An Investigation of the Co-ordination Properties of (2,3,7,8,12,13,17,18-Octamethylcorrolato)iron(III) by Nuclear Magnetic Resonance Spectroscopy†

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The reactivity of (2,3,7,8,12,13,17,18-octamethylcorrolato)iron(III) towards axial ligands such as pyridine, chloride and isocyanide has been studied by means of optical and ^{1}H NMR spectroscopy. Relaxation rate measurements and analysis of the temperature dependence of the isotropic shifts are indicative of an $S = \frac{1}{2}$ spin state for the complex in chloroform solution, whilst its pyridine adduct exhibits a mixed spin state for the metal atom. The existence in chloroform solution of two different species related to a chloride binding equilibrium has been demonstrated by a saturation transfer experiment. Both ^{1}H NMR and electronic spectra of the complex are indicative of the formation of molecular complexes between different macrocyclic rings competing with axial ligation.

Great interest has been devoted to the study of transition-metal complexes of tetrapyrrolic macrocycles because of their similarity to biologically important systems and wide applications in catalysis and photocatalysis.[1,2] Nevertheless little has been published about corrole and its derivatives.[3–7]

The synthesis and characterization of corrole and its metal complexes has been a major concern to us in recent years.[8,9]

Corrole (Fig. 1) is a tetrapyrrolic macrocycle that has a structure intermediate between porphyrin, the prosthetic group of haemoproteins and corrin, the nucleus of the vitamin B_{12} coenzyme; it has a direct link between the A and D pyrrole rings. By lacking a C(20) *meso* carbon bridge the system resembles the corrin skeleton although the hybridization of C(1) and C(19) is believed to be sp^2. An 18-electron π system involving complete conjugation confers to this macrocycle an aromatic character similar to that of the porphyrin ring.[3]

Aromaticity is confirmed by its electronic spectrum, which is characterized by two intense absorptions centred at about 400 and 600 nm. These bands have been attributed to π to π^* transitions similar to the Soret and Q bands observed in the spectra of porphyrins. The marked broadening of the higher energy band, with respect to the corresponding one observed in the spectra of porphyrins, is probably attributed to the existence of two or more unresolved bands due to a number of transitions caused by the lower symmetry of corrole. The C_4 symmetry axis is in fact reduced to a symmetry plane by the presence of the direct pyrrole–pyrrole bond.[4]

The ^{1}H NMR spectrum of corrole shows the existence of downfield shifted resonances due to anisotropic chemical shift effects caused by the local magnetic field induced by the current of electrons of the aromatic ring.[10]

The reactivity of tetrapyrrolic macrocycles with transition-metal ions is relevant both from a co-ordination chemistry point of view and from the formulation of potentially important catalytic compounds.[11] As far as its co-ordination chemistry is concerned, corrole having three amino-like nitrogens acts as a trianionic ligand stabilizing the metal(III) oxidation state with the formation of neutral complexes. We have previously reported on the preparation and characterization of several metal(III) corrolates and established three efficient and reproducible synthetic procedures.[8,9]

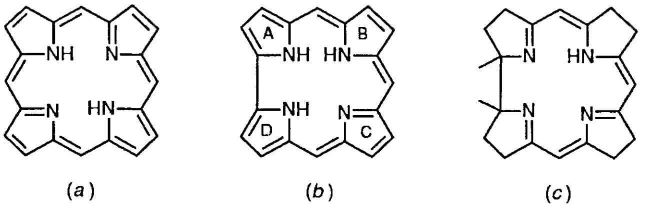

Fig. 1 The structural formulae of porphyrin (*a*), corrole (*b*) and corrin (*c*)

We now report a study on the paramagnetic iron derivative (2,3,7,8,12,13,17,18-octamethylcorrolato)iron(III), [Fe(omc)], which is focused on its electronic state determination and ligand-binding properties in solution. Such information can be extracted from the ^{1}H NMR isotropic shifts and relaxation properties.

Proton NMR provides a powerful tool for investigating paramagnetic complexes: paramagnetism permits the resolution of magnetically non-equivalent environments that cannot be resolved in a comparable diamagnetic system. The presence of unpaired electrons also leads to a great expansion of the chemical shift range of the observed resonances and since the chemical shift differences between exchanging environments are likely to be very large the characterization of fast dynamic processes is made possible.[12] A drawback may be that the presence of paramagnetic centres induces a marked broadening of the resonances with a consequent loss of the spectroscopic detail, *e.g.* splitting due to the proton–proton coupling constant, together with relevant information about the molecular structure or conformation present therein. In our case, however, this effect has not been considered a major problem because all the resonances under examination are expected to be singlets.

