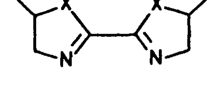
$^5T_2 \rightleftharpoons {}^1A_1$ and $^6A_1 \rightleftharpoons {}^2T_2$ Spin Transitions in Iron(II) and Iron(III) Complexes of 2,2′-Bi-2-imidazoline and Related Ligands

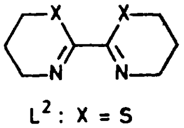
By **Michael G. Burnett, Vickie McKee, and S. Martin Nelson,*** Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland

A series of six-co-ordinate iron(II) complexes $[Fe^{II}L_3]X_2$ (X = ClO_4 or BPh_4) of the bidentate ligands 2,2′-bi-2-imidazoline (L^3), 2,2′-bi-1,4,5,6-tetrahydropyrimidine (L^4), 2,2′-bi-2-oxazoline (L^5), and 5,5′-dimethyl-2,2′-bi-2-oxazoline (L^6) have been prepared and characterised by their physical properties. In all cases co-ordination is *via* the α-di-imine group. Magnetic susceptibility and Mössbauer effect measurements as a function of temperature show that the complexes of L^5 and L^6 are fully high-spin (S = 2) over the temperature range 90—360 K, while for complexes of L^3 (X = ClO_4 but not BPh_4) and L^4 (X = ClO_4 and BPh_4) a $^5T_2 \rightleftharpoons {}^1A_1$ spin transition is observed in this temperature range. Electronic spectra of the corresponding nickel(II) complexes indicate a correlation between Dq(Ni) and the spin ground state of the iron(II) complexes. The iron(III) complex $[Fe^{III}L^3{}_3][ClO_4]_3$ is high-spin ($S = \frac{5}{2}$), while $[FeL^4{}_3][ClO_4]_3$ has a $^2T_2$ ground state but with a thermally accessible $^6A_1$ excited state. Iron(III) complexes of L^5 and L^6 are unstable and could not be isolated. Reaction of the iron(II) complexes of L^3 and L^4 with dioxygen gave the iron(III) complexes $[Fe^{III}L_2(L - H)][ClO_4]_2$ in good yield [(L − H) = mono-deprotonated ligand] which may be reversibly converted to the $[Fe^{III}L_3]^{3+}$ species on treatment with one equivalent of $HClO_4$. The temperature-dependent magnetic moments of the complexes $[FeL_2(L - H)][ClO_4]_2$ are interpreted in terms of $^2T_2 \rightleftharpoons {}^6A_1$ spin equilibria.

MUCH has been published on the properties of metal complexes of ligands containing the α-di-imine group, those of iron(II) having received particular attention. Ligands of this class are of interest because they generate ligand fields, in six-co-ordinate iron(II) complexes, close to the conditions appropriate to the pairing of electrons.[1] We have recently described [2,3] some iron(II) complexes of the nitrogen–sulphur ligands 2,2′-bi-2-thiazoline (L^1) and 2,2′-bi-(4*H*-5,6-dihydrothiazine) (L^2); the six-co-ordinate tris-ligand iron(II) complexes [2] of both these bidentate α-di-imines are low-spin while the mixed-ligand complexes $[FeL^1{}_2(NCS)_2]$ and $[FeL^2{}_2(NCS)_2]$ exhibit quintet–singlet spin crossovers at temperatures below ambient.[3]



L^1 : X = S, R = H
L^3 : X = NH, R = H
L^5 : X = O, R = H
L^6 : X = O, R = Me



L^2 : X = S
L^4 : X = NH

This paper reports on the effect on the spin state of the tris-ligand complexes of iron(II) of an alteration in the nature of the heteroatom X. It will be shown that for some complexes of 2,2′-bi-2-imidazoline (L^3) and 2,2′-bi-1,4,5,6-tetrahydropyrimidine (L^4) a quintet–singlet spin transition occurs within the temperature range 90—380 K while for 2,2′-bi-2-oxazoline (L^5) and its 5,5′-dimethyl derivative (L^6) the tris-ligand complexes are fully in the high-spin form. Evidence for ($S = \frac{5}{2}$) $\rightleftharpoons$ ($S = \frac{1}{2}$) spin transition in two iron(III) complexes of L^4 is also presented.

During the study it was observed that the complex ions $[FeL^3{}_3]^{2+}$ and $[FeL^4{}_3]^{2+}$ react with dioxygen to yield iron(III) complexes in which one ligand molecule has been mono-deprotonated. A description of these complexes is included in this paper; a subsequent paper deals with the kinetics and mechanism of the oxidation reaction.

