Stereochemistry and Spin Configuration of *NN'*-Bis(2-pyridylmethyl)-ethylenediamine Complexes of Iron(III) in the Solid State and in Aqueous Solution

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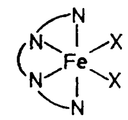
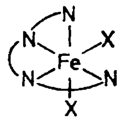
High-spin $[Fe(pmen)Cl_2]Cl$ and low-spin $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$ complexes (pmen is the title ligand), have been prepared and characterized by spectroscopic and magnetic measurements. Electronic and e.p.r. spectra suggest that the complexes have a *cis*-type geometry both in the solid state and in aqueous solution. Peculiar features observed in solution are aquation of the cation of the chloride salt which effects electron pairing, whilst a change from low to high spin, accompanied by a structural rearrangement, occurs when the conjugate dihydroxo-base of both salts is formed. Induced circular dichroism spectra, arising from the interaction of the complexes in aqueous solution with an optically active polyelectrolyte (which does not absorb over the wavelength region explored), make possible an assignment of *cis*-α geometry to the high-spin form and *cis*-β geometry to the low-spin species, in agreement with predictions from qualitative steric considerations. Implications of the stereochemical demands of the complexes on variation of the spin configuration of the iron are also discussed.

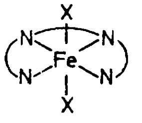
THE way in which the steric constraints of facultative[1] quadridentate ligands affect the stereochemistry of transition-metal complexes has received much attention in the last few years in order to elucidate which factors predominate in determining the most stable configuration.[2-4] We have prepared a set of iron(III) complexes with quadridentate nitrogen ligands, having different conjugative capacity, to be used in a study on the catalase-like activity[5,6] of the corresponding adducts with some polyelectrolytes.[7] Of these complexes, those formed by the facultative ligand *NN'*-bis(2-pyridylmethyl)ethylenediamine (pmen) exhibit stereochemical features closely connected with their magnetic properties.



cis-α (Λ)



cis-β (Λ)



trans

Interconversion between paramagnetic and diamagnetic nickel(II) tetra-amine systems is accompanied by a change in the stereochemistry of the complexes.[8] Furthermore, the influence of the spin state of Fe^{II} and Fe^{III} on the structural characteristics of some macrocyclic complexes[9] or metalloporphyrins[10,11] has been widely investigated. The observed change from a high-spin five-co-ordinate to a low-spin six-co-ordinate species was chiefly ascribed to the radial contraction of the metal ion following the spin variation, which allows it to fit into the in-plane ligand ' hole '.[9-12]

The configuration of the above iron complexes is, however, basically of the *trans* type;[9a,11-12] whereas, in our case, different topological isomers can be formed due to the high flexibility of the quadridentate ligand. This paper presents experimental evidence supporting stereochemical arguments which suggest that the preferred configuration of $[Fe(pmen)X_2]^{n+}$ complexes chiefly depends on the spin state of iron.[12,13]

EXPERIMENTAL

Materials.— *NN'*-Bis(2-pyridylmethyl)ethylenediamine (pmen) was obtained by hydrogenation *via* $Na[BH_4]$ of the corresponding Schiff base bis(pyridinal)ethylenediamine, prepared according to the literature.[14] A typical preparation was as follows.[15] To an 8% methanol solution of the Schiff base, sodium tetrahydridoborate was added in portions. The mixture, after subsidence of an initial vigorous effervescence, was heated on a steam-bath with occasional stirring until the reagent was consumed. The reduction was complete when further addition of $Na[BH_4]$ to the heated solution did not produce any effervescence. After cooling, the reaction mixture was treated with water (25 cm^3) and

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repeatedly extracted with portions of diethyl ether (150 cm^3), enough NaCl being added to saturate the aqueous layer. The ether solution was dried over anhydrous $K_2[CO_3]$ and evaporated *in vacuo*. A pale yellow oil was recovered and converted into the required hydrochloride. The white solid was crystallized three times from water, m.p. 206—208 °C (decomp.) (Found: C, 42.8; H, 5.70; N, 14.4. Calc. for $C_{14}H_{18}N_4 \cdot 4HCl$: C, 43.3; H, 5.70; N, 14.45%). Alternatively, the oil was distilled *in vacuo* (b.p. 169—170 °C, 2 mmHg)* (Found: C, 68.85; H, 7.60; N, 22.95. Calc. for $C_{14}H_{18}N_4$: C, 69.4; H, 7.50; N, 23.1%). The chloride salt of the complex was obtained by adding dropwise a saturated alcoholic solution of $FeCl_2 \cdot 4H_2O$ to a methanolic solution of the ligand (0.5 g), with continuous stirring. The complex was precipitated as a green solid, which was filtered off, washed many times with methanol, and dried. The perchlorate salt was obtained from the chloride by exchange in concentrated aqueous solution with an excess of sodium perchlorate. The complex was precipitated as a brown solid. Because of the very great tendency of iron(II) ions to be oxidized even in the presence of trace amounts of water, iron(III) complexes were prepared (see later).

