16]</sup> or it could reflect the lower crystallinity of the perchlorate salt, which will lead to a more heterogeneous distribution of  $[Fe(L^2Me)_2]^{2+}$  sites in the lattice. Both these hypotheses could explain the LIESST relaxation behavior of the compound, showing multiple relaxation pathways with similar activation energies but different cooperativities. Unfortunately, the absence of crystallographic data for  $[Fe(L^2Me)_2][ClO_4]_2$  prevents us from validating these suggestions.

A second approach to understanding  $[Fe(L^2Me)_2]$ -[ClO<sub>4</sub>]<sub>2</sub> by using Equation (4) is to consider that the  $T_{\frac{1}{2}}$ value of 207 K is correlated with the T(LIESST) value of 95 K, and that the  $T_{\frac{1}{2}}$  step at 171 K with the T(LIESST)value of 47 K. In this case the cooperative (and reversely, the gradual) thermal spin-transition curve is associated with the cooperative (gradual) T(LIESST) regime. Such behavior can be linked to changes in the coordination sphere of two different crystallographic sites, which has been, for example, observed for [Fe(NCS)<sub>2</sub>(PM-BiA)<sub>2</sub>] [PM-BiA = N-(2'-pyridylmethylene)-4-aminobiphenyl], which possesses two distinct isomorphs.<sup>[32,45]</sup>

Whichever explanation is correct, if we relate the resultant  $T(\text{LIESST})/T_{\frac{1}{2}}$  correlations to the T(LIESST) database,<sup>[28]</sup> the stability of the photoinduced high-spin state of  $[\text{Fe}(L^2\text{Me})_2][\text{CIO}_4]_2$  does not lie on the same  $T_0$  line as other complexes of this type.<sup>[6,17,43]</sup> This is only the second compound from the  $[\text{Fe}(\text{bpp})_2]^{2+}$  series that deviates from the T(LIESST) vs.  $T_{\frac{1}{2}}$  relationship [Equation (4)] to be identified.<sup>[46]</sup> This point is particularly interesting because it may allow identification of the factors required to increase the stability of a photoinduced high-spin state at room temperature.

#### **Experimental Section**

**Instrumentation:** Elemental microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. IR spectra were recorded as Nujol mulls pressed between NaCl windows between 600–4,000 cm<sup>-1</sup> by using a Nicolet Avatar 360 spectrophotometer. <sup>1</sup>H NMR spectra were recorded with a Bruker DPX300 spectrometer operating at 300.2 MHz. UV/Vis/NIR spectra were recorded with a Perkin–Elmer Lambda900 spectrophotometer in 1 cm quartz solution cells between 200–3000 nm. Elec-

trospray mass spectra (ESI MS) were obtained with a Waters ZQ4000 spectrometer from MeCN feed solutions. All mass peaks have the correct isotopic distributions for the proposed assignments. Powder X-ray diffraction analyses were performed with a Bruker D8 Advance A25 diffractometer using Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418$  Å).

Magnetic susceptibility measurements were performed by using a Quantum Design SQUID magnetometer in an applied field of 1000 or 5000 G. A diamagnetic correction for the sample was estimated from Pascal's constants;<sup>[33]</sup> a diamagnetic correction for the sample holder was also used. Photomagnetic measurements were performed by using a Spectrum Physics Series 2025 Kr<sup>+</sup> laser ( $\lambda$  = 514 nm) coupled via an optical fibre to the cavity of a MPMS-55 Quantum Design SQUID magnetometer. The optical power at the sample surface was adjusted to 5 mW cm<sup>-2</sup>, and it was verified that this resulted in no change in magnetic response due to heating of the sample. Photomagnetic samples consisted of a thin layer of compound, the weight of which was determined by comparison of the thermal spin-crossover curve with that of a more accurately weighed sample of the same material. Susceptibility measurements in solution were obtained by Evans method using a Bruker DRX500 spectrometer operating at 500.13 MHz.<sup>[38]</sup> A diamagnetic correction for the sample<sup>[33]</sup> and a correction for the variation of the density of the solvent with temperature<sup>[47]</sup> were applied to these data.

**Materials and Methods:** Unless otherwise stated, all reactions were carried out in air and in non-pre-dried AR-grade solvents. 2,6-Di-(pyrazol-1-yl)pyrazine (bppz) was synthesized by the literature method<sup>[11]</sup> and all other reagents were used as commercially supplied.

Synthesis of 2,6-Bis(4-chloropyrazol-1-yl)pyrazine ( $L^2$ Cl): A solution of bppz (1.1 g, 5.2 mmol) in glacial acetic acid (70 cm<sup>3</sup>) was added to a 5% aqueous solution of NaOCl (40 cm<sup>3</sup>) diluted in 100 cm<sup>3</sup> of water. The yellow mixture was stirred at room temperature for 2 h and further heated for 3 h at 70 °C. The mixture was poured onto ice-water (200 cm<sup>3</sup>) and the resultant precipitate extracted into CHCl<sub>3</sub> (200 cm<sup>3</sup>, then  $3 \times 30$  cm<sup>3</sup>). The combined organic layers were washed with saturated aqueous  $K_2CO_3$  (80 cm<sup>3</sup>) and water (80 cm<sup>3</sup>), and then dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure to yield a pale-yellow solid, which was washed with dimethylformamide and diethyl ether to afford a white powder, yield 0.67 g, 46%, m.p. 146-147 °C. <sup>1</sup>H NMR  $[300 \text{ MHz}, (\text{CD})_3\text{SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ SO}]: \delta = 8.02 \text{ (s, 2 H, Pz 3-H)}, 9.01 \text{ and } 9.04 \text{ (both } 10^{-1} \text{ CD})_3 \text{ CD})$ s, 2 H, Pz 5-H and Pyz 3,5-H) ppm. MS (ESI): m/z = 281.9[HL<sup>Cl</sup>]<sup>+</sup>. C<sub>10</sub>H<sub>6</sub>Cl<sub>2</sub>N<sub>6</sub> (281.11): calcd. C 42.7, H 2.15, N 30.0; found C 43.1, H 2.10, N 30.0.