A few metal complexes of L^3 have been briefly reported previously by Wang and Bauman [4] who appear to favour the view that co-ordination is *via* the secondary nitrogen atoms. From results presented in the present work it will be shown that co-ordination is *via* the α-di-imine group.

While the main focus of the present investigation was on the chemistry of the iron complexes, a few complexes of nickel(II) have also been prepared where it was considered that a knowledge of their properties was relevant to the discussion of the iron complexes.

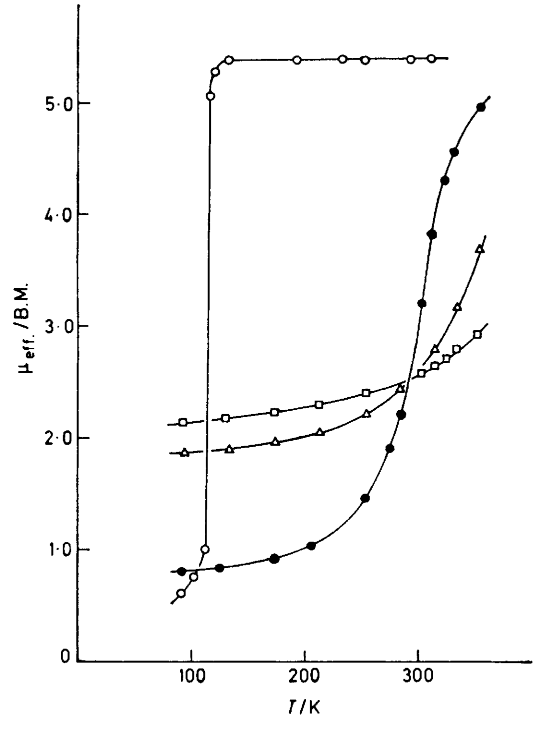
RESULTS AND DISCUSSION

The results are considered in two sections. Part A describes the iron(II) complexes, while Part B discusses the iron(III) complexes. The preparations of the ligands and both sets of complexes are given in the Experimental section.

A. The Iron(II) *Complexes of* L^3, L^4, L^5, *and* L^6.—The complexes examined, along with analytical and selected physical data pertaining to them, are listed in Table 1. The inference based on the stoicheiometry that the complexes are salts of the six-co-ordinate complex cations is supported by the physical properties. All are 2 : 1 electrolytes in acetonitrile solution. With the exception of the complexes of L^3 and L^4, the ν_3 and ν_4 modes of the ClO_4^- ion in the i.r. spectra (Table 2) occur at *ca.* 1 090 and 620—625 cm^{-1} as unsplit bands having band widths no greater than those occurring in reference compounds known to contain ionic ClO_4^-. In contrast, in the spectra of the perchlorate complexes of L^3 and L^4 a marked splitting of ν_3 and ν_4 was usually observed, indicating a reduction in the T_d symmetry of the free ion.[5] In view of the stoicheiometry of the complexes, and of other properties to be considered below, we attribute this splitting not to co-ordination of the ClO_4^- ions to the metal but to a hydrogen-bonding interaction with the N–H groups of the ligands. This is taken as evidence that both L^3 and L^4 are bonded to the metal *via* the α-di-imine groups.

All four ligands exhibit a strong i.r. absorption between 1 570 and 1 640 cm^{-1}. This is the region usually associated with the ν(C=N) stretching vibration, but in these molecules this mode is expected to be strongly coupled with other ring deformations. A total of four to five bands occur between 1 400 and 1 640 cm^{-1} which collectively may be assigned to the interacting ring deformations together with, in the case of L^3 and L^4, the N–H bending mode. On co-ordination there are marked alterations in the position and intensity of these bands; a detailed assignment is beyond the scope of this paper.

In L^3 and L^4 the N–H stretch occurs as an intense broad band at 3 190 cm^{-1} (L^3) and 3 240 cm^{-1} (L^4), due presumably to strong intermolecular hydrogen bonding in the solid state. On co-ordination a more complex pattern is seen, from two to three bands appearing in the 3 100—3 400 cm^{-1} region.



