

*In memory of S. M. Nelson***New Iron(II) Spin-crossover Complexes with Heterocyclic Amine-derived Ligands and STEPS Experiments on Photogenerated Metastable High-spin States****Anthony W. Addison,* Sudhir Burman, and Curtis G. Wahlgren***Chemistry Department, Drexel University, Philadelphia, PA 19104, U.S.A.***Odatt A. Rajan, Teresa M. Rowe, and Ekkehard Sinn****Chemistry Department, University of Virginia, Charlottesville, VA 22901, U.S.A.*

Cationic complexes of the type $[\text{Fe}(\text{L}^{\text{NN}})_3]^{2+}$ and $[\text{Fe}(\text{L}^{\text{NNN}})_2]^{2+}$ have been isolated as Cl^- , ClO_4^- , or BF_4^- salts, where L^{NN} and L^{NNN} represent bidentate and tridentate nitrogen-donor ligands respectively. The bidentate ligands were 2-(2'-pyridyl)benzimidazole (pybzim), 2-(2'-pyridyl)-*N*-methylbenzimidazole (mpybzim); 2-(2'-pyridyl)benzothiazole (pybzt), 2,2'-dipyridylamine (dpya), and the tridentates di(2-pyridylmethyl)amine (dpyma), 2,6-bis(benzimidazol-2'-yl)pyridine (bzimpy), 2,6-bis(*N*-methylbenzimidazol-2'-yl)pyridine (mbzimpy), and 2,6-bis(benzothiazol-2'-yl)pyridine (bztpy). Except for $[\text{Fe}(\text{dpya})_3][\text{ClO}_4]_2$, all these FeN_6 chromophores exhibit strong absorption in the 550 nm region, which is assigned as a metal-to-ligand charge-transfer transition. Between 4 and 320 K, the iron(II) is in the low-spin form in the majority of these compounds; high-spin exceptions are $[\text{Fe}(\text{dpya})_3][\text{ClO}_4]_2$ and $[\text{Fe}(\text{mbzimpy})_2]\text{Cl}_2$. Other complexes show evidence of the onset of a spin transition near 40 °C, while the salt $[\text{Fe}(\text{bztpy})_2][\text{ClO}_4]_2 \cdot \text{CHCl}_3$ is a well defined spin-crossover system. The low-spin complex $[\text{Fe}(\text{bzimpy})_2][\text{ClO}_4]_2$ was excited by irradiation with visible light, and the generation and decay of the resulting high-spin form was observed under cryogenic conditions. In solution, $[\text{Fe}(\text{bzimpy})_2]^{2+}$ acts as a weak diprotic acid and also exhibits quintet $\rightleftharpoons$ singlet spin crossover ($\Delta H^\circ = -42.7 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -140.9 \text{ J K}^{-1} \text{ mol}^{-1}$). The complexes are all electrochemically oxidizable to their iron(III) forms in non-aqueous solution, but the dpyma, bztpy, pybzt, and dpya chelates thus formed are unstable. The iron(III) complex $[\text{Fe}(\text{H}_{-2}\text{bzimpy})_2]^-$ containing the doubly deprotonated ligand was obtained as its low-spin triethylammonium salt. The high-spin chloro complexes $[\text{Fe}(\text{bzimpy})\text{Cl}_3]$, $[\text{Fe}(\text{mbzimpy})\text{Cl}_3]$, $[\text{Fe}(\text{mbzimpy})\text{Cl}_2]$, and the mixed-spin iron(II) complex salt $[\text{Fe}(\text{bzimpy})][\text{FeCl}_4]$ were also isolated.

Transition-metal complexes containing the α -di-imine chromophore are some of the most frequently studied of the coordination compounds which contain strongly bonding ligands,¹ including complexes of 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy), and 2,2':6',2''-terpyridine (terpy) which are probably the best known examples of this class. Such ligands all form low-spin (l.s.) complexes with iron(II), but modification can produce complexes which exhibit magnetic behaviour ranging from completely high-spin (h.s.) character to those which show a spin crossover from the 1A_1 state ($S = 0$) to the 5T_2 state ($S = 2$) with an increase in the ambient temperature.²⁻⁴ Examples of this latter class include ligands studied by Nelson and co-workers, such as the 2,2'-bi-2-thiazolines⁵ and di(2-pyridylmethyl)amine,⁶ as well as 2-(2'-pyridyl)benzimidazole (pybzim),⁷ di(2-pyridyl)amine,^{8,9} and the quadridentate tri(2-pyridyl)amine¹⁰ (tpya).

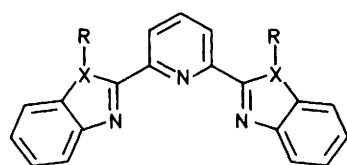
Experiments have been carried out for Fe^{II} (d^6) crossovers as well as for Fe^{III} (d^5), Co^{II} (d^7), and Mn^{III} (d^4)¹¹⁻¹⁴ using STEPS† (susceptibility of transient excited paramagnetic states^{11,15}); these are initiated by photoexcitation of the complex. Subsequent relaxation back to the ground state can occur by non-radiative decay, or with photon emission, or by

internal conversion to other lower excited states. The emissionless decay is dependent on vibrational energy transfer, so that this pathway is slower at lower temperatures, although with simple fluorescent and phosphorescent organic molecules the decay is rapid even at liquid helium temperatures. Complexes exhibiting $\Delta S = 2$ spin-state crossovers exhibit a markedly slower decay rate, exemplified by the $^6A_1 \rightleftharpoons ^2T_2$ crossovers in the octahedral d^5 iron(III) dithiocarbamates¹⁶ and other Fe^{III} complexes,¹⁷ and the $^5T_2 \rightleftharpoons ^1A_1$ crossover, observed in a variety of Fe^{II} complexes.¹⁸ Spin-orbit coupling counteracts the double spin-forbidden barrier, manifesting itself as an increased relaxation rate in $\Delta S = 1$ changes, as in the $^4T_1 \rightleftharpoons ^2E$ crossover observed in Co^{II} complexes¹⁹ and the $^3T_1 \rightleftharpoons ^5E$ crossover in manganese(III).²⁰

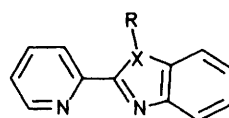
We have prepared and isolated a series of compounds with our recently synthesized^{21,22} bidentate and tridentate ligands including 2,6-bis(benzimidazol-2'-yl)pyridine (bzimpy) and 2,6-bis(*N*-methylbenzimidazol-2'-yl)pyridine (mbzimpy). These bear a structural resemblance to 2,2':6',2''-terpyridine (terpy), and are also closely related to the pybzim ligand which forms tris-chelates with iron having spin-crossover character.²³⁻²⁵

We have investigated the bulk magnetic susceptibility of the present compounds in the range 4–320 K, as well as recording the electronic spectra and redox chemistry in non-aqueous solution. E.s.r. spectra are reported for the iron(III) compounds $[\text{Fe}(\text{bzimpy})\text{Cl}_3]$, $[\text{Fe}(\text{mbzimpy})\text{Cl}_3]$, and $[\text{NH}_4][\text{Fe}(\text{H}_{-2}\text{bzimpy})_2]$.

† The acronym LIESST (light-induced excited spin state trapping) is also used for this process;¹²⁻¹⁴ the two abbreviations have essentially the same meaning here.



	X	R
bzimpy	N	H
mbzimpy	N	CH ₃
bztpy	S	—



	X	R
pybzim	N	H
mpybzim	N	CH ₃
pybzt	S	—

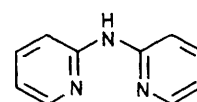
bzimpy)₂]* and a series of STEPS experiments for [Fe(bzimpy)₂][ClO₄]₂.

Experimental

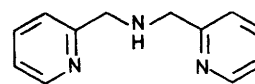
Physical Methods.—Electrochemical measurements were made at $25 \pm 0.2^\circ\text{C}$ in solutions deoxygenated by bubbling purified nitrogen (MG Industrial Gases, boiling liquid N₂). The three-electrode cell configuration was controlled with a system comprising a PAR-173 potentiostat, a PAR-176 i/E converter, a PAR-175 waveform generator, and a McKee-Pedersen 1012A integrator. Potentials in non-aqueous solution were measured with respect to the Ag⁺ (0.01 mol dm⁻³)/[NEt₄][ClO₄] (0.1 mol dm⁻³)/Ag electrode, which we have measured as being at +0.30 V *vs.* a saturated calomel electrode in acetonitrile.²⁶ The potentials may thus be expressed with reference to the standard hydrogen electrode (s.h.e.) by the addition of ca. 545 mV. A Beckman rotating platinum disc electrode (area 0.300 cm²) was used for rotating disc polarography (r.d.p.) and also as a stationary planar electrode for cyclic voltammetry. For coulometry, the counter-electrode compartment was separated from the analyte solution by a porous ('thirsty' Vycor) test-tube. Conductances were measured at ca. 23 °C in dimethylformamide (dmf) using a YSI model 32 meter and 3403 Pt/Ir electrode cell.

