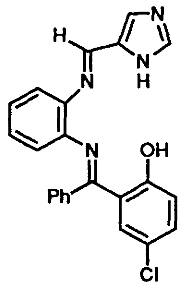
Spin Crossover in Heterodinuclear Iron(III) Schiff-base Complexes

Cynthia T. Brewer, Greg Brewer,* Leopold May, Jennifer Sitar and Ru Wang
Department of Chemistry, Catholic University, Washington DC 20064, USA

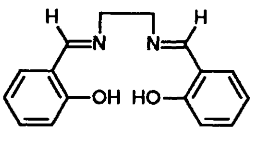
The reaction of a nickel(II) imidazolate complex [NiL^1] (H$_2$L^1 = 5-{*o*-[(5-chloro-2-hydroxyphenyl)phenylmethyleneamino]phenyliminomethyl}imidazole) with iron(III) Schiff-base complexes [FeL^{2}Cl], [FeL^3]$^+$ and [FeL^4]$^+$ [H$_2$L = R(N=CHC$_6$H$_4$OH-*o*)$_2$; R = (CH$_2$)$_2$ (L^1), (CH$_2$)$_3$NH(CH$_2$)$_3$ (L^2) or (CH$_2$)$_3$NMe(CH$_2$)$_3$ (L^3)] yielded the imidazolate-bridged heterodinuclear complexes [FeL^2(NiL^1)Cl], [FeL^3(NiL^1)]BPh$_4$ and [FeL^4(NiL^1)]BPh$_4$, which were characterized by variable-temperature magnetic susceptibility, Mössbauer and ESR spectroscopy. Their spectral and magnetic properties are consistent with high spin/low spin crossover behaviour for the iron(III) atoms. Two analogous copper(II) complexes, [FeL^3(CuL^1)]BPh$_4$ and [FeL^4(CuL^1)]BPh$_4$, were also prepared and the latter characterized as an antiferromagnetically coupled copper(II)–high-spin iron(III) system.

Recent work in this laboratory has been directed at producing imidazolate-bridged heterodinuclear complexes of copper(II) and a high-spin iron(III) porphyrin by treating one equivalent of a copper imidazolate complex [CuL^1] with one equivalent of an iron(III) porphyrin.[1] Complexes of this type are particularly interesting as magnetic mimics of the cytochrome a$_3$–copper(II) pair of cytochrome c oxidase.[2] While dinuclear compounds of the type (porphyrinato)iron(III)–imidazolate–copper(II) have been isolated by this method, the spin state of iron has been found to be intermediate or admixed intermediate spin instead of high spin. The stabilization of the admixed intermediate-spin state is a common occurrence among the distorted iron(III) porphyrin complexes [Fe(por)X][3] or [Fe(por)B]$^+$,[4] where B is a nitrogen-containing base and X is a weakly co-ordinating anion. Because of this tendency it was necessary to investigate the magnetic interaction between copper and iron(III) using a ligand for iron(III) which would promote the high-spin, rather than the admixed intermediate-spin, state. The high-spin iron(III) complexes of tetra- and penta-dentate Schiff bases H$_2$L^2–H$_2$L^4 derived from the condensation of salicylaldehyde and the appropriate di- or tri-amine were chosen. The complexes [FeL^{2}Cl], [FeL^3]$^+$ and [FeL^4]$^+$ are all five-co-ordinate and yield heterodinuclear complexes (see Fig. 1) on reaction with [NiL^1] as was demonstrated previously in a reaction of [FeL^4]$^+$ with a similar metal imidazolate complex.[5]

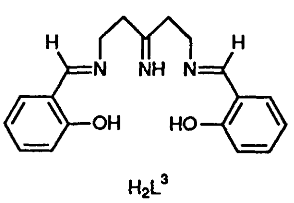
The magnetic exchange pathway of these systems should be similar to that for the metalloporphyrin–imidazolate–copper(II) system, which consists of the $d_{x^2-y^2}$ orbital of copper, the imidazolate π system and the d_{z^2} orbital of the metal of the metalloporphyrin (see Fig. 1). Previous studies in this laboratory showed that, for complexes of this type, the imidazolate bridge fosters both ferromagnetic and antiferromagnetic exchange depending on the electron configuration of the metal in the porphyrin environment. For a metal with unpaired electron density in the t_{2g} level the interaction is ferromagnetic; for a metal with unpaired electron density in the e_g level antiferromagnetism is observed. Thus [Cr(tpp)(CuL^1)Cl][6] [Cr^{III} is $t_{2g}{}^3$; tpp is the dianion of 5,10,15,20-tetraphenylporphyrin) and [Fe(tpp)(CuL^1)$_2$][B$_{11}$CH$_{12}$][7] (Fe^{III} is $t_{2g}{}^5$) are ferromagnetic while [Mn(tpp)(CuL^1)][8] (Mn^{II} is $t_{2g}{}^3e_g{}^2$) is antiferromagnetic.