Temperature dependence of the magnetic moments of $[FeL^3_3][ClO_4]_2$ (○), $[FeL^4_3][ClO_4]_2$ (●), $[FeL^4_2(L^4 - H)][ClO_4]_2$ (△), and $[FeL^4_3][ClO_4]_3$ (□)

Magnetic properties and Mössbauer spectra. The complex $[FeL^3_3][ClO_4]_2$ is fully high-spin ($\mu_{eff.}$ *ca.* 5.40 B.M.*) at temperatures above about 130 K (Table 1). On cooling below this temperature the magnetic moment falls abruptly (see Figure) to a value of 0.59 B.M. at 93 K. An $(S = 2) \rightleftharpoons (S = 0)$ spin transition is clearly indicated, a conclusion fully supported by the Mössbauer data (Table 2). Thus, at 239 K the isomer shift (δ), relative to iron foil standard, and quadrupole splitting (ΔE_Q) have values (1.02 and 1.19 mm s^{-1}) characteristic of high-spin iron(II), while at 77 K these parameters have values (0.38 and <0.2 mm s^{-1}, respectively) in the ranges expected for low-spin ($S = 0$) iron(II).[6] The change in $\mu_{eff.}$ is very abrupt, being *ca.* 90% complete over an interval of a few degrees (cooling curve). This and the fact that rapid quenching of the complex from room temperature to 77 K gave a Mössbauer spectrum which showed that a substantial proportion of the complex was still in the high-spin form suggests that the spin transition is accompanied by associated changes in the crystal lattice. However, experiments in which the transition temperature (T_c *ca.* 116 K, defined as the temperature at which half the molecules are in the low-spin form) was approached slowly (*i.e.* at a rate of *ca.* 1° min^{-1}) gave reproducible results without gross hysteresis effects on ascending temperature runs. In contrast to the perchlorate salt, the BPh_4^- salt is fully high-spin over the entire temperature range (93—293 K) studied. Such dependence of the spin crossover behaviour on the nature of the counter ion is not uncommon and may be regarded as a reflection of the sensitivity of the transition to the relatively minor geometrical effects caused by variations in crystal packing.[1] In the present case a more specific effect may be involved, namely, an alteration in the ligand field by hydrogen bonding between the NH groups and the perchlorate anions. The high values of the isomer shift (1.0—1.1 mm s^{-1}) and the large quadrupole splittings (1.2—3.4 mm s^{-1}) at both 293 and 77 K observed for $[FeL^3_3][BPh_4]_2$ confirm the conclusion, based on the magnetic measurements, that this complex is in the $S = 2$ spin state even at 77 K.

The corresponding iron(II) complexes of L^4 behave similarly. In the case of $[FeL^4_3][ClO_4]_2$, however, the reversible spin transition is much less abrupt and occurs at a higher temperature (T_c *ca.* 310 K), as shown in the Figure (see also Table 1). Mössbauer data (Table 2) are once again in complete accord with the magnetic results. The spectrum at 293 K shows a poorly resolved quadrupole-split doublet centred at 0.29 mm s^{-1}, attributable to the (major) low-spin component. In addition, there is a weak signal having parameters δ and ΔE_Q equal to *ca.* 1.1 and 2.2 mm s^{-1}, respectively. Only the resonance due to the low-spin form was seen at 77 K. As with the L^3 complexes, change of the counter ion from ClO_4^- to BPh_4^- leads to a shift in the crossover position in favour of the high-spin isomer as judged by both the magnetic properties and Mössbauer spectra (Tables 1 and 2). This time, however, the beginnings of a transition from the $S = 2$ to the $S = 0$ spin state are discernible in a fall-off of the magnetic moment from a value of 5.50 B.M. at 293 K to 4.76 B.M. at 93 K. In agreement with this the Mössbauer spectrum at 293 K contains only the high-spin signal ($\delta = 1.05$, $\Delta E_Q = 2.45$ mm s^{-1}), whereas at 77 K two quadrupole-split doublets are clearly seen, the new signal being relatively less intense and having

---

* Throughout this paper: 1 B.M. = 0.927×10^{-23} A m^2.