Ultraviolet-visible absorption spectra were obtained on Perkin-Elmer 320, Lambda-3, and -330 spectrophotometers, the last equipped with an integrating sphere for diffuse reflectance. Mass spectra were from a Finnigan-4000 instrument, and e.s.r. spectra from a Varian E-12 X-band spectrometer, calibrated with diphenylpicrylhydrazyl and [VO(acac)₂] (acac = acetylacetonate) near $g = 2$ (g values are $\pm$ ca. $10^{-3} g^2$). ¹H N.m.r. spectra were obtained on Varian EM-390 (60 MHz) and JEOL FX90Q (90 MHz) spectrometers; chemical shifts are referred to internal SiMe₄.

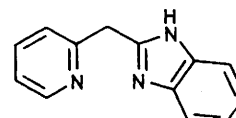
Magnetic susceptibility²⁷ and STEPS^{11,15} measurements were carried out in the range 4–310 K as previously described on a SQUID magnetometer. Photoexcitation of the sample within the susceptometer was carried out as described previously.^{11,15} The sample was mounted at the end of a quartz light-pipe and various visible and u.v. light sources were mounted outside the susceptometer. The nature of the light



dpya



dpyma



pymbzim

source appeared to be immaterial, and most of the experiments were carried out with a Kodak slide projector bulb, using water (1 cm) as an additional i.r. filter. Excitation was carried out with the temperature control set at 4 K; however, the sample temperature rises because of conversion of optical quanta into thermal energy.

Elemental analyses were performed by Canadian Micro-analytical Service (Vancouver), iron analyses by the modified 1,10-phenanthroline method.²⁸

Materials.—Reagents were used as received from Aldrich, Sigma, and Eastman Kodak (organics), and G. F. Smith, Fisher, and Alfa Ventron (iron salts). Tetraethylammonium perchlorate and tetra(n-hexyl)ammonium perchlorate (G. F. Smith) were recrystallized from water and aqueous ethanol respectively, and dried *in vacuo* over phosphorus(v) oxide. Solvents for electrochemistry were distilled *in vacuo* off CaH₂ (dmf), or under dinitrogen off P₄O₁₀ (acetonitrile) or magnesium metal (alcohols). All iron(II) complexes were prepared in a nitrogen atmosphere using deoxygenated solvents.

Preparation of Ligands and Complexes.—2,6-Bis(benzimidazol-2'-yl)pyridine (bzimpy) and 2-(2'-pyridyl)benzimidazole (pybzim). These ligands were prepared by the method of Addison and Burke,²¹ while the syntheses of 2,6-bis(benzothiazol-2'-yl)pyridine (bztpy), 2-(2'-pyridyl)-N-methylbenzimidazole (mpybzim), 2-(2'-pyridyl)benzothiazole (pybzt), and 2-(2'-pyridylmethyl)benzimidazole (pymbzim) followed the procedure of Addison *et al.*²²

2,6-Bis(N-methylbenzimidazol-2'-yl)pyridine (mbzimpy). N-Methyl-o-phenylenediamine dihydrochloride (9.75 g, 50 mmol) was added slowly (allowing for the copious effervescence of HCl gas) to 100 g of vigorously stirred polyphosphoric acid. Pyridine-2,6-dicarboxylic acid (4.2 g, 25 mmol) was then added, the mixture was stirred at 170 °C for 3 h, poured into potassium hydroxide solution, and the solid filtered off from the cooled solution. Recrystallization from aqueous methanol gave off-white needles (2.6 g, 15%) (Found: C, 73.8; H, 5.10; N, 20.6. Calc. for C₂₁H₁₇N₅: C, 74.3; H, 5.05; N, 20.6%). Mass spectrum (*m/e*): 340 (12), 339 (*M*⁺, 66), 338 (100), 324 (9), 235 (10), 208 (14), 169 (34), 104 (11), 78 (17), 77 (53), 64 (11), 63 (17), 51 (30%). N.m.r. (CD₃OD): δ 4.2 (s, CH₃), 7.3–7.8 (m, benzene ring), 8.1–8.4 (m, pyridine ring). This compound can also be prepared by the method of Phillips²⁹ in comparable yield.

[Fe(bzimpy)₂][FeCl₄]. The ligand bzimpy (0.31 g, 1.0 mmol) in hot methanol (>60 °C, 40 cm³) was added to a methanol

* The anions formed by single and double deprotonation of the ligand bzimpy are represented as H₋₁bzimpy and H₋₂bzimpy respectively.

solution (20 cm³) of FeCl₂·4H₂O (0.20 g, 1.0 mmol). The deep purple solution was refluxed for 1 h. On cooling, the solution yielded purple crystals which were filtered off, washed with cold methanol, and dried under vacuum at 120 °C (Found: C, 52.5; H, 2.80; N, 15.9. Calc. for C₃₈H₂₆Cl₄Fe₂N₁₀: C, 52.1; H, 3.00; N, 16.0%).

[Fe(bzimpy)₂]Cl₂·CH₃OH. A methanol solution (40 cm³) of FeCl₂·4H₂O (0.10 g, 0.5 mmol) was added to a hot methanol solution (20 cm³) of bzimpy (0.31 g, 1.0 mmol). The deep violet solution was heated at reflux for 1 h, then cooled and the violet crystals filtered off. These were recrystallized from methanol and dried under vacuum at 120 °C (Found: C, 59.6; H, 3.65; N, 17.5. Calc. for C₃₉H₃₀Cl₂FeN₁₀O: C, 59.9; H, 3.85; N, 17.9%).

[Fe(bzimpy)₂][ClO₄]₂. A hot ethanol solution (40 cm³) of ligand (0.31 g, 1.0 mmol) was combined with an ethanol solution (20 cm³) of FeCl₂·4H₂O (0.10 g, 0.5 mmol) to give a deep red solution. After 24 h (no solid had formed) an ethanol solution (15 cm³) containing excess sodium perchlorate (0.24 g, 2.0 mmol) was added, resulting in the formation of a magenta coloured precipitate of the product (Found: C, 51.6; H, 2.85; N, 15.6. Calc. for C₃₈H₂₆Cl₂FeN₁₀O₈: C, 52.0; H, 3.00; N, 16.0%).

[Fe(H₂bzimpy)₂]·H₂O. An ethanol solution (20 cm³) of Fe(ClO₄)₂·6H₂O (0.91 g, 2.5 mmol) and a hot ethanol solution (70 cm³) of bzimpy (1.56 g, 5.0 mmol) were combined and triethylamine (1.4 cm³, 10 mmol) added. The deep blue product was filtered off from the resulting deep blue solution and dried *in vacuo* over P₄O₁₀ (Found: C, 65.7; H, 4.15; N, 19.6. Calc. for C₃₈H₂₆FeN₁₀·H₂O: C, 65.5; H, 4.05; N, 20.1%).

Fe(mbzimpy)Cl₂. Addition of a hot methanol solution (40 cm³) of mbzimpy (0.34 g, 1.0 mmol) to a methanol solution (20 cm³) of FeCl₂·4H₂O (0.20 g, 1.0 mmol) resulted in a purple solution which was refluxed briefly and then cooled to give purple crystals which were dried *in vacuo* over P₄O₁₀ (Found: C, 54.0; H, 3.20; N, 14.9. Calc. for C₂₁H₁₇Cl₂FeN₅: C, 54.1; H, 3.68; N, 15.0%).

[Fe(mbzimpy)₂]Cl₂·H₂O. This was prepared by combining a hot methanol solution (40 cm³) of mbzimpy (0.34 g, 1.0 mmol) and a methanol solution (20 cm³) of FeCl₂·4H₂O (0.10 g, 0.5 mmol), heating under reflux for 30 min and allowing the solution to cool. The resulting dark purple solid was filtered off and dried *in vacuo* over P₄O₁₀ (Found: C, 60.9; H, 4.15; Fe, 7.45; N, 17.1. Calc. for C₄₂H₃₆Cl₂FeN₁₀O: C, 61.2; H, 4.40; Fe, 6.80; N, 17.0%).

