bond-rupture mechanism.[11] The activation parameters for these changes in chlorobenzene are similar to one another. Thus an intramolecular bond-rupture mechanism can be suggested for the racemization of $Cr(acac)_3$. The $\Delta H^{\ddagger}$ value for the racemization of $Cr(acac)_3$ is not very different from our $\Delta H^{\ddagger}$ for the k_i and k_w paths in the low Hacac concentration region (Table II). These $\Delta H^{\ddagger}$ values may reflect the ease of breaking the Cr–O bond, and we may expect a common intermediate II for both racemization and isotopic exchange. The large difference in the first-order rate constants can be accounted for by the contribution of the term $k_3/(k_{-2} + k_3)$ in eq 14.

In the gaseous phase containing 3.5×10^{-5} mol of $Cr(acac)_3$ and 3.9×10^{-5} mol of [^{14}C]Hacac l.$^{-1}$, the ligand isotopic exchange was observed in a temperature region over 160 °C. The apparent first-order rate constant with respect to the complex "concentration" is of the order of 10^{-4} s^{-1} at 190 °C.[12] Not very different data were obtained in a glass vessel and a Teflon-coated metal chamber. Influence of various factors including the pressure and the wall of the vessel should be carefully examined for discussing the mechanism in more detail. However, so far as the observed rate constant is concerned, there seems to be no marked discontinuity between the isotopic exchange in the gaseous phase and in AN solution.

Among octahedral tris(acetylacetonato) complexes of various metal ions,[5] the chromium(III) complex gives the most inert example of intermolecular isotopic exchange, i.e., more inert than $Co(acac)_3$[13] and $[Ge(acac)_3]ClO_4$.[14]

Acknowledgment. The authors thank the Ministry of Education of the Japanese Government for financial support.

Registry No. $Cr(acac)_3$, 13681-82-8; Hacac, 123-54-6.

References and Notes

(1) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
(2) R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Am. Chem. Soc.*, **92**, 7056 (1970).
(3) C. Kutal and R. E. Sievers, *Inorg. Chem.*, **13**, 897 (1974).
(4) R. W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).
(5) K. Saito, *Pure Appl. Chem.*, **38**, 325 (1974).
(6) W. C. Fernelius and J. E. Blanch, *Inorg. Synth.*, **5**, 130 (1957).
(7) K. Saito and K. Masuda, *Bull. Chem. Soc. Jpn.*, **41**, 384 (1968).
(8) D. W. Thompson and A. L. Allred, *J. Phys. Chem.*, **75**, 433 (1971).
(9) S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967).
(10) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, **11**, 56, 92 (1974).
(11) A. Y. Girgis and R. C. Fay, *J. Am. Chem. Soc.*, **92**, 7061 (1970).
(12) K. Saito and H. Kido, Abstracts, XVIIIth National Conference on Coordination Chemistry, Kyoto, Japan, 1968, p 67.
(13) K. Saito and M. Murakami, *Bull. Chem. Soc. Jpn.*, **45**, 2472 (1972).
(14) A. Nagasawa and K. Saito, to be submitted for publication.

Contribution from the Istituto di Fisica e
Istituto di Chimica Fisica, Università di Roma, Rome, Italy

Magnetic Properties of Some Iron(III) Binuclear Complexes in Aqueous Solution

M. CERDONIO,*[1a,c] F. MOGNO,[1a] B. PISPISA,*[1b] G. L. ROMANI,[1a] and S. VITALE[1a]

Received July 26, 1976 AIC60524H

Magnetic properties of frozen aqueous solutions of two configurationally different iron(III) oxy-bridged dimeric complexes were determined. The compounds may be formulated as *trans*-$[(Fe(tetpy))_2O(H_2O)_2]^{4+}$ and *cis*-$[(Fe(bmen))_2O(H_2O)_2]^{4+}$, where tetpy and bmen are quadridentate nitrogen ligands with different conjugative capacity, e.g., 2,2′:6′,2″:6″,2‴-tetrapyridyl and *N,N′*-bis(2-methylpyridyl)ethylenediamine, respectively. The stability of the bridging unit Fe–O–Fe is seen to be [H$^+$] dependent only in the case of the trans derivative. In weakly acid solutions (pH ~5) the oxy-bridged unit of this complex is transformed into a dihydroxy-bridged structure, whose fragmentation occurs only at higher pH values (>6). In contrast, the cis derivative retains essentially the original antiferromagnetic character within the whole range of pH explored. The diverse behavior of these complexes in an aqueous medium is briefly discussed in the light of the different stereochemical features.