**2,6-Bis(4-bromopyrazol-1-yl)pyrazine** ( $L^2$ **Br**): A solution of 4-bromopyrazole (5.00 g, 34 mmol) in dry dmf (100 cm<sup>3</sup>) was added to NaH (0.90 g, 37 mmol) under N<sub>2</sub>, and the resultant suspension was stirred at 50 °C for 20 min. Solid 2,6-dichloropyrazine (2.43 g, 16 mmol) was then added in one portion and the mixture was stirred at 90 °C for a further 16 h. After cooling, a large excess of cold water was added to the mixture to yield a yellow solid. The solid was collected and washed with ethyl acetate to yield a white powder, yield 1.95 g, 31%, m.p. 140–142 °C. <sup>1</sup>H NMR [300 MHz, (CD)<sub>3</sub>SO]:  $\delta$  = 7.74 (s, 2 H, Pz 3-H), 8.50 (s, 2 H, Pz 5-H), 9.17 (s, 2 H, Pyz 3,5-H) ppm. MS (ESI): m/z = 392.9 [Na $L^{\text{Br}}$ ]<sup>+</sup>. C<sub>10</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>6</sub> (370.01): calcd. C 32.5, H 1.63, N 22.7% found C 32.2, H 1.55, N 22.3.

**2,6-Bis(4-iodopyrazol-1-yl)pyrazine**  $(L^2I)$ : Method as for  $L^2Br$ , but by using 4-iodopyrazole (6.60 g, 34 mmol). The crude yellow solid was washed with ethyl acetate to afford the pure product as a white



powder, yield 1.67 g, 21%, m.p. 140–142 °C. <sup>1</sup>H NMR [300 MHz, (CD)<sub>3</sub>SO]:  $\delta$  = 8.01 (s, 2 H, Pz 3-H), 9.13 (s, 2 H, Pz 5-H), 9.25 (s, 2 H, Pyz 3,5-H) ppm. MS (ESI): *m*/*z* = 486.9 [Na*L*<sup>1</sup>]<sup>+</sup>. C<sub>10</sub>H<sub>6</sub>I<sub>2</sub>N<sub>6</sub> (464.01): calcd. C 25.9, H 1.30, N 18.1; found C 25.6, H 1.20, N 17.7.

**2,6-Bis(4-methylpyrazol-1-yl)pyrazine** ( $L^2$ Me): Method as for  $L^2$ Br, but by using 4-methylpyrazole (2.79 g, 34 mmol). The resultant yellow solid was purified by flash silica column chromatography in dichloromethane/ethyl acetate/hexane (1:1:2) to give  $L^{Me}$  as a white powder, yield 1.89 g, 46%, m.p. 147–148 °C. <sup>1</sup>H NMR [300 MHz, (CD)<sub>3</sub>SO]:  $\delta$  = 2.18 (s, 6 H, CH<sub>3</sub>), 7.61 (s, 2 H, Pz 3-H), 8.24 (s, 2 H, Pz 5-H), 9.08 (s, 2 H, Pyz 3,5-H) ppm. MS (ESI): m/z = 263.1 [Na $L^{Me}$ ]<sup>+</sup>. C<sub>12</sub>H<sub>12</sub>N<sub>6</sub> (240.27): calcd. C 60.0, H 5.03, N 35.0; found C 60.0, H 5.00, N 35.2.

**2,6-Bis(4-nitropyrazol-1-yl)pyrazine** ( $L^2NO_2$ ): Method as for  $L^2Br$ , but by using 4-nitropyrazole (3.85 g, 34 mmol). This yielded a yellow powder, which was purified by washing with ethyl acetate to give a white solid, yield 1.72 g, 33%, m.p. 151–153 °C. <sup>1</sup>H NMR [300 MHz, (CD)<sub>3</sub>SO]:  $\delta$  = 8.84 (s, 2 H, Pz 3-H), 9.35 (s, 2 H, Pyz 3,5-H), 10.49 (s, 2 H, Pz 5-H) ppm. MS (ESI): m/z = 302.3  $[L^{NO2}]^+$ . C<sub>10</sub>H<sub>6</sub>N<sub>8</sub>O<sub>4</sub> (302.23): calcd. C 39.7, H 2.00, N 37.1; found C 39.8, H 1.95, N 37.1.

**2,6-Bis(4-aminopyrazol-1-yl)pyrazine** ( $L^2$ NH<sub>2</sub>): A mixture of  $L^2$ NO<sub>2</sub> (0.66 g, 2.2 mmol), iron powder (0.73 g, 3.7 mmol), and ammonium chloride (1.17 g, 21.9 mmol) was suspended in a ethanol/water (2:1, 20 cm<sup>3</sup>) under N<sub>2</sub>. The mixture was heated at reflux for 30 min. The black mixture was filtered whilst hot and the yellow filtrate concentrated to around 5 cm<sup>3</sup> under reduced pressure. Storage at 0 °C for 1 h afforded a yellow precipitate, which was collected, repeatedly washed with water, and dried. Although there were no organic impurities in the product by <sup>1</sup>H NMR, its poor microanalysis may indicate a minor inorganic salt contaminant that we were unable to remove, yield 0.20 g, 56%. <sup>1</sup>H NMR [300 MHz, (CD)<sub>3</sub>SO]:  $\delta$  = 5.60 (br. s, 4 H, NH<sub>2</sub>), 7.71 and 7.89 (both s, 2 H, Pz 5-H and 5-H), 9.01 (s, 2 H, Pyz 3,5-H) ppm. MS (ESI): *m/z* = 265.5 [NaL<sup>NH2</sup>]<sup>+</sup>. C<sub>10</sub>H<sub>10</sub>N<sub>8</sub> (242.24): calcd. C 49.6, H 4.16, N 46.3; found C 48.0, H 4.10, N, 43.2.