[Fe(mbzimpy)₂][ClO₄]₂·0.5CH₃OH. A methanol solution (30 cm³) of FeCl₂·4H₂O (1.0 g, 5.0 mmol) was added to a hot methanol solution (80 cm³) of mbzimpy (6.8 g, 10 mmol) and the resulting mixture heated under reflux for 30 min. Solid sodium perchlorate (1.33 g, 10 mmol) was added and the solution heated under reflux for 2 h. Cooling the solution gave a dark purple precipitate which was filtered off and dried *in vacuo* at 120 °C (Found: C, 53.4; H, 3.45; N, 14.7. Calc. for C_{42.5}H₃₆Cl₂FeN₁₀O_{8.5}: C, 53.8; H, 3.80; N, 14.8%).

[Fe(bzimpy)Cl₃]. A methanol solution (20 cm³) of FeCl₃·6H₂O (0.14 g, 0.5 mmol) was added to a hot methanol solution (40 cm³) of bzimpy (0.31 g, 1.0 mmol) and the brown solution heated under reflux for 30 min. Cooling, filtering, and drying *in vacuo* over P₄O₁₀ gave a brown solid (Found: C, 47.9; H, 2.45; Fe, 11.6; N, 14.6. Calc. for C₁₉H₁₃Cl₃FeN₅: C, 48.2; H, 2.75; Fe, 11.8; N, 14.8%).

[NHET₃][Fe(H₂bzimpy)₂]·4H₂O. A hot ethanol solution (70 cm³) of bzimpy (1.55 g, 5.0 mmol) was added to an ethanol solution (20 cm³) of iron(III) perchlorate (5.0 cm³ of a 1.0 mol dm⁻³ solution). This was followed by addition of excess triethylamine (3 cm³). The deep blue solution was filtered after 2 h and the precipitate discarded. The filtrate was (rotary) evaporated to reduce the volume of solvent; the dark blue crystals which formed after 15 h were filtered off and dried over P₄O₁₀. The compound is a weak conductor in dmf (46 S cm²

mol⁻¹, *cf.* 98 S cm² mol⁻¹ for [NEt₄][ClO₄], both at 1 mmol dm⁻³) (Found: C, 60.7; H, 5.05; Fe, 6.6; N, 17.4. Calc. for C₄₄H₄₆FeN₁₁O₄: C, 61.1; H, 5.35; Fe, 6.45; N, 17.8%).

[Fe(mbzimpy)Cl₃]·0.5H₂O. A methanol solution (20 cm³) of FeCl₃·6H₂O (0.14 g, 0.5 mmol) was mixed with a hot methanol solution (40 cm³) of mbzimpy (0.31 g, 1.0 mmol) and the resulting solution was heated under reflux for 30 min. Filtering and drying *in vacuo* over P₄O₁₀ gave a finely divided orange solid (Found: C, 49.6; H, 3.35; N, 13.7. Calc. for C₂₁H₁₈Cl₃FeN₅O_{0.5}: C, 49.4; H, 3.55; N, 13.7%).

[Fe(mpybzim)₃][ClO₄]₂. An aqueous solution (20 cm³) of iron(II) ammonium sulphate (0.39 g, 1.0 mmol) was added to a hot ethanol solution (60 cm³) of ligand (0.63 g, 3.0 mmol). An aqueous (10 cm³) sodium perchlorate solution (0.24 g, 2 mmol) was then added to give a blue-purple solution and a fine purple precipitate. The solid was filtered off and discarded. The filtrate was cooled overnight before filtering again to give a fine, purple solid. The final product (0.40 g, 45%) was obtained by recrystallizing this second solid from acetonitrile (Found: C, 52.8; H, 3.65; N, 14.3. Calc. for C₃₉H₃₃Cl₂FeN₉O₈: C, 53.1; H, 3.75; N, 14.3%).

[Fe(bztpy)₂][ClO₄]₂·CHCl₃. An ethanol solution (20 cm³) of iron(II) perchlorate (0.36 g, 1 mmol) was added to a chloroform solution (60 cm³) of ligand (0.69 g, 2 mmol); then triethyl orthoformate, HC(OC₂H₅)₃ (teof), was added to this mixture. The resulting purple-red crystals were filtered off and dried *in vacuo* over P₄O₁₀ (Found: C, 43.7; H, 1.70; N, 7.80. Calc. for C₃₉H₂₃Cl₅FeN₆O₈: C, 44.0; H, 2.20; N, 7.90%).

[Fe(pybzim)₃][ClO₄]₂. This was prepared as described previously.⁷

[Fe(pybzim)₃][PF₆]₂. This was prepared from a hot ethanol solution (20 cm³) of ligand (0.59 g, 3 mmol) and an aqueous solution (20 cm³) FeCl₂·4H₂O (0.20 g, 1 mmol). To the resulting deep-red purple solution was added aqueous KPF₆ (0.55 g, 3 mmol; 10 cm³). The solution was then (rotary) evaporated to reduce the volume of solvent and the brick red solid formed (0.90 g, 96%) was filtered off, washed, and dried *in vacuo* over P₄O₁₀ (Found: C, 46.5; H, 2.95; N, 13.5. Calc. for C₃₆H₂₇F₁₂FeN₉P₂: C, 46.4; H, 2.90; N, 13.5%).

[Fe(dpyma)₂][BF₄]₂. An aqueous solution (20 cm³) of FeCl₂·6H₂O (1.0 g, 5.0 mmol) was combined with a methanol solution (40 cm³) of di(2-pyridylmethyl)amine (dpyma) (2.2 g, 11 mmol). The deep red solution was filtered and an aqueous solution (15 cm³) containing excess NaBF₄ (2.4 g, 22 mmol) added. The resulting deep red prisms were filtered off and air-dried (1.48 g, 47%). The same product is obtained for ligand:iron ratios ranging from 2:1 to 4:1. **CAUTION:** The perchlorate salt of this complex is a dangerous contact explosive (Found: C, 45.6; H, 4.10; N, 13.3. Calc. for C₂₄H₂₆B₂F₈FeN₆: C, 45.9; H, 4.15; N, 13.4%).

[Fe(dpya)₃][ClO₄]₂. An aqueous solution (20 cm³) of iron(II) ammonium sulphate (1.0 g, 2.5 mmol) was added to an ethanol solution (50 cm³) of ligand (1.32 g, 7.8 mmol) to yield a pale yellow solution. Addition of aqueous (20 cm³) sodium perchlorate (2.0 g, 15 mmol) produced a lemon-yellow precipitate which was dried *in vacuo* over P₄O₁₀ to give 1.6 g of product (83% yield) (Found: C, 46.8; H, 3.60; N, 16.1. Calc. for C₃₀H₂₇Cl₂FeN₉O₈: C, 46.9; H, 3.55; N, 16.4%).

Because of its low stability, the complex [Fe(pybzt)₃]²⁺ was prepared in CH₃NO₂ solution for electrochemistry by adding an excess of ligand to a teof-treated solution of iron(II) perchlorate in CH₃NO₂. Attempts to isolate [Fe(pybmzim)₃]²⁺ and [Fe(mbzimpy)₂]³⁺ salts were not successful.

Results and Discussion

Synthetic Aspects.—Ligand syntheses relied on the convenient acid-catalyzed condensation of the appropriate carb-