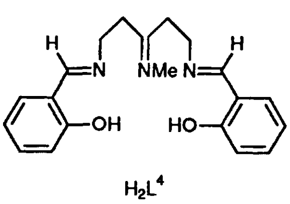
H$_2$L^1



H$_2$L^2



H$_2$L^3



H$_2$L^4

The synthesis and magnetic characterization of the adducts of [FeL]$^+$ (L = L^2–L^4) with [NiL^1] and the synthesis and preliminary characterization of adducts of [FeL]$^+$ (L = L^3 or L^4) with [CuL^1] are described herein. All of the heterodinuclear nickel complexes prepared in this work are spin-crossover complexes. Spin-crossover complexes for homodinuclear iron-(II)[9] and -(III)[10] involving two identical iron atoms in identical donor environments have been reported. In these cases both iron atoms undergo spin crossover. In the iron(II) dinuclear case a weak antiferromagnetic interaction is observed between iron atoms in the high-spin state. Spin crossover in cobalt(III)[11] and iron(III)[12] heterotrinuclear compounds has also been reported in which only the central metal participates in a spin-state change. The present complexes appear to be the first heterodinuclear spin-crossover systems reported. In these complexes a second metal which does not undergo spin crossover, a 'spectator metal', is linked to iron(III) *via* a ligand which has been shown to promote magnetic exchange. This spectator metal may be useful as a probe to investigate spin-state changes in the neighbouring iron(III) ion or to study the effects of a spin crossover on magnetic exchange. One intriguing possibility is a temperature-dependent transition from ferromagnetism to antiferromagnetism when the spectator metal is Cu^{II}. Such behaviour is predicted since it has been established that the magnetic interactions between square-planar copper(II) and low-spin iron(III)[7] are ferromagnetic and between square-

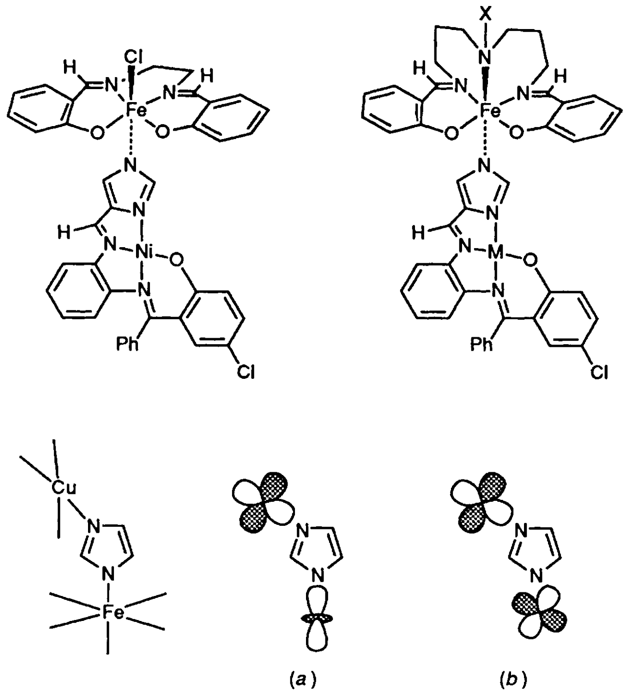


Fig. 1 Dinuclear complexes and magnetic exchange pathways of heterodinuclear complexes of square-planar copper(II) and octahedral iron(III); M = Ni^{II} or Cu^{II}, X = H or Me. Antiferromagnetic coupling (*a*) for high-spin case and ferromagnetic (*b*) for low-spin case

planar copper(II) and high-spin iron(III)[13] or manganese(II)[8] are antiferromagnetic. Complexes of the present class seem to be ideal systems to examine this possibility and also the broader effects of spin exchange on spin-crossover behaviour. One of the present examples involving copper(II), $[FeL^4(CuL^1)]BPh_4$, is described as an antiferromagnet while the other, $[FeL^3(CuL^1)]BPh_4$, may be a candidate for a spin-coupled crossover system.