Introduction

Solution properties of Fe(III) dimeric complexes have received much attention in the last few years either to elucidate the structural features of this type of compound in aqueous medium[2-4] or to investigate their behavior as model systems of naturally occurring materials.[2c,5] Comparison between solution properties of configurationally different iron(III) derivatives is generally lacking, however, despite the obvious interest in the relationship between stereochemistry and stability as well as reactivity of such compounds.

We have prepared and characterized two novel oxy-bridged Fe(III) binuclear complexes, which exhibit a different configuration depending upon the different conjugative capacity of the quadridentate nitrogen ligands used. In the solid state they may be formulated as *cis*-$[(Fe(bmen))_2O(H_2O)_2](SO_4)_2\cdot H_2O$ (I) and *trans*-$[(Fe(tetpy))_2O](SO_4)_2\cdot 7H_2O$ (II) (bmen = *N,N′*-bis(2-methylpyridyl)ethylenediamine and tetpy = 2,2′:6′,2″:6″,2‴-tetrapyridyl), in which pairs of $S = {}^5/_2$ Fe(III) ions interact antiferromagnetically with $J = -89$ (I) and -83 cm^{-1} (II), respectively.[6] Furthermore, evidence has been produced that both dimeric species are stable in acid solution but complex II undergoes a monomer–dimer equilibrium, at variance with complex I,[6] at pH around neutrality.

In order to explain this peculiar behavior, an extensive study on the magnetic properties of frozen aqueous solutions (25–250 K) at various pH's was undertaken. It is the aim of this paper to present the results of this investigation which definitely indicate that, upon increase in pH, the dimeric complexes behave differently.

Experimental Section

Materials. $[(Fe(bmen))_2O(H_2O)_2](SO_4)_2\cdot H_2O$ and $[(Fe(tetpy))_2O](SO_4)_2\cdot 7H_2O$ were prepared as described.[6] Measurements were performed on freshly prepared aqueous samples using doubly distilled water with a conductivity less than 2×10^{-6} Ω^{-1} cm^{-1} (20 °C). Concentrations (based on molecular weights of half the dimers) never exceeded 1.2×10^{-2} and 8.5×10^{-3} M, respectively, since these figures almost represent the maximum solubility in water at room temperature of the complexes.

Methods. Samples for magnetic susceptibility measurements had typical volumes in the range of 0.1 ml. Total volume susceptibilities of the frozen solutions were measured by a novel oscillating-sample version[7] of the superconducting magnetometer,[8] within the temperature range of 25–250 K. As previously shown,[7] the method effectively nulls any contribution from the holder. Paramagnetic and antiferromagnetic contributions show up in the raw data as deviations from the dominant diamagnetic background of the frozen solution. The two contributions can be easily separated when the absolute value of the antiferromagnetic coupling constant J is of the order of 70 cm^{-1}, since in this case the antiferromagnetic contribution in the lowest temperature range explored is negligible. When the coupling constant J is smaller, a trial and error procedure of fitting on raw data must be followed. Paramagnetic and antiferromagnetic contributions were reduced to

