Seven-co-ordination in Metal Complexes of Quinquedentate Macrocyclic Ligands. Part III.[1,2] Preparation and Properties of some Iron(II) Complexes of 2,13-Dimethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene and 2,14-Dimethyl-3,6,10,13,19-penta-azabicyclo[13.3.1]nonadeca-1(19),13,15,17-pentaene

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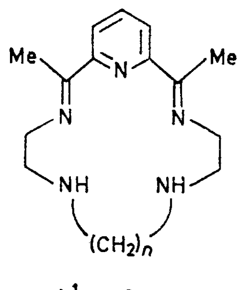
Iron(II) complexes of stoicheoimetry $FeLX_2 \cdot xH_2O$ and $FeClL(ClO_4) \cdot 2H_2O$ (L = the 15- or 16-membered N_5 title macrocycles; X = halide or pseudohalide) have been prepared by dithionite reduction of the corresponding iron(III) complexes, $[FeLX_2][ClO_4]$. The complexes may also be prepared by direct template synthesis from 2,6-diacetylpyridine and the appropriate tetra-amine in the presence of iron(II) salts. The physical properties of the complexes provide evidence for an approximately pentagonal-bipyramidal structure in which the macrocycle lies in the pentagonal plane and the axial positions are occupied by halide and/or water; the magnetic moments and Mössbauer spectra indicate $S = 2$ ground states. All the complexes exhibit an intense visible absorption, the energy of which is dependent on the nature of both the macrocycle and of the axial ligands. This absorption is ascribed to a charge transfer from the metal to the tri-imine segment of the macrocycle. The assignment is supported by electrochemical-potential measurements of the oxidation of the metal and of the reduction of the co-ordinated macrocycle. In aqueous solution, the iron(II) complexes catalyse electrochemical reduction of the hydrated proton to hydrogen.

IN Parts I[1] and II[2] the synthesis and properties of two series of seven-co-ordinate iron(III) complexes of the type $[FeLX_2]Y$ (L = quinquedentate macrocycle, X = halide or pseudohalide ion, and Y = non-co-ordinating counter anion, *e.g.* $[ClO_4]^-$ or $[PF_6]^-$) were described. These contained the 15- and 16-membered quinquedentate N_5 macrocyclic ligands L^1 and L^2. Single-crystal *X*-ray analysis[2] of one complex (X = NCS, Y = ClO_4) from each series established the approximate planarity of the five donor atoms of the two macrocycles and the approximate pentagonal-bipyramidal symmetry of the central metal ion. The complexes were prepared by Schiff-base condensation, in 1 : 1 : 1 molar ratio, of 2,6-diacetylpyridine and the appropriate tetra-amine in the presence of an iron(II) salt in water or aqueous alcohol solution. No attempt was made to exclude air and the ultimate products of the reactions carried out in this way were invariably complexes of Fe^{III}. We were interested to extend the synthesis to pentagonal-bipyramidal complexes of other metal ions. We have had success in this regard in the cases of Mn^{II},[3] Zn^{II}, and Cd^{II}, and, by using a suitable reductant, in the case of Fe^{II} also. A preliminary report[4] of some of these results has appeared. This paper discusses in detail the preparation and properties of the iron(II) macrocyclic complexes; in the following paper[5] the crystal and molecular structures of two members of the series are described. They are the first macrocyclic pentagonal-bipyramidal complexes of Fe^{II}. Recently, another, non-macrocyclic, iron(II) complex of approximate D_{5h} symmetry has been briefly reported.[6]



$L^1, n = 2$
$L^2, n = 3$

RESULTS AND DISCUSSION

Synthesis of the Complexes.—Cyclic voltammetry and coulometry of the iron(III) complexes $[FeLX_2]Y$ in aqueous solution revealed two one-electron reductions in the ranges +0.2 to 0 and −0.4 to −0.5 V *versus* the standard calomel electrode (s.c.e.). The former reduction, which is reversible, was ascribed to reduction of Fe^{III} to Fe^{II} and suggested that iron(II) macrocycles might be stable with respect to oxidation. (Previous attempts to prepare such derivatives from diketone and tetra-amine in the presence of Fe^{2+} under anaerobic conditions had not been successful.) In accord with this expectation, chemical reduction of the $[FeCl_2L]Y$ complexes with aqueous sodium dithionite in the presence of an excess of NaX yielded deep blue or blue-green crystals of $FeLX_2 \cdot nH_2O$ or, in one case, $FeClL(ClO_4) \cdot 2H_2O$. Analytical data are in Table 1. The complexes are stable for long periods in the solid state and in non-oxidising solvents in the absence of air. They are readily soluble in water and in most organic solvents of moderate polarity.

The syntheses of the parent iron(III) complexes is con-

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[1] S. M. Nelson and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1859; see also S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Comm.*, 1966, 611.

[2] M. G. B. Drew, A. H. Othman, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1975, 2507; see also E. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, 1967, **89**, 720.

[3] M. G. B. Drew, A. H. Othman, S. G. McFall, and S. M. Nelson, unpublished work.