Experimental

Spectra.—Visible spectra were obtained on a computer-controlled Perkin Elmer Lamda 4 UV/VIS spectrometer using software obtained from Softways, IR spectra on a Perkin Elmer model 1750 FT IR instrument using IDRIS software and ESR spectra on polycrystalline samples at 80 K on a Varian E9 or E3 spectrophotometer. The Mössbauer spectra were obtained on a Ranger Scientific model MS-900 spectrometer in the acceleration mode with moving-source geometry at 80 K or room temperature. The resultant spectra were analysed by a constrained, least-squares fit to Lorentzian-shaped lines. The samples were mounted in polyethylene cells. The velocity range was calibrated with $Na_2[Fe(CN)_5(NO)]$, and the isomer shift values converted into the iron standard by subtracting 0.257 mm s^{-1}.

Magnetism.—The magnetic susceptibilities were measured between 80 and 295 K on a computer-controlled Faraday system which consists of a Cahn 2000 microbalance, Applied Magnetics electromagnet, Lake Shore Cryotronics temperature controller, platinum-resistance thermometer, and Abbess instrument cryostat. A Data Translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with $HgCo(NCS)_4$.[14] The raw data were corrected for the susceptibility of the holder and the diamagnetism of the ligand atoms by Pascal's constants,[15] and converted into molar susceptibilities from which the magnetic moments were calculated as $\mu = 2.828(\chi_M T)^{\frac{1}{2}}$. The experimental data were fitted to the appropriate theoretical equations by a non-linear least-squares fitting program, GRAFIT, as described previously.[16]

Starting Materials.—The iron Schiff-base complexes $[FeL^2Cl]$,[17] $[FeL^3Cl]$[18] and $[FeL^4Cl]$[5] and the metal imidazolate[19] complexes $[NiL^1]$ and $[CuL^1]$ were prepared as described previously.

Synthesis of Dinuclear Complexes.—The dinuclear complexes $[FeL(ML^1)]BPh_4$ (L = L^3 or L^4) were synthesised by similar methods as exemplified by the preparation of $[FeL^4(NiL^1)]$ described below. The synthesis of $[FeL^2Cl(NiL^1)]$ differed slightly and is also described below.

$[FeL^4(NiL^1)]BPh_4\cdot 0.5CHCl_3$. To a solution of $[FeL^4Cl]$ (0.0663 g, 0.150 mmol) in methanol was added a solution of $[NiL^1]$ (0.0693 g, 0.150 mmol) in $CHCl_3$ (10 cm^3). This solution was stirred, then filtered and a solution of $NaBPh_4$ (0.0513 g, 0.150 mmol) in methanol (5 cm^3) added. The resulting solution was warmed for 10 min and set aside to stand overnight. The black crystals which formed were filtered off, yield 45% (Found: C, 65.95; H, 5.20; N, 7.75. Calc. for $C_{68}H_{60}BClFeN_7NiO_3\cdot 0.5CHCl_3$: C, 66.0; H, 4.85; N, 7.85%).

$[FeL^2(NiL^1)Cl]\cdot H_2O$. To a solution of $[FeL^2Cl]$ (0.040 g, 0.11 mmol) in 95% ethanol was added a solution of $[NiL^1]$ (0.050 g, 0.11 mmol) in chloroform. The solution was heated to reflux and filtered whilst hot. The dark reddish brown crystals which formed overnight were filtered off, yield 50% (Found: C, 55.50; H, 4.10; N, 10.30. Calc. for $C_{39}H_{29}Cl_2FeN_6NiO_3\cdot H_2O$: C, 56.20; H, 3.75; N, 10.1%).

All new complexes were analysed by MHW Laboratories (Found: C, 67.9; H, 4.90; N, 8.75. $[FeL^3(NiL^1)]BPh_4\cdot MeOH$ requires C, 67.9; H, 5.15; N, 8.15. Found: C, 64.40; H, 4.90; N, 7.60. $[FeL^3(CuL^1)]BPh_4\cdot MeOH\cdot 0.5CH_2Cl_2$ requires C, 64.90; H, 4.95; N, 7.70. Found: C, 65.65; H, 4.90; N, 7.85. $[FeL^4(CuL^1)]BPh_4\cdot 0.5CHCl_3$ requires C, 65.90; H, 4.85; N, 7.85%).

Results and Discussion

Synthesis.—The synthesis of all the dinuclear complexes was easily accomplished by the reaction of equimolar amounts of the iron(III) Schiff base and the metal imidazolate complex in an alcohol–chloroform mixed solvent. The $[FeL^3(ML^1)]^+$ and $[FeL^4(ML^1)]^+$ complexes were precipitated as their tetraphenylborate salts by the addition of sodium tetraphenylborate. Their formation could be monitored in solution by observing the shift in the band of the reactant at 430 nm to that of the product at 528 nm. This spectral change was also observed[5] on addition of 1-methylimidazole to a solution of $[FeL^4]BPh_4$ and indicates co-ordination of the imidazole group in both cases. The IR spectra revealed the presence of bands attributable to the tetraphenylborate anion and the starting complexes.