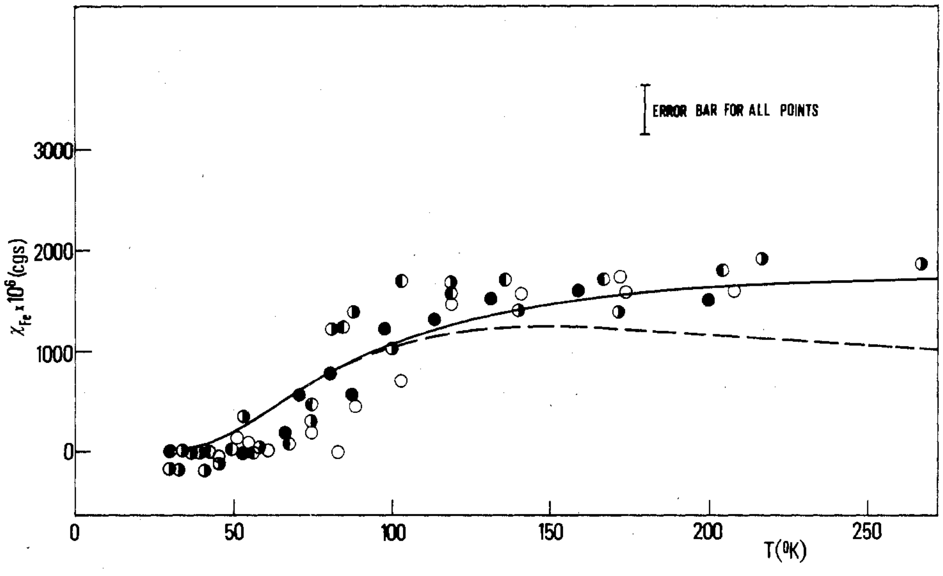


Figure 1. Atomic magnetic susceptibility as a function of temperature of $[(Fe(bmen))_2OX_2]^{n+}$ at various pH's (referred to room temperature): ○, pH 4.5; ◑, pH 5.4; ◐, pH 6.0; ●, pH 6.9. Solid line is the theoretical curve for $S_1 = S_2 = {}^5/_2$; $J = -85$ cm^{-1}, $g = 2.00$, and TIP = 0. Dashed line is the theoretical curve for $S_1 = S_2 = {}^1/_2$; $J = -85$ cm^{-1}, $g = 2.00$, and TIP = 0.

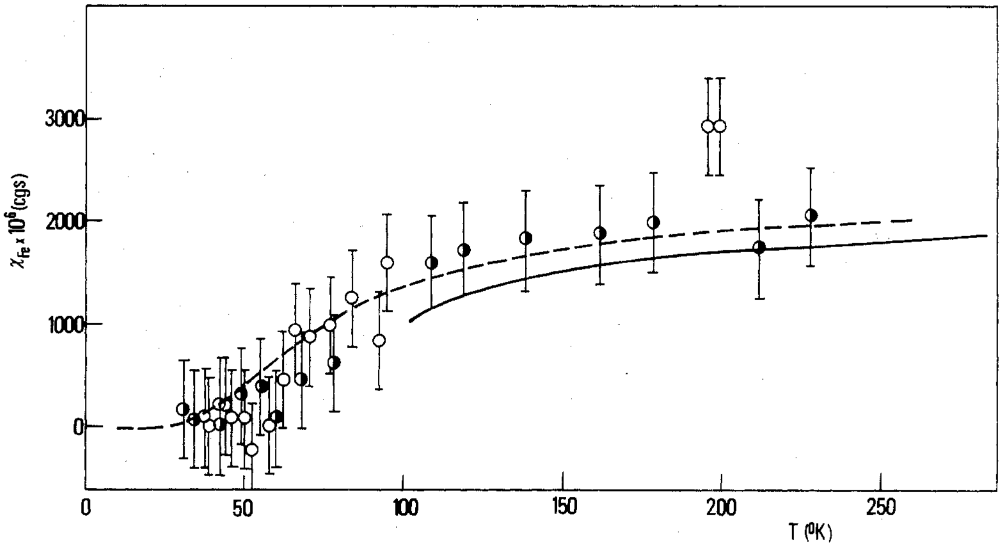


Figure 2. Atomic magnetic susceptibility as a function of temperature of $[(Fe(tetpy))_2O(H_2O)_2]^{4+}$ at pH 3.5 (○) and 3.8 (◑): dashed line, theoretical curve for $S_1 = S_2 = {}^5/_2$, $J = -75$ cm^{-1}, $g = 2.00$, TIP = 0; solid line, atomic susceptibility of solid $[(Fe(tetpy))_2O](SO_4)_2 \cdot 7H_2O$ from the experimental data of ref 6.

Fe atomic susceptibilities using the temperature-dependent density of pure ice given by Kell[9] and the reported molar susceptibility of pure ice.[10] The systematic errors introduced by the use of properties of pure ice rather than those of the frozen aqueous solutions were negligible in comparison with errors arising from resolving the deviations from the diamagnetic background. The temperature was controlled within ±1 K. Measurements were taken well after thermal equilibrium had been established at each temperature. Details on the experimental method and its accuracy were already reported.[8]

EPR spectra of aqueous sample 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. Electronic spectra were performed at room temperature by a Beckman DK-2A apparatus with appropriate quartz cells. pH values were determined by a Radiometer 26 pH meter with the use of standard semimicroelectrodes.