2,6-Bis[4-(phenylethynyl)pyrazol-1-yl]pyrazine Hemihydrate (L<sup>2</sup>CCPh·  $\frac{1}{2}$ H<sub>2</sub>O): This ligand was prepared under N<sub>2</sub>.  $L^2$ I (0.36 g, 0.78 mmol) was dissolved in fresh triethylamine (10 cm<sup>3</sup>) and dioxane  $(2 \text{ cm}^3)$ , and the mixture was stirred for 15 min. [Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub>] (55 mg, 0.078 mmol), PPh<sub>3</sub> (41 mg, 0.156 mmol), and CuI (20 mg, 0.1 mmol) were then added, followed by phenylacetylene (0.35 g, 3.5 mmol). The resultant mixture was heated at 80 °C for 30 min until it became a dark orange. It was then cooled to room temperature and left to stir for 1 h during which a light-orange product precipitated. The mixture was neutralized in an ice-bath with dilute HCl and the product was extracted with  $CH_2Cl_2$  (3 × 20 cm<sup>3</sup>). The orange organic phase was collected, washed with a saturated solution of NH<sub>4</sub>Cl, and dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give a dark-orange solid, which was washed with ethanol (50 cm<sup>3</sup>) to give a white powder, yield 0.26 g, 78%, m.p. 126–128 °C. <sup>1</sup>H NMR [300 MHz, (CD)<sub>3</sub>SO]:  $\delta$  = 7.47 (m, 3 H, Ph 3,4,5-H), 7.56 (m, 2 H, Ph 2,6-H), 8.38 (s, 2 H, Pz 3-H), 8.50 (s, 2 H, Pz 5-H), 9.56 (s, 2 H, Pyz 3,5-H) ppm. MS (ESI):  $m/z = 413.1 \ [\text{H}L^{\text{CCPh}}]^+$ .  $C_{26}H_{16}N_6 \cdot \frac{1}{2}H_2O$  (421.46): calcd. C 74.1, H 4.07, N 19.9; found C 73.7, H 3.80, N 19.5.

**Synthesis of the Complexes:** The same basic method, described here for  $[Fe(L^2Me)_2][BF_4]_2$ , was used for the synthesis of all the complexes. A solution of  $L^2Me$  (0.20 g, 0.83 mmol) and  $Fe[BF_4]_2$ ·6H<sub>2</sub>O (0.14 g, 0.42 mmol) in nitromethane (15 cm<sup>3</sup>) and triethyl orthoformate (3 drops) was heated at reflux until all the solid had dissolved

(ca. 3 h). The cooled solution was concentrated in vacuo to around 5 cm<sup>3</sup>. Slow diffusion of diethyl ether vapor into the filtered solution afforded orange crystals of the product. The other complex salts were prepared using appropriate amounts of the relevant  $L^2R$  ligand and/or Fe[ClO<sub>4</sub>]<sub>2</sub>·6H<sub>2</sub>O, as required. Yields after recrystallization ranged from 42–77%. Microanalytical data for the complexes are listed below.

 $[Fe(L^2Me)_2][BF_4]_2$ : C<sub>24</sub>H<sub>24</sub>B<sub>2</sub>F<sub>8</sub>FeN<sub>12</sub> (709.99): calcd. C 40.6, H 3.41, N 23.7; found C 40.7, H 3.35, N 23.7.

**[Fe(L<sup>2</sup>Me)<sub>2</sub>][CIO<sub>4</sub>]<sub>2</sub>:** C<sub>24</sub>H<sub>24</sub>Cl<sub>2</sub>FeN<sub>12</sub>O<sub>8</sub> (735.28): calcd. C 39.2, H 3.29, N 22.9; found C 39.4, H 3.25, N 23.0.

 $[Fe(L^2Cl)_2][BF_4]_2: C_{20}H_{12}B_2Cl_4F_8FeN_{12}$  (791.67): calcd. C 30.3, H 1.53, N 21.2; found C 30.2, H 1.72, N 21.2.

**[Fe(***L***<sup>2</sup>Br)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub>·CH<sub>3</sub>NO<sub>2</sub>:** C<sub>20</sub>H<sub>12</sub>B<sub>2</sub>Br<sub>4</sub>F<sub>8</sub>FeN<sub>12</sub>·CH<sub>3</sub>NO<sub>2</sub> (1030.51): calcd. C 24.4, H 1.47, N 17.7; found C 24.3, H 1.75, N 17.5.

 $[Fe(L^2Br)_2][CIO_4]_2$ : C<sub>20</sub>H<sub>12</sub>Br<sub>4</sub>Cl<sub>2</sub>FeN<sub>12</sub>O<sub>8</sub> (994.76): calcd. C 24.1, H 1.22, N 16.9; found C 23.9, H 1.50, N 16.8.

 $[Fe(L^2I)_2][BF_4]_2: C_{20}H_{12}B_2F_8FeI_4N_{12}$  (1157.47): calcd. C 20.8, H 1.05, N 14.5; found C 20.8, H, 1.04, N 14.5.

**[Fe(L<sup>2</sup>I)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub>:** C<sub>20</sub>H<sub>12</sub>Cl<sub>2</sub>FeI<sub>4</sub>N<sub>12</sub>O<sub>8</sub> (1182.76): calcd. C 20.3, H 1.02, N 14.2; found C 20.3, H 1.35, N 14.6.