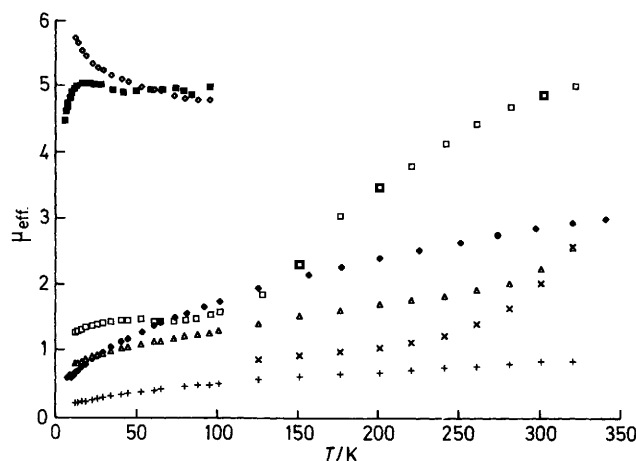


Figure 1. Plots of magnetic moment vs. temperature data: (+) $[\text{Fe}(\text{dpya})_2][\text{BF}_4]_2$, (x) $[\text{Fe}(\text{mpybzim})_3][\text{ClO}_4]_2$, (Δ) $[\text{Fe}(\text{bzimpy})_2] \cdot \text{Cl}_2 \cdot \text{CH}_3\text{OH}$; (◆) $[\text{Fe}(\text{bzimpy})_2][\text{ClO}_4]_2$, ($\square$) $[\text{Fe}(\text{bztpy})_2][\text{ClO}_4]_2 \cdot \text{CHCl}_3$, (■) $[\text{Fe}(\text{bzimpy})_2][\text{FeCl}_4]$, ($\diamond$) $[\text{Fe}(\text{mbzimpy})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$

oxylic acid with *o*-phenylenediamines or *o*-aminothiophenol. The latter, in either polyphosphoric acid or a melt of the neat reactants, yields the benzothiazole.²² *N*-Methyl-*o*-phenylenediamine was used here to yield the corresponding *N*-methylbenzimidazole, this type of reaction generally being performed in either polyphosphoric acid or in 4 mol dm⁻³ HCl under reflux.²⁹ The higher temperatures accessible with the former medium afford shorter reaction times, but sometimes promote decarboxylation of the acids.²² Syntheses of the iron(II) chelates usually required an inert atmosphere, because the iron(II) solutions are susceptible to hydrolysis and, more so, to aerial oxidation to iron(III) in the presence of these basic ligands, until an adequate amount of ligand is present to form a stable low-spin FeN_6 chromophore.

Magnetic Susceptibility.—For $[\text{Fe}(\text{bzimpy})_2]\text{Cl}_2 \cdot \text{CH}_3\text{OH}$, the magnetic moment ($\mu_{\text{eff.}}$) varies gradually from 0.8 at 10 K to 2.2 at 300 K, which we attribute to the effects of temperature-independent paramagnetism and to the (not uncommon) presence of some paramagnetic impurity [probably iron(III)], since the molar susceptibility increases sharply at low temperature. The system is essentially low spin, but with some evidence of an upturn in magnetic moment at the upper instrumental temperature limit (Figure 1). Otherwise, in the range 10–200 K, it is analogous to the well known $[\text{Fe}(\text{terpy})_2]^{2+}$ systems which are low spin at room temperature.³⁰ It is not unexpected for some temperature dependence of moment to be manifested by the bzimpy system since substitution of five-membered heterocyclic rings for pyridine generally has been found to induce a spin transition in the normally low-spin bipyridine^{1,31,32} and terpyridine complexes.^{33–35} It is also interesting to compare this to the bromide salt $[\text{Fe}(\text{pybzim})_3]\text{Br}_2$, for which Sams *et al.*⁷ found an incomplete, gradual spin crossover (with a magnetic moment varying from 3.6 to 5.3 between 100 and 300 K). One could account for the higher moment of this latter compound as resulting from the ligands being bidentate, while bzimpy is a tridentate ligand and should have a stronger co-ordination to the iron and greater ligand-field strength.

$[\text{Fe}(\text{bzimpy})_2][\text{ClO}_4]_2$ shows much the same behaviour as the chloride salt listed above, but there is slightly more of an upturn of the moment near 350 K, with values of 0.6 at 6 K and 2.8 at 300 K. Anion-dependence of magnetic moment has been noted previously in systems containing ligands of intermediate field strength.^{2,36} For both the $[\text{Fe}(\text{bzimpy})_2]^{2+}$ salts, the onset

Table 1. Magnetic data

Compound	Curie constant	Weiss constant (K)
$[\text{Fe}(\text{mbzimpy})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	3.1379 ± 0.0008	8.0 ± 1.6
$[\text{Fe}(\text{bzimpy})_2][\text{FeCl}_4]$	3.0462 ± 0.0004	-1.14 ± 0.07
$\text{Fe}(\text{mbzimpy})\text{Cl}_2$	3.5011 ± 0.0006	1.95 ± 0.09
$[\text{Fe}(\text{dpya})_3][\text{ClO}_4]_2$	3.5082 ± 0.0005	2.12 ± 0.08
$[\text{Fe}(\text{mbzimpy})_2][\text{ClO}_4]_2 \cdot 0.5\text{CH}_3\text{OH}$	Diamagnetic	

of spin crossover is also suggested by departure from the Curie-Weiss law at higher temperature.

$[\text{Fe}(\text{mbzimpy})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ is a high-spin complex with a magnetic moment of 5.0 at 300 K but the sample seems to contain some paramagnetic impurity since the moment increases steadily as the temperature falls below 100 K. There is good correlation with the Curie-Weiss law (Table 1).

$[\text{Fe}(\text{mbzimpy})_2][\text{ClO}_4]_2 \cdot 0.5\text{CH}_3\text{OH}$ was found to be completely diamagnetic at room temperature. In comparison with its bzimpy (perchlorate) analogue, the total absence of any onset of paramagnetism in the accessible temperature range could be attributed to the increased basicity of the imidazole nitrogen when a methyl group is present.³⁷ This would probably lead to a stronger co-ordination to the iron. The contrast in behaviour of this perchlorate with that of the previous chloride salt highlights the major influence of the anion on the magnetism; there must be a significant change in the solid-state environment when the anion is changed.

Transformation of the benzimidazole groups into benzothiazoles, as in $[\text{Fe}(\text{bztpy})_2][\text{ClO}_4]_2 \cdot \text{CHCl}_3$, weakens the ligand strength so that the iron(II) shows an essentially complete spin crossover in the temperature range accessed. For the trihydrate, Livingstone and Nolan³⁴ observed a less complete spin crossover ($\mu_{\text{eff.}} = 2.2$ –4.5) in a comparable temperature range.

The compounds FeLCl_2 (L = bzimpy or mbzimpy) have quite different magnetic behaviour. For $\text{Fe}(\text{bzimpy})\text{Cl}_2$, $\mu_{\text{eff.}} = 3.5$ per iron, while for the methylated ligand, $\mu_{\text{eff.}} = 5.2$ per iron; in both cases, the values are only slightly temperature dependent from 4 to 94 K, and the data fit the Curie-Weiss law well (Table 1). Possible formulations for these FeLCl_2 compounds are: (i) monomeric, five-co-ordinate $[\text{FeLCl}_2]$; (ii) strongly antiferromagnetically coupled chloro-bridged six-co-ordinate dimer, $[\text{Fe}_2\text{L}_2\text{Cl}_4]$; (iii) complex salt, $[\text{FeL}_2][\text{FeCl}_4]$. In the case of $\text{Fe}(\text{bzimpy})\text{Cl}_2$, the apparent $\mu_{\text{eff.}}$ per iron indicates it to be $[\text{Fe}(\text{bzimpy})_2][\text{FeCl}_4]$, in which the cation and anion are respectively purely low and high spin, the latter thus having $\mu_{\text{eff.}} = 4.9$. Indeed, intermediate-spin monomers of the type (i) are known only for pseudo-square-planar FeN_4 systems,³⁸ while a dimer of type (ii) is ruled out by the absence of the expected variation of moment with temperature. For $\text{Fe}(\text{mbzimpy})\text{Cl}_2 \cdot \text{H}_2\text{O}$, the value of $\mu_{\text{eff.}} = 5.2$ and obedience to the Curie-Weiss law suggest it to be a simple monomer, $[\text{Fe}(\text{mbzimpy})(\text{OH}_2)\text{Cl}_2]$, though formulation as a very weakly coupled dimer cannot be excluded.

$[\text{Fe}(\text{mpybzim})_3][\text{ClO}_4]_2$ shows evidence of a gradual onset of spin crossover with the magnetism varying from $\mu_{\text{eff.}} = 0.84$ at 125 K to 2.00 at 300 K. This can be compared to $[\text{Fe}(\text{pybzim})_3][\text{ClO}_4]_2 \cdot x\text{H}_2\text{O}$, for which the moment depends on the amount of water in the lattice;³⁹ for $x = 1$ $\mu_{\text{eff.}} = 2.00$ at 80 K, while for $x = 2$ the value was 1.29 at the same temperature. Both compounds have a moment of ca. 5.4 at 300 K. The generally lower paramagnetism of the methylated compound may again be attributable to the increase in basicity caused by the methyl group on the benzimidazole nitrogen, as in the mbzimpy and bzimpy systems.