Results

Magnetic Data. A feature common to both complexes in aqueous solution at pH ~4 is a temperature-dependent susceptibility which is characteristic of an antiferromagnetic coupled system (Figures 1 and 2). Assuming $S_1 = S_2 = {}^5/_2$, $g = 2.00$, a temperature-independent paramagnetism (TIP) contribution of zero, the experimental data can be satisfactorily fitted with $J = -85$ and -75 cm^{-1} for *cis*-$[(Fe(bmen))_2O(H_2O)_2]^{4+}$ and *trans*-$[(Fe(tetpy))_2O(H_2O)_2]^{4+}$ ions, respectively.

In this connection, it must be noted that a χ^2 test analysis[11] of the goodness of fit for the $S_1 = S_2 = {}^5/_2$ and $S_1 = S_2 = {}^1/_2$ theoretical curves for the cis derivative (Figure 1), within the temperature range of 120–250 K where the curves diverge, assigns more than 95% level of confidence to the $S_1 = S_2 = {}^5/_2$ model, while the $S_1 = S_2 = {}^1/_2$ system gets less than 5%. In the case of the trans compound the two models cannot be discriminated with such a high degree of confidence because of a somewhat poorer quality of the experimental data. Nevertheless, the good overlapping between the susceptibility curves of the solid and aqueous samples within the temperature range of 100–250 K (Figure 2), together with the finding that in no case did a $S_1 = S_2 = {}^1/_2$ treatment prove satisfactory for the solid material at 100–300 K,[6] makes it reasonable to assume a sextet model also for *trans*-$[(Fe(tetpy))_2O(H_2O)_2]^{4+}$

Table I. Electronic Spectral Data of $[(Fe(bmen))_2OX_2]^{n+}$ Ions in Aqueous Solution[a]

pH 4.5			pH 7.3	
Band position	Assignment	Calcd energy[b]	Band position	Calcd energy[e]
10.5 b (~3)	$^6A_1 \rightarrow {}^4T_1$	10.7	11.4 b (~2)	11.6
15.9 b (60)	$\rightarrow {}^4T_2$	16.1	16.7 b (60)	16.7
20.4 sh (235)	$\rightarrow ({}^4A_1, {}^4E)$	20.4	20.8 (140)	20.8
21.0 sh (280)	*c*	21.0		
22.4 (382)	$\rightarrow {}^4T_2$	22.4	22.7 sh (210)	22.7 (or 22.8[c])
24.1 sh (450)	$\rightarrow {}^4E$	25.1	24.4 sh (300)	25.2
27.8 (3500)	Charge transfer		27.8 sh (2000)	Charge transfer
31.4 (5300)	Charge transfer		32.2 (3700)	Charge transfer
39.5 (11 800)	Ligand localized[d] ($\pi \rightarrow \pi_1{}^*$)		39.7 (11 400)	$\pi \rightarrow \pi_1{}^*$
			43.5 sh (11 100)	

[a] X = H_2O or OH^-, depending on pH. Band positions are in $cm^{-1} \times 10^{-3}$; b = broad, sh = shoulder. Samples are approximately 10^{-3} M (per mol of iron(III)); ϵ given in parentheses. [b] Calculated using $Dq = 1244$, $B = 678$, and $C = 2726$ cm^{-1}. [c] Calculated sum $[({}^6A_1 \rightarrow {}^4T_1) + ({}^6A_1 \rightarrow {}^4T_1)]$. [d] bmen ligand alone absorbs at 37.7×10^3 (sh), 38.5×10^3, and 39.2×10^3 cm^{-1} (sh). [e] Calculated using $Dq = 1212$, $B = 633$, and $C = 2899$ cm^{-1}.

