Preparation and Characterisation of some New 12- and 14-Membered Dibenzotetraaza Macrocyclic Complexes of Iron(III)

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The iron(III) macrocyclic complexes of some 12- and 14-membered dibenzo tetraaza macrocycles have been synthesised by the template process using o-phenylenediamine and the appropriate diketone. This affords a method to prepare these complexes with different ring substituents and varying degrees of unsaturation. All complexes were characterised by elemental analysis, molar conductance, magnetic susceptibility, visible and infrared spectra. They are all high spin and six coordinate. These macrocycles tend to attain a 'saddle shape' which favours a cis-geometry. This is supported by the infrared and Mössbauer spectra.

Introduction

The potentialities of the N_4-synthetic macrocyclic complexes as models for more complex natural systems is now well recognised [1–3]. The catalytic decomposition of hydrogen peroxide to water and oxygen by catalase [4–8] has attracted considerable attention, but studies on the mechanism of the reaction using an iron(III) macrocyclic complex (A) as a model system for catalase have been reported only recently [9]. Although this report shows that iron-(III) macrocyclic systems can function as substitutes for catalase, nothing is as yet known on the role of the macrocyclic environment on the extent of catalytic activation at the iron(III) centre. It is therefore of interest to prepare some new iron(III) macrocyclic complexes and to investigate their catalytic activity towards the decomposition of hydrogen peroxide. In this paper our results on the preparation and characterisation of some 12- and 14-membered iron(III) macrocyclic complexes with varying degrees of unsaturation are reported. The iron(III) complexes with the following macrocyclic ligand environment have been prepared:

I   R = CH_3
II R = C_6H_5

III

IV

V $R_1 = R_2 = CH_3$
VI $R_1 = CH_3; R_2 = C_6H_5$
VII $R_1 = R_2 = C_6H_5$

(A)

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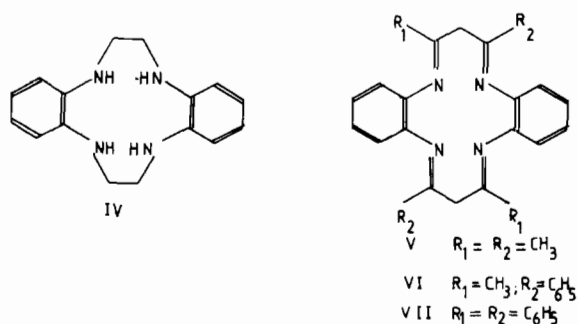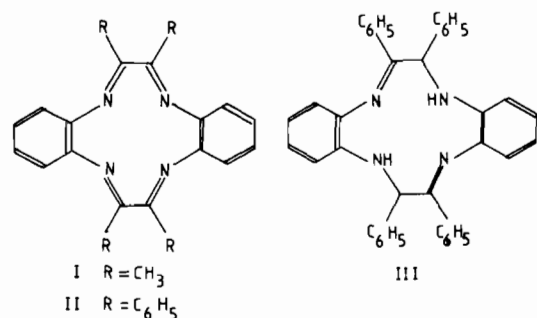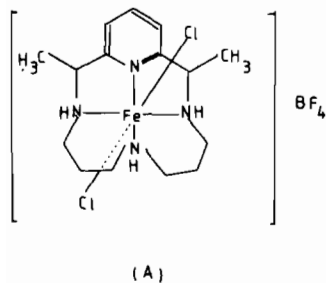
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TABLE I. Analytical Data of the Iron(III) Macrocyclic Complexes.