 $[Fe(L^2CCPh)(OH_2)_4]_x[Fe(L^2CCPh)(OH_2)_3]_{1-x}[BF_4]_2$  ( $x \approx 0.5$ ): Complexation of Fe[BF<sub>4</sub>]<sub>2</sub>·6H<sub>2</sub>O (0.14 g, 0.42 mmol) with  $L^2$ CCPh (0.34 g, 0.83 mmol, 2 equiv.) following the above procedure gave this 1:1 metal/ligand product as a yellow solid, yield 0.20 g, 45%. ( $C_{26}H_{24}B_2F_8FeN_6O_4$ )\_{0.5}( $C_{26}H_{22}B_2F_8FeN_6O_3$ )\_{0.5} (704.96): calcd. C 44.3, H 3.29, N 11.9; found 44.8, H 3.80, N 11.3.

**Single-Crystal Structure Analyses:** Single crystals of the complexes were all obtained by slow diffusion of diethyl ether vapor into nitromethane solutions of the compounds. All diffraction data were collected with a Bruker X8 Apex diffractometer using graphitemonochromated Mo- $K_a$  radiation ( $\lambda = 0.71073$  Å) generated by a rotating anode. The structure was solved by direct methods (SHELXS-97)<sup>[48]</sup> and then developed by least-squares refinement on  $F^2$  (SHELXL-97).<sup>[48]</sup> Crystallographic figures were prepared by using XSEED,<sup>[49]</sup> which incorporates POVRAY.<sup>[50]</sup> Experimental data obtained from the structure determinations are presented in Table 2.

**Structure Refinement of**  $L^2$ **CI:** The asymmetric unit contains half a molecule with N(1) and N(4) lying on the crystallographic  $C_2$  axis  $[x, 1 - x, \frac{1}{4}]$ . No restraints were applied in the final model. All non-H atoms were refined anisotropically. All H atoms were located in the Fourier map and allowed to refine freely with a common  $U_{iso}$  thermal parameter of 0.027(3) Å<sup>2</sup>. The refined C–H distances were in the range of 0.92(2)–1.01(2) Å.

Structure Refinement of  $[Fe(L^2Me)_2][BF_4]_2$ : The compound was originally solved in the space group  $P2_1$  and then transformed into  $P\overline{4}2_1c$  by using the ADSYMM routine in PLATON.<sup>[51]</sup> The crystal was refined as a racemic twin. The asymmetric unit contains a quarter of the complex dication, with Fe(1) occupying the crystallographic  $S_4$  site [0, 1, 1] and N(2) and N(5) lying on the  $C_2$  axis [0, 1, *z*], and half a BF<sub>4</sub><sup>-</sup> anion that is disordered about the  $C_2$ axis [0,  $\frac{1}{2}$ , *z*]. Two equally occupied partial environments for this disordered half-anion were refined subject to the refined restraints B–F 1.40(2) Å and F…F 2.29(2) Å. All non-H atoms except the disordered anion were refined anisotropically and all H atoms were placed in calculated positions and refined by using a riding model.



	$L^2$ Cl	$[Fe(L^2Me)_2][BF_4]_2$	$[Fe(L^2Cl)_2][BF_4]_2 \cdot 3.33CH_3NO_2 \cdot (C_2H_5)_2O$
Formula	C <sub>10</sub> H <sub>6</sub> Cl <sub>2</sub> N <sub>6</sub>	C <sub>24</sub> H <sub>24</sub> B <sub>2</sub> F <sub>8</sub> FeN <sub>12</sub>	C <sub>27,33</sub> H <sub>32</sub> B <sub>2</sub> Cl <sub>4</sub> F <sub>8</sub> FeN <sub>15,33</sub> O <sub>7,67</sub>
$M_{\rm r} [{\rm gmol}^{-1}]$	281.11	710.02	1069.29
Crystal system	tetragonal	tetragonal	monoclinic
Space group	$P4_{1}2_{1}2$	$P\bar{4}2_1c$	C2/c
a [Å]	5.1884(3)	9.7297(14)	40.025(4)
b [Å]	_	_	17.0702(17)
	41.708(3)	17.5425(16)	19.958(2)
<i>B</i> [°]	_	_	101.775(4)
$V[A^3]$	1122.77(13)	1660.7(4)	13349(2)
	150(2)	300(2)	100(2)
7	1	2	12
$D \sim [\alpha \text{ cm}^{-3}]$	1 663	1 420	1 596
$D_{\text{calcd.}}$ [genn ]	0.567	0.525	0.675
$\mu$ [IIIII ] Min (may transmission)	0.307	0.555	0.075
	0.770/0.902	0.055/0.900	0.099/0.831
$\theta_{\max}$	30.61	27.60	28.50
Measured reflections	27/46	20/13	144862
Unique reflections	1744	1926	16845
Reflections $[F_{\rm o} > 4\sigma(F_{\rm o})]$	1727	1561	13010
R <sub>int</sub>	0.043	0.061	0.064
Parameters	93	128	983
$R_1^{[a]}[F_o > 4\sigma(F_o)]$	0.031	0.039	0.058
$wR_2^{[b]}$ [all data]	0.076	0.112	0.200
Gof	1.286	1.062	1.074
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}$ [e Å <sup>-3</sup> ]	0.32/-0.25	0.25/-0.24	1.86/-0.77
Flack parameter	0.01(9)	0.46(3)	_
	$[Fe(L^2Br)_2][BF_4]_2 \cdot 3CH_3NO_2$	$[Fe(L^2I)_2][BF_4]_2 \cdot 3CH_3NO_2$	$[Fe(L^2CCPh)(OH_2)_4]_x [Fe(L^2CCPh)(OH_2)_3]_{1-x}$ - [BF <sub>4</sub> ] <sub>2</sub> (x = 0.4)
Formula	Ca2Ha1BaBr4FeFeN15Oc	Ca2Ha1BaL4FeFeN15Oc	CaoHaa BaFeFeNcO4 4
M [gmol <sup>-1</sup> ]	1152.66	1340.62	777 29
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2./c	P2./c	C2/c
	17.678(4)	18 320(3)	18 9558(15)
$u [\Delta]$	17.076(4) 17.144(3)	17 445(3)	13,6788(12)
	17.144(3) 14.190(2)	1/.7+3(3) 1/.502(2)	17.029(2)
	14.160(3)	14.302(2)	17.920(2)
$p \begin{bmatrix} 1 \\ 1 \end{bmatrix}$	2048 2(14)	112.800(8)	120.731(3)
	3948.2(14) 150(2)	42/0.0(11)	5995.9(7) 150(2)
	150(2)	150(2)	150(2)
	4	4	4
$D_{\text{calcd.}} [\text{gcm}^{-5}]$	1.939	2.085	1.292
$\mu [\text{mm}^{-1}]$	4.527	3.335	0.455
Min./max. transmission	0.644/1.029	0.574/0.979	0.763/0.972
$\theta_{\max}$ [°]	27.53	29.02	28.46
Measured reflections	75061	166820	53701
Unique reflections	9056	11348	5056
Reflections $[F_{\rm o} > 4\sigma(F_{\rm o})]$	6445	9191	4110
R <sub>int</sub>	0.077	0.075	0.050
Parameters	553	518	257
$R_1^{[a]}[F_o > 4\sigma(F_o)]$		0.022	0.086
$wR_2^{[b]}$ [all data]	0.036	0.033	0.080
4-1 I	0.036 0.084	0.033 0.080	0.283
Gof	0.036 0.084 1.008	0.033 0.080 1.031	0.283 1.096
Gof $\Delta \rho_{max} / \Delta \rho_{min} [e Å^{-3}]$	0.036 0.084 1.008 0.77/-0.57	0.033 0.080 1.031 1.26/-1.21	0.080 0.283 1.096 1.82/-0.56

