Oxo-bridged Binuclear Iron(III) Complexes with *NN'*-Bis(2-methylpyridyl)ethylenediamine and 2,2' : 6',2'' : 6'',2'''-Tetrapyridyl

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Two oxo-bridged complexes of iron(III), having different configurations depending on the different conjugative capacity of the quadridentate nitrogen ligands used, have been isolated and characterized. They are formulated as *cis*-$[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2\cdot H_2O$ and *trans*-$[\{Fe(tetpy)\}_2O][SO_4]_2\cdot 7H_2O$, in which pairs of iron(III) ions ($S = \frac{5}{2}$) interact antiferromagnetically [bmen = *NN'*-bis(2-methylpyridyl)ethylenediamine and tetpy = 2,2':6',2'':6'',2'''-tetrapyridyl]. Evidence is produced that the dimeric form of both complexes also predominates in an aqueous medium. As the pH is increased, the stability between the oxo-bridged units of the two complexes in solution differs; this is briefly discussed in the light of the different stereochemical features of the molecules.

THE wide interest in binuclear iron(III) complexes,[1-4] which may also represent useful model systems of biological significance,[4,5] prompts us to report the physical and chemical properties of two novel iron(III) oxo-bridged dimeric complexes in the solid state and in aqueous solution, $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2\cdot H_2O$ (I) and $[\{Fe(tetpy)\}_2O][SO_4]_2\cdot 7H_2O$ (or $[\{Fe(tetpy)\}_2O(H_2O)_2][SO_4]_2\cdot 5H_2O$) (II) [bmen and tetpy are quadridentate nitrogen ligands, *NN'*-bis(2-methylpyridyl)ethylenediamine and 2,2':6',2'':6'',2'''-tetrapyridyl].

RESULTS AND DISCUSSION

Owing to the marked difference in flexibility between the ligands, the complexes are expected to exhibit a different configuration. According to molecular models, the rigidity of porphyrin-like tetpy makes possible only a *trans* arrangement around the central metal ion.[6,7] In contrast, complex (I) very likely assumes a *cis*-type geometry, in agreement with the available data on chelate systems of Ni^{II} and Co^{III} which show that *cis*-$[MN_4X_2]$ species are definitely favoured over *trans* [8,9] when a ' facultative ' ligand,[10] such as bmen, is used (see later).

Elemental analyses were in good agreement with the proposed formulae which were also substantiated by the i.r. spectra. For instance, of the four ring-deformation vibrations, that at the highest frequency shifted on co-ordination by *ca.* 14 (I) and 8 cm^{-1} (II) towards higher wavenumbers when compared with the free ligands. This, together with the absence of any band at *ca.* 1 590 cm^{-1}, is consistent with bonding of pyridyl groups.[11a] The N–H stretching absorption of complex (I) was at 3 260 cm^{-1}, *i.e. ca.* 60 cm^{-1} lower than that of the free ligand, indicating bond formation between the aliphatic nitrogen atoms and iron.[11b] Furthermore, in the frequency region where the antisymmetric Fe–O–Fe stretch is expected to occur [1-3] $[\{Fe(tetpy)\}_2O][SO_4]_2$ exhibited a medium broad band (832 cm^{-1}) whilst $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2$ showed several bands, those at 840 or 828

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cm^{-1} being very likely ascribable to this vibration since they are not observed in some parent mononuclear derivatives.[12]