The complex $[\text{Fe}(\text{dpya})_3][\text{ClO}_4]_2$ remains high spin down

Table 2. Electron spin resonance data

Compound	Medium	Temperature	g Values			
[Fe(bzimpy)Cl ₃]	Powder	77 K	3.1 ^a			
[Fe(mbzimpy)Cl ₃].0.5H ₂ O	Powder	Ambient	4.88			
Fe(mbzimpy)Cl ₂	Powder	77 K	4.20			1.981
[Fe(mbzimpy) ₂][ClO ₄] ₂ .0.5CH ₃ OH	Powder	77 K	4.23			1.975
[NHEt ₃][Fe(H ₂ bzimpy) ₂].4H ₂ O	Powder ^b	Ambient	2.248	2.141		1.929
[NHEt ₃][Fe(H ₂ bzimpy) ₂].4H ₂ O	dmf	Ambient	2.253	2.147	2.003	1.930

^a Bandwidth *ca.* 0.16 T. ^b Weak resonance at *g* = 9.4.

to 4 K with a magnetic moment that varies only between 5.1 and 5.4 below 100 K (Table 1). Prevailing views would predict that this compound should be high spin since the α -diimine π -electron conjugation present in the low-spin [Fe(bipy)₃]²⁺ analogues is interrupted by the amine nitrogen. Our results are in accord with the room-temperature value $\mu_{\text{eff.}} = 5.4$ reported previously for the ClO₄⁻ salt by McWhinnie *et al.*⁹

The complex [Fe(dpyma)₂][BF₄]₂ is essentially low spin with only a trace of temperature dependence in the $\mu_{\text{eff.}}$ The values range from 0.19 at 11 K to 0.81 at 300 K, probably attributable to a paramagnetic impurity in the sample, since the susceptibility increases sharply at low temperature. Above 200 K the susceptibility is essentially independent of temperature. Nelson and Rodgers⁶ showed that the chloride, bromide, and thiocyanate salts of this cation and its (amino) *N*-methylated analogue are low spin at ambient temperature, and proposed that the strength of the metal-ligand interaction is due to (i) the ability of the iron *t*_{2g} electrons to be delocalized into the pyridine antibonding π orbitals and (ii) the flexibility of the dpyma ligand enabling a favourable (for co-ordination) arrangement of the donor atoms around the metal. Ligands of the α -diimine class are more geometrically constrained. Anent this proposal is the comparison of [Fe(dpyma)₂]²⁺ with the dipyridylamine complex [Fe(dpya)₃]²⁺. Neither have α -diimine character but their magnetic behaviour is completely different. Although relative flexibility of the ligand is a factor, we suggest that it is more important that the di(pyridylmethyl)-amines provide two secondary aliphatic nitrogens of increased basicity relative to the aromatic nitrogens of the dipyridylamine ligands, leading to greater σ -donor strength.

Electron Spin Resonance.—The occurrence of a single resonance at *g* = 4.88 for [Fe(mbzimpy)Cl₃].0.5H₂O (Table 2) is clearly an indication of high-spin iron(III). There are no other distinguishing peaks for this compound. For [Fe(bzimpy)Cl₃] the only observed resonance is very broad but clearly indicates high-spin iron(III). The compound [NHEt₃][Fe(H₂bzimpy)₂].4H₂O has strong resonances at *g* = 2.253 and *g* = 2.147 which indicate low-spin iron(III). There is a weak feature at *g* = 9.4 which indicates a small amount of high-spin iron(III), but even at room temperature the low-spin iron is greatly predominant. In solution, an additional signal (*g* = 2.003) suggests the presence of some molecules in which there is ligand radical character present. The diamagnetism of [NHEt₃][Fe(H₂bzimpy)₂].4H₂O is readily rationalized by considering the strongly basic nature of the anionic benzimidazole donors. The data in Table 2 also reveal the traces of iron(III) in the mbzimpy-iron(II) preparations.

Electronic Spectra.—The optical spectra are summarized in Table 3. The *d*-*d* electronic transition which has been observed^{9,40} for [Fe(dpya)₃]²⁺ at 12 000 cm⁻¹ appears to be obscured in most of the above complexes by an intense charge-

transfer (c.t.) band at *ca.* 20 000 cm⁻¹. Some of the bzimpy and mbzimpy compounds show a broad shoulder on the low-energy side of an intense peak at *ca.* 18 000 cm⁻¹. We attribute this shoulder to a *d*-*d* (*t*_{2g} → *e*_g) transition. It is not seen in the spectra of all the compounds we studied and is somewhat difficult to locate with accuracy.

There is a correlation between the spin state of the bis(triimine)iron(II) complex salts and the appearance of the ambient-temperature absorption spectrum in the solid state. A weak, broad band (probably a *d*-*d* transition) is present near 10 500 cm⁻¹ in the high-spin complexes, but absent in the low-spin complexes. A pronounced shoulder is present in the low-spin perchlorate salt of [Fe(mbzimpy)₂]²⁺ at 13 900 cm⁻¹. In the high-spin chloride, it is red-shifted by 700 cm⁻¹ and less clearly apparent, while in the spin-crossover perchlorate of [Fe(bzimpy)₂]²⁺, the band is of intermediate character. In Me₂SO solution, the longer wavelength side is enhanced in intensity for both the [Fe(mbzimpy)₂]²⁺ salts, but less so for the [Fe(bzimpy)₂]²⁺ salt. Interpretation of the solvent ¹H n.m.r. shifts (Evans' method⁴¹) induced by these complexes in Me₂SO yields ambient-temperature effective solution moments of *ca.* 4.2 for [Fe(bzimpy)₂]²⁺ and *ca.* 2.2 (70% low spin) for its methylated analogue. The absorption spectra in methanol show that the spin-state details are solvent dependent. Differences in the absorption spectra amongst the bis-complexes are therefore not necessarily direct inductive consequences of ligand modifications such as *N*-methylation, but mainly result from the spin-state differences caused by these modifications.

The intense absorption in the visible region (occurring in all but the dipyridylamine complexes) near 18 000 cm⁻¹ undoubtedly involves ligand-based orbitals as well as metal *d* orbitals. These bands in low-spin tris(diimine)iron(II) complexes are widely considered to be associated with metal-to-ligand charge transfer transitions (*d* → π_1^* m.l.c.t.).⁴²⁻⁴⁵ This assignment is originally based on convincing evidence presented for tris(1,10-phenanthroline)iron(II) complexes, and then extended by similarity to the tris(2,2'-bipyridyl)iron(II) systems.⁴⁶ Within this assignment, simple charge and inductive effects could not account for the red shifts observed on methylation, deprotonation, and oxidation of the [Fe(bzimpy)₂]²⁺ complex at constant spin state, since direct or inductive increase of electronic charge on the ligand should raise the energies of the ligand π orbitals. The m.l.c.t. assignment is nonetheless consistent with the properties of the [Fe(mbzimpy)₂]²⁺ complex. The red shift observed for the iron(III) bis-complex shows that the c.t. transition direction is reversed, as in [Fe(phen)₃]³⁺, in which these l.m.c.t. bands are in the visible region⁴⁶ because in contrast to the iron(II) system, (a) the *d*_π subshell has a vacancy and (b) the metal orbitals are at considerably lower energy. It seems apparent that the latter may also be effective for the H₂bzimpy system. This broad peak has a shoulder at 1 200–1 600 cm⁻¹ to higher energy for the bzimpy complexes and 800 cm⁻¹ in the same direction for the mbzimpy complexes. Such behaviour is characteristic of both