TABLE 1

Element analyses and some physical properties of the iron(III) complexes

	Analysis [a](%)				$\mu_{eff.}$[b]	Λ[c]
	C	H	N	Cl	B.M.	S cm^2 mol^{-1}
$[Fe(pmen)(OH_2)(OH)][ClO_4]_2$	31.35 (31.55)	4.1 (3.95)	10.45 (10.5)	12.95 (13.3)	2.08 [d]	206 (H_2O)
$[Fe(pmen)Cl_2]Cl \cdot H_2O$	40.2 (39.8)	4.6 (4.75)	13.15 (13.25)	25.3 (25.15)	5.96	84 ($MeNO_2$) 90 (MeOH) 355 (H_2O)

[a] Calculated values are given in parentheses. [b] Magnetic moment at room temperature, corrected for ligand and anion diamagnetism. [c] At 25 °C (for *ca.* 10^{-3} mol dm^{-3} solutions); the solvent is given in parentheses. [d] See Table 3.

Elemental analyses, by Alfred Bernhardt Laboratories, are in Table 1. All reagents were of analytical grade and were employed without further purification. Measurements in aqueous solution were made on freshly prepared samples, using double distilled water with a conductivity of less than 2.5×10^{-6} S cm^{-1} at 20 °C.

Methods and Apparatus.—Magnetic measurements were made as a function of temperature (100—300 K) by the Gouy method. The magnetic moments were corrected for ligand and anion diamagnetism.[16] Conductivities (Table 1) were determined by a Philips PR 9500 apparatus at 25 ± 0.2 °C at 1 000 Hz, using a cell with a constant of 1.46 cm^{-1}. The concentration of the samples was *ca.* 10^{-3} mol dm^{-3}.

Infrared spectra were obtained with a Perkin-Elmer model 337 spectrophotometer, using Nujol mulls or KBr discs. Only very small differences were noted for the two methods. E.p.r. spectra of aqueous samples were recorded at liquid-nitrogen temperature on a Varian E-9 spectrometer. Microwave frequencies were of the order of 9.16 GHz with 100 KHz field modulation. Reflectance spectra were obtained with a Beckman DK-1 apparatus, electronic spectra of solutions with a Beckman DK-2A instrument and appropriate quartz cells. Mössbauer spectra at room temperature were recorded with a ^{57}Co-in-Cu source and a constant-acceleration 400-channel Laben spectrometer, calibrated by $Na_2[Fe(CN)_5(NO)]$ and natural iron absorbers. The spectra were fitted to Lorentzian lines by use of a computer program. Circular dichroism (c.d.) spectra were recorded on a Cary 61 instrument, with quartz cells of 2, 1, or 0.1 cm pathlength, and optical rotatory dispersion (o.r.d.) measurements were made with a Perkin-Elmer 141 M apparatus. The molar absorption coefficient, ε, and the molar ellipticity, $\varepsilon_L - \varepsilon_R$, were obtained on the basis of the total iron concentration.

pH Values were determined on a Radiometer 26 pH meter with the use of standard semimicroelectrodes. Potentiometric titrations were carried out at 20 °C, using the same apparatus. The temperature was maintained constant (±0.2 °C) by an external water-bath. In all experiments no electrolyte was added. Pure nitrogen, saturated with the solvent, was passed over the sample during the titrations in order to eliminate carbon dioxide.

RESULTS

The conductance data agree with the proposed structures (Table 1). The perchlorate salt had a conductance in water of 206 S cm^2 mol^{-1}, as expected for a 2 : 1 electrolyte, whereas the chloride salt behaved as a 1 : 1 electrolyte, with conductance values of 84 in nitromethane and 90 S cm^2 mol^{-1} in methanol.[17] Since the molar conductivity in aqueous solution of the chloride salt was 355 S cm^2 mol^{-1}, as expected for a 3 : 1 electrolyte,[18] it may be concluded that the co-ordinated chloride ions are ionized in water, possibly yielding a diaqua-species (see later).

I.r. Spectra.—The i.r. spectra (Table 2) substantiate the proposed formulae. The four pyridine-ring deformation vibrations occurred in the range 1 430—1 610 cm^{-1}.[19a] Of these, the one at higher wavenumber is shifted on co-ordination towards wavenumbers higher than those in the 'free' ligand. This, together with the absence of any band at *ca.* 1 590 cm^{-1}, is consistent with bonding of both pyridyl groups.[20] All spectra had N–H stretching absorptions in the range 3 150—3 260 cm^{-1}, which are appreciably lower (60—140 cm^{-1}) than that of the free ligand (Table 2). This is indicative of bond formation between the aliphatic nitrogen atoms and the iron.[19b]

The perchlorate salt exhibited an additional N–H stretching vibration at 3 180m cm^{-1}, besides that at 3 260 cm^{-1}. Since in both salts investigated there is a significant possibility of hydrogen bonding between the NH groups and anions or water,[3, 20b] this finding may suggest that the two NH groups

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* 1 mmHg ≈ 13.6 × 9.8 Pa, 1 B.M. ≈ 9.27×10^{-24} A m^2, 1 G = 10^{-4} T.