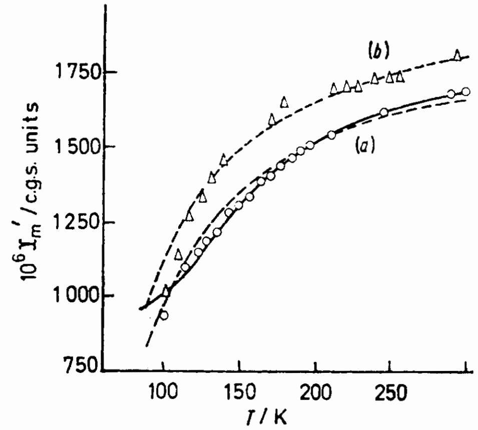

FIGURE 1 Magnetic susceptibilities per iron(III) ion as a function of T for $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2 \cdot H_2O$ (*a*) and $[\{Fe(tetpy)\}_2O][SO_4]_2 \cdot 7H_2O$ (*b*). The symbols refer to experimental values whilst the broken lines were calculated for $S = \frac{5}{2}$, $g = 2.00$, t.i.p. = 0, $J = -89$ (*a*) and -83 cm^{-1} (*b*); the full line was calculated for $S = \frac{1}{2}$, $g = 2.35$, t.i.p. = 860×10^{-6} c.g.s. units, and $J = -175$ cm^{-1}. χ_m' values refer to a molecular weight of one half of the dimers

Magnetic susceptibilities at 100—300 K can be satisfactorily fitted by the usual spin–spin interaction model, assuming for both compounds that $S = (\frac{5}{2},\frac{5}{2})$, $g = 2.00$, a temperature-independent paramagnetic (t.i.p.) contribution of zero, and $J = -89$ (I) and -83 cm^{-1} (II), respectively. In no case did an $S = (\frac{1}{2},\frac{1}{2})$ treatment prove satisfactory for $[\{Fe(tetpy)\}_2O][SO_4]_2$ whilst the experimental data for $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2$ could also be fitted assuming $S = (\frac{1}{2},\frac{1}{2})$, $g = 2.35$, and t.i.p. = 860×10^{-6} c.g.s. units (J -175 cm^{-1}), as illustrated in Figure 1. These values, however, are much too high to be acceptable.[3b] The complexes may therefore be described as dimeric species with antiferromagnetic exchange between the two iron ions, both formally in an $S = \frac{5}{2}$ state.

Room-temperature Mössbauer measurements (relative to natural iron) support this conclusion in that they gave isomer shifts of 0.71 and 0.66 mm s^{-1} and quadrupole splittings of 1.41 and 1.79 mm s^{-1} for (I) and (II), respectively. These values are of the same order of magnitude as those found for a number of high-spin d^5 oxo-bridged complexes.[3a,5b,13] Whilst the relation between quadrupole splitting and the spin state of iron in a complex is not obvious,[3b] the values of the isomer shift fall in the range (*ca.* 0.7 mm s^{-1}) [13a] where the iron(III) ions are in a spin-sextet ground state. On the other hand, if the surrounding ligands are similar, five-co-ordinate iron(III) complexes are expected to give rise to smaller isomer shifts and higher quadrupole splittings than six-co-ordinate derivatives.[14] The Mössbauer results might suggest, therefore, that complex (II) is five-co-ordinate. The observation that $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2 \cdot H_2O$ exhibits two medium-intensity i.r. bands at 1 011 and 967 cm^{-1}, ascribable to co-ordinated water,[12,15] whereas $[\{Fe(tetpy)\}_2O][SO_4]_2 \cdot 7H_2O$ does not, provides further support to this hypothesis.

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

Solid	Assignment		Calc. energy [b]	Aqueous solution [c]
(*a*) $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2 \cdot H_2O$ (I)				
10.5 (b)	$^6A_1 \longrightarrow {}^4T_1$	(1)	10.7	10.5 (b, *ca.* 3) [d]
15.9 (sh)	$\longrightarrow {}^4T_2$	(2)	16.1	15.9 (b, 60)
20.4 (sh)	$\longrightarrow ({}^4A_1, {}^4E)$	(3)	20.4	20.4 (sh, 235)
21.3	(1 + 1)		(21.0) [e]	21.0 (sh, 280)
22.7	$\longrightarrow {}^4T_2$	(4)	22.4	22.4 (382)
27.4	Charge transfer			24.1 (sh, 450)
32.2 (sh)	Charge transfer			27.8 (sh, 3 500)
				31.4 (5 300)
				39.5 (11 800)
(*b*) $[\{Fe(tetpy)\}_2O][SO_4]_2 \cdot 7H_2O$ (II)				
11.8 (b)	$^6A_1 \longrightarrow {}^4T_1$	(1)	11.8 [f]	
18.9 (sh)	$\longrightarrow {}^4T_2$	(2)	18.9	18.2 (sh, 135) [g]
23.8 (sh)	$\longrightarrow ({}^4A_1, {}^4E)$	(3)	23.8	25.0 (sh, 3 800)
	(and/or 1 + 1)		(23.6) [e]	28.0 (11 150)
27.0	*h*			33.3 (14 400)
32.2 (sh)	*h*			(45.4 sh, 38 200)
				47.6 (42 400)