Table 3. Absorption spectra of ligands and complexes^a

Table 3. Absorption spectra of ligands and complexes ^a															
Complex	Solvent														
bzimpy ^b	CH ₃ OH														
mbzimpy ^b	CH ₃ OH														
[Fe(H ₋₁ bzimpy) ₂].H ₂ O	CH ₃ OCH ₂ CH ₂ OH	13.5(sh) (2.40)	16.9 (3.8)	18.5(sh) (2.8)	21.7(sh) (1.5)	26.0(sh) (27.2)	27.4(sh) (7.5)	29.4(sh) (29.7)	30.6 (33.7)	32.3(sh) (29.3)	39.7(sh) (10.7)	41.3(sh) (13.4)	43.9(sh) (19.3)	46.1(sh) (32.8)	
[Fe(bzimpy) ₂][FeCl ₄]	CH ₃ OH		18.0 (3.4)	19.6(sh) (2.5)											
[Fe(bzimpy) ₂].Cl ₂	CH ₃ OH	14.0(sh) (0.19)	18.0 (1.4)	19.5(sh) (1.1)											
[Fe(bzimpy) ₂][ClO ₄] ₂	CH ₃ OH	14.5(sh) (0.22)	18.0 (3.9)	19.6(sh) (2.8)											
[Fe(mbzimpy) ₂].Cl ₂ .H ₂ O	Solid CH ₃ OH	11.1(sh) ^c 13.9(sh) (0.42)	14.1(sh) 17.4 (8.4)	15.2(sh) 18.2(sh) (7.1)	18.9 20.6(sh) (3.7)	26.3 ^d	27.2 (41.3)	28.7 (37.0)	31.7 (51.0) ^e	32.3(sh) (29.3)	32.8(sh) (34.0)	32.5(sh) (45.5)	32.1 (55.0)	30.5 (55.0)	45.9(sh) (66.0)
[Fe(mbzimpy) ₂][ClO ₄] ₂ .0.5CH ₃ OH	Solid CH ₃ OH	10.3(sh) ^c 13.9(sh) (0.44)	13.2(sh) 17.4 (8.3)	14.9(sh) 17.2(sh) (6.7)	18.2 20.4(sh) (3.4)		27.4 (37.8)	28.7 (35.3)	31.8 (49.2) ^e	31.8 (49.2) ^e					46.3(sh) (37.5)
[Fe(bzimpy)Cl ₃]	Solid Dmf	13.9(sh)	17.2(sh) (0.26)	20.1(sh) (0.48)											46.5(sh) (72.6)
[NHEt ₃][Fe(H ₋₂ bzimpy) ₂].4H ₂ O	CH ₃ OH		17.2 (4.3)		21.7(sh) (1.3)	26.0(sh) (19.0)	27.8(sh) (26.6)	29.0(sh) (32.0)	30.3 (33.5)	30.3 (33.5)					
[Fe(mbzimpy)Cl ₃].0.5H ₂ O	Dmf		17.2(sh) (0.11)						31.1 (53.0)						
[Fe(mpybzim) ₃][ClO ₄] ₂	CH ₃ CN		18.9 (4.9)	19.6(sh) (4.7)		26.3 (2.2)							43.5 (43.0)		
[Fe(bztpy) ₂][ClO ₄] ₂ .CHCl ₃ ^e	CH ₃ NO ₂	14.4(sh) (0.07)	17.6(sh) (0.57)	19.4 (0.62)		26.3 (5.65)									
[Fe(pybzim) ₃][ClO ₄] ₂	CH ₃ CN		18.9 (4.85)	19.6(sh) (4.7)		26.3(sh) (2.15)			30.8(sh) (55.5)	32.3 (61.0)			43.5 (43.0)		
[Fe(dpyma) ₂][BF ₄] ₂	Dmf				22.7 (8.8)	25.6(sh) (6.7)					37.6 (28.0)				
[Fe(dpya) ₃][ClO ₄] ₂	Solid CH ₃ CN			18.9(sh)		25.0				31.7 (40.5)	37.7 (37.5)	40.0 (44.4)			

^a Band positions ($\times 10^{-3}$) in cm^{-1} ; molar absorptivity ($\times 10^{-3}$) in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ is given in parentheses. ^b Several ligand u.v. absorptions are also observed as peaks or shoulders in the metal complexes. ^c Instrumental limitations prevent observation of this band in solution. ^d Several relatively narrow shoulders are observed about these maxima. ^e The spectrum of bztpy is reported in ref. 22.

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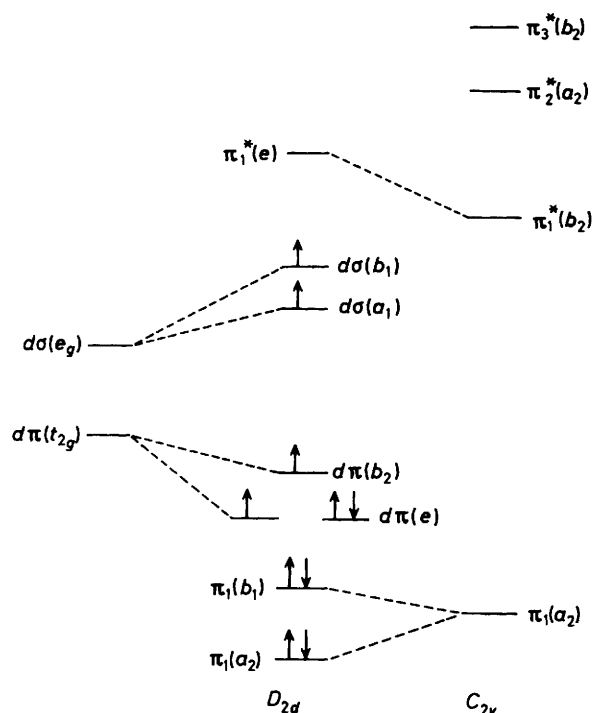


Figure 2. Molecular orbital scheme for $[\text{Fe}(\text{bzimpy})_2]^{2+}$

the terpy- and bipy-iron systems but the band is broader than that observed for the terpy complex,^{29,47,48} which has a narrow peak at $18\,100\text{ cm}^{-1}$. $[\text{Fe}(\text{bipy})_3]^{2+}$ has a broad absorption centred at $19\,200\text{ cm}^{-1}$ which resembles the shape of the bands due to the pyridylbenzimidazole complexes in this region, despite the fact that the bzimpy compounds and $[\text{Fe}(\text{terpy})_2]^{2+}$ have the same symmetry (D_{2d}) and similar types of ligands. However, the frequency at which the $[\text{Fe}(\text{bzimpy})_2]^{2+}$ peak appears corresponds to the absorptions of the terpy, rather than the bipy, complex.

A molecular orbital (m.o.) scheme is presented in Figure 2. Free bzimpy ligands have C_{2v} symmetry and the π and π^* orbitals transform as a_2 or b_2 . In a bis-chelate the two a_2 bzimpy orbitals give a_2 and b_1 m.o.s in the D_{2d} point group, and the two b_1 bzimpy orbitals transform together as one m.o. of e symmetry. The metal $d\pi$ (d_{xy} , d_{xz} , d_{yz}) orbitals transform as b_2 and e in the D_{2d} point group. It seems likely that the absorption which occurs at $18\,000\text{ cm}^{-1}$ is due to the $d\pi(b_2) \rightarrow \pi_1^*(e)$ electronic transition. The shoulder at higher energy may be due to a $d\pi(e) \rightarrow \pi_1^*(e)$ transition.

It is noteworthy, that although di(2-pyridylmethyl)amine contains no α -di-imine unit, it nonetheless exhibits fairly intense absorption in the visible region, which is consistent with the low-spin $d\pi \rightarrow \pi_1^*$ assignments. A suspicion that the dpyma ligand may have become oxidatively dehydrogenated to yield the imine is countered by the observations (i) that the intense colour of $[\text{Fe}(\text{dpyma})_2]^{2+}$ in aqueous solution is not dispelled by addition of excess sodium tetrahydroborate and (ii) the corresponding dehydrogenated complex has a different absorption spectrum.[†]

By analogy with the band assignments⁴⁴ for $[\text{Fe}(\text{bipy})_3]^{2+}$, the peak at $27\,800\text{ cm}^{-1}$ is assigned as a $d\pi \rightarrow \pi_1^*$ transition. The bands at ca. $30\,000\text{ cm}^{-1}$ would be $\pi \rightarrow \pi_1^*$ transitions and

[†] In $[\text{Fe}(2,2'\text{-C}_5\text{H}_4\text{NCH}=\text{NCH}_2\text{C}_5\text{H}_4\text{N})_2]^{2+}$ the absorption bands are at $16\,800$ and $27\,500\text{ cm}^{-1}$ (A. W. Addison and C. G. Wahlgren, unpublished work).