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in the perchlorate are not equivalent and, therefore, that the chloride and perchlorate salts have a different stereochemistry. This is supported by *X*-ray powder patterns * which show marked differences between the two samples, and is not unreasonable in view of the fact that (3,6-diazaoctane-1,8-diamine)cobalt(III) complexes assume a *cis*-β structure in the diaqua-form but a *cis*-α geometry in the dichloro-species,[21] whilst the $[CoCl_2(pmen)]^+$ complex prefers a *cis*-α configuration, the *cis*-β isomer being only formed from the dinitro-derivative by exchange with HCl.[3]

Finally, the weak broad band at *ca.* 1 650 cm^{-1}, together with the O–H stretching vibrations in the 3 450—3 300 cm^{-1} region, confirms the presence of water in the complexes. There were two medium bands at 1 013 and 968 cm^{-1} in the spectrum of the perchlorate which could be attributed to co-ordinated water in agreement with data for some aqua-complexes.[22]

TABLE 2

Prominent infrared stretching bands (cm^{-1}) of the complexes [a]

Compound	O–H [b]	N–H	Ring stretching vibrations	C–N	Anion
pmen		3 320m, b	1 592s, sp	1 150s, sp	
			1 570m, sp		
			1 475m, sp		
			1 433s, sp		
$[Fe(pmen)(OH_2)(OH)][ClO_4]_2$	3 400w (sh) [c]	3 260m (sh)	1 610s, sp	1 165m, sp	1 120vs, sp
	3 300m, b	3 180m	1 572w, sp		1 105vs, sp
			1 480m, sp		627s
			1 432m, sp		
$[Fe(pmen)Cl_2]Cl\cdot H_2O$	3 600w (sh) [d]	3 210m	1 610s, sp	1 162w	
	3 540m, sp		1 571w, sp		
	3 350m, b		1 486m, sp		
			1 440s, sp		

[a] The spectra refer to paraffin oil mulls or KBr discs; s = strong, m = medium, w = weak, sh = shoulder, b = broad, sp = sharp, and v = very. [b] In all cases where O–H stretching frequencies are assigned, there were bands corresponding to the H_2O bending in the range 1 640—1 670w, b cm^{-1}. [c] This complex exhibits two additional medium sharp bands at 1 013 and 968 cm^{-1} which could be attributed to co-ordinated water. [d] This band is not assigned to O–H stretching modes, although it occurs near to this frequency region.

Magnetic Properties and Mössbauer Data.—The magnetic moment of $[FeCl_2(pmen)]Cl$ is 5.96 B.M. (Table 1) and independent of temperature (down to 100 K), as predicted for a $^6A_1$ ground state. This agrees with preliminary room-temperature Mössbauer data which are normal for high-spin six-co-ordinate iron(III) derivatives[23] (isomer shift 0.74, quadrupole splitting 0.45 mm s^{-1}). In contrast, $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$ is a low-spin species with a magnetic moment at room temperature of 2.08 B.M., slightly less than that found for typical octahedral low-spin iron(III) complexes[16,18] but similar to that obtained with spin-paired d^5 complexes formed with quinque- or sexidentate nitrogen ligands.[24] The magnetic data as a function of temperature are given in Table 3. The formulation of the ground state as a spin doublet is justified. Treating the data according to Figgis[25] for $^2T_{2g}$ systems in an axially distorted cubic field, a good fitting of the observed moments was obtained assuming a spin-orbit coupling constant, λ, of 85 cm^{-1}, a delocalization constant, *k*, of 1.0, and an axial distortion, Δ, of -170 cm^{-1}. No particular significance should be placed, however, on the value of these parameters since other sets with a positive value of Δ also gave a reasonable fit to the experimental data. In all cases the susceptibilities were independent of field strength.

Mössbauer measurements on $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$ gave an isomer shift and quadrupole splitting at 293 K of 0.65 and 1.33 mm s^{-1}, respectively. The quadrupole splitting, therefore, substantiates the magnetic data in predicting a low distortion from cubic symmetry, as compared, for instance, with the value of 3.09 mm s^{-1} (Δ $-1\ 750$ cm^{-1}) found for $[Fe(terpy)_2][ClO_4]_3$ (terpy = 2,2′ : 6′,2″-terpyridyl).[18] On the other hand, an axial distortion near zero and a quadrupole splitting of 1.09 mm s^{-1} (290 K) was observed for $[Fe(en)_3]Cl_3$ (en = ethylenediamine).[26]

Finally, it is worth anticipating that the dihydroxo-conjugate base $[Fe(pmen)(OH)_2]^+$ exhibits a high-spin configuration (see later). This implies that the ligand-field splitting of H_2O is larger than $[OH]^-$, as commonly observed in simple inorganic hydroxo- and aqua-complexes, but, at the same time, indicates that there is a close balance between the ligand-field and electron-pairing energies.

TABLE 3

Magnetic-susceptibility data and calculated magnetic moments for $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$

T/K	$10^6\chi_m$/c.g.s. units	$\mu_{eff.}$/B.M.
288	1 862	2.08
244	2 076	2.02
215	2 262	1.98
183	2 614	1.96
176	2 638	1.93
162	2 736	1.89
144	2 880	1.83
135	2 975	1.80
128	3 002	1.76
119	3 190	1.75
102	3 302	1.64

Electronic Spectra.—The overall features of the electronic spectra of solid samples or methanol solutions confirm the foregoing considerations (Table 4). Although the symmetry

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* We thank Professor M. Calligaris (University of Trieste) for making these measurements.

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of the complexes is lower than O_h, it might be expected that their electronic spectra would conform approximately to those of d^5 systems in octahedral symmetry. In such a case, the most reasonable assignment of the first three visible ligand-field bands of $[FeCl_2(pmen)]Cl$, which have very low molar absorption coefficients (Table 4), seems to be the spin forbidden $^6A_1 \rightarrow {}^4T_1$, $^6A_1 \rightarrow {}^4T_2$, and $^6A_1 \rightarrow ({}^4A_1, {}^4E)$ transitions. They fall within the wavelength range of those reported for a number of high-spin iron(III) complexes.[18,27] These assignments lead to the values of Dq = 1 294, B = 981, and C = 2 038 cm^{-1} and to the energies reported in the Table, which agree satisfactorily with the experimental values.