Experimental

(2,3,7,8,12,13,17,18-Octamethylcorrolato)iron(III) was prepared according to the procedure reported previously[9] and purified by recrystallization from diethyl ether–pentane (1:2).

All chemicals (Farmitalia) were reagent grade and used as received. Deuteriated solvents were purchased from Aldrich and used without further purification.

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† *Non-SI unit employed:* BM = 9.274×10^{-24} J T^{-1}.

Table 1 Electronic absorption data for [Fe(omc)] in different solvents

Solvent	λ_{max}/nm	$10^{-4}\ \varepsilon$/dm^3 mol^{-1} cm^{-2}
Benzene	370	3.23
Chloroform	370	2.52
Tetrahydrofuran	385	4.66
	546	0.97
Pyridine	395	4.04
	546	0.92

Table 2 Spectral properties for [Fe(omc)] in pyridine[a]

			Variable temperature plot			
Label	I[b]	δ	10^{-4} slope/K^{-1}	Intercept	T_1[c]/ms	T_2[c]/ms
A	3	131.0	3.91	4.53	1.6	1.3
B	3	75.0	1.80	17.16	4.8	3.2
C	3	56.4	*d*	*d*	6.1	3.9

[a] Resonances are assigned to the methyl group protons. [b] Intensity. [c] ±10%. [d] The Curie plot relative to this resonance is not linear (see text).

Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature, IR spectra on a Perkin-Elmer Model 983 spectrophotometer as chloroform solutions and NMR spectra on a Bruker WP 80 SY spectrometer at the probe temperature (305 K). Typical NMR spectra consist of 1024 transients of 8192 data points over a 31 kHz bandwidth using a 2.8 μs 90° pulse. Chemical shifts are given from tetramethylsilane ($SiMe_4$) referenced against residual solvent signals. The concentrations of [Fe(omc)] solutions were in the range 10^{-2}–10^{-4} mol dm^{-3}.

The T_1 relaxation times were measured using the standard (180–τ–90) inversion recovery pulse sequence with a repetition rate of 1.1 s^{-1}. Data were analysed by a linear regression routine on semilogarithmic plots. Mean-square errors did not exceed 10%. The T_2 spin–spin relaxation times were estimated from the half-height linewidth of the resonances.

Magnetic susceptibilities in solution were determined according to literature methods.[13,14] Magnetic moments were calculated according to Timkovich and Cork.[15]

Saturation transfer experiments were carried out with a recycle time of 2 s, irradiating the resonance of interest with a selective decoupling pulse length corresponding to a bandwidth of about 3–5 Hz and substracting the spectrum from that obtained in the same experimental conditions but irradiating off-resonance.

Results and Discussion

Optical Spectroscopy.—The electronic spectrum of [Fe(omc)] in pyridine is characterized by an intense Soret-like absorption in the high-energy region and by an additional band at 546 nm (Table 1).

The spectrum is very similar to that reported for the same complex in tetrahydrofuran (thf)[9] and confirms the hypothesis that the low-energy band may be correlated to axial co-ordination.

The spectra in non-co-ordinating solvents such as benzene or chloroform show only one resolved band centred at 370 nm.

NMR Spectroscopy.—The 80 MHz NMR spectra of [Fe(omc)] have been found to be characterized, as expected, by resonances which show rather large linewidths. This is mainly due to the presence of effective transverse relaxation caused by the presence of unpaired electrons interacting with the aromatic macrocyclic ring. Large isotropic shifts due to coupling of the σ orbital of the metal ion with the nuclear dipole of hydrogen nuclei of the macrocyclic ring are also present.