The reaction of $[NiL^1]$ with $[FeL^2Cl]$ yielded $[FeL^2(NiL^1)Cl]$, which is structurally different from the monoadducts discussed above in that the sixth ligand around iron is either the chloride counter ion or a water. Monoadducts of substituted $[FeL^2]^+$ complexes with imidazoles and pyrazoles have been observed previously.[20] In contrast the reaction of $[FeL^2Cl]$ and $[CuL^1]$ gives only the metal-exchange products, $[CuL^2]$ and $[FeL^1Cl]$. The former product was identified on the basis of its UV/VIS and IR spectra while the latter was tentatively identified on the basis of its IR and ESR spectra. The unexpected outcome of this reaction is attributed to the preference of the copper ion for H_2L^2. Investigation of alternative reaction conditions has not resulted in the isolation of the desired product to date.

Magnetism.—The susceptibility of all samples was measured between 80 and 295 K. The susceptibility and moment data for $[FeL^4(NiL^1)]BPh_4$ are shown in Fig. 2. The sharp change in susceptibility at ≈120 K and the other physical measurements

Table 1 Data for nickel(II)–iron(III) dinuclear complexes

	Magnetic susceptibility		Mössbauer			
Compound	E/cm^{-1}	C	T	q.s./mm s^{-1}	i.s./mm s^{-1}	ESR (g)
[FeL^2(NiL^1)Cl]	−298(1)	0.446(4)	N$_2$(l)	2.29(1)	0.238(2)	l.s. 2.40, 2.11, 1.94, 2.15 (av.)
			r.t.	1.30(3)	0.41(1)	h.s. 8.10, 4.30
[FeL^3(NiL^1)]BPh$_4$	−291(2)	0.160(3)	N$_2$(l)	2.97(3)	0.342(8)	l.s. 2.56, 2.05, 1.47, 2.03 (av.)
				0.98(2)	0.428(4)	h.s. 8.19, 4.22
			r.t.	—	—	
[FeL^4(NiL^1)]BPh$_4$	−75.7(47)	18.5(10)	N$_2$(l)	3.06(3)	0.363(7)	l.s. 2.78, 2.00, 1.73, 2.17 (av.)
			r.t.	1.04(8)	0.24(2)	h.s. 9.27, 4.34

r.t. = Room temperature, l.s. = low spin, h.s. = high spin.

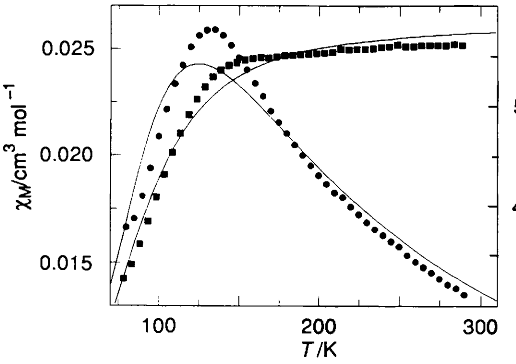


Fig. 2 Plot of magnetic susceptibility (●) and moment (■) against temperature for [FeL^4(NiL^1)]BPh$_4$. The solid line represents the best fit by equation (1) using the values in Table 1 and λ = 375 cm$^-$1

(ESR and Mössbauer) clearly indicate a spin-state crossover for this compound. The magnetic susceptibility data of [FeL^2(NiL^1)Cl] and [FeL^3(NiL^1)]BPh$_4$ lack the abrupt change that [FeL^4(NiL^1)]BPh$_4$ exhibits but do show a gradual increase in magnetic moment with increasing temperature. The magnetic moments of [FeL^2(NiL^1)Cl] and [FeL^3(NiL^1)]BPh$_4$ varied from 3.5 and 2.86 at 80 K to 4.5 and 3.60 at 295 K, respectively. No thermal hysteresis was observed.