TABLE 1

Analytical, magnetic, and electrical conductance data for the complexes

Complex	Analysis (%)						$\mu_{eff.}$[a]/B.M.		Λ[b]/S cm^2 mol^{-1} (MeCN)
	Found			Calc.					
	C	H	N	C	H	N	293 K	93 K	
$[Fe^{II}L^3_3][ClO_4]_2$	32.2	4.5	24.9	32.2	4.5	25.1	5.40	0.59	319
$[Fe^{II}L^3_3][BPh_4]_2$	71.5	6.3	14.9	71.0	6.4	15.1	5.61	5.47	*c*
$[Fe^{II}L^4_3][ClO_4]_2$	38.4	5.8	22.1	38.3	5.6	22.3	2.58	0.84	225
$[Fe^{II}L^4_3][BPh_4]_2$	71.7	7.0	13.6	72.4	6.9	14.1	5.50	4.76	*c*
$[Fe^{II}L^5_3][ClO_4]_2$	30.3	3.5	11.9	32.0	3.6	12.3	5.60	5.33	307
$[Fe^{II}L^6_3][ClO_4]_2$	38.4	4.8	10.8	38.0	4.8	11.0	5.38	5.14	295
$[NiL^3_3][ClO_4]_2$	33.3	4.4	25.9	32.2	4.5	25.0	3.18		292
$[NiL^4_3][ClO_4]_2$	38.4	5.8	22.0	38.1	5.6	22.3	3.32		226
$[NiL^5_3][ClO_4]_2$	32.9	3.6	12.6	31.9	3.6	12.4	3.12		315
$[NiL^6_3][ClO_4]_2$	37.9	4.6	10.8	37.8	4.7	11.0	3.22		310
$[Fe^{III}L^3_3][ClO_4]_3$	28.1	3.9	21.9	28.1	3.9	21.9	5.91	5.84	384
$[Fe^{III}L^4_3][ClO_4]_3$	33.9	5.2	19.5	33.8	5.0	19.7	2.53	2.14	353
$[Fe^{III}L^3_2(L^3 - H)][ClO_4]_2$	32.2	4.5	25.2	32.3	4.4	25.2	5.91	5.58	325
$[Fe^{III}L^4_2(L^4 - H)][ClO_4]_2$	38.0	5.5	21.8	38.3	5.5	22.3	2.50	1.87	

[a] Corrected for diamagnetism of ligands. [b] For 10^{-3} mol dm^{-3} solutions at 25 °C. [c] Insoluble.

δ and ΔE_Q values (0.38 and 0.25 mm s^{-1}, respectively) appropriate to the spin singlet state.[6]

For the iron(II) complexes of the two oxygen-containing ligands L^5 and L^6 both the magnetic (Table 1) and Mössbauer (Table 2) spectral measurements reveal that these remain in the high-spin ($S = 2$) state over the complete temperature range investigated.

TABLE 2

Mössbauer parameters for the iron complexes

Complex	T/K	δ [a,b]/ mm s^{-1}	ΔE_Q[b]/ mm s^{-1}
$[Fe^{II}L^3_3][ClO_4]_2$	293	1.02	1.19
	77	0.38	<0.2
$[Fe^{II}L^3_3][BPh_4]_2$	293	1.00	<1.26
	77	1.09	2.33
$[Fe^{II}L^4_3][ClO_4]_2$	293	0.29(1.1) [c]	$<0.2(2.2)$ [c]
	77	0.38	0.22
$[Fe^{II}L^4_3][BPh_4]_2$	293	0.92	1.20
	77	1.05(0.38) [d]	2.45(0.25) [d]
$[Fe^{II}L^5_3][ClO_4]_2$	293	1.01	0.63
	77	1.09	1.29
$[Fe^{II}L^6_3][ClO_4]_2$	293	1.01	0.72
	77	1.10	1.52
$[Fe^{III}L^3_3][ClO_4]_3$	293	0.24	<0.2
	77	0.25	<0.2
$[Fe^{III}L^4_3][ClO_4]_3$	293	0.03	1.50
	77	0.12	1.70
$[Fe^{III}L^3_2(L^3 - H)][ClO_4]_2$	293	0.33	0.93
	77	0.35	*e*
$[Fe^{III}L^4_2(L^4 - H)][ClO_4]_2$	293	0.08	2.17
	77	0.16	2.31

[a] Relative to natural iron. [b] Estimated error ± 0.02 mm s^{-1}. [c] Resonance due to high-spin form (± 0.05 mm s^{-1}). [d] Resonance due to low-spin form. [e] Asymmetric, broad, and unresolved resonance.