Table 2. Experimental data for the crystal structure determinations in this work.

 $\overline{[\mathbf{a}] \ R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|} \ [\mathbf{b}] \ w R_2 = \{ \Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{\frac{1}{2}}.$ 

Structure Refinement of  $[Fe(L^2Cl)_2][BF_4]_2\cdot 3.33CH_3NO_2\cdot (C_2H_5)_2O$ : The asymmetric unit contains 1.5 formula units with one half-molecule of the complex spanning the crystallographic  $C_2$  axis  $[0, y, \frac{1}{4}]$ . All three of the unique  $BF_4^-$  ions are disordered and were modeled over two or three sites by using the refined restraints B–F 1.40(2) Å and F···F 2.29(2) Å. Five nitromethane solvent sites were also identified. Three of these are wholly occupied and the other two are half-occupied. A half-molecule of diethyl ether was also located overlying the two half-occupied nitromethane sites. Finally, a badly disordered region near the inversion center at  $[0, \frac{1}{2}, \frac{1}{2}]$  forms channels parallel to the unit cell *c* axis of approximate dimensions  $5.0 \times 3.3$  Å (measured from the ordered solvent molecules lining the edges of the channels). A SQUEEZE analysis<sup>[51]</sup> found four voids of 445 Å<sup>3</sup> each per unit cell, containing a total of 602 electrons. That equates to 151 electrons per void, or 75 electrons per asymmetric unit, which could correspond to one molecule



of nitromethane (32 electrons) plus one molecule of diethyl ether (42 electrons). This formula was used for the density and F(000) calculations.

The original dataset, rather than that obtained by SQUEEZE, was used for the final refinement cycles. The more intense Fourier peaks in the disordered channels were refined as 0.2-occupied C atoms, but no attempt was made to assign these to individual partial solvent sites. All wholly occupied non-H atoms and the partial anion sites with an occupancy  $\geq 0.5$  were refined anisotropically, whereas H atoms were placed in calculated positions and refined by using a riding model. There were 14 residual Fourier peaks of  $1.0-2.0 \text{ e} \text{ Å}^{-3}$  in the final model, most of which also lie within the unassigned region of the disordered solvent.

Structure Refinement of  $[Fe(L^2Br)_2][BF_4]_2 \cdot 3CH_3NO_2$ : Both  $BF_4^-$  ions are disordered over two sites. The refined occupancy ratio for the disordered orientations of anion B(38)–F(42) was 0.5:0.5, whereas that for anion B(43)–F(47) was 0.72:0.28. The refined restraints B–F = 1.38(2) and F…F = 2.25(2) Å were applied to the anions. All wholly non-H atoms with an occupancy >0.5 were refined anisotropically and all H atoms were placed in calculated positions and refined by using a riding model.

Structure Refinement of  $[Fe(L^2I)_2][BF_4]_2 \cdot 3CH_3NO_2$ : The two BF<sub>4</sub> ions are disordered over two sites. The sites of disorder for anion B(38)-F(42) were refined with a common wholly occupied B atom, B(38), with a refined occupancy ratio of 0.8:0.2. The refined occupancies of the disordered orientations of the other anion B(43)-F(47) were 0.6:0.4. The refined restraints B-F 1.40(2) and F…F 2.29(2) Å were applied to the anions. One of the three nitromethane molecules C(52)-O(55) is also disordered over two orientations with a 0.60:0.40 occupancy ratio. This was modeled by using the fixed restraints C-N 1.47(2), N-O 1.21(2), O···O 2.10(2), and C···O 2.30(2) Å. All wholly occupied non-H atoms were refined anisotropically and all H atoms were placed in calculated positions and refined by using a riding model. There are five residual Fourier peaks of 1.0–1.3 eÅ<sup>-3</sup> within the disordered anion B(38)–F(42), which may represent another, minor site of disorder for that residue. The deepest Fourier hole of  $-1.3 \text{ e}\text{\AA}^{-3}$  is also located in the same anion.