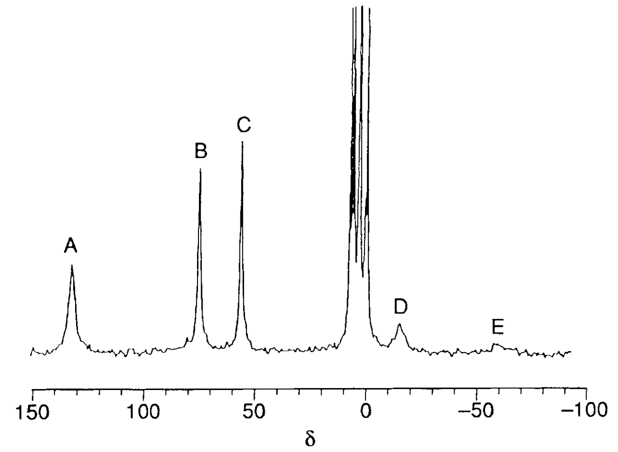

Fig. 2 ^{1}H NMR spectrum of [Fe(omc)] in [$^2H_5$]pyridine. Labels refer to the assignments reported in Table 2.

The spectra were found to be largely dependent on the nature of the solvent. Such dependence is only partially a result of the solvent effect usually observed in NMR spectroscopy and must be ascribed to the possibility of axial co-ordination of the iron inserted in the corrole ring. Thus a study in different solvents such as pyridine and chloroform, with some complication with respect to its acidic impurities, has been carried out in order to understand the difference in the co-ordination behaviour.

NMR spectra in pyridine. The 80 MHz ^{1}H NMR spectrum of [Fe(omc)] in pyridine is reported in Fig. 2 and reveals three isotropically shifted resonances of equal intensity that are clearly due to the methyl groups present in the pyridine adduct of the complex (labelled A, B and C). Since four peaks are expected on the basis of symmetry considerations we conclude that the fourth most probably lies under the intense diamagnetic resonances due to the solvent residual signals. The weak peaks at high field (D and E) can be attributed to the residual protons of deuteriated pyridine bound axially to iron. The chemical shift values are given in Table 2. The large values of the isotropic shifts and the values of the relaxation rates (see later) seem to indicate a high-spin ground state for the metal ion.[16]

A magnetic moment (μ) measurement was thus performed in order to ascertain the correct metal spin state for [Fe(omc)] in pyridine. The value obtained, 4.30 BM, is consistent with a mixed spin state ($S = \frac{1}{2}, \frac{5}{2}$) for iron in this complex.[17]

NMR spectra in chloroform. The 80 MHz ^{1}H NMR spectrum of [Fe(omc)] in chloroform is shown in Fig. 3(*a*). The chemical shifts of the isotropically shifted resonances are reported in Table 3. together with other spectral properties. The assignments were made by using a variety of arguments that are summarized as follows.

The most downfield shifted resonances [M_1 and M_2, inset of Fig. 3(*a*)] have been assigned to the *meso* protons of the corrole ring because of their proximity to the paramagnetic centre. The relative value of the integral ratio, *i.e.* 1:2, is in agreement with the existence of a C_2 symmetry plane secating the C(1)–C(19) bond and the C(10) atom.

The same symmetry considerations should lead to the observation in the ^{1}H NMR spctrum of [Fe(omc)] of four resonances due to the eight methyl groups. The similarity of the linewidths of the methyl group proton resonances indicates that they lie at essentially identical distances from the paramagnetic centre.

The observation of eight resonances of equal intensity may be explained either by the disruption of the symmetry or, most probably, by the existence of different chemical species that could be either isomers or species in equilibrium with low exchange rate dynamics.

The X-ray crystal structure of [Rh(omc)($AsPh_3$)][9] shows, at least in the solid state, that the complex does not deviate significantly from planarity. The complex [Fe(omc)] is not