[4] M. G. B. Drew, A. H. Othman, W. E. Hill, P. D. A. McIlroy, and S. M. Nelson, *Inorg. Chim. Acta*, 1975, **12**, L25.

[5] M. G. B. Drew, A. H. Othman, and S. M. Nelson, *J.C.S. Dalton*, following paper.

[6] D. Wester and G. J. Palenik, *J. Amer. Chem. Soc.*, 1973, **95**, 6505.

sidered to involve a template action by the metal ion. Control experiments in which the diketone and tetraamine were allowed to react in the absence of metal ion yielded only resinous materials which showed bands at 1 700 cm^{-1} in the i.r. spectra characteristic of residual carbonyl groups; these materials are probably oligomeric in nature. Our initial failure with the direct template synthesis of complexes of Fe^{II} and also of Co^{II}, Ni^{II}, and Cu^{II} and our success with Mn^{II}, Zn^{II}, and Cd^{II} at first suggested either (*i*) that only symmetrically occupied (d^0, d^5, or d^{10}) *d*-shell configurations can readily accommodate a pentagonal-bipyramidal stereochemistry or (*ii*) that the template synthesis of planar quinquedentate macrocycles is not favoured by transition-metal ions having a non-spherical *d*-electron occupancy.[4]

TABLE 1

Analytical, conductance, magnetic, and Mössbauer data for the iron(III) complexes

		Analysis (%)															
		Found				Calc.				Λ [a]/S cm^2 mol^{-1}			μ_{eff} [b]	Isomer shift [c,d] mm s^{-1}		Quadrupole splitting [d] mm s^{-1}	
Complex	Colour	C	H	N	halogen	C	H	N	halogen	H_2O	MeCN	$C_2H_4Cl_2$	B.M.	293	77 K	293	77 K
$FeClL^1(ClO_4)\cdot2H_2O$	Blue-violet	36.0	5.4	14.0		36.1	5.4	13.9		243	167	10.8	5.32	1.09	1.21	0.93	1.57
$FeBr_2L^1\cdot H_2O$	Blue-green	35.5	4.9	14.0	31.7	35.5	5.0	13.8	31.5	246	149	2.3	5.36	1.05	1.12	2.12	2.66
$FeI_2L^1\cdot2H_2O$	Blue-green	28.9	4.5	11.2	40.7	29.1	4.4	11.2	41.0	250	240	3.1	5.29	1.03, 1.00	1.14, 1.14	2.14, 0.47	2.65, 0.72
$FeL^1(NCS)_2$	Blue-green	45.6	5.3	21.8	14.3 [e]	45.8	5.2	22.0	14.4 [e]	234	94	0.4	5.27	0.98	1.11	2.27	2.87
$FeBr_2L^2\cdot2H_2O$	Blue	35.9	5.2	13.1	29.7	35.7	5.4	13.0	29.7	264	152	1.6	5.32	1.08	1.20	2.14	2.61
$FeI_2L^2\cdot3H_2O$	Blue-violet	29.7	4.7	10.6	38.9	29.5	4.8	10.7	39.0	260	263	1.4	5.39	1.11	1.21	2.46	2.95
$FeL^2(NCS)_2$	Blue	46.6	5.6	20.9		47.0	5.5	21.3		225	88	0.2	5.32	1.03	1.14	1.82	2.44

[a] For 10^{-3} mol dm^{-3} solutions. [b] Corrected for the diamagnetism of the ligands; estimated error, ±0.05 B.M. [c] Relative to natural iron. [d] Estimated error, ±0.05 mm s^{-1}. [e] Sulphur analysis.

However, subsequent experiments have shown that the iron(II) series of complexes can be prepared by the template method using iron(II) salts in the presence of dithionite. Thus, we have no firm evidence so far that the d^n configuration of the metal is important either in its template action or in regard to the stability of the macrocyclic product.

Information about the nature of the co-ordination polyhedra in the various complexes was gained from measurements of the i.r. and electronic spectra and of the electrical conductances of solutions.

Infrared Spectra.—These bear a close similarity in important respects to the spectra of the parent iron(III) complexes.[1,2] None showed any absorption at 1 700 cm^{-1} characteristic of ν(C=O) of diacetylpyridine which might result from hydrolysis of the macrocyclic ring during the reduction procedure in aqueous solution. All the complexes showed medium to strong bands at *ca.* 1 640 and *ca.* 1 590 cm^{-1} as expected for the C=N stretch and the highest energy pyridine ring vibration. Both bands occur at slightly lower wavenumbers (8—15 cm^{-1}) than in corresponding complexes of Fe^{III}. The position, intensity, and breadth of the N–H stretching vibration was variable and, in the case of the hydrates, was strongly overlapped by O–H absorption. No doubt hydrogen-bonding effects are important here. The bands at 1 090 and 620 cm^{-1} due to $[ClO_4]^-$ in $FeClL^1(ClO_4)\cdot2H_2O$ were not split and indicate that this ion is unco-ordinated.[7] The asymmetric stretching, symmetric stretching, and bending vibrations of the NCS groups, on the other hand, had positions [2 065, 790, and 483 cm^{-1}, respectively, in $FeL^1(NCS)_2$ and 2 067, 790, and 483 cm^{-1} in $FeL^2(NCS)_2$] and intensities consistent with co-ordination *via* the nitrogen atom.[8] The spectra of all the hydrated complexes showed, in addition to the stretching vibration at 3 200—3 500 cm^{-1} and the bending vibration at 1 620—1 630 cm^{-1}, a broad band of moderate intensity at 550 cm^{-1} (L^1 series of complexes) or 580—600 cm^{-1} (L^2 series). Absorption in this region is usually assigned to wagging or rocking modes of co-ordinated water.[9] For example, the band at 575 cm^{-1} in the spectra of salts of the aqua-cation $[Fe(OH_2)_6]^{2+}$ has been assigned to the wagging mode.[10]