TABLE 4

Electronic spectra of the iron(III) complexes [a]

Perchlorate salt

Solid	Aqueous soln [b]	Assignment	Energy [c]
9.7b	9.5b (*ca.* 3)	$^2T_2 \rightarrow {}^4T_1$	9.7
17.9 (sh)	17.9 (58)	$^2T_2 \rightarrow {}^4T_2$	17.7
21.0 (sh)	20.6 (sh) (125)	$^2T_2 \rightarrow {}^2A_2$	20.6
	22.0 (sh) (185)	$^2T_2 \rightarrow {}^2T_1$	21.6
27.8	28.6 (sh) (2 420)	charge transfer	
32.3 (sh)	32.1 (3 800)	charge transfer	
	39.7 (10 180)	$\pi \rightarrow \pi_1^*$ (pyridine)	

Chloride salt

Solid	Methanol soln.	Assignment	Energy
9.1b		$^6A_1 \rightarrow {}^4T_1$	9.1
16.9	17.2 (10)	$^6A_1 \rightarrow {}^4T_2$	16.9
20.0	19.6 (sh) (14)	$^6A_1 \rightarrow ({}^4A_1, {}^4E)$	20.0
27.4	27.9 (4 000)	charge transfer	
32.3 (sh)	34.5 (sh) (5 800)	charge transfer	
	39.7 (15 200)	$\pi \rightarrow \pi_1^*$(pyridine)	

[a] Band positions in 10^3 cm^{-1}; b = broad, sh = shoulder. [b] *ca.* 10^{-3} mol dm^{-3}, pH 3.7; absorption coefficient (ε/dm^3 mol^{-1} cm^{-1}) given in parentheses. [c] Calculated using 10 Dq = 26 555, B = 995, and C = 2 970 cm^{-1}; at pH 7.1 the predominant species in solution is the dihydroxo-conjugate base (see text) whose visible ligand-field bands are at 10 200b (*ca.* 1), 15 385 (30), 20 830 (125), 22 730 (sh) (185), and 24 100 (sh) (235) cm^{-1}; the energies (in 10^3 cm^{-1}), calculated using 10 Dq = 13 650, B = 673, and C = 2 820 cm^{-1}, are: $^6A_1 \rightarrow {}^4T_1$, 10.0; $^6A_1 \rightarrow {}^4T_2$, 15.4; $^6A_1 \rightarrow ({}^4A_1, {}^4E)$, 20.8. [d] Calculated using 10 Dq = 12 940, B = 981, and C = 2 038 cm^{-1}.

On the other hand, for the diffuse-reflectance and the electronic spectrum of an aqueous solution of $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$, the first two ligand-field bands, having low molar absorption coefficients (Table 4), are reasonably assigned to the spin-forbidden $^2T_2 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_2$ transitions.[26,28] The next two bands, having molar absorption coefficients within the range 120—200 dm^3 mol^{-1} cm^{-1}, may be assigned to the spin-allowed, almost degenerate, pair $^2T_2 \rightarrow {}^2A_2$ and $^2T_2 \rightarrow {}^2T_1$, at energies of $10Dq - 3B - C$ and $10Dq - 2B - C$, respectively.[26] These assignments lead to the values of Dq = 2 655, B = 995, and C = 2 970 cm^{-1} and to the energies reported in the Table. The agreement between the calculated and observed energies is generally good. Furthermore, the condition for spin pairing of a d^5 system ($20Dq > 15B + 10C$) is clearly met and the value of Dq appears reasonable in view of the values of 2 525—2 500 cm^{-1} for some pseudo-octahedral spin-paired ion(III) complexes formed with quinque- or sexi-dentate ligands.[24]

The other bands in the spectra of both samples must arise from Laporte-allowed transitions because of their high intensities. The first two of these, located at *ca.* 28 000 and 32 000 cm^{-1}, may be assigned as charge-transfer transitions whilst the last band within the accessible region of the ultraviolet can be assigned to the $\pi \rightarrow \pi_1^*$ transition of the pyridine groups.[29] Finally, since the visible *d–d* bands of $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$ do not appear to be split, as might be expected from the above Mössbauer results, the complex may be thought to have a *cis* configuration, as for the more widely known octahedral MN_4X_2 chromophores of Co^{III} and Ni^{II}.[3,30] Room-temperature reflectance spectra of *trans* species show a marked splitting of the visible ligand-field bands, in agreement with prediction.[30]

Solution Properties.—The close similarity between the diffuse-reflectance spectrum and the electronic spectral patterns of aqueous solutions of the perchlorate salt (Table 4) seems to suggest that the complex has a similar structure in the solid and in the aqueous state. According to the magnetic and i.r. data, this finding makes it reasonable to formulate the complex as a simple low-spin six-co-ordinate species also in aqueous solution. This is further supported by the fact that for both $[Fe(pmen)(OH_2)(OH)]^{2+}$ and $[Fe(pmen)(OH)_2]^+$ (see later) Beer's law is obeyed over a wide range of concentration (2×10^{-4}—2×10^{-3} mol dm^{-3}), as shown in Figure 1. The occurrence of a monomer–oxo- or hydroxo-bridged dimer equilibrium in solution may be excluded therefore, since the percentage of dimerization should be concentration dependent.