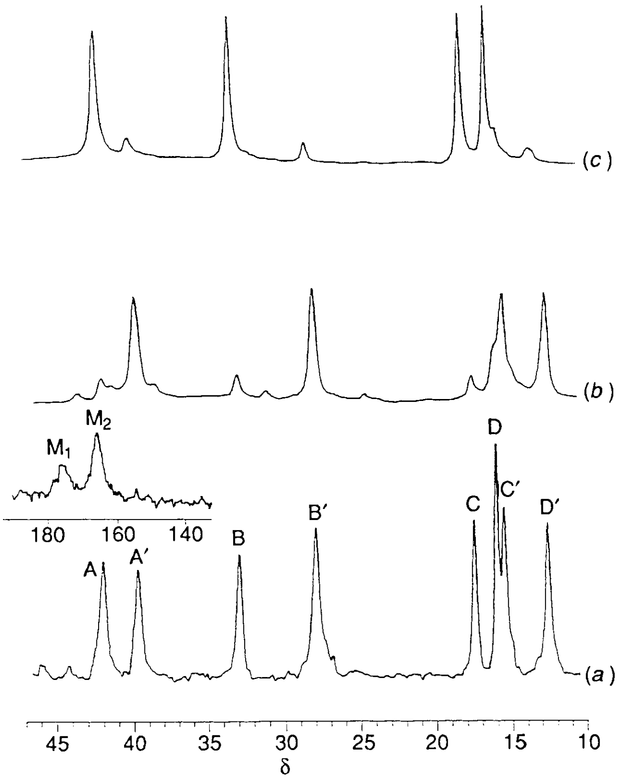

Fig. 3 ^{1}H NMR spectra of [Fe(omc)] in $CDCl_3$. Inset, δ 130–190, refers to spectrum (*a*). (*a*) In $CDCl_3$, (*b*) resulting from the elimination of chloride by treatment of the same sample with $AgNO_3$ and (*c*) the sample of (*a*) after addition of an excess (1:100) of $NEt_3(CH_2Ph)Cl$

Table 3 Spectral properties for [Fe(omc)] and [Fe(omc)(Bu^{t}NC)]^a in $CDCl_3$

			Variable temperature plot			
Label	I^b	δ	10^{-4} slope/K^{-1}	Intercept	$T_1{}^c$/ms	$T_2{}^c$/ms
M_1	1	175.1	5.29	−3.65	*d*	0.8
M_2	2	165.6	5.76	−8.67	*d*	1.1
A	3	41.9	1.54	−8.06	20	12
A′	3	39.7	1.43	−6.48	20	10
B	3	31.4	1.32	−9.71	22	14
B′	3	28.2	1.06	−6.25	28	11
C	3	18.1	0.79	−8.03	28	15
D	6	16.6	0.61	−3.35	37	*e*
C′		16.1	—	*d*	26	*e*
D′	3	13.3	0.51	−3.66	21	13
A_i	3	41.9	*d*	*d*	21	16
B_i	3	32.9	*d*	*d*	21	14
C_i	3	17.8	*d*	*d*	29	16
D_i	3	16.5	*d*	*d*	34	19

[a] The resonances due to the isocyanide complex have been labelled with subscript i. [b] Intensity as the number of protons. [c] ±10%. [d] Not determined. [e] The peaks are buried under envelopes.

expected to behave differently from the analogous rhodium complex and does not probably exhibit any distortion that can lead to an alteration of the C_2 symmetry axis. Nevertheless the multiplicity of resonances found for the methyl groups indicates that the macrocyclic ring exists in two major chemical and magnetic environments. The hypothesis that these environments stem from the existence of axial ligation in one of the two species has thus been explored. The possibility that chloride ions present in the deuteriochloroform (as hydrogen chloride impurity) could act as axial ligands has therefore been considered.

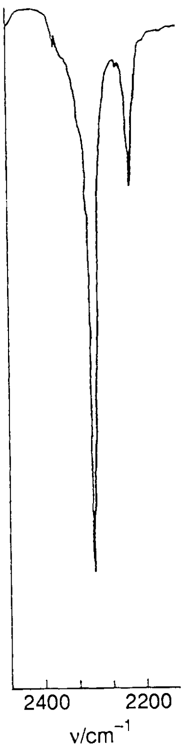

Fig. 4 IR spectrum of [Fe(omc)(Bu^{t}NC)] in chloroform

Addition to the sample of silver nitrate, vigorous shaking of the mixture, centrifugation and elimination of the supernatant, gave a sample whose ^{1}H NMR spectrum showed the almost complete disappearance of some of the resonances observed previously [Fig. 3(*b*)]. The resonances now observed are labelled A′, B′, C′ and D′ thus indicating that they correspond to protons belonging to the same chemical species which is not involved in the interaction with chloride ions. The sample tends to return back to the equilibrium condition and the second chemical species is regenerated with time. After a few hours an increase in intensity of resonances A, B, C and D was observed. Equilibrium is reached after 3 d when the original spectrum was again observed, completely recovered. The reason for such reversibility may be ascribed to the oxidative decomposition of chloroform generating $COCl_2$, Cl_2 and HCl.[18]

The hypothesis of axial ligation was explored further and chloride ion (in the form of benzyltriethylammonium chloride) was added to the solution. The resulting spectrum, consisting of only four major peaks (*i.e.*, A, B, C and D), is shown in Fig. 3(*c*).