Electronic Spectra.—Spectra of the solid complexes and of their solutions in water, acetonitrile, and 1,2-dichloroethane were recorded in the range 5 000—30 000 cm^{-1}. With one exception ($FeI_2L^1\cdot2H_2O$) the spectra of the complexes are similar in that they all comprised a broad absorption band of rather high intensity (ε = 500—1 200 dm^3 mol^{-1} cm^{-1}) in the 13 000—19 000 cm^{-1} region (Table 2). Comparison of the spectra of the different complexes in the solid state and in solution in different solvents, in conjunction with electrical conductivity data for the latter (Table 1), allows an assignment of the nature of the axially co-ordinated ligands to be made in most cases.

The complexes $FeL^1(NCS)_2$ and $FeL^2(NCS)_2$ had similar spectra in the solid state and in dichloroethane solution in which they are also non-electrolytes. It is concluded, therefore, that both NCS groups are co-ordinated in the solid complexes. This conclusion is confirmed by the results of single-crystal *X*-ray structure determinations (see following paper [5]). The spectra of the two complexes in acetonitrile and in water differed from those of the solids and from each other. Conductance measurements showed, in both cases, that the complexes are somewhat less than 1 : 1 electrolytes in the former solvent and 1 : 2 electrolytes in water, consistent with partial displacement of co-ordinated NCS by MeCN and virtually complete displacement by H_2O. It is noteworthy that all the complexes of a given macrocycle

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

[8] J. L. Burmeister, *Co-ordination Chem. Rev.*, 1966, **1**, 205; 1968, **3**, 225.

[9] J. R. Ferraro, ' Low-frequency Vibrations of Inorganic and Co-ordination Compounds,' Plenum Press, New York, 1971, p. 65.

[10] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1964, **20**, 429.

have identical spectra in water, and that they are all 1 : 2 electrolytes. Moreover, the solid complexes $FeClL^1(ClO_4)\cdot 2H_2O$ and $FeI_2L^2\cdot 3H_2O$ have very similar spectra to those of their respective aqueous solutions.

TABLE 2

Electronic spectra of the iron(II) complexes

Complex	State	Band maxima, $\nu/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1} for solutions)
$FeClL^1(ClO_4)\cdot 2H_2O$	Solid	16.4
	H_2O	16.0 (740)
	MeCN	14.5 (1 150)
	$C_2H_4Cl_2$	14.0 (600)
$FeBrL^1\cdot H_2O$	Solid	25.5, 16.0 (sh), 14.0
	H_2O	16.0 (750)
	MeCN	14.5 (1 090)
	$C_2H_4Cl_2$	13.2 (1 200)
$FeI_2L^1\cdot 2H_2O$	Solid	17.6, 14.4
	H_2O	16.0 (750)
	MeCN	18.2 (sh), 16.4 (1 100)
	$C_2H_4Cl_2$	13.9 (1 200)
$FeL^1(NCS)_2$	Solid	16.0 (sh), 13.5
	H_2O	16.0 (750)
	MeCN	14.7 (1 200)
	$C_2H_4Cl_2$	16.0 (sh), 13.6 (780)
$FeBr_2L^2\cdot 2H_2O$	Solid	26.0, 19.0 (sh), 15.4
	H_2O	21.0 (sh), 17.2 (570)
	MeCN	15.6 (710)
	$C_2H_4Cl_2$	13.9 (720)
$FeI_2L^2\cdot 3H_2O$	Solid	19.5 (sh), 16.5
	H_2O	20.5 (sh), 17.2 (560)
	MeCN	17.4 (700)
	$C_2H_4Cl_2$	14.5 (760)
$FeL^2(NCS)_2$	Solid	14.2
	H_2O	20.8, 17.3 (560)
	MeCN	15.2
	$C_2H_4Cl_2$	14.2 (760)

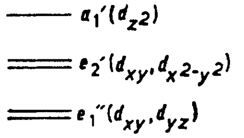
These are therefore formulated as $[FeL^1(OH_2)_2]Cl\cdot ClO_4$ and $[FeL^2(OH_2)_2]I_2\cdot H_2O$ in the solid state. However, there is evidence for a measure of anion co-ordination in solution in acetonitrile (chloro-complex) and in dichloroethane (both complexes). The structural assignment for $[FeL^1(OH_2)_2]Cl\cdot ClO_4$ has been verified by an *X*-ray analysis.[11]