The data for the three dinuclear nickel–iron complexes were analysed by the equation (1) of Ewald *et al.*,[21] for a spin

$$\mu^2 = \frac{0.75g^2 + 8kT/\lambda(1 - \mathrm{e}^{-3\lambda/2kT}) + 105C\,\mathrm{e}^{(-\lambda-E)/kT}}{1 + 2\,\mathrm{e}^{-3\lambda/2kT} + 3C\,\mathrm{e}^{(-\lambda-E)/kT}} \qquad (1)$$

equilibrium between the $^2T_2$ and $^6A_1$ states. In this equation g is the spectroscopic splitting factor of the $^2T_2$ state, λ is the spin–orbit coupling term, E is the separation of the zero-point energies between the $^2T_2$ and $^6A_1$ states, and C is the ratio of the molecular vibrational partition functions, Q_a/Q_t. In practice the C term is used to incorporate a variety of effects such as lattice forces, higher-order terms, and distortion from pure octahedral geometry. In order to avoid overparameterization of the problem the fitting procedure was used to determine the best values of C and E only. The average of the three ESR low-spin g values was used along with a value of 375 cm^{-1} for λ, which was used in interpreting the data for [FeL^2(Him)$_2$]ClO$_4$[22] (Him = imidazole) by the same approach. This method of analysis for the nickel–iron complexes is appropriate since the square-planar nickel complex [NiL^1] is diamagnetic and incapable of undergoing magnetic exchange with the iron atom. The results of the fit are given in Table 1 and the solid line in Fig. 2 represents the best fit of the data by the theoretical function. All three complexes exhibit a negative E value which indicates that the $^6A_1$ state lies below the $^2T_2$ state as was observed previously for several tris(dithiocarbamato)iron complexes.[23] This behaviour differs from that of the previously mentioned [FeL^2(Him)$_2$]ClO$_4$, which exhibits an energy separation of 772 cm^{-1}.

The [FeL^2(NiL^1)Cl] and [FeL^3(NiL^1)]BPh$_4$ complexes are best described as gradual and incomplete spin-crossover systems whereas [FeL^4(NiL^1)]BPh$_4$ is a more abrupt but still incomplete spin-crossover system. The observation of spin crossover is not surprising for [FeL^3(NiL^1)]BPh$_4$ and [FeL^4(NiL^1)]BPh$_4$ since the donor set around the iron is N_4O_2 in both cases. Spin crossover for [FeL^2(NiL^1)Cl] is somewhat unexpected for this N_3O_2Cl donor set in light of the fact that related complexes with a N_3O_3 donor set are pure high spin.[20] The observation of spin crossover in [FeL^2(NiL^1)Cl] may reflect a greater donor strength of [NiL^1], which is a formal imidazolate, over neutral imidazole donors.

The magnetic moment of [FeL^4(CuL^1)]BPh$_4$ increases from 5.09 at 80 K to 6.62 at 295 K and overall resembles that of a related copper-containing dinuclear complex of [FeL^4]BPh$_4$.[5] The moments of these copper(II)–iron(III) heterodinuclear complexes clearly indicate the presence of high-spin iron and both are antiferromagnets as predicted theoretically. The susceptibility data for [FeL^4(CuL^1)]BPh$_4$ were analysed by equation (2) for an interacting $S = \frac{1}{2}$–$S = \frac{5}{2}$ system,[24] where N

$$\chi = \frac{Ng^2\beta^2}{kT}\cdot\frac{10 + 28\,\mathrm{e}^{6J/kT}}{5 + 7\,\mathrm{e}^{6J/kT}} + N\alpha \qquad (2)$$

is Avogadro's number, g is the gyromagnetic ratio of the electron, β is the Bohr Magneton, k is Boltzman's constant, J is the magnetic coupling constant, and $N\alpha$ is the temperature-independent paramagnetism, to give a g of 2.14 and J of −31 cm^{-1} with $N\alpha = 200 \times 10^{-6}$ cm^3 mol^{-1}. The interaction is weak and cannot be elaborated on without structural information. The lack of spin-crossover behaviour for [FeL^4(CuL^1)]BPh$_4$ in the temperature region examined contrasts with that of the analogous nickel complex and emphasizes the delicate energy balance in these systems. The 1-methylimidazole complex of [FeL^4]BPh$_4$, prepared by Motsumoto *et al.*, [5] and examined as part of this study is also pure high spin with a temperature-independent magnetic moment of 5.7.

The magnetic moment of [FeL^3(CuL^1)]BPh$_4$ increases gradually from 3.83 at 80 K to 4.81 at 295 K. Clearly these values exclude pure high-spin and pure low-spin behaviour for the iron(III) atom. If a spin-crossover exists for the iron in this complex its magnetic behaviour cannot be interpreted in terms of equation (1) because the paramagnetic copper(II) ion can experience magnetic exchange with the iron(III). Ferromagnetic exchange with the low-spin form and antiferromagnetic exchange with the high-spin form are both possible and must be considered. The total susceptibility would be given by equation (3) where α represents the fraction of the low-spin (l.s.)