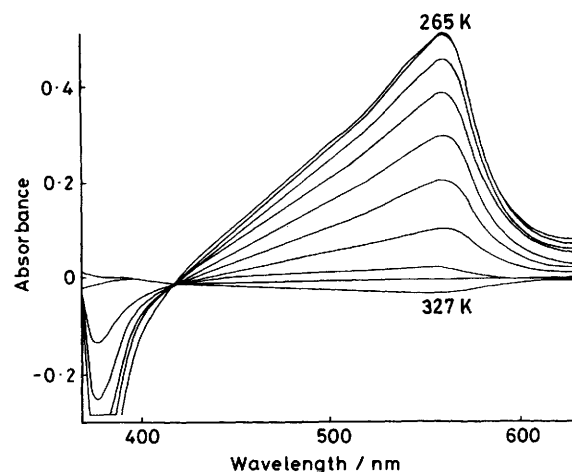


Figure 3. Temperature dependence of difference absorption for $[\text{Fe}(\text{bzimpy})_2][\text{ClO}_4]_2$ in dmf solution

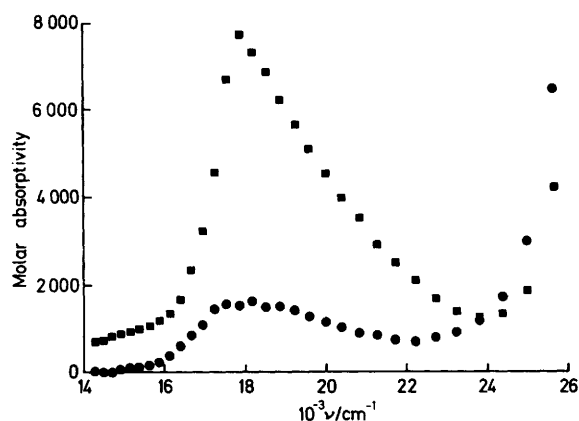
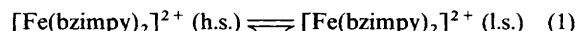


Figure 4. Upper-(●) and lower-temperature (■) limiting spectra computed from thermochromism data for $[\text{Fe}(\text{bzimpy})_2][\text{ClO}_4]_2$ in dmf solution

the absorptions at $40\,000\text{ cm}^{-1}$ and above would be $\pi \rightarrow \pi_2^*$ transitions. The appearance of several shoulders or closely spaced distinct peaks in the vicinity of $30\,000$ and $40\,000\text{ cm}^{-1}$ are taken as evidence for vibrational fine structure ($1\,000$ – $2\,000\text{ cm}^{-1}$ spacing) associated with the $\pi \rightarrow \pi^*$ bands.

Difference Spectra.—Spin-equilibrium processes have been explored in solution both for iron(III) proteins⁴⁹ and iron(II) co-ordination complexes⁵⁰ using spectrophotometric methods. The co-operativity and hysteresis which have been observed^{23,51} for solid-state samples are expected to be absent in solution. We have applied the analytical method of Neya *et al.*⁴⁹ to $[\text{Fe}(\text{bzimpy})_2]^{2+}$. Since the molar absorptivity at a given wavelength and temperature results from a combination of contributions from the high- and low-temperature forms of the complex, it can be expressed as: $\epsilon = f\epsilon_h + (1-f)\epsilon_l$ where f is the fraction of complex in the low-spin form, and ϵ_h and ϵ_l are the molar absorptivities for the high- and low-temperature limiting forms of the complex respectively. Since the equilibrium constant for a process such as (1) can be written as $K = f/(1-f)$,



then $K = (\epsilon_h - \epsilon)/(\epsilon - \epsilon_l)$. Using the observed values of ϵ and T at a single wavelength, the best combination of values for ϵ_h and ϵ_l was obtained from a least-squares fit to the Van t'Hoff

equation (2), yielding values of ΔH° and ΔS° for the equilibrium

$$\ln[(\epsilon_h - \epsilon)/(\epsilon - \epsilon_l)] = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (2)$$

in question. These values can be fed back into a pair of spectra obtained at different temperatures to generate the limiting spectra of the low-temperature and high-temperature forms of the complex ion. The spectral changes (Figures 3 and 4) are quite similar to those obtained by Wilson and co-workers⁵⁰ in their study of the spin equilibrium of the cation tris[2-(2'-pyridyl)imidazole]iron(II) and suggest that the equilibrium indeed involves a h.s. $\rightarrow$ l.s. conversion. The values of ΔH° and ΔS° (-42.7 ± 0.01 kJ mol⁻¹ and -140.9 ± 0.04 J K⁻¹ mol⁻¹ respectively*) are a little larger, but of the same order of magnitude as those for tris[2-(2'-pyridyl)imidazole]iron(II). This same procedure was applied to a solution of [Fe(dpyma)₂][BF₄]₂ in nitromethane under dinitrogen, but the spectra indicated that the process was an irreversible one. Similar results were obtained when dmf was used as the solvent and also when the complex was formed in aqueous solution by adding dpyma to iron(II) chloride. The nature of the reaction is not clear but dissociation of the complex at elevated temperatures, followed by irreversible reaction of the amine ligand with nitromethane solvent is clearly one possibility.

STEPS Measurements.—The low-spin complex, [Fe(bzimpy)₂][ClO₄]₂ was chosen as a candidate for STEPS measurements, as the cation is strongly absorbing over a broad region of the visible spectrum and has an accessible high-spin state. The electronic excited states are therefore all considerably higher in energy than the quintet state, so are suitable for initiating the process of conversion to the metastable high-spin state. In particular, this will involve mainly the iron $\rightarrow$ ligand charge-transfer excitation, and any spin-allowed $d-d$ transitions, such as to the ¹T₁ and ¹T₂ excited states (or to the distortion-split remnants of these states) in the real pseudo-octahedral complex.

Photoexcitation was immediately followed by an initial rise in magnetism, due to an increase in paramagnetic species, succeeded by a dramatic fall in the magnetism, due to the Curie law decrease in magnetic susceptibility with the associated increase in temperature (see Experimental section). This phenomenon limits the light intensity that can be used, as a rise above the catastrophic (explosive) decay temperature (see above) must be prevented; otherwise, the conversion is easy to attain; very low-intensity light sources would be adequate, but for the impractically long excitation times which would be required.

In the region 30–35 K, the decay of the photoexcited sample was explosive: the energy released with each decay of a molecule from the high- to the low-spin state is more than sufficient to raise at least one more molecule over the activation energy and the process readily becomes self-sustaining. Detailed measurement of the onset temperature of explosive decay was not possible because of the associated temperature fluctuations produced in the thermostat control.

Near 20 K a very slow and apparently exponential decay is observed, with a half-life of 4 d. This implies first-order kinetics and is compatible with a unimolecular process. Such a mechanism would imply a spontaneous decay process, where only occasional molecules attain sufficient energy to go over (or tunnel through) the activation barrier. Spin-crossover systems are known to be highly co-operative in the solid state,^{18,51} and

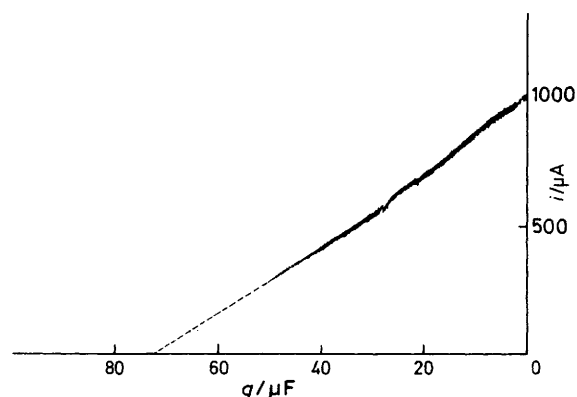


Figure 5. Recorder trace of current (*i*) vs. charge (*q*) plot for [Fe(bzimpy)₂][ClO₄]₂ (72.7 μmol) in dmf-[NEt₄][ClO₄]

undoubtedly, the detailed mechanism is more complicated than a simple random decay process. We presume that generation of the metastable high-spin state involves internal conversion of part of the photoexcited population to low-lying triplet states and then finally to the quintet.

After excitation is stopped, the complex must be cooled back to 4 K for low-temperature observations. At this temperature, the complex appears able to remain indefinitely in a metastable state. For as long as the apparatus could reasonably be kept in operation, there was no measurable decay, and the paramagnetism persisted as the sample temperature was gradually raised toward 20 K.

Electrochemistry.—Electrolytic oxidation of a dimethylformamide solution of [Fe(bzimpy)₂]²⁺ (72.2 μmol) at a Pt-gauze anode at +500 mV yielded the *i* vs. *q* plot⁵² of Figure 5, extrapolation to zero current showing that complete oxidation corresponds to passage of 76.3 μF (*n* = 1.05) (*n* = no. of electrons per molecule involved in the redox process). The r.d.p. limiting currents associated with the oxidation of the other iron(II) compounds reported here are comparable to that of [Fe(bzimpy)₂]²⁺, so the oxidation waves are assigned to *n* = 1 oxidations, formally of iron(II) to iron(III).