The solid-state spectra of $FeBr_2L^1\cdot H_2O$ and $FeBr_2L^2\cdot 2H_2O$ differ from those of their aqueous solutions not only in regard to the positions of the visible bands but also in having strong bands at 25 500 ($FeBr_2L^1\cdot H_2O$) and 26 000 cm^{-1} ($FeBr_2L^2\cdot 2H_2O$). These bands were also apparent in the spectra of the acetonitrile and dichloroethane solutions in which the complexes are, respectively, 1 : 1 electrolytes and non-electrolytes. This band is attributed to a metal–bromide charge-transfer absorption. These observations, in conjunction with the data for the visible spectra, indicate that the structures of the complexes are probably $[FeBrL(OH_2]^+$, $[FeBrL(NCMe)]^+$, and $[FeBr_2L]$ in the solid state, in acetonitrile, and in dichloroethane, respectively.

Data for the complex $FeI_2L^1\cdot 2H_2O$ indicate that the dominant species in water and acetonitrile are, respectively, $[FeL^1(OH_2)_2]^{2+}$ and $[FeL^1(NCMe)]^{2+}$. However, the structure in the solid is uncertain. The spectrum consisted of a very broad unstructured absorption at 13 000—20 000 cm^{-1} and a further more intense broad band at *ca.* 26 000 cm^{-1}. There is thus some evidence for the formulation $[FeIL^1(OH_2)]I\cdot H_2O$. However, the real situation is clearly more complex since the Mössbauer spectra (see below) provide evidence for two different sites for the metal ions. Different preparations of the complex showed similar properties.

Origin of the Visible Spectra.—The following paper [5] shows that $FeL^1(NCS)_2$ and $FeL^2(NCS)_2$ have pentagonal-bipyramidal stereochemistry, the N_5 macrocycle defining the equatorial plane containing the metal with the thiocyanate nitrogen atoms occupying the axial positions. *X*-Ray analysis [11] has also demonstrated a similar structure for $[FeL^1(OH_2)_2]Cl\cdot ClO_4$. In view of the close similarity in properties, it is a reasonable assumption that the conformation of the macrocycles is the same in all the complexes and that the sixth and seventh ligands, halide and/or water, are axially co-ordinated.

In D_{5h} symmetry the five degenerate *d* orbitals of the ' free ' ion split as shown below. It is assumed here that the a_1' level is of highest energy, although it is conceivable that in situations where the axial field is small compared to the equatorial field it may drop below the e_2' level. For the case of high-spin iron(II), two spin-allowed Laporte-forbidden transitions are expected. These are $^5E_1'' \rightarrow {}^5E_2'$ and $^5E_1'' \rightarrow {}^5A_1'$. Since these are the first reported spectra for pentagonal-bipyramidal complexes of Fe^{II}, no comparisons are available. In trigonal-bipyramidal iron(II) complexes, which have a similar splitting pattern, two bands of low intensity are observed in the 5 000—10 000 cm^{-1} region.[12] Rather higher transition energies might be expected for at least one of the transitions in D_{5h} symmetry. However, none of the complexes exhibited any bands in the region between 5 000 and 13 000 cm^{-1}. It follows that either the *d–d* bands are masked by (or mixed in with) the strong visible absorption or the visible bands are actually the *d–d* transitions.



The latter proposal is unsatisfactory on two counts. First, the intensities of these bands are much higher than would be expected for Laporte-forbidden transitions. Secondly, the response of band position to change in the nature of the axial ligand contravenes expectations based on the spectrochemical series. The results of the previous section, summarised in Table 2, indicate that the position of maximum absorption moves to higher energies as the axial ligand is changed in the sequence $[NCS]^- \sim Br^- < H_2O$. This is the order of decreasing reducing power of the axial ligands. This fact, coupled with the rather high intensity of the absorption bands, seems to point to a charge-transfer origin. Yet the

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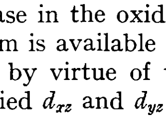
[11] M. G. B. Drew, A. H. Othman, P. D. A. McIlroy, and S. M. Nelson, *Acta Cryst.*, in the press.

[12] W. S. J. Kelly, G. H. Ford, and S. M. Nelson, *J. Chem. Soc.* (*A*), 1971, 388.

absorption cannot be due to an axial ligand→Fe^{II} charge-transfer mechanism in view of (*i*) the fact that the iron(II) ion is readily oxidised to Fe^{III}, and (*ii*) the fact that the axial ligand→Fe^{III} charge-transfer bands in the iron(III) series of complexes occur at higher energies.[1,2]

These considerations lead us to propose that the strong visible absorption is due to an Fe^{II}→macrocycle charge-transfer transition and that the energy of this transition decreases with increase in the oxidisability of the axial ligand. A mechanism is available for a charge-transfer process of this kind by virtue of the fact that in D_{5h} symmetry the occupied d_{xz} and d_{yz} metal orbitals have suitable symmetry for overlap with vacant delocalised p_{π}^* antibonding orbitals derived from the p_z atomic orbitals of the pyridine and imino-carbon and nitrogen atoms. Support for the spectral assignment is provided by the results of structure determinations of $FeL^1(NCS)_2$ and $FeL^2(NCS)_2$.[5] These show that the metal atom lies relatively closer to the unsaturated (sp^2 hybridised) nitrogen atoms than is the case in the iron(III) complexes where such $d_{\pi} \rightarrow p_{\pi}^*$ bonding does not occur. It is noteworthy also that these bond-distance effects are more pronounced in the L^1 complex than in that of the larger macrocycle L^2 for which the visible absorption occurs at higher energy. Finally, the spectral assignment is consistent with the observation of the electrochemical reduction of the ligand (see below).