Structure Refinement of  $[Fe(L^2CCPh)(OH_2)_4]_x[Fe(L^2CCPh)-$ (OH<sub>2</sub>)<sub>3</sub>]<sub>1-x</sub>[BF<sub>4</sub>]<sub>2</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O: The asymmetric unit contains half a complex dication, with Fe(1), N(2), N(5), and O(20B) lying on the crystallographic  $C_2$  axis  $[0, y, \frac{3}{4}]$ , and one BF<sub>4</sub><sup>-</sup> anion and a halfoccupied, disordered diethyl ether molecule occupying general lattice sites. In addition to the  $L^2$ CCPh ligand and the wholly occupied water ligand O(19), there are three weaker Fourier peaks close to the  $C_2$  axis. These are at appropriate distances from Fe(1) to be considered partial water ligands and they were modeled as such, as O(20A) (occupancy 0.4), O(20B) (lying on the  $C_2$  axis, occupancy 0.1), and O(20C) (occupancy 0.2). O(20A) and its symmetry equivalent O(20A<sup>i</sup>) [symmetry code: (i) -x, y, 3/2 - z] are 2.76 Å from each other, so these sites can be simultaneously occupied. The proximity of O(20B) and O(20C) to O(20A) and to each other means that only one of those sites can be occupied at any one time. We interpret this as implying that the crystal contains a mixture of seven-coordinate  $[Fe(L^2CCPh)(OH_2)_4]^{2+}$  when O(20A) and  $O(20A^{i})$  are both occupied and six-coordinate [Fe(L<sup>2</sup>CCPh)- $(OH_2)_3$ <sup>2+</sup> when either O(20B), O(20C), or O(20C<sup>i</sup>) is occupied.

The BF<sub>4</sub><sup>--</sup> ion is crystallographically ordered, but the diethyl ether molecule is disordered over two sites labeled "A" (occupancy 0.3) and "B" (0.2). The fixed restraints C–C 1.52(2), C–O 1.43(2), 1,3-C···O 2.42(2), and 1,3-C···C = 2.34(2) Å were applied to this residue. All wholly occupied non-H atoms and O(20A) were refined

anisotropically and all carbon-bound H atoms were placed in calculated positions and refined by using a riding model. The water H atoms bound to O(19) were located in the Fourier map, and this water molecule was refined as a rigid group in the final leastsquares cycles. The H atoms bound to O(20A)-O(20C) were not located, but are included in the density calculation.

CCDC-899454 {for  $[Fe(L^2Cl)_2][BF_4]_2 \cdot 3.33CH_3NO_2 \cdot (C_2H_5)_2O$ }, -899455 {for  $[Fe(L^2Me)_2][BF_4]_2$ }, -899456 {for  $[Fe(L^2I)_2][BF_4]_2 \cdot 3CH_3NO_2$ }, -899457 {for  $[Fe(L^2Br)_2][BF_4]_2 \cdot 3CH_3NO_2$ }, -899458 {for  $[Fe(L^2CCPh)(OH_2)_4]_x[Fe(L^2CCPh)(OH_2)_3]_{1-x}[BF_4]_2 \cdot (C_2H_5)_2 - O$ }, and -899459 (for  $L^2Cl$ ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): Additional crystallographic figures, magnetic susceptibility and LIESST relaxation data, and powder diffraction simulations.

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- P. Gutlich, H. A. Goodwin (Eds.), Spin-Crossover in Transition-Metal Compounds I–III, in: Topics in Current Chemistry, vol. 233–235, Springer, Berlin, 2004.
- [2] a) P. Gamez, J. S. Costa, M. Quesada, G. Aromí, *Dalton Trans.* 2009, 7845–7853; b) I. Šalitroš, N. T. Madhu, R. Boča, J. Pavlik, M. Ruben, *Monatsh. Chem.* 2009, 140, 695–733; c) A. Bousseksou, G. Molnár, L. Salmon, W. Nicolazzi, *Chem. Soc. Rev.* 2011, 40, 3313–3335; d) M. A. Halcrow, *Chem. Soc. Rev.* 2011, 40, 4119–4142.
- [3] M. A. Halcrow, Coord. Chem. Rev. 2009, 253, 2493-2514.
- [4] M. A. Halcrow, Coord. Chem. Rev. 2005, 249, 2880–2908.
- [5] R. Pritchard, C. A. Kilner, M. A. Halcrow, *Chem. Commun.* 2007, 577–579.
- [6] C. Carbonera, J. S. Costa, V. A. Money, J. Elhaïk, J. A. K. Howard, M. A. Halcrow, J.-F. Létard, *Dalton Trans.* 2006, 3058–3066.
- [7] a) M. Nihei, L. Han, H. Oshio, J. Am. Chem. Soc. 2007, 129, 5312–5313; b) C. A. Tovee, C. A. Kilner, S. A. Barrett, J. A. Thomas, M. A. Halcrow, Eur. J. Inorg. Chem. 2010, 1007–1012.
- [8] a) C. Rajadurai, O. Fuhr, R. Kruk, M. Ghafari, H. Hahn, M. Ruben, *Chem. Commun.* 2007, 2636–2638; b) J. Elhaïk, C. M. Pask, C. A. Kilner, M. A. Halcrow, *Tetrahedron* 2007, 63, 291–298.
- [9] a) M. Nihei, N. Takahashi, H. Nishikawa, H. Oshio, *Dalton Trans.* 2011, 40, 2154–2156; b) Y. Hasegawa, K. Takahashi, S. Kume, H. Nishihara, *Chem. Commun.* 2011, 47, 6846–6848; c) R. González-Prieto, B. Fleury, F. Schramm, G. Zoppellaro, R. Chandrasekar, O. Fuhr, S. Lebedkin, M. Kappes, M. Ruben, *Dalton Trans.* 2011, 40, 7564–7570.
- [10] M. S. Alam, M. Stocker, K. Gieb, P. Müller, M. Haryono, K. Student, A. Grohmann, *Angew. Chem.* **2010**, *122*, 1178; *Angew. Chem. Int. Ed.* **2010**, *49*, 1159–1163.
- [11] M. Loï, M. W. Hosseini, A. Jouaiti, A. De Cian, J. Fischer, *Eur. J. Inorg. Chem.* **1999**, 1981–1985.
- [12] J. C. Rodriguez-Ubis, R. Sedano, G. Barroso, O. Juanes, E. Brunet, *Helv. Chim. Acta* 1997, 80, 86–96; *corrigendum*: J. C. Rodriguez-Ubis, R. Sedano, G. Barroso, O. Juanes, E. Brunet, *Helv. Chim. Acta* 1997, 80, 621.