[a] Band positions in 10^3 cm^{-1}; b = broad, sh = shoulder. [b] From $Dq = 1\,244$, $B = 678$, and $C = 2\,726$ cm^{-1}. [c] *Ca.* 10^{-3} mol dm^{-3} of sample (per mol of Fe^{III}); ε (dm^3 mol^{-1} cm^{-1}) values are given in parentheses. [d] pH 4.6. [e] Calculated sum of $({}^6A_1 \longrightarrow {}^4T_1) + ({}^6A_1 \longrightarrow {}^4T_1)$. [f] From $Dq = 1\,502$, $B = 887$, and $C = 2\,985$ cm^{-1}. [g] pH 4.0. [h] Ligand-localised and/or ligand $\longrightarrow$ Fe^{III} charge-transfer bands (tetpy ligand alone absorbs in the same frequency region at 31.3 and 36.0 10^3 cm^{-1}).

The diffuse-reflectance spectra of these complexes were characterized by anomalously intense visible ligand-field bands as compared to those of a parent high-spin mononuclear iron(III) derivative.[12] This may be ascribed to exchange coupling interaction between neighbouring ions, as recently found for some manganese(II) salts [16]

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and iron(III) complexes,[2b] where the metal ions are bridged by a single anion. The assignment of the transitions from an $^6A_1$ ground state leads to the values of $Dq = 1\,244$ and $1\,502$, $B = 678$ and 887, and $C = 2\,726$ and $2\,985$ cm^{-1} for complexes (I) and (II), respectively, and to calculated energies which are in good agreement with the experimental energies (Table). The observation that in both cases only one band probably falls within the calculated positions for the simultaneous pair electronic (s.p.e.) excitations [2b,16] is most likely due to the fact that in these complexes s.p.e. bands are masked by intense charge-transfer or ligand-localized bands.

Solution Properties.—The electronic spectrum of $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2$ in aqueous solution (pH *ca.* 4.5) still showed intense visible ligand-field bands when compared to those of a parent mononuclear low-spin derivative,[12] *i.e.* $[Fe(bmen)(H_2O)(OH)]^{2+}$. These bands are reminiscent of but better resolved than those of the solid material (Table). In addition, at the same pH, this complex (*i*) strictly follows Beer's law over the concentration range allowed by its poor solubility in water at room temperature (*ca.* 1.4×10^{-2} mol dm^{-3}, based on a molecular weight of one half that of the dimer), and (*ii*) exhibits antiferromagnetic behaviour similar to that of the solid sample, according to magnetic measurements as a function of temperature on frozen aqueous solutions.[17] All these features support the formulation of complex (I) as a binuclear species also in an aqueous medium. On the other hand, potentiometric data (20 °C, Figure 2), indicate the occurrence of two protolytic equilibria, characterized by an average pK_a of 6. On inspection of the curve it appears that, within experimental error, the amount of base consumed is twice that necessary for a single proton. For instance, at pH 7.5, 0.102 mmol of Na[OH] were consumed per 0.053 mmol of the binuclear complex [Figure 2(*a*)].