It is significant, also, that the high-spin five- and six-co-ordinate iron(II) complexes of the related quadridentate macrocycle shown below, which also co-ordinates in a planar fashion, do not exhibit any intense visible



absorption. Instead, these show one or two bands of low intensity ($\varepsilon > 10$ dm^3 mol^{-1} cm^{-1}) in the range 4 000—11 000 cm^{-1}, clearly attributable to *d–d* transitions. This difference in the spectra of the two series of complexes can be readily understood since the quadridentate macrocycle contains no unsaturated (C=N) functions outside the pyridine ring. Thus, no delocalised p_{π} molecular orbital embracing three nitrogen donors can be constructed.

Magnetic Properties and Mössbauer Spectra.—Magnetic susceptibilities were determined by the Gouy method over the temperature range 90—300 K. The moments at 293 K fell in the range 5.2—5.4 B.M. (Table 1).* The susceptibilities obeyed the Curie–Weiss law, $\mu_{\text{eff.}} = 2.84 [\chi_m^{\text{corr}}(T - \theta)]^{\frac{1}{2}}$, over the entire temperature range, the Weiss constant, θ, being numerically less than $-5°$ in all cases. The moments characterise all the complexes as having $S = 2$ ground states as predicted for high-spin Fe^{II} in D_{5h} symmetry. There is significant orbital contribution to the moments as expected for the degeneracy of the d_{xz} and d_{yz} orbitals in this symmetry.

Mössbauer spectra were recorded at 293 and 77 K. With one exception, the spectra consisted of one quadrupole-split doublet. The complex $FeI_2L^1 \cdot 2H_2O$ was unique in showing two quadrupole-split doublets. Isomer shifts (quoted relative to natural iron) and quadrupole splittings are in Table 1. These are the first reported Mössbauer parameters for Fe^{II} in D_{5h} symmetry. The ranges of values observed for both the isomer shift (δ) and the quadrupole splitting (ΔE_Q) are consistent with a non-spherical occupation (d^6) of the five *d* orbitals. Indeed, the magnitudes of both parameters fell within the ranges usually observed for high-spin iron(II) compounds in six-co-ordinate environments.[13] There are two main contributions to the magnitude of ΔE_Q: (*i*), the unsymmetrical electron density about the nucleus already referred to; and (*ii*), the asymmetry of the ligand field. The electric-field gradients from these two sources may have the same or opposite signs and thus may reinforce or partially cancel each other. Inspection of the ΔE_Q data for the various complexes indicates no clear correlation with the nature of the axial ligands and their expected field strengths. Further discussion of the Mössbauer parameters is therefore deferred until measurements at liquid-helium temperature and in applied magnetic fields can be made.

The complex $FeI_2L^1 \cdot 2H_2O$ is exceptional in displaying two quadrupole-split doublets, the outer having an integrated intensity of about three times that of the inner doublet at both 293 and 77 K. Neither ΔE_Q value corresponds with that observed for $[FeL^1(OH_2)_2]Cl \cdot ClO_4$ which rules out the presence of a diaqua-cation. The quadrupole splitting for the outer (more intense) doublet is very similar to that of $FeBr_2L^1 \cdot H_2O$, considered from spectral evidence to be $[FeBrL^1(OH_2)]Br$. It seems probable, therefore, that the dominant species in this complex is $[FeIL^1(OH_2)]I \cdot H_2O$. The origin of the inner doublet is unknown; possibly it is due to $[FeI_2L^1] \cdot 2H_2O$.

Electrochemical Measurements.—Cyclic voltammetry was carried out on dilute (10^{-3} mol dm^{-3}) solutions of the iron(III) complexes $[FeLX_2]Y$ in water and in acetonitrile using 10^{-1} mol dm^{-3} NaCl and $[NEt_4][ClO_4]$, respectively, as supporting electrolyte. In some cases the cyclic voltammograms were checked with those for the corresponding complexes of Fe^{II} in acetonitrile. Two reduction waves were observed for both L^1 and L^2 series of complexes in both solvents. The reduction occurring at the more positive potential is ascribed to a reduction of the metal from the III to the II oxidation state. Coulometric measurements on $[FeCl_2L^1][ClO_4]$ established the one-electron nature of this process.