Complex		% Carbon		% Hydrogen		% Nitrogen		% Iron	
		calc.	found	calc.	found	calc.	found	calc.	found
I	[Fe(Me$_4$,Bzo$_2$[12]tetraene-N$_4$)Cl$_2$]Cl	50.2	50.0	4.2	4.3	11.7	11.6	11.7	11.8
II	[Fe(Ph$_4$, Bzo$_2$[12]tetraene-N$_4$)Cl$_2$]Cl	66.1	66.0	3.9	4.0	7.7	7.8	7.7	8.0
III	[Fe(Ph$_4$,Bzo$_2$[12]diene-N$_4$)Cl$_2$]Cl	65.9	66.1	4.1	4.0	7.7	7.7	7.7	7.9
IV	[Fe(Bzo$_2$[12]tetrane-N$_4$)Cl$_2$]Cl	44.6	44.8	4.7	4.8	13.0	13.2	13.0	12.7
V	[Fe(Me$_4$,Bzo$_2$[14]tetraene-N$_4$)Cl$_2$]Cl	52.1	52.5	4.8	4.7	11.1	11.3	11.1	10.9
VI	[Fe(Me$_2$,Ph$_2$Bzo$_2$[14]tetraene-N$_2$)Cl$_2$]Cl	60.9	61.0	4.5	4.6	8.9	8.7	8.9	8.8
VII	[Fe(Ph$_4$Bzo$_2$[14]tetraene-N$_4$)Cl$_2$]Cl	66.8	66.5	4.3	4.1	7.4	7.6	7.4	7.4
VIII	[Fe(Me$_4$,Bzo$_2$[14]tetraene-N$_4$)py$_2$]Cl	57.8	57.6	5.2	5.1	12.6	12.8	8.4	8.6
IX	[Fe(Me$_4$,Bzo$_2$[14]tetraene-N$_4$)py$_2$]Cl	56.5	56.6	4.7	4.6	13.2	13.4	8.9	8.7

Experimental

These macrocyclic complexes of iron(III) can be readily prepared by template condensation of o-phenylenediamine and the appropriate diketone in the presence of iron(III) in methanolic solutions. The following method was employed:

1.35 g of pure o-phenylenediamine was dissolved in 100 cm^3 of methanol and cooled in an ice bath to about 5 °C. To this was added 1.69 g of anhydrous ferric chloride with stirring, followed by 1.1 cm^3 of biacetyl diluted to 10 cm^3 with methanol. The solution was slowly heated and refluxed for 2 h. Air was bubbled through the solution for 30 min after cooling to room temperature and the volume reduced to about 20 cm^3 on a rotary evaporator using a water bath maintained at 40–50 °C. The concentrated solution was filtered and cooled to 0 °C in an ice bath and treated with a few drops of conc. HCl. On standing for about an hour, a reddish brown precipitate formed which was suction filtered and washed with ice cold methanol. The crude product was recrystallised at least twice from methanol containing a few drops of conc. HCl to obtain the analytically pure sample. The other complexes were prepared using 2.62 g benzil, 2.65 g benzoin, 10.8 cm^3 1,2-dibromoethane, 1.3 cm^3 2,4-pentanedione, 2.02 g 1-phenyl-1,3-butane dione and 2.8 g of 1,3-diphenyl-1,3-propane dione.

The pyridine substituted derivatives of complexes I and V were prepared as follows:

1.35 g of o-phenylenediamine was dissolved in a minimum amount of dry methanol, cooled in an ice bath and mixed with 1.69 g of anhydrous ferric chloride followed by 1.3 cm^3 of acetyl acetone. The solution was refluxed for 2 h and 10 cm^3 of freshly distilled pyridine added slowly. It was further refluxed for 1 h and the volume reduced to one fourth on a rotary evaporator, followed by cooling in an ice

bath. Addition of a few drops of conc. HCl resulted in precipitation of the complex, which was suction filtered and washed with ice cold methanol. The crude product was recrystallised twice from methanol, washed with ether and dried in a vacuum.

o-phenylenediamine was recrystallised from water-methanol mixtures after treatment with charcoal and sodium dithionate. The dry, recrystallised sample was sublimed before use. Impure o-phenylenediamine leads to considerable tarry products and the final product is difficult to purify.

Benzil, benzoin, 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione were prepared in the laboratory using literature methods [10–12].

Iron in the complexes was determined spectrophotometrically [13] on a Bausch and Lomb Spectronic 20 Spectrophotometer using 1,10-phenanthroline. About 0.1 g of the complex was decomposed by heating with conc. HNO$_3$ for a few hours and then taking the solution slowly to dryness. The residue was extracted with dil. HCl and Fe(III) reduced to Fe(II) with hydroxylamine hydrochloride. The analytical data is presented in Table I.