In order to verify the occurrence of axial ligation t-butyl isocyanide was added to a chloroform solution of [Fe(omc)]. Only one of the two patterns of hyperfine shifted resonances observed in pure chloroform (*i.e.*, A, B, C and D) was present in the resulting ^{1}H NMR spectrum (not shown). The resonance due to the t-butyl group fell in the diamagnetic region of the spectrum. Spectral data for the isocyanide derivative are also reported in Table 3.

Together with the NMR evidence the presence of a band at 2250 cm^{-1} in the IR spectrum of the mixture confirms the co-ordination of isocyanide (Fig. 4). The frequency of the ν(C≡N) vibrational motion is increased upon co-ordination (Δν = 200 cm^{-1}) indicating a higher bond order in the complex than in the free ligand that can be attributed to the good donor properties of isocyanides to Fe^{III}.[19,20]

Saturation transfer experiment. In order to assess that the two species observed belong to a unique equilibrium, either chemically as different compounds or conformationally as different conformers, a saturation transfer experiment was carried out.

Selective saturation of one resonance with a proper (see

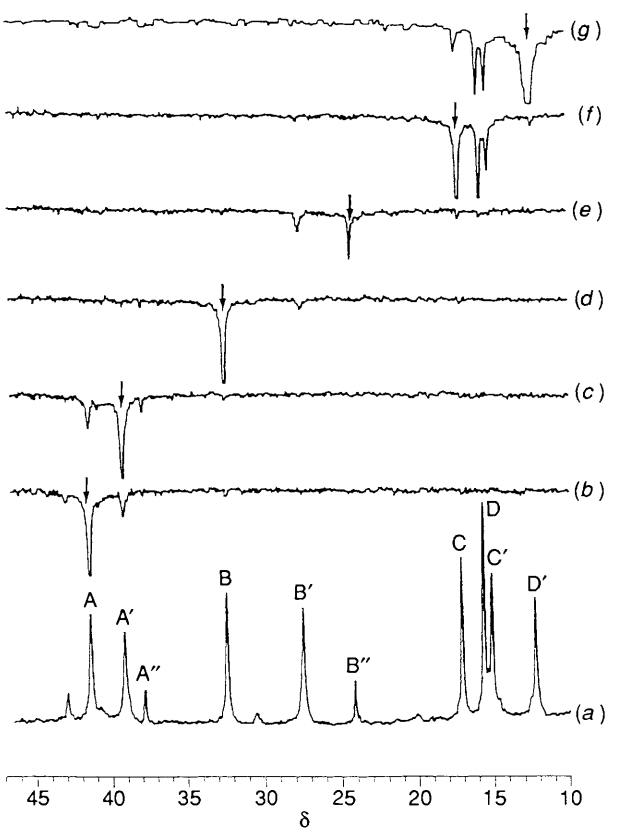

Fig. 5 ^{1}H NMR saturation transfer experiment. Traces (*b*)–(*g*) [expanded vertically four times with respect to trace (*a*)] show the difference spectra obtained by subtracting the reference spectrum (*a*) from the irradiated spectrum. Arrows indicate the saturated resonances

Experimental) irradiation power with acquisition by a non-selective pulse after a delay time, gives a spectrum where the irradiated resonance disappears. In the absence of magnetization transfer due to chemical or conformational exchange dynamics, the subtraction from such a spectrum of a reference spectrum obtained by irradiating far from the region of interest should give a trace where the only peak would be that corresponding to the irradiated resonance.

In the case of exchange, the excited nuclei share their saturation in the different magnetic environments which are in equilibrium. Thus the intensity of the resonances due to the same proton during its migration in a different chemical or magnetic environment are altered. The difference spectrum will give difference peaks indicating the saturation transfer and thus proving the existence of the chemical or conformational equilibrium.

The results reported in Fig. 5 clearly demonstrate that the multiplicity of the resonance observed is due to an equilibrium between different compounds. In fact spectra (*b*), (*c*) and (*d*) indicate the transfer of saturation bwetween resonances A A′ and B B′ respectively.

The presence and intensity of resonances A″, B″ *etc.* is largely dependent on the batch of deuteriated chloroform used.

The difference spectrum (*e*) where the resonance labelled B″ was irradiated indicates that this resonance belongs to a minor equilibrium also involving B.