Electronic spectra of the iron(II) *complexes.* Spectra were measured for the solid complexes and for their solutions in O_2-free acetonitrile in the range 5 000—30 000 cm^{-1}; data for these are in Table 3. Good agreement between the spectra in the two phases was obtained. The spectra are characterised by an intense absorption, attributed to the co-ordinated ligand, tailing into the visible from the ultraviolet, together with a number of charge-transfer and/or ligand-field bands at lower energies. All the iron(II) complexes exhibit a strong absorption in the range 17 000—24 000 cm^{-1}. The apparent intensities, which vary from ε_M *ca.* 800 to *ca.* 3 600 dm^3 mol^{-1} cm^{-1}, are too large for *d–d* spectra and are assigned as charge-transfer bands. We suggest that they originate from overlap of the filled metal t_{2g} orbitals with the vacant p_π* antibonding orbitals of the ligand α-di-imine groups, *i.e.* they are metal-oxidation charge transfers. Significantly, strong absorption in this region is not observed for the corresponding complexes of Co^{II} and Ni^{II} for which metal ions the metal-oxidation potentials have higher values. Alone among the iron(II) complexes, $[FeL^4_3]^{2+}$ exhibits two absorption maxima in this region, at 17 200 and 19 600 cm^{-1}. Measurements carried out over the temperature range 5—40 °C showed that the relative intensities of the two bands are temperature dependent, the band at 19 600 cm^{-1} becoming relatively more intense at the lower temperatures, and the other band becoming less intense. Since salts of this complex ion exhibit spin-state transitions in the solid state we deduce from these observations that the spin equilibrium also occurs in solution. Accordingly, the band at 17 200 cm^{-1} is assigned to the high-spin form and that at 19 600 cm^{-1} to the low-spin form.

TABLE 3

Electronic spectra of the iron(II) and nickel(II) complexes in acetonitrile solution

Complex	Absorption maxima */10^3 cm^{-1}	
$[FeL^3_3][ClO_4]_2$	21.2(900)	11.5(20)
$[FeL^4_3][ClO_4]_2$	19.6(3 500)	17.2(3 500)
$[FeL^5_3][ClO_4]_2$	23.6(850)	10.9(10)
$[FeL^6_3][ClO_4]_2$	24.5(sh)	10.9(10)
$[NiL^3_3][ClO_4]_2$	17.1(17)	10.3(14)
$[NiL^4_3][ClO_4]_2$	17.9(15)	11.0(12)
$[NiL^5_3][ClO_4]_2$	16.8(12)	10.1(9)
$[NiL^6_3][ClO_4]_2$	17.3(15)	10.4(13)

* Absorption coefficients ϵ(dm^3 mol^{-1} cm^{-1}) in parentheses; (sh) = shoulder.

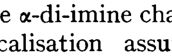
In addition to the charge-transfer bands discussed above, solutions of $[FeL^3_3]^{2+}$, $[FeL^5_3]^{2+}$, and $[FeL^6_3]^{2+}$ exhibited a weak absorption (ε_M *ca.* 10 dm^3 mol^{-1} cm^{-1}) at 11 000—12 000 cm^{-1}. This is assigned to the $^5T_{2g} \rightarrow$

^5E_g transition (in O_h symmetry). This absorption was not discernible in the spectra of $[FeL^4_3]^{2+}$ which, as mentioned above, exists partly in the spin singlet state.

Spectra of the nickel(II) complexes of the four bidentate ligands were also recorded (Table 3). All consisted of two low intensity symmetrical bands at 16 500—18 000 and 10 000—11 000 cm^{-1}, entirely consistent with the anticipated octahedral structure. The two bands are thus assigned to the $^3A_{2g}\rightarrow{}^3T_{2g}$ and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ transitions, respectively; the $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ band is obscured by the much more intense co-ordinated ligand absorption.

The mode of co-ordination of the ligands. The stoicheiometry of the complexes together with the evidence of the i.r. and electronic spectra, the electrical conductivity, and magnetic data are collectively sufficient to establish a six-co-ordinate (approximately octahedral) configuration. It remains to consider the mode of bonding of the bidentate ligands, *i.e.* whether they are bonded to the metal *via* the α-di-imine group or *via* the secondary nitrogen atoms (L^3 and L^4) or the oxygen atoms (L^5 and L^6).* As mentioned above, Wang and Bauman [4] suggested that for L^3 it may be the secondary nitrogens that are co-ordinated. This view was based on the apparent absence of the characteristic iron(II) α-di-imine chromophore in *e.g.* $[FeL^3_3][NO_3]_2$ and of the ' low ' Dq value obtained for the nickel(II) complex $[NiL^3_3]^{2+}$. It is true that Dq(Ni) in this complex is somewhat low in relation to values obtained for most other complexes of α-di-imine ligands.[7] It is not true, however, that the iron(II) α-di-imine chromophore is absent. As shown in the preceding section this feature is present in the spectra of all the iron(II) complexes, though at higher energies than often observed. Secondly, there is the evidence of the $^5T_2 \rightleftharpoons {}^1A_1$ spin-state transition in the L^3 and L^4 complexes. Spin singlet ground states are commonplace for octahedral iron(II) complexes of α-di-imines and related ligands [1,7] but, to our knowledge, are unknown for octahedral complexes containing only saturated nitrogen donors. Thirdly, the apparent absence of any steric consequences, for example, in stoicheiometry, or in the Dq value for the nickel(II) complex, of the introduction in L^6 of methyl substituents at the carbon centres alpha to the oxygen atoms argues strongly for a co-ordination mode involving the unhindered nitrogens. Finally, there is the evidence of the splitting of the ν_3 and ν_4 perchlorate bands in the i.r. spectra of the L^3 and L^4 complexes, referred to above.