**FULL PAPER** 

- [13] See, for example: a) K. H. Sugiyarto, D. C. Craig, A. D. Rae, H. A. Goodwin, *Aust. J. Chem.* **1993**, *46*, 1269–1290; b) M. Ostermeier, M.-A. Berlin, R. M. Meudtner, S. Demeshko, F. Meyer, C. Limberg, S. Hecht, *Chem. Eur. J.* **2010**, *16*, 10202– 10213; c) N. Chandrasekhar, R. Chandrasekar, *Dalton Trans.* **2010**, *39*, 9872–9878.
- [14] J. Elhaïk, V. A. Money, S. A. Barrett, C. A. Kilner, I. R. Evans, M. A. Halcrow, *Dalton Trans.* 2003, 2053–2060.
- [15] V. A. Money, I. R. Evans, J. Elhaïk, M. A. Halcrow, J. A. K. Howard, *Acta Crystallogr., Sect. B* 2004, 60, 41–45.
- [16] V. A. Money, J. Elhaïk, I. R. Evans, M. A. Halcrow, J. A. K. Howard, *Dalton Trans.* 2004, 65–69.
- [17] R. Pritchard, H. Lazar, S. A. Barrett, C. A. Kilner, S. Asthana, C. Carbonera, J.-F. Létard, M. A. Halcrow, *Dalton Trans.* 2009, 6656–6666.
- [18] a) G. Zoppellaro, M. Baumgarten, *Eur. J. Org. Chem.* 2005, 2888–2892; *corrigendum*: G. Zoppellaro, M. Baumgarten, *Eur. J. Org. Chem.* 2005, 4201; b) S. Basak, P. Hui, R. Chandrase-kar, *Synthesis* 2009, 4042–4048.
- [19] R. Pritchard, Ph. D. Thesis, University of Leeds, UK, 2008.
- [20] a) C. A. Bessel, R. F. See, D. L. Jameson, M. R. Churchill, K. J. Takeuchi, J. Chem. Soc., Dalton Trans. 1992, 3223–3228; b)
  M. A. Halcrow, C. A. Kilner, M. Thornton-Pett, Acta Crystallogr., Sect. C 2000, 56, 213–214; c) F. Calderazzo, U. Englert, C. Hu, F. Marchetti, G. Pampaloni, V. Passarelli, A. Romano, R. Santi, Inorg. Chim. Acta 2003, 344, 197–206; d) G. Zoppellaro, A. Geies, V. Enkelmann, M. Baumgarten, Eur. J. Org. Chem. 2004, 2367–2374; e) N. Chandrasekhar, R. Chandrasekar, Chem. Commun. 2010, 46, 2915–2917; f) S. Basak, R. Chandrasekar, Adv. Funct. Mater. 2011, 21, 667–673.
- [21] Twinned single crystals of  $L^2NO_2$  were also obtained. A preliminary refinement showed that the molecule adopts the same conformation as  $L^2Cl$  (see the Supporting Information). This structure has not been deposited with the CCDC. Unit cell data for  $L^2NO_2$ :  $C_{10}H_6N_8O_4$ ,  $M_r$  302.23, monoclinic,  $P2_1/c$ , a= 5.3564(6), b = 10.1292(12), c = 23.201(3) Å,  $\beta$  = 96.463(6)°, V = 1250.8(2) Å<sup>3</sup>, Z = 4.
- [22] R. Lungwitz, S. Spange, New J. Chem. 2008, 32, 392-394.
- [23] a) M. L. Scudder, H. A. Goodwin, I. G. Dance, New J. Chem.
  1999, 23, 695–705; b) J. McMurtrie, I. Dance, CrystEngComm
  2005, 7, 216–229; c) J. McMurtrie, I. Dance, CrystEngComm
  2010, 12, 2700–2710.
- [24] a) J. K. McCusker, A. L. Rheingold, D. N. Hendrickson, *Inorg. Chem.* 1996, *35*, 2100–2112; b) P. Guionneau, M. Marchivie, G. Bravic, J.-F. Létard, D. Chasseau, *Top. Curr. Chem.* 2004, 234, 97–128.
- [25] J. M. Holland, J. A. McAllister, C. A. Kilner, M. Thornton-Pett, A. J. Bridgeman, M. A. Halcrow, J. Chem. Soc., Dalton Trans. 2002, 548–554.
- [26] a) J. Elhaïk, D. J. Evans, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2005, 1693–1700; b) C. A. Kilner, M. A. Halcrow, *Polyhedron* 2006, 25, 235–240; c) M. Haryono, F. W. Heinemann, K. Petukhov, K. Gieb, P. Müller, A. Grohmann, *Eur. J. Inorg. Chem.* 2009, 2136–2143.
- [27] S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* 1984, 105, 1–4.
- [28] a) J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcén, G. Chastanet, M. Marchivie, L. Capes, *Chem. Eur. J.* 2005, 11, 4582–4589; b) J.-F. Létard, *J. Mater. Chem.* 2006, 16, 2550–2559; c) J.-F. Létard, G. Chastanet, P. Guionneau, C. Desplanches, *Optimising the stability of trapped metastable spin states*, in: *Spin-crossover materials properties and applications* (Ed.: M. A. Halcrow), Wiley, Chichester, UK, 2013, in the press.
- [29] a) J.-F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, O. Kahn, *Inorg. Chem.* 1998, 37,