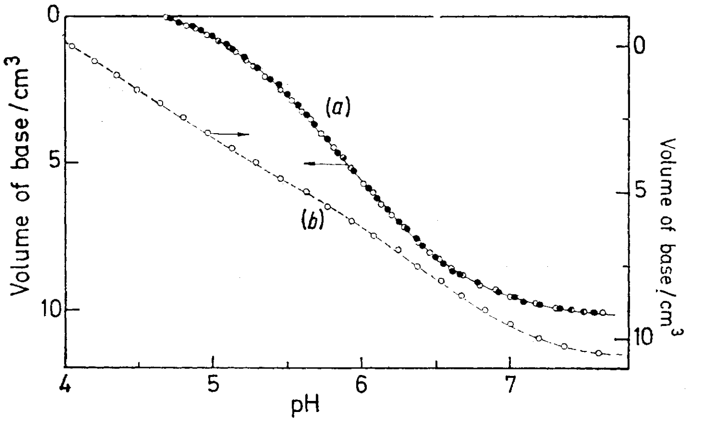

FIGURE 2 Typical potentiometric titration curves of the binuclear complexes with 0.01N Na[OH]: (*a*) 0.053 mmol of $[\{Fe(bmen)\}_2O(H_2O)_2]^{4+}$ (the two symbols refer to different runs); and (*b*) 0.050 mmol of $[\{Fe(tetpy)\}_2O(H_2O)_2]^{4+}$ (see text)

On the basis of these results, it may be inferred that in solution complex (I) undergoes equilibria (1) and (2),

$$[\{Fe(bmen)\}_2O(H_2O)_2]^{4+} \rightleftharpoons [\{Fe(bmen)\}_2O(H_2O)(OH)]^{3+} + H^+ \quad (1)$$

$$[\{Fe(bmen)\}_2O(H_2O)(OH)]^{3+} \rightleftharpoons [\{Fe(bmen)\}_2O(OH)_2]^{2+} + H^+ \quad (2)$$

whose dissociation constants, calculated according to known methods,[18] are p$K_{a,1}$ 5.7 and p$K_{a,2}$ 6.2 (20 °C).

With increased pH, a parallel slower reaction leading to mononuclear species may occur, however, to some extent. This is suggested by the following observations: (*i*) on back titration, the visible spectrum of the dimeric complex exhibited molar absorption coefficients which were somewhat lower than those of the original complex; and (*ii*) at *ca.* pH > 6, e.s.r. spectra of frozen aqueous solutions (*X* band, *ca.* 90 K) began to show a resonance at 1 520 G {$g_{eff.}$ 4.29,* already observed for the high-spin mononuclear $[Fe(bmen)(OH)_2]^+$ ion, characterized by rhombic anisotropy}.[12] Nevertheless, under the experimental conditions, the dihydroxo-conjugate base $[\{Fe(bmen)\}_2O(OH)_2]^{2+}$ is expected to predominate, since the protolytic reactions should be much faster than dissociation of the dimer.[2c] This is indeed the case, as confirmed by magnetic data on frozen aqueous solutions, which showed antiferromagnetic coupling between iron ions also at pH *ca.* 7, and by the fact that, at the same pH, Beer's law is obeyed, a result which is incompatible with a monomer–oxo-bridged dimer equilibrium which should obviously be concentration dependent.

A final point is worth mentioning. It has been found that $[\{Fe(bmen)\}_2O(H_2O)_2]^{4+}$ is rather labile at room temperature. According to spectrophotometric measurements, the dissociative process giving rise to the free ligand in solution has a half-life of 45 h (25 °C). At *ca.* 5 °C, however, this reaction was strongly depressed, the spectral patterns remaining practically unaltered for more than 15 d. It is interesting that the low-spin mononuclear $[Fe(bmen)(H_2O)(OH)]^{2+}$ ion exhibits a

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* 1 G = 10^{-4} T.

[17] M. Cerdonio, F. Mogno, B. Pispisa, and G. L. Romani, unpublished work.