A consideration of both the magnetic properties of the iron(II) complexes and the electronic spectra of the nickel(II) complexes indicates a gradation in ligand-field strength in the sequence $L^1 > L^3 > L^5$, *i.e.* as the non-co-ordinating heteroatom is changed from S to N(H) to O, the order of increasing electronegativity. Possibly, there is an increasing contribution to the bonding from the valence-bond structure (below) in this order which serves to diminish the α-di-imine character of the ligand. Such electron delocalisation assumes a certain sp^2 character on the part of the oxygen (or secondary nitrogen) atom, a not unexpected situation in unsaturated five-membered rings. The apparently greater ligand-field strength of L^4 (which contains six-membered rings) over L^3 may be due to a smaller degree of electron delocalisation or, possibly, to an improved ' bite '.



B. The Products of Reaction of the Iron(II) *Complexes of* L^3 *and* L^4 *with Dioxygen.*—The complexes $[Fe^{II}L_3][ClO_4]_2$ ($L = L^3$ or L^4) were observed to become dark green on exposure of their solutions to air or O_2. Dark green crystalline solids could be isolated from the solutions. The complex $[Fe^{II}L^4_3][ClO_4]_2$ also undergoes the oxidation in the solid state, although more slowly. The green oxidation products were characterised as the iron(III) complexes $[Fe^{III}L_2(L-H)][ClO_4]_2$, where $(L-H)$ denotes the anionic mono-deprotonated ligand, by elemental analysis, magnetic susceptibility, and Mössbauer effect studies and by their interconversion with the tris neutral ligand iron(III) complexes $[Fe^{III}L_3]^{3+}$ *via* acid–base reactions.

Addition of one equivalent of $HClO_4$ to a solution of either green complex yielded the $[Fe^{III}L_3][ClO_4]_3$ complexes, shown by analysis and physical properties to be identical to authentic samples prepared directly from iron(III) salts and the free ligands L^3 or L^4 (see Tables 1, 2, and 3). The neutralisation was followed spectrophotometrically in MeCN for the case of the L^3 complex. The reaction is reversible. Addition of one equivalent of $HClO_4$ to a solution of $[FeL^3_2(L^3-H)]^{2+}$ ($\nu_{max.}$ 14 800 cm^{-1}, ε_M 4 000 dm^3 mol^{-1} cm^{-1}) produced a spectrum ($\nu_{max.}$ 22 600 cm^{-1}, ε_M 8 800 dm^3 mol^{-1} cm^{-1}) identical to that of $[Fe^{III}L^3_3][ClO_4]_3$ in the same solvent. Subsequent addition of one equivalent of Na[OMe] regenerated the spectrum of the green complex, an isosbestic point being observed at 17 500 cm^{-1}. Spectrophotometric evidence for further deprotonation on addition of more than one equivalent of base was also obtained; discussion of these equilibria is deferred.

The complex $[Fe^{III}L^3_3][ClO_4]_3$ has a virtually temperature independent magnetic moment (Table 1) close to the value of 5.92 B.M. expected for high-spin iron(III). In agreement, the Mössbauer spectra (Table 2) at both 293 and 77 K consist of a single resonance (δ *ca.* 0.25 mm s^{-1}) with small (unresolved) quadrupole splitting as expected for a $^6A_1$ spin ground state.[6] The complex $[Fe^{III}L^4_3][ClO_4]_3$, on the other hand, has a $^2T_2$ spin ground state at 93 K as judged by the value of $\mu_{eff.} = 2.14$ B.M. found at this temperature. There is a reversible increase in $\mu_{eff.}$ on increase in temperature, reaching a value of 2.93 B.M. at 353 K which we attribute

---

* The free ligands L^3 and L^4 can be considered as tautomeric systems for which there is an effective equivalence of the four nitrogens; this is seen clearly in both the ^1H and ^{13}C n.m.r. spectra (see Experimental section). Such equivalence vanishes, of course, on complexation.

to a thermally controlled equilibrium between high- and low-spin forms of the centrally co-ordinated iron(III) ion (Figure). No separate resonance attributable to the high-spin species was discernible in the Mössbauer spectrum at 293 K, but this is scarcely to be expected since only a small proportion of the molecules can be in the $^6A_1$ state at this temperature [$\mu_{eff.}$ (293 K) = 2.53 B.M.].