The saturation transfer between C and C′ and between D and D′ is confirmed from the difference spectra (*f*) and (*g*) although the spillover of the irradiation power produces some effects because of the close proximity of the resonances.

The possibility arises that the observed species consist of macrocycles where a chloride ion is bound axially to iron, the unligated complex or aggregates where the axial position is essentially free and the electronic π system gives rise to stacking interactions. In this last case the chemical shift difference observed can be accounted for by the summation over a short distance of contributions due to different ring current effects arising from the overlap of different corrole rings.[21]

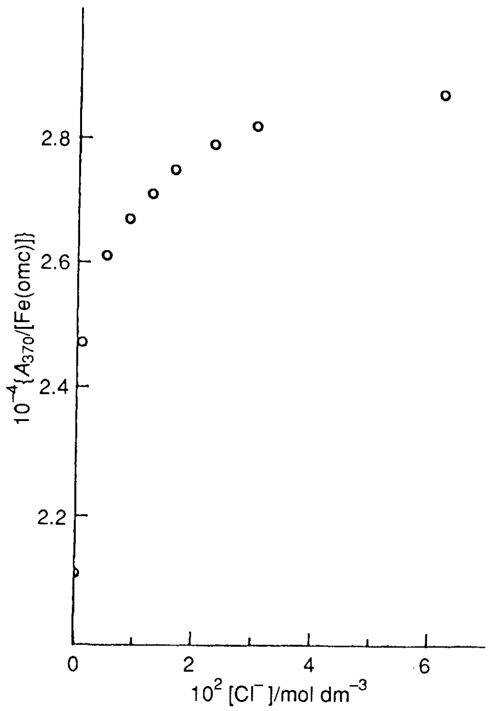

Fig. 6 Effect of chloride concentration on the intensity of the 370 nm absorption in the electronic spectrum of [Fe(omc)] in chloroform

The electronic spectra of [Fe(omc)] in the presence of several anions has been recorded. No variation was observed upon addition of non-co-ordinating anions such as perchlorate or tetrafluoroborate to a chloroform solution of [Fe(omc)], whilst the addition of chloride ions caused a marked increase in intensity of the absorption at 370 nm (Fig. 6). It has been reported that formation of molecular complexes between metalloporphyrinates and electron acceptors can be evidenced by loss of intensity and red shifts in the Soret region.[22] The formation of π complexes is a well established property of porphyrins and is demonstrated by their tendency to form aggregates with themselves or other aromatic molecules. Furthermore it is easier for intermolecular interactions to occur in the case of corrole than in analogous complexes of porphyrins or chlorin since no repulsion between electrically charged species has to be overcome in order for two or more macrocycles to come close to each other. The data presented in Fig. 6 have been analysed by using a plot of $[L]/\alpha$ *vs.* $(1/1 - \alpha)$, where [L] is the chloride concentration and α is the fraction of bound complex. The plot (not shown) exhibits linear behaviour and gives a value of $K = 309 \pm 40$ for the chloride binding equilibrium.

Such a value, together with the absence of any dependence on concentration in the range suitable for an NMR investigation, *i.e.* 10^{-2}–10^{-4} mol dm^{-3}, indicates that the aggregation equilibrium is shifted strongly towards the aggregated form.

Temperature dependence. The temperature dependences of the isotropic shifts of the protons of [Fe(omc)] in chloroform and pyridine are shown in Figs. 7 and 8 respectively.

In chloroform solution it can be seen that the shifts vary linearly with reciprocal temperature in the Curie plots reported in Fig. 7.

It is well known[12] that a linear Curie temperature dependence can be expected when co-ordination occurs between ligand orbitals and a paramagnetic metal in a pure spin state. In this case the extrapolated values should be close to the corresponding values from the ^{1}H NMR spectrum of