$$\chi = \alpha\chi_{\mathrm{l.s.}} + (1 - \alpha)\chi_{\mathrm{h.s.}} \qquad (3)$$

form and the susceptibilities of the Cu^{II}–Fe$^{III}_{\mathrm{l.s.}}$ and Cu^{II}–Fe$^{III}_{\mathrm{h.s.}}$ species are given by the Bleaney–Bowers equation and equation

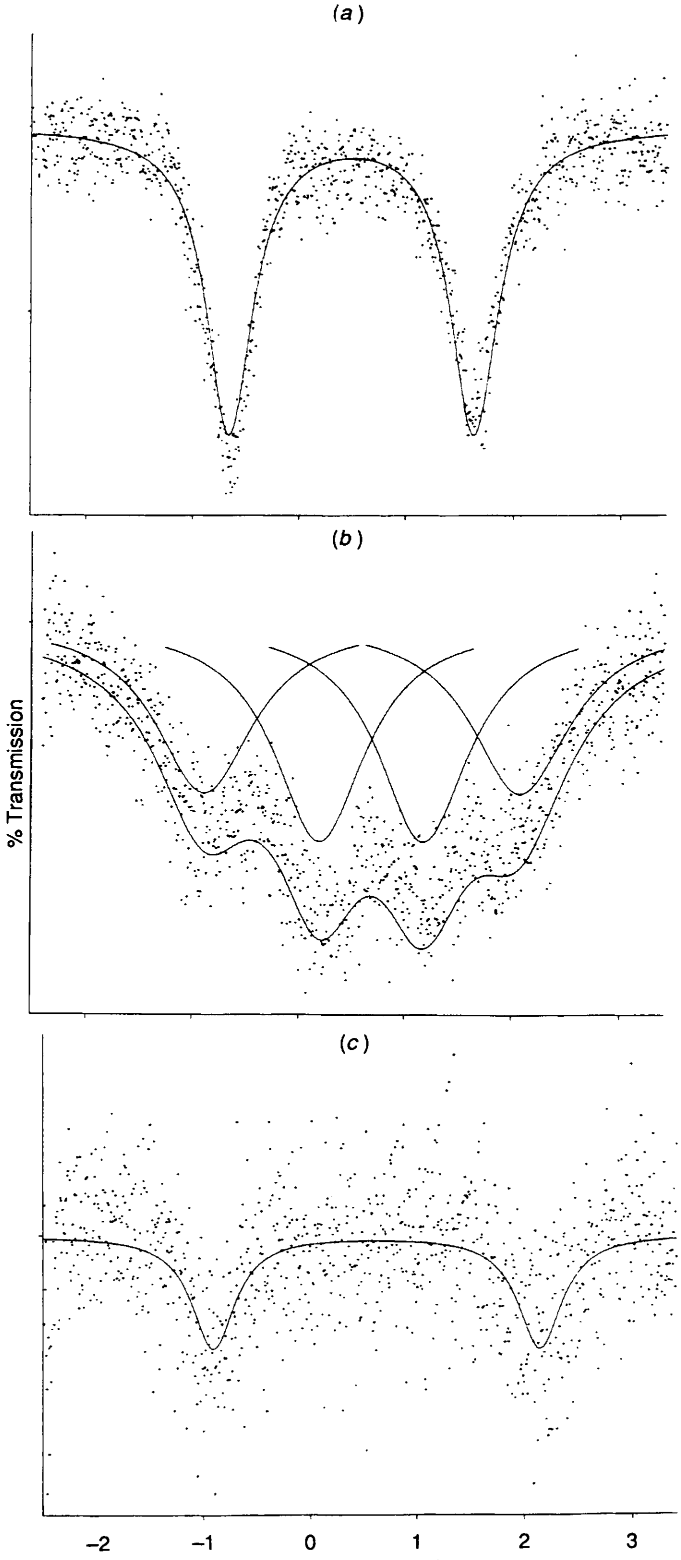


Fig. 3 Mössbauer spectra of (*a*) [FeL^2(NiL^1)Cl], (*b*) [FeL^3(NiL^1)]BPh$_4$ and (*c*) [FeL^4(NiL^1)]BPh$_4$ at 80 K. Velocity values are relative to Na$_2$[Fe(CN)$_5$(NO)] (subtract 0.257 mm s^{-1} to convert into iron metal standard)