The *E*₁ values (Table 4) for [Fe(bipy)₃]^{3+/2+} and [Fe(terpy)₂]^{3+/2+} are in fact quite comparable (within 2 and 12 mV respectively) with previously reported values of +1 087⁵³ and +1 130 mV⁵⁴ [in acetonitrile vs. Ag/AgCl/NaCl(saturated), which is +197 mV vs. s.h.e.⁵⁵]. Nonetheless, Table 4 reveals that the redox potentials of the Fe³⁺/Fe²⁺ couples are no less sensitive to small variations in donor type than are the magnetic properties, the *E*₁ values encompassing a range of almost 700 mV, despite the similarities amongst the donors. Complexes are tabulated as having reversible redox behaviour where the peak-to-peak potential separation is comparable to that for a Nernstian *n* = 1 standard such as ferrocene or 1,1'-dimethyl-4,4'-bipyridinium hexafluorophosphate⁵⁶ at the same scan rate.

As the content of benzothiazole nitrogen in the co-ordination sphere is increased, *E*₁ increases; benzothiazoles are much less σ-basic than benzimidazoles. Apart from this, there seem to be few clear correlations between the *E*₁ values and other properties of the chelates. N-Methylation (mpybzim vs. pybzim; mbzimpy vs. bzimpy) might have been expected to (inductively) uniformly lower *E*₁,^{26,46} but the opposite is in fact observed (opposite to the effect of methylation on the magnetic susceptibility of the bzimpy compounds). The thermodynamic origin of this effect is not clear to us, but may be connected with the apparent instability of [Fe(mbzimpy)₂]³⁺ noted in the Experimental section.

* The parameters ΔH° and ΔS° are referred to a standard state of 1 mol dm⁻³; the σ values account only for residual random errors, which are minimized by the procedure forcing the data to linearity.⁴⁹

Table 4. Redox properties of the complexes

Complex	Solvent	E_1^a /mV	ΔE_p^b /mV	$10^8 D\eta^c$ /g cm s ⁻²	Comments
[Fe(bipy) ₃][BF ₄] ₂	CH ₃ CN	+742 ^d	85	2.5	Reversible
[Fe(terpy) ₂][ClO ₄] ₂	CH ₃ NO ₂	+795 ^d	80	3.1	Reversible
[Fe(dpva) ₂][ClO ₄] ₂	CH ₃ CN	+630		2.9	Irreversible
[Fe(pybzt) ₃] ²⁺ ^e	CH ₃ NO ₂	+1 080		1.1	Irreversible
[Fe(pybzim) ₃][PF ₆] ₂	CH ₃ NO ₂	+440	115	3.1	Quasi-reversible
[Fe(mpybzim) ₃][ClO ₄] ₂	CH ₃ CN	+525	80	2.5	Reversible
[Fe(bzimpy) ₂][ClO ₄] ₂	CH ₃ CN	+415	80	1.6	Reversible
[Fe(mbzimpy) ₂][ClO ₄] ₂	CH ₃ CN	+445	83	1.9	Reversible
[Fe(dpyma) ₂][BF ₄] ₂	CH ₃ NO ₂	+445	90	3.7	Following reaction
		+760 ^f	120		Quasi-reversible
[Fe(bztpy) ₂][ClO ₄] ₂	CH ₃ NO ₂	+880	108	2.1	Following reaction
[Fe(mbzimpy)Cl ₃]	Dmf	-390		3.3	Irreversible

^a Values vs. Ag⁺ (0.01 mol dm⁻³)/[NEt₄][ClO₄](0.1 mol dm⁻³)/Ag electrode. ^b In cyclic voltammogram at 0.1 V s⁻¹, without *iR* correction. ^c From r.d.p. data (or $10^{-13} D\eta$ in kg m s⁻²); *D* = diffusion coefficient, η = absolute viscosity. ^d Data from cyclic voltammetry only. ^e Treated with teof, and prepared by addition of excess pybzt to iron(II) perchlorate in CH₃NO₂. ^f Second oxidation process for dpyma, data from cyclic voltammetry.

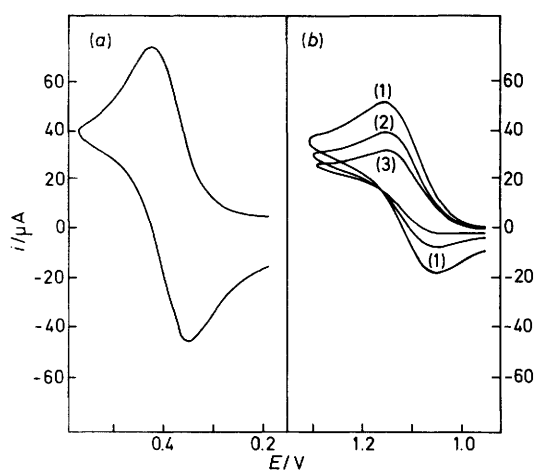


Figure 6. (a) Cyclic voltammetry of [Fe(bzimpy)₂][ClO₄]₂ vs. the non-aqueous Ag⁺/Ag reference electrode in CH₃CN-[NEt₄][ClO₄]; scan rate 100 mV s⁻¹. (b) Cyclic voltammetry of [Fe(bztpy)₂][ClO₄]₂ in CH₃NO₂-[NEt₄][ClO₄]; scan rates, (1) 400, (2) 200, (3) 100 mV s⁻¹; current ratio ($i_{p,c}/i_{p,a}$), (1) 0.798, (2) 0.689, (3) 0.550

Those couples wherein the iron(II) complex is high spin (dipyridylamine) or observed to be of low thermodynamic stability (benzothiazoles) tend to be less reversible electrochemically. It is noted, in this regard, that [Fe(bztpy)₂]²⁺ and [Fe(pybzt)₃]²⁺ are dominantly high spin near 298 K.^{34,57} The known tendency for the iron(III) complexes to hydrolyze^{58,59} may well be amplified in these weaker N-donor systems. The great variability of the E_1 values as a function of the type of heterocyclic N-donor ligand contrasts with their relatively constant, systematic effect on the E_1 values of Cu²⁺/Cu⁺ systems.⁶⁰ This further points to the importance of potential spin-state variability in both the iron(II) and iron(III) states as significant thermodynamic influences.

In the case of [Fe(bztpy)₂]^{3+/2+} the increasing value of the ratio of cyclic voltammetric peak currents as the scan rate increases (with a limiting value of 1.0, Figure 6) is diagnostic of a chemical reaction following the electron-transfer (e.c.) process.⁶¹ Using the working curve of current ratio vs. τk_f developed by Nicholson and Shain,^{62,*} a value of 0.44 s⁻¹ was obtained for the forward rate constant, k_f , of the irreversible

reaction in this e.c. process. This is likely to involve displacement of co-ordinated nitrogens by solvent in the iron(III) form of the couple. [Fe(dpyma)₂][BF₄]₂ undergoes similar chemistry, for which the same treatment gives a value of 0.21 s⁻¹ for the rate constant of the reaction following oxidation.

In the r.d.p. of [Fe(bzimpy)₂]²⁺ in dmf, the wave for Fe²⁺ → Fe³⁺ occurs at +345 mV. Addition of triethylamine causes the development of current at more negative potential, until the first wave is replaced by one at -680 mV, while the visible region absorption band simultaneously increases in intensity (by 36%) and shifts from 18 000 cm⁻¹ to 17 100 cm⁻¹, causing the colour of the solution to change from purple to indigo. The emergence of the wave at -680 mV reaches a current limit at a ratio of 2.5 mol of NEt₃ per mol of Fe, interpretable in terms of formation of the neutral iron(II) species [Fe(H₋₁bzimpy)₂] in solution, *via* deprotonation of the benzimidazole N-H fragment. Overlapping intermediate polarographic waves attributed to redox equilibria involving deprotonation of both iron(II) and iron(III) species are discernible. The indigo species is also generated spontaneously when a dmf solution of [Fe(bzimpy)₂]²⁺ is allowed to stand for several hours, due to the generation of dimethylamine from this solvent. [Fe(H₋₁bzimpy)₂] was also prepared in and isolated from ethanol solution. The similarity between the absorption spectra of the two species, one [Fe(H₋₂bzimpy)₂]⁻, associated with metal ion oxidation, the other with only ligand deprotonation of [Fe(bzimpy)₂]²⁺ is striking, and supports the same (l.m.c.t.) assignment to both these lowest-energy absorptions.

Finally, we note that the pybzim, bzimpy, and bztpy iron(II) chelates show an additional *n* = 1 reduction wave at quite low potentials. However, only in the case of [Fe(bzimpy)₂]²⁺ does this process (-1 450 mV) appear to be reversible on the cyclic voltammetry time-scale used.

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* Rate behaviour first order in the reactive species is presumed; τ is the time elapsed from scan direction reversal.

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