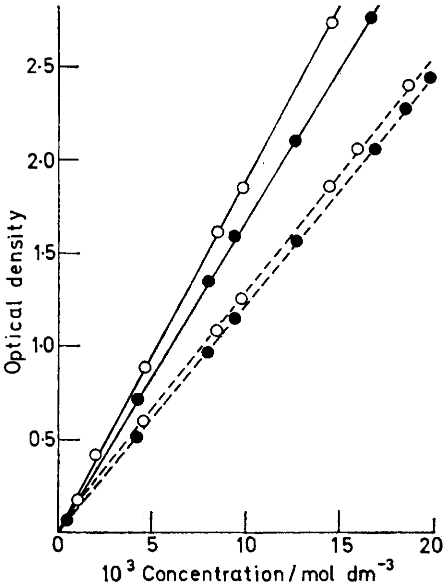

FIGURE 1 Optical density at 450 (——) and 480 nm (— — —) as a function of complex concentration: (○), pH 3.7 ± 0.1; (●), pH 7.2 ± 0.1 (see text). All measurements were normalized for an optical pathlength of 1 cm

Potentiometric titrations (20 °C) indicate that the same complex exhibits the following equilibrium in solution: $[Fe(pmen)(OH_2)(OH)]^{2+} \rightleftharpoons [Fe(pmen)(OH)_2]^+ + H^+$

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($pK_{a,2}$ 4.4 ± 0.1), the visible ligand-field bands of the species being reported in Table 4. On the other hand, conductimetric data on the chloride salt in water indicate that co-ordinated Cl^- ions ionize within the time of solubilization, yielding a diaqua-species. This, according to potentiometric titrations, can give rise to the aquahydroxo- ($pK_{a,1}$ 2.70 ± 0.05) and dihydroxo-forms, whose visible *d–d* transitions are quite similar to those of the perchlorate salt (Table 4). This implies that aquation of $[FeCl_2(pmen)]^+$ effects electron pairing, which is not surprising in view of the fact that low-spin $[Fe(pmen)(OH_2)(OH)][ClO_4]_2$ was obtained from aqueous solutions of the chloride salt. The molar absorption coefficients of the aquahydroxo-cation of the chloride salt (pH *ca.* 3.9) are, however, some 20% lower than those of the perchlorate. This suggests that the chloride solution still contains some high-spin species, possibly the aquachloro-derivative arising from incomplete ionization of Cl^- ions (see later).

E.p.r. measurements at the *X* band on frozen aqueous solutions * of $[Fe(pmen)(OH_2)(OH)]^{2+}$ (pH *ca.* 3.9) apparently contradict the above conclusion. In fact, under the experimental conditions used, the spectra did not show any detectable resonance in the $g_{eff.}$ 2 region, which is characteristic of spin-paired d^5 systems.[31,32] It has been reported recently, however, that anomalously weak signals are often observed in low-spin iron(III) complexes,[31] as also found in some spin-paired iron(III) derivatives of biological significance.[33] In contrast, weak lines were detected in the 800—1 600 G region, where signals from a $S = \frac{5}{2}$ system might be expected. A solution of the chloride (pH 3.9) showed a weak–medium resonance at 1 520 G ($g_{eff.}$ 4.29), known to be characteristic of high-spin iron(III) complexes in certain stereochemistries [31,34] (Figure 2). With increased pH, *i.e.* when $[Fe(pmen)(OH)_2]^+$ becomes predominant, this signal increased sharply in all samples, as illustrated in Figure 3, where the e.p.r. titration curve of $[Fe(pmen)(OH_2)(OH)]^{2+}$ is shown together with the corresponding potentiometric curve. Therefore the weak resonance at 1 520 G detected in the aqueous acidic solutions (pH *ca.* 3.9) may be reasonably ascribed to small amounts of the dihydroxo-complex, in agreement with the above equilibrium. On the other hand, the finding that the same resonance is somewhat reinforced in the acid solution of the chloride salt (Figure 2) may be ascribed to the presence of some additional high-spin species (aquachloro-derivative), as already suggested from the absorption spectra. It may be concluded that the dihydroxo-conjugate base is a high-spin complex characterized by rhombic anisotropy. Consistently, the assignment of the visible ligand-field bands of $[Fe(pmen)(OH)_2]^+$ to transitions from a spin sextet ground state leads to calculated energies which agree satisfactorily with the experimental energies (Table 4).

E.p.r. signals with *g* values of *ca.* 4.29 have been found for a number of non-haem iron(III) proteins [33] and have been reported to occur in high-spin ($S\ \frac{5}{2}$) systems having certain stereochemistries.[34] For example, the MX_3Y_3 chromophore with a pseudo-octahedral meridional configuration (C_{2v}) can give rise to such a resonance.[31,34] The signal with a *g* value of 4.29 observed in the spectra of $[Fe(pmen)(OH)_2]^+$ (Figure