[18] K. H. Schröder, *Acta Chem. Scand.*, 1966, **20**, 1401.

higher lability, the half-life of the dissociative process being 30 h (25 °C).[12]

Investigation of the solution properties of *trans*-$[\{Fe(tetpy)\}_2O][SO_4]_2$ is complicated by the lack of knowledge of the behaviour of well established mononuclear parent derivatives, but a relatively recent study suggests unusually high stability in aqueous medium for Fe^{3+} ions co-ordinated to all the four nitrogens of tetpy in the equatorial plane.[7] On the other hand, at pH *ca.* 4: (*i*) this complex is highly inert in solution (25 °C); (*ii*) Beer's law is strictly followed, over the whole concentration range explored; and (*iii*) magnetic measurements on frozen aqueous solutions indicate antiferromagnetic behaviour consistent with the presence of an oxo-bridged structure.[17] All these features strongly suggest that this complex is also a binuclear species in an aqueous medium. Furthermore, under the experimental conditions, two water molecules are probably co-ordinated in apical positions. This hypothesis is based on potentiometric-titration experiments [Figure 2(*b*)], which clearly show the occurrence of two protolytic equilibria ($pK_{a,1}$ 4.3 ± 0.1, $pK_{a,2}$ 6.2 ± 0.1, 20 °C), in agreement with the finding that amount of base consumed (mol) is approximately twice that of the binuclear complex in solution. Such a change in co-ordination could also account for the difference in the ligand-field bands between the solid and aqueous samples (Table).

It is worth noting that in almost neutral solutions, concentration-dependence measurements as well as magnetic data suggest the occurrence of dimer dissociation, in contrast to the finding on complex (I). The mechanism of this process could be similar to that already proposed for other oxo-bridged complexes,[2c] *i.e.* the assistance of an entering water molecule and the formation of an unstable strained seven-co-ordinate dihydroxo-bridged structure.

The difference in stability between the oxo-bridged units of the two binuclear complexes in aqueous solution, once the Fe–O–Fe bonds are weakened by replacement of H_2O groups by electron-releasing $[OH]^-$ ions, probably depends on the different stereochemical environments. According to molecular models and steric arguments,[12] a *cis*-α arrangement of bmen around the high-spin central ions would be favoured either because it alleviates 'E-strain'[8b,12] or because it optimizes non-bonded interactions between neighbouring atoms or groups in the dimeric molecule. A rather compact structure with hydrophobic character is thus expected to arise. This would make the oxygen bridge less accessible to water molecules, which are suggested to assist the dimer dissociation, than the more open structure of the *trans*-iron(III) binuclear derivative, as experimentally observed.

X-Ray diffraction analysis of the solid complexes is in progress.

EXPERIMENTAL

The complex $[\{Fe(bmen)\}_2O(H_2O)_2][SO_4]_2\cdot H_2O$ (I) was prepared by addition of a concentrated aqueous solution of iron(II) sulphate to a concentrated solution of the ligand (1 : 1 molar ratio), bmen being obtained by hydrogenation *via* $Na[BH_4]$ of the corresponding Schiff base.[12] The resulting red mixture was slowly evaporated on a steam-bath until addition of an excess of ethanol caused precipitation of the complex as a pink solid. The complex was washed several times with alcohol and dried. The complex $[\{Fe(tetpy)\}_2O][SO_4]_2\cdot 7H_2O$ (II) was prepared by adding a concentrated aqueous solution of $Fe[SO_4]$ to an alcoholic solution of the ligand (1 : 1 molar ratio), obtained as described.[6] The mixture was gently boiled to eliminate alcohol and concentrated. After cooling the complex precipitated as a brown-red solid. Owing to the very great tendency of iron(II) ions to oxidize even in the presence of trace amounts of water, in all cases iron(III) complexes were obtained. Elemental analyses were by A. Bernhardt, West Germany [Found: C, 39.0; H, 5.15; N, 13.0; S, 7.45. Calc. for $C_{28}H_{42}Fe_2N_8O_{12}S_2$ (I): C, 39.15; H, 4.95; N, 13.05; S, 7.45. Found: C, 45.35; H, 3.80; N, 10.1; S, 5.85. Calc. for $C_{40}H_{42}Fe_2N_8O_{16}S_2$ (II): C, 45.05; H, 3.95; N, 10.5; S, 6.00%]. Methods and apparatus have been reported.[12]

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