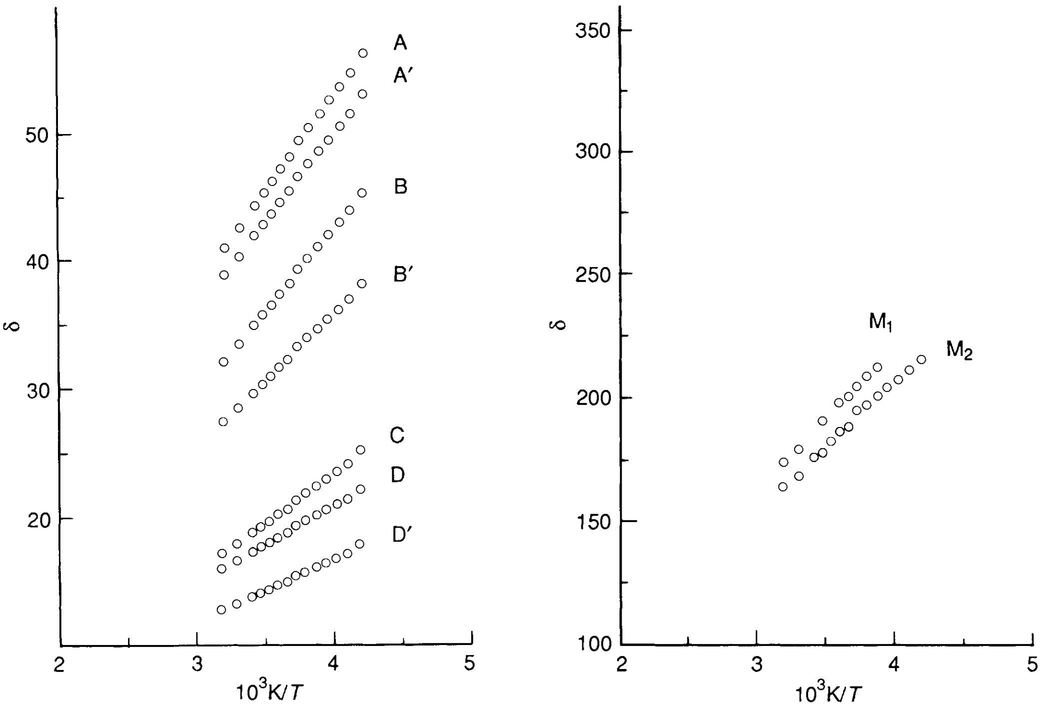

Fig. 7 Temperature dependence of the isotropic shifts of the resonances due to the methyl groups and *meso* protons of [Fe(omc)] in $CDCl_3$. Labels refer to the assignments reported in Table 3

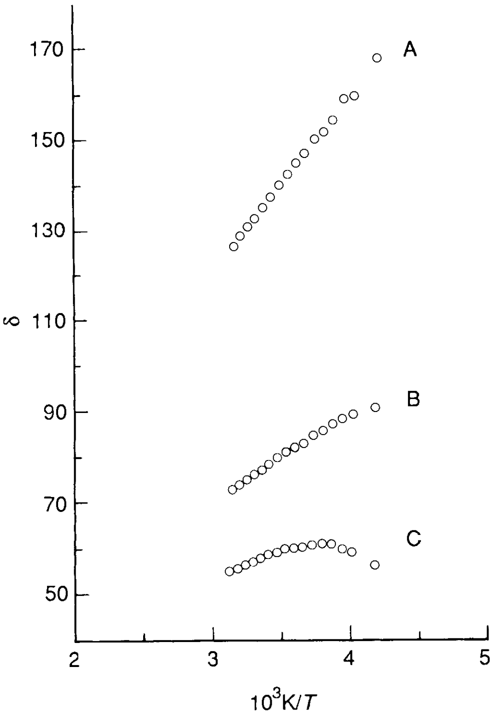

Fig. 8 Temperature dependence of the isotropic shifts of the resonances of the methyl protons of [Fe(omc)] in pyridine. Labels refer to the assignments reported in Table 2

the diamagnetic ligand. Deviation from linearity is indicative of a different distribution of the unpaired electron density in the complex.

For a d^5 high-spin ion such as Fe^{III} the *g* tensor is highly isotropic which would normally lead to a negligible dipolar component of the isotropic shift. Sizable dipolar shifts can however arise as a result of the anisotropy of the zero-field splitting. Such dipolar shifts have a characteristic dependence on the reciprocal of the square of temperature in contrast to the contact contribution to the shift.[23]

The temperature dependences of the shifts for the pyridine adduct of [Fe(omc)] (Fig. 8) show deviations from linearity which are most evident in the plot relative to resonance C where a maximum is observed for $T = 265$ K. Such deviations have been attributed[24] to the existence of a spin equilibrium. Since a single resonance is observed for each set of protons at all temperatures, with no marked difference in linewidth, the rate of exchange between the two spin states must be larger than that of the frequency shift difference of the protons in the two environments.