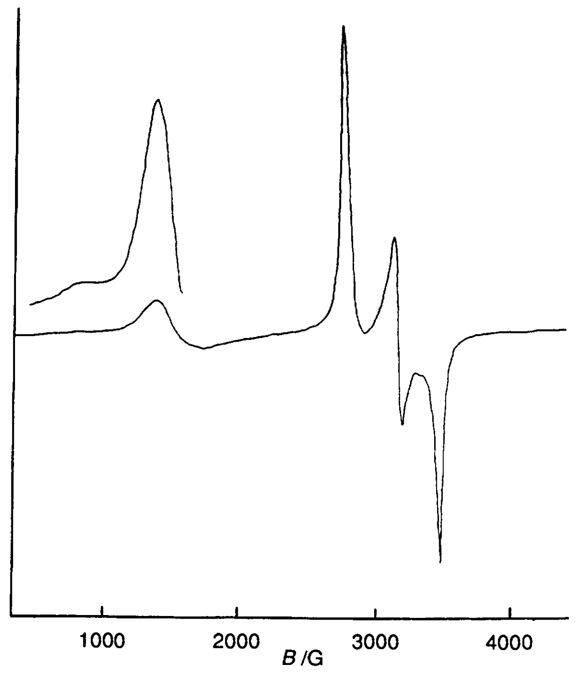


Fig. 4 Electron spin resonance spectrum of solid [FeL^2(NiL^1)Cl] at 80 K; G = 10^{-4} T

(2), respectively. In the case of an abrupt transition α would be either zero or one. In the case of a gradual transformation the spin-exchange operator and the spin-orbit promoted crossover must be considered simultaneously. Complete analysis of this complex is a significant problem that will require detailed Mössbauer and low-temperature magnetic data as was described for a related ferromagnetic copper(II)–iron(III) system[25] and is currently under investigation.

Mössbauer.—The Mössbauer data for the three nickel(II)–iron(III) dinuclear complexes are given in Table 1 and the spectra at liquid-nitrogen temperature are shown in Fig. 3. At 80 K the spectra of [FeL^2(NiL^1)Cl] and [FeL^4(NiL^1)]BPh$_4$ exhibit single quadrupole splittings of 2.29 and 3.06 mm s^{-1}, respectively. At 295 K these values decrease to 1.30 and 1.04 mm s^{-1}, respectively. Failure to observe both spin states by Mössbauer spectroscopy for iron(III) spin equilibrium systems is fairly common due to the normally fast relaxation rates for this ion.[26] For these two compounds the relaxation rate is faster than the Mössbauer time-scale, 10^{-7} s, and the spectrometer sees an average environment. In contrast, [FeL^3(NiL^1)]BPh$_4$ exhibits two sets of quadrupole doublets of 2.97 and 0.98 mm s^{-1} for the low-and high-spin forms, respectively. From the area of the Mössbauer peak the fraction of the sample present in the low-spin form at 80 K is 0.46 which differs from the magnetic susceptibility data value of 0.67. This lack of agreement has been observed previously and is attributed to the differences in the Debye–Waller factors for the two spin states.[27]

Electron Spin Resonance.—The ESR values for the dinuclear nickel–iron compounds are given in Table 1 and the spectrum of [FeL^2(NiL^1)Cl] is shown in Fig. 4. These complexes exhibit the characteristic features of low-spin iron(III), three signals in the $g = 2$ region and those of distorted high-spin iron(III), a signal at g of ≈4.3 and a lower-field signal at g between 8 and 9.5. This rhombic distortion is easily explained when the asymmetric nature of the iron environment is considered.

The ESR data for the dinuclear copper–iron complexes are not as easily interpreted as those of the nickel–iron dinuclear complexes since the copper(II) is paramagnetic and interacts with the iron(III). Neither compound exhibits the typical low-spin iron(III) spectrum that was observed for the analogous nickel complexes. This is not surprising for [FeL^4(CuL^1)]BPh$_4$ since its iron atom is high spin as shown by magnetic susceptibility. Further ESR work on [FeL^3(CuL^1)]BPh$_4$ is necessary to understand the effects of a spin crossover and magnetic exchange on the spectrum.

Conclusion

Imidazolate-bridged heterodinuclear complexes of nickel(II) or copper(II) with Fe$^{\text{III}}$ can be prepared by treating stoichiometric quantities of the imidazolate complexes with iron(III) Schiff-base complexes. The nickel(II) complexes are spin-crossover systems as shown by magnetic susceptibility, Mössbauer and ESR spectroscopy. The analogous copper(II) complexes are of great interest since they potentially have a temperature-dependent transition from ferromagnetism to antiferromagnetism. Further investigation of these systems may result in a reinterpretation of the magnetic susceptibility data for cytochrome c oxidase in terms of a spin-crossover model as has been shown for a number of haem proteins.[28] The widely held belief that cytochrome c oxidase contains a strongly antiferromagnetically coupled ($J < -200$ cm^{-1}) high-spin iron(III)–copper(II) pair resulting in a $S = 2$ system is not supported by current model systems, which lack such strong coupling.