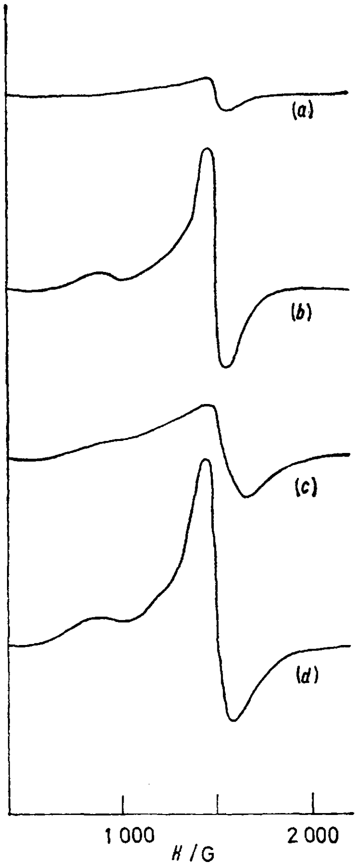

FIGURE 2 E.p.r. spectra of frozen aqueous solutions of the perchlorate, (*a*) and (*b*), and chloride, (*c*) and (*d*), salts at the *X* band. Curves (*a*) and (*c*), pH 3.9 ± 0.1; (*b*) and (*d*), 7.1 ± 0.1 (referred to room temperature). The concentration was *ca.* 5×10^{-3} mol dm^{-3}

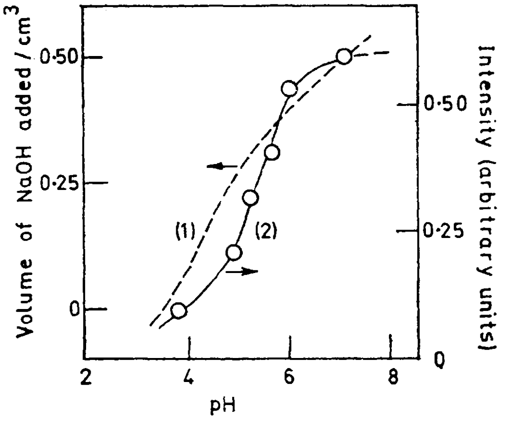

FIGURE 4 Potentiometric [curve (1)] and e.p.r. [(2)] titration of $[Fe(pmen)(OH_2)(OH)]^{2+}$ (perchlorate salt). Curve (1), 293; (2), 90 K (the intensity refers to a signal at 1 520 G)

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* Measurements were carried out at *ca.* 90 K in order to minimize the effects of spin–lattice relaxation and spin–spin interaction, both of which can broaden the e.p.r. lines. $g_{eff.}$ Is defined as $h\nu/\beta H$. We thank Professor D. Cordinschi for these data.

[31] S. A. Cotton and J. F. Gibson, *J. Chem. Soc.* (*A*), 1971, 803, 1696.

[32] R. E. De Simone, *J. Amer. Chem. Soc.*, 1973, **95**, 6238.

[33] J. Peisach and W. E. Blumberg, 'Metalloproteins as Studied by Electron Paramagnetic Resonance,' in 'Electron Spin Resonance of Metal Complexes,' ed. Teh Fu Yen, A. Hilger, London, 1969, p. 73, and refs. therein; G. Palmer and H. Brintzinger, *Nature*, 1966, **211**, 189.

[34] J. S. Griffith, *Mol. Phys.*, 1964, **8**, 213.

2) could be interpreted, therefore, as arising from a $[FeN_4O_2]$ chromophore in a pseudo-octahedral *cis* configuration (C_{2v}). This assignment is consistent with stereochemical considerations in that a *trans* arrangement of the facultative ligand around the metal ion would be destabilized chiefly by steric hindrance between the hydrogen atoms of the adjacent pyridyl residues. Most of the available data on quadridentate nitrogen chelate systems of Co^{III} and Ni^{II} show that *cis*-$[MN_4X_2]$ species are definitely favoured over *trans*.[3,35] The same arguments apply to the low-spin complexes and the diffuse-reflectance spectrum of the perchlorate has already been shown to be suggestive of a *cis* configuration.