NMR relaxation time measurements. The measurement of NMR relaxation parameters of the resonances observed can be used to characterize the electronic properties of co-ordination compounds. In the presence of a paramagnetic centre the nuclear relaxation parameters are greatly dependent on the unpaired spin state.

Thus measurement of the spin lattice relaxation time T_1 and an estimate of the transverse relaxation time T_2 from the half-height linewidths was carried out. The results are reported in Tables 2 and 3.

In chloroform solution (Table 3) both species give very similar T_1 and T_2 values. As far as the nuclear relaxation is concerned the metal–proton distance and the electronic orbital symmetry can be considered the most important parameters. Hence these parameters are not substantially different in the chloride bound complex and in the species where the macrocyclic rings are stacked on top of one another.

The literature data reported for similar complexes indicate a value compatible with a $S = \frac{1}{2}$ ground state for the iron atom in [Fe(omc)] in chloroform.[23]

Measurement of the magnetic moment in chloroform has been carried out in the presence of an excess of chloride ions in order to obtain a single species in solution. The value obtained, 1.70 BM, confirms the low-spin state for the metal atom.

In the presence of pyridine both T_1 and T_2 (Table 2), are rather shorter than those measured in chloroform confirming that in this complex the iron atom exists in an higher spin state.

Iron porphyrinates exhibit different spin states as a function of the co-ordination number and nature of the axial ligands. Six-co-ordinate bis(pyridine) iron porphyrinates are reported to be low-spin.[25] In pyridine(py)–water mixtures both synthetic and natural iron porphyrinates are reported to form six-co-ordinate aqua complexes [FeP(py)(H_2O)]Cl (P = porphyrinate).[17] Such complexes show a thermal spin equilibrium between the $S = \frac{5}{2}$ and $\frac{1}{2}$ spin states with the $S = \frac{1}{2}$ state lying lower. Finally, extended Hückel calculations on high- and low-spin Fe^{III} porphyrinates have shown that the high-spin state occurs only when the metal atom is out of the macrocyclic plane.[26] The only exceptions to this rule reported are two compounds having two weak-field ligands: a diaqua and a bis(tetrahydrothiophene-*S*-oxide) 5,10,15,20-tetraphenylporphyrin iron(III) complex.[27] In these species the iron(III) atom is accommodated by a radial expansion of the porphyrin core. Both compounds show an average Fe–N distance of 2.045 Å *versus* a value of 1.986 Å observed in low-spin species. The corrole core is smaller than that of porphyrin but it can accommodate large metal ions: although no crystal structures have been reported for iron corrolates, in [Rh(omc)($AsPh_3$)] the average Rh–N distance is 1.945 Å *versus* 2.040 Å observed in rhodium porphyrinates without substantial deviation from planarity.

Although no detailed molecular orbital calculations have been reported for corrole or its metal complexes our results seem to indicate that [Fe(omc)] exists in pyridine as a complex where the metal binds one molecule of pyridine axially without being displaced from the macrocyclic plane. The sixth co-ordination site may be occupied by a water molecule.

Conclusion

Evidence has been obtained to indicate some differences in the ligand-field effects between corrole and other tetrapyrrolic macrocycles. In pyridine, [Fe(omc)] exhibits a behaviour similar to that of synthetic iron porphyrins where the metal atom is in a mixed spin state.

The peculiarity of metallocorrolates is that they represent the first examples of Fe^{III} complexes with tetrapyrrolic macrocycles that exist as neutral species.

The ^1H NMR study clarifies the structural as well as the electronic characteristics of [Fe(omc)] in the presence of different solvents and axially co-ordinating ligands. It has been demonstrated that pyridine binds axially to the iron atom whilst in the presence of chloroform wide aggregation between macrocyclic rings competing with axial co-ordination has been observed. Chloride ions act as electron donors, eliminate intermolecular stacking and lead to the observed increase in intensity of the Soret band in the electronic spectrum of the complex favouring, at the same time, the low spin state for the metal ion. This is an unusual spin state for a chloroform solution of an iron(III) macrocyclic complex: iron derivatives of porphyrins, chlorin and 5,15-dihydroporphydrins are in fact all high-spin in this solvent.[28,29]

Further investigations are in progress in order to assign the resonance patterns of the ^1H NMR spectra fully and thus characterize the electronic properties of the corrole system.

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