Conductance measurements of 1 mM solutions of the complexes in nitromethane and water were carried out on a Systronics Conductivity Meter 302 at 25 ± 0.1 °C. pH titrations were carried out under an atmosphere of nitrogen on a Radiometer PHM60 digital pH meter using a composite glass electrode. The pH meter was standardised with phthalate (pH = 4.01 and borax (pH = 9.28) buffer. The absorption spectra were recorded on a Carl Zeiss Specord recording spectrophotometer using 10 mm silica cells. The infrared spectra were recorded on a Beckmann IR-20 spectrophotometer in KBr pellets in 4000–600 cm^{-1} range and as nujol mull on polythene sheets in 700–250 cm^{-1} range.

Magnetic measurements were carried out using a Princeton Applied Research Model 155 vibrating

TABLE II. Infrared and Conductance Data of the Iron(III) Macrocyclic Complexes.

Complex	Absorption band at (cm^{-1})				Molar Conductance Ω^{-1} cm^{-1} Nitromethane	Water
	NH	C=N	phenyl	$-CH_2-$		
I	–	1660	1610, 1580	–	120	520
II	–	1660	1600, 1580	–	130	540
III	3250, 3200, 890, 850, 840	1650	1610, 1570	–	125	500
IV	3240, 3200, 880, 845, 835	–	1610, 1580	805, 785	150	520
V	–	1660	1630, 1600	800, 790	140	500
VI	–	1680	1610, 1575	800, 790	132, 515	515
VII	–	1670	1600, 1570	805, 790	146	560
VIII	–	1670	1600, 1570	805, 795	125	–
IX	–	1680	1610, 1585	–	130	–

sample magnetometer incorporating a digital read-out. The electromagnet was fed from a Polytronic Constant Current Regulator Type CP-200, with the current adjusted to produce a magnetic field of 5000 gauss. The instrument was calibrated with a standard nickel pellet and cross checked against Hg[Co-(CNS)$_4$]. The complex samples were made into pellets using a stainless steel die.

Mössbauer spectra of the complexes were recorded at room temperature (20 ± 1.0 °C) using a Harwell Mössbauer Spectrometer in the acceleration mode, coupled with an ORTEC Model 6240 multichannel analyser. The source was a 25 mCi ^{57}Co in Rh matrix. The spectrophotometer was calibrated against a standard iron foil using the inner four lines.
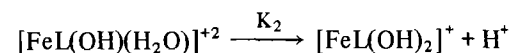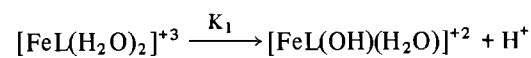
Results and Discussion

The 12- and 14-membered macrocyclic complexes with different ring substituents have been obtained *in situ* by the condensation of *o*-phenylenediamine and some diketones. The synthetic route for the preparation of the different complexes is similar but the ease of isolation was governed by the solubility of the individual complexes in methanol. The yields of the complexes ranged from 20 to 40%. Air was bubbled through the solutions to avoid Fe(II) contamination of the samples obtained from unaerated solutions. Any oxobridged dimers which may be expected to form during aeration seem to decompose on standing after addition of conc. HCl. Recent investigation by Endicott [14] on oxo-bridged dimers in cobalt(III) complexes have shown that these compounds undergo fairly rapid decomposition on addition of HCl. The complexes were found to show a fair degree of solubility in water, methanol, acetonitrile, nitromethane, DMF and DMSO. The complexes are deep reddish—brown in colour and are fairly stable

in the solid state. The Mössbauer spectra start showing changes after about three weeks.

The molar conductance of the complexes in nitromethane (Table II) at 25 °C lie in the range of 120–150 Ω^{-1} cm^{-1}, which corresponds to the uni—univalent formulae assigned. In water the conductance values are around 500 Ω^{-1} cm^{-1}, which is in accord with the expected rapid hydrolysis of these complexes:

$$[FeLCl_2]^+ \xrightarrow{H_2O} [FeL(H_2O)_2]^{+3}$$
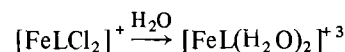
A rapid titration of complex V in H$_2$O against carbonate-free sodium hydroxide under an atmosphere of nitrogen shows two inflection points corresponding to one and two equivalents of the base consumed. The pK values from the titration work out as pK$_1$ = 4.5 and pK$_2$ = 6.25, according to the following equations:

$$[FeL(H_2O)_2]^{+3} \xrightarrow{K_1} [FeL(OH)(H_2O)]^{+2} + H^+$$

$$[FeL(OH)(H_2O)]^{+2} \xrightarrow{K_2} [FeL(OH)_2]^+ + H^+$$

The spectra of complex V show a shift in λ_{max} from 450 nm (<pH 4.5) to 435 nm (pH 6.0) and 330 nm (pH 10) in accord with the above reactions. The titration is carried out rapidly to avoid the dimerisation [9] of the hydrolysis products:

$$[2FeL(OH)(H_2O)]^{+2} \xrightarrow{-2H_2O} \left[LFe \underset{OH}{\overset{OH}{\diagup\diagdown}} FeL \right]^{+4}$$
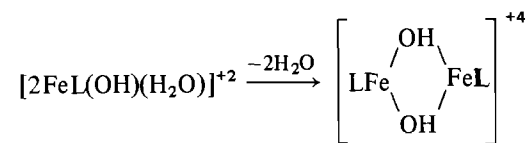
A slow decrease in absorbances in the spectra of complex V in water provides evidence for the dimerisation reaction.

The infrared spectra (Table II) shows the appearance of the C=N absorption [15–17] at around 1650

TABLE III. Magnetic, Ultraviolet and Visible Spectral Data of the Iron(III) Macrocyclic Complexes.

Complex	λ_{max} (nm)			μ_{eff}, B.M.
I	215, 240, 260, 370, 480			5.71
II	225, 245, 265, 345, 455			5.73
III	218, 348, 350, 410, 470			5.88
IV	262, 285,	440		5.93
V	235, 264, 282,	460		6.19
VI	220, 230, 265, 280,	480		5.91
VII	260, 290,	450		5.78
VIII	212, 260,	440, 460, 480		6.24
IX	210, 238, 258, 360,	460		5.77
	solvent methanol			

cm^{-1} (except in complex IV). The appearance of this band, coupled with the absence of the C=O band around 1700 cm^{-1}, provide conclusive evidence of condensation of the amine with the diketone. Complexes III and IV also show the presence of an NH frequency as a doublet around 3200 cm^{-1}. The phenyl ring absorptions [17] appear in the 1600–1400 cm^{-1} region. The infrared spectra in the 900–700 cm^{-1} region give important information regarding the *cis–trans* geometry [18, 19] of the complexes. The bands in this region can be exclusively assigned to the imine and $-CH_2-$ absorptions of the macrocycle and the multiplicity of these bands is dependent on the geometry of the complexes. The secondary imine vibrations in complexes III and IV appear as a triplet while in complexes IV, V, VI and VII the $-CH_2-$ absorption shows two bands (Table II). The multiplicity of these bands [20] suggests a *cis* configuration for these complexes. Complexes I and II do not carry any NH or $-CH_2-$ groups and hence no such information can be derived from their infrared spectra, but they are also expected to have a *cis*-geometry. The far infrared spectra are somewhat complex, which prevents the unambiguous assignment of the (M–X) frequency.

However, the multiplicity of the bands in the 300–200 cm^{-1} region appears to be a result of the *cis*-geometry.

Magnetic measurements (Table III) show the complexes to be paramagnetic with five unpaired spins (S = 5/2). It is interesting to note that the complexes with pyridine as axial ligands are also paramagnetic. This contrasting behaviour to other iron macrocyclic complexes [19, 21–23] (complexes with strong axial ligands like pyridine have been found to be low spin) is due to the 'sitting atop' of the iron(III) centre with respect to the N_4-macrocyclic plane. This 'sitting atop' is due to the 'saddle shape' of the macrocycle. In a detailed crystallographic analysis of the macrocycle obtained from o-phenyl-

enediamine and acetylacetone (V), the pronounced 'saddle shape' for the ligand has been observed [24–27]. The 'saddle shape' arises from the steric interaction of the benzenoid rings with the methyl substituents on the macrocyclic ring. The resulting strain is relieved through a distortion of the ring to give a non-planar structure. The strain is relieved through the twisting of the torsional angles about the C–N bonds on the N_4-ring, which is the most readily deformable site. The extent of deviations from the dihedral angle in an ideally planar structure depends on the single and double bond characters of the various bonds in the macrocyclic ring. In the 'saddle shape' the nitrogen lone pairs are directed [25] out of the N_4-plane, so that the metal 'sits atop' and not inside the N_4 cavity. Since the macrocycle is folded and the metal ion is lying outside the N_4-plane on the side opposite to the folding, it is quite exposed so as to promote a *cis*-orientation of the axial ligands. With the 'sitting atop' of iron(III), the ligand field exerted by the N_4 system is very weak which results in high spin complexes even with strong donor ligands like pyridine as the extraplanar ligands. The 12-membered macrocycles also give high spin complexes with iron(III) due to this 'sitting atop'. It is known that a 12-membered ring is a good fit cavity for iron(III), exerting a sufficiently strong ligand field to give low spin complexes even with weak axial ligands [27].