Acknowledgements

Support of this work under National Institutes of Health contract DK41425-01 is gratefully acknowledged.

References

1 C. T. Brewer and G. Brewer, *J. Chem. Soc., Dalton Trans.*, 1992, 1669; G. Brewer and R. Wang, *Inorg. Chim. Acta.*, in the press.
2 M. F. Tweedle, L. J. Wilson, L. Garcia-Iniguez, G. T. Babcock and G. Palmer, *J. Biol. Chem.*, 1978, **253**, 8065.
3 C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Schiedt, K. Spartalian and G. Lang, *J. Am. Chem. Soc.*, 1979, **101**, 2948.
4 W. R. Scheidt, D. K. Geiger, Y. J. Lee, C. A. Reed and G. Lang, *Inorg. Chem.*, 1987, **26**, 1039.
5 N. Motsumoto, Y. Maeda, H. Okawa, T. Akui, T. Kawaji, A. Ohyoshi, M. Kodera, H. Oshio and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1989, 943.
6 G. A. Brewer and R. Wang, *J. Chem. Soc.*, Chem. Commun., 1990, 583.
7 C. A. Koch, C. A. Reed, G. A. Brewer, N. P. Rath, W. R. Scheidt, G. Gupta and G. Lang, *J. Am. Chem. Soc.*, 1989, **111**, 7645.
8 C. A. Koch, C. A. Reed, B. Wang and G. Brewer, *J. Chem. Soc., Chem. Commun.*, 1989, 1754.
9 A. Real, J. Zarembowitch, O. Kahn and X. Solans, *Inorg. Chem.*, 1987, **26**, 2939.
10 S. Ohta, C. Yoshimura, N. Matsumoto, H. Okawa and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 155.
11 W. Eberspach, N. El Murr and W. Klaui, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 915; G. Navon and W. Klaui, *Inorg. Chem.*, 1984, **23**, 2722.
12 G. Vos, R. A. G. De Graaff, J. G. Haasnoot, A. M. Van Der Kraan, P. de Val and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 2305.
13 N. Matsumoto, H. Tamaki, K. Inoue, M. Koikawa, Y. Maeda, H. Okawa and S. Kida, *Chem. Lett.*, 1991, **8**, 1393.
14 E. Sinn and C. J. O'Connor, *Inorg. Chim. Acta*, 1979, **32**, 29.
15 A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, New York, 1968.
16 G. Brewer, *J. Chem. Educ.*, in the press.
17 M. Gerloch, J. Lewis, F. E. Mabbs and A. Richards, *J. Chem. Soc. A*, 1968, 112.
18 N. Matsumoto, S. Ohta, C. Yoshimura, A. Ohyoshi, S. Kohata, H. Okawa and Y. Maeda, *J. Chem. Soc., Dalton Trans.*, 1985, 2575.
19 R. Atkins, G. Brewer, E. Kokot, G. M. Mockler and E. Sinn, *Inorg. Chem.*, 1985, **24**, 127.
20 B. J. Kennedy, G. Brain, E. Horn, K. S. Murray and M. R. Snow, *Inorg. Chem.*, 1985, **24**, 1647.
21 A. H. Ewald, R. L. Martin, I. G. Ross and A. H. White, *Proc. R. Soc. London, Ser. A*, 1964, **280**, 235.
22 B. J. Kennedy, A. C. McGrath, K. S. Murray and B. W. Skelton, *Inorg. Chem.*, 1987, **26**, 483.
23 A. H. Ewald, R. L. Martin, E. Sinn and A. H. White, *Inorg. Chem.*, 1969, **8**, 1837.
24 C. J. O'Connor, *Prog. Inorg. Chem.*, 1982, **29**, 203.
25 C. A. Reed, C. A. Koch, W. R. Scheidt and G. R. Lang, *Inorg. Chem.*, 1990, **29**, 4234.
26 P. Gütlich, *Mössbauer Spectroscopy Applied to Inorganic Chemistry*, ed. G. L. Long, Plenum, New York, 1984, vol. 1, ch. 11, p. 333.
27 M. S. Haddad, M. W. Lynch, W. D. Federer and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 123, 131.
28 M. F. Peurtz, J. K. M. Sanders, D. H. Chenerv, R. W. Noble, R. R. Pennley, L. W. M. Fund, C. Ho, I. Biannini, D. Porschke and H. Winkler, *Biochemistry*, 1978, **17**, 3640; S. G. Sligar, *Biochemistry*, 1976, **15**, 5399.

Received 8*th July* 1992; *Paper* 2/03597I