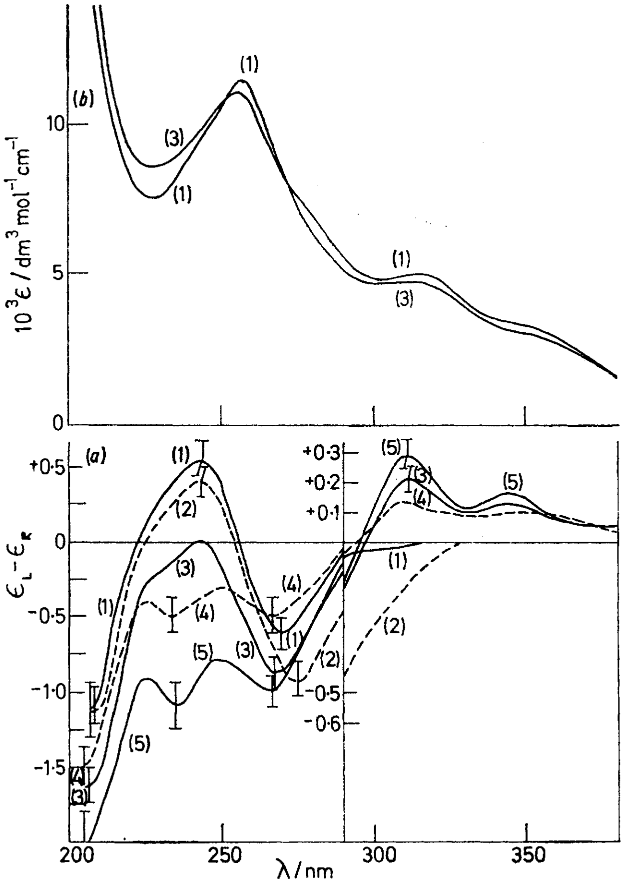

FIGURE 4 Circular dichroism, (*a*), and absorption spectra, (*b*), of the complexes in aqueous solution, in the presence of sodium dextran sulphate. Curve (1), pH 5.0; (2), 5.8; (3), 7.0; (4), 7.4; (5), 7.8. At pH 5 the predominant species in solution is $[Fe(pmen)(OH_2)(OH)]^{2+}$ whilst at pH 7.8 it is $[Fe(pmen)(OH)_2]^+$ (pK_a 6.5; see text). Curves (1), (3), and (5) refer to chloride, (2) and (4) to the perchlorate salt. Complex to polymer molar ratio, 0.15 : 1 (degree of association >90%); polymer concentration, 7.4×10^{-4} mol dm^{-3} (referred to monomeric unit)

Finally, the aquahydroxo-species were rather labile at room temperature. According to spectrophotometric measurements, the dissociative process (giving rise to the free ligand) takes place with a half-life of 30 h (25 °C). Below 10 °C, the reaction was much slower and at *ca.* 5 °C the samples were unaltered for more than 15 d, within the pH region (3.0—7.5) explored ([Fe] = 0.01 mol dm^{-3}). We did not make any systematic investigation of the effect of ionic strength on this reaction.

Circular-dichoism Spectra.—Figure 4 illustrates the c.d. spectra arising from the interaction of the complexes, at different pH values, with an optically active polyelectrolyte, namely sodium dextran sulphate (Na[ds] *M* 500 000, Sigma Chemical Co, U.S.A.). It is well known that the interactions of the enantiomers of an asymmetric molecule with a dissymmetric environment must be different.[36] This also happened when the present iron(III) complexes were allowed to interact with Na[ds] in aqueous solution. The chiral *cis* arrangement of the ligand around the central metal ion gives rise to two enantiomers (Λ and Δ) [37] for each geometrical isomer. The dichroic bands in Figure 4 must arise, therefore, because the dissymmetric substrate perturbs the two forms differently (see later), though they might also arise from some selective binding.[38] Preliminary back-dialysis experiments rule out, however, the latter possibility.

The most important result is the dramatic variation of the spectral patterns as the pH is increased, which suggests the occurrence of a stereochemical change in going from low-spin $[Fe(pmen)(OH_2)(OH)]^{2+}$ to high-spin $[Fe(pmen)(OH)_2]^+$. In this connection, it is stressed that: (*i*) the c.d. bands in Figure 4 arise solely from electronic transitions of the complex molecules because the macroion absorbs only beyond the accessible region of ultraviolet; (*ii*) under the same experimental conditions, no optical activity was observed when iron(III) ions or the free ligand were added to an aqueous solution of dextran sulphate; (*iii*) the change in sign of the rotational strength of the bands centered at *ca.* 310 and 240 nm as the pH is increased from 5 to 7.8 does not reflect any conformational transition of the polymer. [In fact, the o.r.d. of dextran sulphate, within the range 250—550 nm, is quite similar at both pH 4.8 and 7.5, as illustrated in Figure 5. In the same Figure, it can be seen that the polyelectrolyte follows the simple Drude equation $\alpha_m = K/(\lambda^2 - \lambda_c^2)$, within the wavelength region explored ($K = 3.5 \times 10^6$, $\lambda_c = 136$ nm)]; (*iv*) the different c.d. patterns of the aquahydroxo- and dihydroxo-cations cannot be ascribed to different degrees of association with the macroion since, according to equilibrium dialysis measurements at 8 °C (data not given here), in all cases the per-

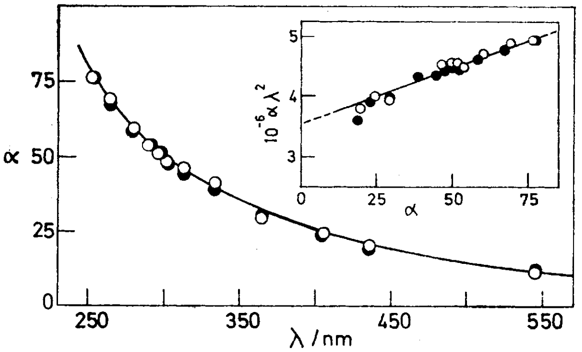

FIGURE 5 Optical rotatory dispersion of sodium dextran sulphate in aqueous solution: (○), pH 4.8; (●), 7.5. Insert: plot of the one-term Drude equation

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[35] R. D. Gillard and H. M. Irving, *Chem. Rev.*, 1965, **65**, 603.

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[37] *Inorg. Chem.*, 1970, **9**, 1.

[38] V. Crescenzi and B. Pispisa, *J. Polymer Sci.*, 1968, **6**, 1093.

centage of the complex which is associated is comparable ($>90\%$); and (*v*) the pK_a of the equilibrium $[Fe(pmen)(OH_2)(OH)]^{2+} \rightleftharpoons [Fe(pmen)(OH)_2]^+ + H^+$, referred to bound molecules, is 6.5 ± 0.1 in all cases, according to potentiometric titrations (20 °C) in the presence of dextran sulphate.