Earlier studies [1-3] have shown that the $[FeLX_2]^+$ complex ions are virtually exclusively (X = Cl, Br, or I) or predominantly (X = NCS) dissociated to the diaqua-cations $[FeL(OH_2)_2]^{3+}$ in 10^{-3} mol dm^{-3} aqueous solution. Accordingly, in aqueous solution, the same redox potential $E^{\ominus}$ for the Fe^{III}–Fe^{II} interconversion would be

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* 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

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

expected for all the complexes of a given macrocycle. This was found to be the case (see Table 3). For each series the value of $E_{pc} - E_{pa}$ was close to the theoretical value [14] of 0.058 V for a reversible one-electron-transfer process, $E^{\ominus} = \frac{1}{2}(E_{pc} + E_{pa})$ being +0.08 and +017 V *versus* the s.c.e. for the L^1 and L^2 series, respectively.

TABLE 3

Cyclic-voltammetric data for the complexes (10^{-3} mol dm^{-3}); supporting electrolyte, 10^{-1} mol dm^{-3} NaCl; potentials measured in V *versus* the s.c.e., sweep rate 0.015 V s^{-1}

	First redox step,[a]	Second redox step [b]	
Complex	$E^{\ominus} = \frac{1}{2}(E_{pc} + E_{pa})$	E_{pc}	E_{pa}
$[FeCl_2L^1][ClO_4]$	+0.08	−0.52	−0.42
$FeL^1(NCS)_2$	+0.05		
$[FeCl_2L^2][ClO_4]$	+0.16	−0.52	−0.42
$[FeBr_2L^2][ClO_4]$	+0.18		
$FeL^2(NCS)_2$	+0.13		

[a] This step was reversible with $E_{pa} - E_{pc} = 0.06$ V and $I_{pc}/I_{pa} = 1.05$. [b] Peak potentials and heights were pH dependent.

TABLE 4

Results from cyclic voltammetry of the complexes $[FeLX_2][ClO_4]$ (10^{-3} mol dm^{-3}) in acetonitrile. The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4][ClO_4]$ unless otherwise stated; potentials in V *versus* the s.c.e., sweep rate 0.08 V s^{-1}

Complex		First redox step				Second redox step	
L	X	E_{pc}'	E_{pa}'	I_{pc}/I_{pa}	$E^{\ominus\prime} = \frac{1}{2}(E_{pc} + E_{pa})$	E_{pc}''	E_{pa}''
L^1	N_3	−0.42	−0.34	1.1	−0.38	−1.48	−1.35
	Cl	−0.28	−0.16	1.3		−1.43	−1.33
	Cl [a,b]	−0.26	−0.20	*b*	−0.23		
	Br	−0.18	+0.01	1.2		−1.43	−1.33
	Br [a]	−0.12	−0.05	1.0	−0.09		
	NCS [c]	−0.09	−0.13	1.1	−0.06	−1.42	−1.33
	I [d]	+0.49	+0.63	*d*			
L^2	N_3	−0.37	−0.30	1.1	−0.34	−1.50	−1.40
	Cl	−0.20	−0.07	1.3		−1.42	−1.33
	Cl [a]	−0.19	−0.13	1.1	−0.16		
	Br	−0.02	+0.08	1.2		−1.40	−1.31
	Br [a]	−0.03	+0.04	1.0	+0.01		
	NCS [c]	−0.01	+0.08	1.1	+0.04	−1.42	−1.32
	I [d]	+0.53	+0.61	*d*	+0.57	−1.43	−1.35

[a] The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4]X$. [b] The counter ion was $[FeCl_4]^-$ in place of $[ClO_4]^-$. This ion shows a reduction wave with $E_{pc} = -0.05$ and $E_{pa} = +0.04$ V which partly overlaps the first redox step. [c] Identical peak potentials are shown by $FeL(NCS)_2$ but, of course, at electrode potentials positive of the first redox step the current is anodic due to the reaction $Fe^{II} \longrightarrow Fe^{III}$. [d] The complex $FeI_2L{\cdot}xH_2O$ was used which exists in solution as $[FeL(NCMe)_2]^{2+}$. The redox reaction $2I^- \rightleftharpoons I_2$ with $E_{pc} = +0.08$ and $E_{pa} = +0.23$ V overlaps the first redox step.

In contrast, the more positive of the two redox processes occurring in acetonitrile solutions is dependent on the nature of the anionic ligand X. For these solutions, earlier measurements [2,3] have established that there is little dissociation so that we are dealing with reduction of the complex ion $[FeLX_2]^+$. The cyclic voltammograms for the complexes with X = N_3 or NCS indicate reversible behaviour for this first electron-transfer step (Table 4). Those for the complexes with X = Cl or Br showed small departures from reversible behaviour when $[NEt_4][ClO_4]$ was used as supporting electrolyte, but the redox couple became reversible when 0.1 mol dm^{-3} $[NEt_4]X$ was present. The additional X^- ion is sufficient to suppress slight dissociation of the complexes in these cases. The complexes $FeI_2L{\cdot}xH_2O$ have been shown above to be virtually completely dissociated in 10^{-3} mol dm^{-3} acetonitrile solution, so the reversible redox couple observed for X = I is due to the solvated complex ion $[FeL(NCMe)_2]^{3+}$. A third redox couple was observed in the cyclic voltammetry of the iodo-complexes and this is due to the dissociated iodide–iodine couple. The peaks on the cyclic voltammogram ascribed to this third couple were enhanced by the addition of iodide ion to the solutions.