In the case of iron(III) complexes, a detailed ligand field analysis of the d → d spectra has not been carried out so far. A number of high spin complexes of iron(III) have been reported [28–32] in which d → d band in the visible region has not been observed due to its spin forbidden character. In some cases bands with high extinction coefficients are observed in the visible region which have been assigned to charge transfer transitions. The present complexes also show a similar type of spectra (Table III).

TABLE IV. Mössbauer Spectral Data of the Iron(III) Macrocyclic Complexes.[a]

Complex	Isomer shift δ, mm/s		Quadrupole splitting ΔE, mm/s	
	cis	trans	cis	trans
I	0.36	0.37	0.62	1.03
IV	0.35	0.35	0.55	1.24
V	0.39	0.39	0.49	1.04
VI	0.42	0.39	0.67	1.44
VIII	0.36	0.26	0.56	1.22
IX	0.37	0.37	0.59	1.13

[a]All values are with respect to iron. Estimated error in values: ±0.02 mm/s.

Fig. 1. Mössbauer spectra of [Fe(Me$_4$,Bzo$_2$[14]tetraene-N$_4$)Cl$_2$]Cl.

The Mössbauer spectra of these complexes shows a typical two line spectrum with considerable broadening of the lines (Fig. 1). In the case of complex VIII two distinct additional lines appear at higher velocities. The values of the isomer shift (Table IV) are in accord with six coordinate high spin iron-(III) complexes [32, 33]. An analysis of the spectra through least square curve fitting of the data shows that two quadrupole splitting values can be worked out. The second quadrupole splitting value is double the first value, an observation indicating the presence of both *cis*- and *trans*-isomers in the sample [34, 35]. Two factors contribute to the value of ΔE: (i) The asymmetry of the electron density about the nucleus, and (ii) The asymmetry of the ligand field. Using a point charge model, the electric field gradient can be calculated [34] for the *cis*- and *trans*-isomers. These calculations show that $\Delta E_{trans}/\Delta E_{cis}$ turns out to be ~2. Our values of the first ΔE corresponding to the *cis*-isomer are close to the values reported earlier by Busch *et al.* [29] for *cis*-high spin iron(III)N$_4$ macrocyclic complexes. The Mössbauer spectra further shows that the amount of the *trans*-isomer is small as compared to the *cis*-isomer.

An attempt was made to separate the *cis*- and *trans*-isomers by ion exchange chromatography using Dowex 50 W resin, mesh 100–200, and 0.1 *M* HCl as eluent. Only one band could be obtained. It was evaporated to dryness and its Mössbauer spectra showed it to be mostly *cis*- with some *trans*-contamination. Further attempts to separate the isomers using different HCl concentrations to elute the solution gave similar results. Since these Fe(III) complexes are labile, the eluted product is an equilibrium mixture of the more stable *cis*- and the less stable *trans*-isomer. The standard free energy difference ($\Delta F^{\circ}_{25\,^{\circ}C}$) for the equilibrium *cis* $\right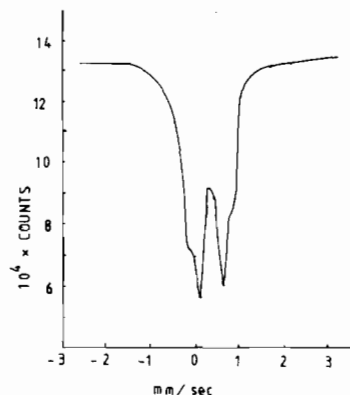leftharpoons$ *trans* is quite small [36] (around 2400 J mol^{-1}), with the equilibrium lying largely towards *cis*. This small value of $\Delta F^{\circ}_{25\,^{\circ}C}$ apparently prevents the complete resolution of the isomers.

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