On the basis of the above results and on the finding that electronic and e.p.r. spectra of complex–dextran sulphate systems closely resemble those of the iron(III) complexes in the absence of dextran sulphate, it may be concluded that, under the experimental conditions used, the overall structural features of the associated molecules are practically the same as those of the complexes in the absence of added polyelectrolyte.

DISCUSSION

Stereochemical considerations suggest that the iron(III) complexes investigated have a *cis* configuration, consistent with the overall spectral data obtained in the solid state and in aqueous solution. Furthermore, it has been shown that for a number of quadridentate nitrogen chelate systems of Ni^{II} and Co^{III} a *cis* geometry is preferred over *trans*.[3,35] Nevertheless, there is no significant experimental evidence yet to distinguish with confidence which of possible *cis* configurations is favoured, but c.d. data can afford good insight into the problem on the assumption that the complex–polymer interaction does not alter the structural features of the complexes under examination, as suggested by the electronic and e.p.r. spectra.

Much of the observed behaviour may be explained by the stereochemical demands of the complexes on variation of the spin state of the iron. The reduced paramagnetism of the aquahydroxo-cation would imply shorter iron–nitrogen bond distances than those of the high-spin dihydroxo-species.[12,13] According to molecular models, in this case non-bonded interactions between neighbouring hydrogen atoms of the aliphatic NH groups and the terminal pyridyl residues would make the *cis*-α configuration the more crowded the closer the ethylenediamine ring is to a *gauche* conformation, which represents the best approximation to an unstrained arrangement for a five-membered ring.[39] In the notation of some authors,[2a,3] we could say that the low-spin complex would prefer a *cis*-β configuration, because it alleviates ' B strain '. In contrast, a radial expansion of the central metal ion, as expected for the high-spin species, accentuates conformational strains in the five-membered ring [2a] (' E strain ') but relieves ' B strain '. In this case the *cis*-α geometry would be preferred because it reduces ' E strain '. These assignments, based on qualitative stereochemical considerations, are supported by the results of the induced c.d. bands for the pyridine $\pi\rightarrow\pi^*$ transitions. We confine the discussion to these transitions since at present only the ligand-localized bands can be used to connect the configuration of metal complexes with the sign of c.d. on a purely spectroscopic basis.[40]

When the *cis*-α geometry is taken into account, one would expect a lack of coupling between the transition moments of the pyridyl residues, since they are far away in the molecule. On the other hand, when the *cis*-β arrangement is considered, exciton coupling may be predicted,[40] giving rise to a c.d. with negative and positive components. This is indeed the case (Figure 4). High-spin $[Fe(pmen)(OH)_2]^+$, whose configuration was assumed to be of the *cis*-α type, exhibits c.d. spectral patterns which are characterized by the overlapping of negative bands centered at *ca.* 263 and 235 nm. In contrast, low-spin $[Fe(pmen)(OH_2)(OH)]^{2+}$, to which a *cis*-β configuration was assigned, shows a spectrum consisting of two bands of opposite sign centered at 273 and 240 nm.

The finding that in the latter case the rotational strength of the positive and negative bands is markedly different may be ascribed to the presence of a negative band at *ca.* 235 nm (as found in the other spectra), which subtracts rotational strength from the positive band at 240 nm. The pronounced asymmetry of this band is clear confirmation of such a conclusion. It is to be noted that the trend of this spectrum [curves (1) and (2) of Figure 4] could also fit qualitatively to a *trans* (distorted) [3] configuration; however, this was excluded on the basis of electronic and e.p.r. spectra as well as on stereochemical considerations.

Finally, if the Λ and Δ enantiomers of a given geometrical isomer had been resolved (attempted resolutions were unsuccessful), each stereoisomer, in the absence of the optically active polyelectrolyte, would have obviously displayed equal chiroptical properties although of opposite sign. In contrast, our samples are racemic mixtures. Therefore, on addition of dextran sulphate the complexes show c.d. patterns which are actually difference spectra, *i.e.* spectra of a mixture of diastereoisomers, due to the fact that the dissymmetric substrate perturbs the *d* and *l* forms to different extents.[36] This accounts for the low value of the ellipticity (Figure 4) compared, for example, with those exhibited (within the same range of wavelength, corresponding to $\pi\rightarrow\pi^*$ transitions of the ligands) by $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl)[40] or $[Co\{(+)mpmen\}X_2]^+$ [mpmen = *N*-methyl-*N′N′*-bis(2-pyridylmethyl)ethylenediamine] [41] complexes.

It is worth noting, however, that the c.d. spectra of *cis*-β isomers of $[Co\{(+)mpmen\}X_2]^+$ display a negative–positive pattern [41] reminiscent of that found for the low-spin iron(III) complex to which was assigned a *cis*-β configuration. The *cis*-α cobalt(III) complexes, on the other hand, do not present any exciton splitting,[41] as also predicted for our complex with the same geometry. These results provide additional support for the above assignments and thus for the idea that the stereochemistry

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[41] J. Cragel, jun., and G. R. Brubaker, *Inorg. Chem.*, 1972, **11**, 303.

of the complexes investigated is closely connected with the spin configuration of the iron. A definite confirmation must await the *X*-ray structure determination, which is in progress. Further experiments are needed to elucidate the mechanism of the stereochemical rearrangement which accompanies the variation of the spin state of iron.

We thank Mr. G. Minelli for assistance in some experiments.

[5/704 *Received*, 14*th April*, 1975]