The green complex $[Fe^{III}L^3{}_2(L^3 - H)][ClO_4]_2$ obtained *via* aerial oxidation of $[Fe^{II}L^3{}_3][ClO_4]_2$ has a $^6A_1$ ground state as judged by the magnetic moment of 5.91 B.M. (293 K) and the isomer shift (δ 0.33 mm s^{-1}) in the Mössbauer spectrum at 293 K. The rather large quadrupole splitting (0.93 mm s^{-1} at 293 K) presumably reflects the ligand-field asymmetry expected for a complex in which one bidentate ligand is anionic and two are uncharged. On decreasing the temperature to 93 K a small, but definite fall in the magnetic moment was observed. Since the $^6A_1$ state is orbitally non-degenerate and since there is no apparent mechanism for antiferromagnetic coupling in this complex the most likely explanation of the temperature dependence of the magnetic moment is that, once again, there is an equilibrium between high- and low-spin forms of the complex at the lower temperatures. The Mössbauer spectrum at 77 K of this complex consisted of a broad, asymmetric, and poorly resolved doublet centred at *ca.* 0.35 mm s^{-1}. Since different, analytically pure, preparations gave the same spectrum this behaviour appears to be a genuine property of the complex. Possibly, it is due to spin–spin relaxation effects.[8] A possible alternative explanation for the line broadening may be found in dynamic spin interconversion where the rate of spin interconversion is commensurate with the lifetime of the excited Mössbauer state of the ^{57}Fe nucleus (1.4×10^{-7} s).[6] Intersystem crossing rates in six-co-ordinate iron(III) complexes having values both above and below 10^7 s^{-1} are known.[6,9,10]

A similar, though more pronounced, temperature dependence of the magnetic moment was observed for the green oxidation product $[FeL^4{}_2(L^4 - H)][ClO_4]_2$. Here the moment is 1.87 B.M. at 93 K indicating that the metal ion is completely in the $^2T_2$ state. The moment rises reversibly with increase in temperature to a value of 3.70 B.M. at 353 K (Figure). The Mössbauer spectrum at 77 K gave parameters (Table 2) fully consistent with the low-spin nature of the iron(III) ion at this temperature. At 293 K, where as indicated by the magnetic measurements *ca.* 20% of the ions are in the high-spin state, only a single quadrupole split doublet of normal linewidth was observed. From this it appears that, in this case, the spin interconversion rate is greater than Mössbauer experiment time-scale rate so that only an 'averaged' spectrum is seen, or that the high-spin resonance is too weak to be discernible.

The magnetic data for the iron(III) complexes show, as do the results for the iron(II) and nickel(II) complexes, that the ligand L^4 containing six-membered heterocyclic rings exercises a somewhat greater ligand-field than does L^3, containing five-membered rings. The ligand L^4 is the only one we are aware of that generates spin-crossover conditions in both iron(II) and iron(III) complexes.

EXPERIMENTAL

Preparation of the Ligands.—2,2′-Bi-2-imidazoline was prepared by the method of Forssel as modified by Wang and Bauman.[4] It was characterised by elemental analysis and by i.r. and ^{1}H n.m.r. spectra.

2,2′-*Bi*-1,4,5,6-*tetrahydropyrimidine*. This was prepared by a similar method but using 1,3-diaminopropane instead of 1,2-diaminoethane. The crude product was recrystallised from CCl_4 in 70% yield. It was characterised by elemental analysis, mass and ^{1}H n.m.r. spectra.

2,2′-*Bi*-2-*oxazoline*. Oxamide (0.17 mol) was suspended in ethanolamine (*ca.* 1 mol) and the mixture refluxed for 2 h. The resulting *NN*′-bis(2-hydroxyethyl)oxamide was recrystallised from ethanol and the synthesis was continued by Wenker's method [11] with slight modifications. *NN*′-Bis(2-hydroxyethyl)oxamide (0.11 mol) was suspended in toluene (100 cm^3) and heated to 60 °C. Excess of thionyl chloride (0.33 mol) was added in two portions. Vigorous reaction occurred after addition of the second portion. The mixture was maintained at 60 °C for 30 min and then heated for 90 min on a boiling water-bath. After cooling, the crystals of 2,2′-bi-2-oxazoline dihydrochloride were filtered off. The chloride was refluxed for 1 h in a methanol solution of K[OH], the solution filtered and allowed to stand. The product separated as white needles in 65% yield. It was characterised by elemental analysis, i.r., mass, and ^{1}H n.m.r. spectra.