The more negative reduction in acetonitrile solution was found to be reversible but the reduced species has a half-life of *ca.* 5 s. The potential for this reduction was virtually independent of the nature of X and the change in size of the saturated carbon chain between macrocycles L^1 and L^2. However, replacement of the Me substituents on the imine groups by H (giving macrocycle L^3) and by Ph (giving macrocycle L^4) resulted in a positive shift of the potential for this second reduction and, in both cases, the appearance of a third and yet more negative reduction (Table 5). It seems probable that the second reduction wave in the complexes $[FeLX_2][ClO_4]$ corresponds to the addition of an electron to the lowest antibonding orbital of the conjugated imino-system giving a radical anion. The third reduction wave of the complexes $[FeL^3(NCS)_2][ClO_4]$ and $[FeL^4(NCS)_2][ClO_4]$ corresponds to addition of a second electron to the radical anion; this reaction is not observed with macrocycles L^1 and L^2 before the back-

TABLE 5

Effect of imino-substituent R on the redox potentials of the complexes $FeL(NCS)_2$ in acetonitrile. The supporting electrolyte was 0.1 mol dm^{-3} $[NEt_4][ClO_4]$; potentials in V *versus* the s.c.e., sweep rate 0.08 V s^{-1}

Complex		First redox step		Second redox step		Third redox step	
L	R	E_{pc}'	E_{pa}'	E_{pc}''	E_{pa}''	E_{pc}'''	E_{pa}'''
L^1	Me	−0.09	−0.03 *	−1.42	−1.33		
L^2	Me	−0.01	+0.08 *	−1.42	−1.32		
L^3	H	−0.00	+0.07	−1.23	−1.15	−1.53	
L^4	Ph	+0.01	+0.08	−1.22	−1.12	−1.47	−1.35

* Compare with data for $[FeL(NCS)_2][ClO_4]$ (Table 4).

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[14] R. S. Nicholson and I. Shain, *Analyt. Chem.*, **1964**, **36**, 706.

ground current becomes excessive due to solvent decomposition.

The electrochemical data show that in the iron(II) complexes, $FeLX_2$, the metal may be readily oxidised to Fe^{III} and that the co-ordinated macrocycle may be reduced to the radical anion. Associating these two processes we have, in effect, a metal-to-macrocycle charge transfer. Recalling that the visible absorption of these complexes was ascribed to such a process, we might therefore expect some correspondence in the energies of the electrochemical reactions and the spectral processes. $F(E^{\ominus\prime} - E^{\ominus\prime\prime})$ is the free energy associated with removal of an electron from Fe^{II} in $FeLX_2$ and addition of an electron to L in $FeLX_2$. It is compared in Table 6 with the spectral charge-transfer energy derived from the position of maximum absorption. Exact agreement of the two energies is, of course, not expected since in the electrochemical process the electron (from the electrode) is being added to the macrocycle co-ordinated to Fe^{II}, while in the spectral process the electron (from the metal) is excited to a molecular orbital mainly localised on the macrocycle. Moreover, reorganisation of the outer co-ordination sphere of solvent and counter ions may occur during the redox reactions but not during the spectral transition. Nonetheless, as Table 6 shows, the agreement is remarkably good. Probably even more significant is the correlation in the direction of the energy changes as X is varied. These observations reinforce the conclusions reached above concerning the origin of the visible spectra.

TABLE 6

Comparison of the energies of the charge-transfer bands in the complexes $FeLX_2$ with those of the metal ⟶ macrocycle redox process

Complex	Energy/kJ mol^{-1}	
	Charge transfer	$F(E^{\ominus\prime} - E^{\ominus\prime\prime})$
$FeBr_2L^1$	158 [a]	124
$FeL^1(NCS)_2$	162 [a]	127
$[FeL^1(NCMe)_2]^{2+}$	196 [b]	187 [b]
$FeBr_2L^2$	166 [a]	133
$FeL(NCS)_2$	170 [a]	136
$[FeL^2(NCMe)_2]^{2+}$	208 [b]	188 [b]

[a] In $C_2H_4Cl_2$. [b] For iodo-complex in MeCN.

The more negative wave in aqueous solutions occurred in the range −0.4 to −0.5 V. Its height was pH dependent, increasingly markedly at low pH so that at pH 2.5 it was 10—15 times the height of the first reduction wave. This wave is therefore ascribed to hydrogen evolution at the smooth platinum electrode, catalysed by the hydrated ion $[FeL(OH_2)_2]^{2+}$. The overpotential necessary for hydrogen evolution at a smooth platinum electrode is usually more negative. However, amine salts and some complex ions, particularly of Co^{II}, are known to lower the activation energy for hydrogen evolution giving rise to the ' catalytic hydrogen waves ' which have been studied at the dropping mercury electrode.[15]

EXPERIMENTAL

Preparation of the Complexes.—*Method* (*a*). All operations were made under an atmosphere of N_2 and all solvents were deoxygenated by heating to their boiling points and subsequently cooling under N_2.