4432–4441; b) J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard, J.-A. Real, O. Kahn, *Chem. Phys. Lett.* **1999**, *313*, 115–120; c) S. Marcén, L. Lecren, L. Capes, H. A. Goodwin, J.-F. Létard, *Chem. Phys. Lett.* **2002**, *358*, 87–95.

- [30] O. Kahn, Molecular Magnetism, VCH Verlagsgesellschaft, Weinheim, Germany, 1993.
- [31] a) A. Hauser, Coord. Chem. Rev. 1991, 111, 275–290; b) A. Hauser, Comments Inorg. Chem. 1995, 17, 17–40; c) A. Hauser, Top. Curr. Chem. 2004, 234, 155–198; d) A. Hauser, C. Enaschescu, M. L. Daku, A. Vargas, N. Amstutz, Coord. Chem. Rev. 2006, 250, 1642–1652.
- [32] J.-F. Létard, G. Chastanet, O. Nguyen, S. Marcèn, M. Marchivie, P. Guionneau, D. Chasseau, P. Gütlich, *Monatsh. Chem.* 2003, 134, 165–182.
- [33] C. J. O'Connor, Prog. Inorg. Chem. 1982, 29, 203-283.
- [34] J. Elhaïk, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2006, 823–830.
- [35] See, for example: a) G. S. Matouzenko, A. Bousseksou, S. Lecocq, P. J. van Koningsbruggen, M. Perrin, O. Kahn, A. Collet, *Inorg. Chem.* 1997, 36, 5869–5879; b) H. Z. Lazar, T. Forestier, S. A. Barrett, C. A. Kilner, J.-F. Létard, M. A. Halcrow, *Dalton Trans.* 2007, 4276–4285; c) R. Pritchard, S. A. Barrett, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2008, 3159–3168; *corrigendum:* R. Pritchard, S. A. Barrett, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2009, 10622.
- [36] a) J. P. Jesson, S. Trofimenko, D. R. Eaton, J. Am. Chem. Soc. 1967, 89, 3158–3164; b) M. A. Hoselton, L. J. Wilson, R. S. Drago, J. Am. Chem. Soc. 1975, 97, 1722–1729; c) M. F. Tweedle, L. J. Wilson, J. Am. Chem. Soc. 1976, 98, 4824–4834; d) W. Linert, M. Konecny, F. Renz, J. Chem. Soc., Dalton Trans. 1994, 1523–1531.
- [37] a) H. L. Chum, J. A. Vanin, M. I. D. Holanda, *Inorg. Chem.* 1982, 21, 1146–1152; b) T. Zhu, C. H. Su, D. Schaeper, B. K. Lemke, L. J. Wilson, K. M. Kadish, *Inorg. Chem.* 1984, 23, 4345–4349; c) S. A. Barrett, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2011, 40, 12021–12024.
- [38] a) D. F. Evans, J. Chem. Soc. 1959, 2003–2005; b) E. M. Schubert, J. Chem. Educ. 1992, 69, 62.
- [39] R. Pritchard, C. A. Kilner, S. A. Barrett, M. A. Halcrow, *Inorg. Chim. Acta* 2009, *362*, 4365–4371.
- [40] H. Toftlund, J. J. McGarvey, *Top. Curr. Chem.* **2004**, *233*, 151–166.
- [41] J. Elguero, E. Gonzalez, R. Jacquier, Bull. Soc. Chim. Fr. 1968, 5009–5017.
- [42] R. J. Smithson, C. A. Kilner, A. R. Brough, M. A. Halcrow, *Polyhedron* 2003, 22, 725–733.
- [43] V. A. Money, J. S. Costa, S. Marcén, G. Chastanet, J. Elhaïk, M. A. Halcrow, J. A. K. Howard, J.-F. Létard, *Chem. Phys. Lett.* **2004**, *391*, 273–277.
- [44] V. Mishra, R. Mukherjee, J. Linares, C. Baldé, C. Desplanches, J.-F. Létard, E. Collet, L. Toupet, M. Castro, F. Varret, *Inorg. Chem.* 2008, 47, 7577–7587.
- [45] M. Marchivie, P. Guionneau, J.-F. Létard, D. Chasseau, Acta Crystallogr., Sect. B 2005, 61, 25–28.
- [46] V. A. Money, C. Carbonera, J. Elhaïk, M. A. Halcrow, J. A. K. Howard, J.-F. Létard, *Chem. Eur. J.* 2007, 13, 5503–5514.
- [47] a) J. C. Philip, H. B. Oakley, J. Chem. Soc. Trans. 1924, 125, 1189–1195; b) W. A. Felsing, S. A. Durban, J. Am. Chem. Soc. 1926, 48, 2885–2893.
- [48] G. M. Sheldrick, Acta Crystallogr., Sect. A 2008, 64, 112-122.
- [49] L. J. Barbour, J. Supramol. Chem. 2001, 1, 189–191.
- [50] POVRAY, v.3.5, Persistence of Vision Raytracer Pty. Ltd., Williamstown, Victoria, Australia, 2002 (http://www.povray.org).
- [51] A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7-13.

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