5,5′-Dimethyl-2,2′-bi-2-oxazoline was prepared similarly except that 2-methylethanolamine was used in place of ethanolamine.

Preparation of the Complexes.—In preparations of the complexes of Fe^{II} all operations were carried out under an atmosphere of N_2 using deoxygenated solvents. The same general method of preparation was used for the complexes of Ni^{II}. A solution of $M[ClO_4]_2\cdot 6H_2O$ (M = Fe or Ni) (2 mmol) in ethanol (10 cm^3) was added to a gently refluxing solution of L in ethanol (75 cm^3). Crystals of $[ML_3][ClO_4]_2$ separated on cooling in >50% yield. The products were recrystallised from acetonitrile. Tetraphenylborate salts were obtained if $Na[BPh_4]$ (6 mmol) was present in the solution before the addition of the metal perchlorate.

The salt $[Fe^{III}L^3{}_3][ClO_4]_3$ was prepared by the addition of solid $Fe[ClO_4]_3\cdot 6H_2O$ (1.3 mmol) to a hot solution of L^3 (0.45 mmol) in 100 cm^3 ethanol. Dark red crystals of product separated on cooling and concentrating.

The salt $[FeL^4{}_3][ClO_4]_3$ was prepared by the addition of $Fe[ClO_4]_3\cdot 6H_2O$ (9 mmol) in 2,2-dimethoxypropane, previously stirred for 2 h at *ca.* 50 °C, to a solution of L^4 (3 mmol) in 75 cm^3 ethanol. On mixing, the solution turned brown and a small quantity of brown solid soon separated; $HClO_4$ was added dropwise until this precipitate redissolved. On reducing the volume, the product was obtained as orange crystals.

$[FeL^3{}_2(L^3 - H)][ClO_4]_2$ *and* $[FeL^4{}_2(L^4 - H)][ClO_4]_2$. These were prepared by allowing a solution of the corresponding iron(II) complex (0.5 g) in dry ethanol (50 cm^3), containing 1 cm^3 of 2,2-dimethoxypropane, to react with air *via* a $CaCl_2$ drying tube for several days. The dark green products which separated were washed with dry ethanol. The salt $[FeL^4_2(L^4 - H)][ClO_4]_2$ could alternatively be obtained merely by storage of $[FeL^4_3][ClO_4]_3$ over dry air (P_4O_{10}) for about 8 weeks.

Physical measurements were carried out as described in earlier papers.[2,3]

We thank the Department of Education (N. Ireland) for a Research Award (to V. M.).

[0/1965 *Received, 22nd December*, 1980]

REFERENCES

[1] For reviews see E. König, *Coord. Chem. Rev.*, 1968, **3**, 471; R. L. Martin and A. H. White, *Transition Met. Chem.*, 1969, **5**, 113; E. K. Barefield, D. H. Busch, and S. M. Nelson, *Q. Rev. Chem. Soc.*, 1968, 457; H. A. Goodwin, *Coord. Chem. Rev.*, 1976, **18**, 293.

[2] J. Nelson, S. M. Nelson, and W. D. Perry, *J. Chem. Soc., Dalton Trans.*, 1976, 1282.

[3] G. Bradley, V. McKee, S. M. Nelson, and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1978, 522.

[4] J. C. Wang and J. E. Bauman, *Inorg. Chem.*, 1965, **4**, 1613.

[5] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

[6] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

[7] S. M. Nelson and J. Rodgers, *J. Chem. Soc. A*, 1968, 272.

[8] M. Blume, *Phys. Rev. Lett.*, 1965, **14**, 96; 1967, **18**, 305.

[9] R. H. Petty, E. V. Dose, M. F. Tweedle, and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1064; K. A. Reeder, E. V. Dose, and L. J. Wilson, *ibid.*, p. 1071.

[10] D. N. Hendrickson, M. S. Haddad, W. D. Federer, and M. W. Lynch, *Proc. 21st Int. Conf. Coord. Chem.*, Toulouse, 1980, p. 62.

[11] H. Wenker, *J. Am. Chem. Soc.*, 1938, **60**, 2152.