A solution of $[FeCl_2L][ClO_4]$ (5 g) in water (250 cm^3) was heated to near its boiling point and $Na_2[S_2O_4]$ (3 g) was added. The solution turned a deep royal blue (L = L^1) or blue-violet (L = L^2). This solution was filtered into a second solution containing NaX (X = Cl, Br, I, or NCS) (20 g) in water (100 cm^3). The resulting solution was maintained at 60—70 °C under a N_2 gas stream until it was reduced to a third of its volume or less. It was then cooled in an ice-bath. Deep blue or blue-green crystals separated. These were filtered off and washed with small quantities of cold water containing $Na_2[S_2O_4]$ (*ca.* 0.1 g per 100 cm^3). Yields were related to the solubility of the complex in water, varying from *ca.* 30 (chloride and iodides) to *ca.* 40% (thiocyanates). The products were recrystallised from water containing $Na_2[S_2O_4]$ (0.1 g per 100 cm^3).

Method (*b*). To a solution of $FeCl_2 \cdot 4H_2O$ (4 g) in methanol (200 cm^3) and water (50 cm^3) were added $Na_2[S_2O_4]$ (2 g), 2,6-diacetylpyridine (3.2 g), and an equimolar quantity of 3,6-diazaoctane-1,8-diamine (or 3,7-diazanonane-1,9-diamine). The reaction mixture was heated gently under reflux for 12 h and then filtered into a solution of NaX (20 g) and $Na_2[S_2O_4]$ (1 g) in water (100 cm^3). The filtrate was reduced in volume to *ca.* 100 cm^3 by passing a rapid stream of N_2 through it while being maintained at 50 °C. Crystals of the products separated on cooling. These were isolated and purified as in method (*a*); yields were generally 10—20% higher.

Physical Measurements.—Infrared spectra were recorded in the range 250—4 000 cm^{-1} as Nujol mulls and as KBr pellets using a Perkin-Elmer 457 grating spectrometer. A Unicam SP 700 spectrophotometer was used in measurements of the electronic spectra. The spectra of the solids are transmittance spectra of mulls. A conductivity cell of cell constant 0.0368 and constructed from bright platinum electrodes was used in conjunction with a conventional resistance–capacitance bridge for electrical-conductance measurements. Magnetic measurements were made by the Gouy method using a Newport Instruments variable-temperature magnetic balance. Mössbauer spectra were recorded at 293 ± 3 and 77 K with a ^{57}Co-in-Pd source using a Harwell constant-acceleration spectrometer. The equipment was calibrated with an iron-foil standard at 293 K. Absorber thicknesses were not more than 50 mg cm^{-2}. Isomer shifts and quadrupole splittings were determined by visual inspection to ± 0.015 mm s^{-1}; values were checked by repeating the measurements using different samples. Approximately equal line intensities were found in all the spectra.

Electrochemical experiments were made under a nitrogen atmosphere deoxygenated with the BTS catalyst[16] and dried by molecular sieves. All electrode potentials were measured with respect to an aqueous saturated calomel electrode (s.c.e.) (1.0 mol dm^{-3} $Na[NO_3]$) salt bridge containing the electrolysis solution so as to avoid precipitation of $K[ClO_4]$ at liquid junctions where the salt bridge contains $[ClO_4]^-$ ions.[17] Liquid junctions were made through short 3-mm diameter plugs of porous Vycor glass which were attached to the glassware by poly(tetrafluoroethylene)

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[15] S. G. Mairanovskii, ' Catalytic and Kinetic Waves in Polarography,' Plenum Press, New York, 1968.

[16] M. Schutze, *Angew. Chem.*, 1958, **70**, 697; Badische Anilin- and Soda-Falnk AG, Technical Bulletin, ' BTS Catalyst.'

[17] B. McDaffie, L. B. Anderson, and C. Reilly, *Analyt. Chem.*, 1966, **38**, 883.

tubes.[18] The cyclic-voltammetry cell had a s.c.e. as reference, a platinum-wire anode, and an appropriate cathode, and was controlled by an operational amplifier potentiostat unit built in this Department. The potential waveform came from a Hewlett-Packard 3310A function generator and current–voltage curves were recorded on a Bryant 2 600 series XY recorder. The bright Pt cathode was allowed to reach equilibrium at the starting potential, and the result from a single triangular-voltage sweep was then recorded. The cathode was formed from a Pt sphere, made by melting Pt wire (0.30-mm diameter) in a hydrogen–oxygen flame, and supported in soda glass. The cell contained the substrate complex (1.0×10^{-3} mol dm^{-3}) and the electrolyte (0.1 mol dm^{-3}) in either acetonitrile or water. In the coulometric experiment, a solution of $[FeCl_2L^1][ClO_4]$ (0.1 g) in acetonitrile (15 cm^3) containing $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}) was contained in one limb of an H-type electrolysis vessel and reduced at a platinum-gauze cathode maintained at -0.5 V *versus* the s.c.e. A hydrazine coulometer was placed in series;[19] uptake, 1.05 F mol^{-1}.

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[19] J. A. Page and J. J. Lingane, *Analyt. Chim. Acta*, 1957, **16**, 175.