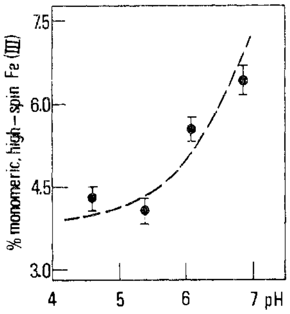


Figure 3. Paramagnetic contribution of aqueous solutions of $[(Fe(bmen))_2OX_2]^{n+}$ as a function of pH. Data are expressed as percent of monomeric high-spin Fe(III).

ions. On the basis of these results it may be concluded that, under the reported experimental conditions, both compounds are dimeric species with antiferromagnetic exchange between the two iron ions, both very likely in a $S = {}^5/_2$ state. Furthermore, it clearly appears that the extent of antiferromagnetic interaction is high and similar to that of the solid samples. This may account for the observation that the solutions do not give rise to any EPR signal (X band, 90 K).

With increased pH, the complexes behave as weak acids; e.g., they undergo two protolytic equilibria characterized by the following dissociation constants (20 °C): $pK_{a,1} = 5.7$ and $pK_{a,2} = 6.2$ for the cis compound and 4.3 and 6.2, respectively, for the trans derivative.[6] At the same time, a remarkable difference between their magnetic properties is observed. Within the whole range of pH explored, complex I is seen to retain essentially the original antiferromagnetic features, as illustrated in Figure 1. For example, at pH ~7, where the dihydroxo conjugate base $[(Fe(bmen))_2O(OH)_2]^{2+}$ predominates, the susceptibility can be fitted, within experimental errors, by the same parameters used for the diaquo oxy-bridged dimeric compound. In these conditions, only a few percent of paramagnetic species is present in solution, as suggested by the results of Figure 3 where the paramagnetism of the aqueous samples is reported as a function of pH. This effect is very likely due to the presence of some high-spin $[Fe(bmen)(OH)_2]^+$ ions, descendent from a minor dimer dissociation. The finding that above about pH 6, EPR spectra exhibit a weak–medium resonance at 1520 G ($g_{eff} = 4.29$), already observed for the parent mononuclear derivative characterized by a certain rhombic anisotropy,[12] provides a support to this hypothesis.

In contrast, at pH above about 4, the susceptibility of complex II shows a trend quite different from that illustrated in Figure 2, an antiferromagnetic interaction much smaller than that observed in the original $[(Fe(tetpy))_2O(H_2O)_2]^{4+}$ ions being detected. In fact, within the pH range of 4.2–5.5, the susceptibility of the solutions can be satisfactorily fitted only if one assumes the presence of two dimeric species in equilibrium (whose concentrations are predictable by the $pK_{a,1}$ of the complex), characterized by coupling constants $J = -75$ and -14.5 cm^{-1}, respectively. The other parameters were $S_1 = S_2 = {}^5/_2$, $g = 2.0$, and TIP = 0 (Figure 4).

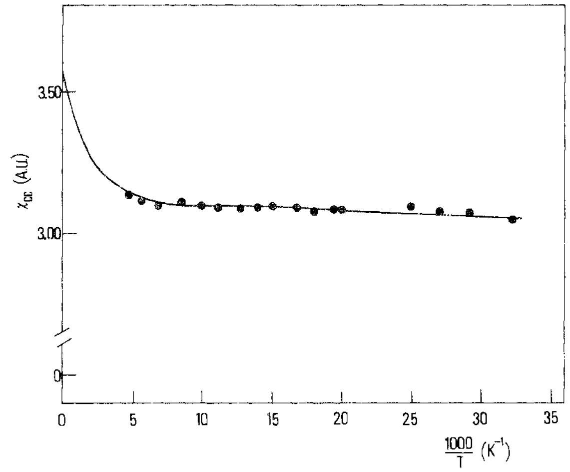
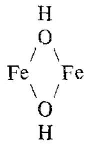


Figure 4. Volume magnetic susceptibility of an 8.55 mM solution of the trans complex at pH 4.6 as a function of inverse temperature. Solid line is the theoretical curve for two dimeric species in equilibrium with $J = -75$ cm^{-1} (2.15 mM) and -14.5 cm^{-1} (6.40 mM); see text.

According to a number of examples, which indicate that a reduced antiferromagnetic interaction with $J \approx -10$ cm^{-1} is ascribable to a bridging unit of the type[2,5-15]



the aforementioned results strongly suggest that, upon increase in pH, the dimeric trans compound utilizes dihydroxo bridging in its coordination structure. Such a bridging unit was supposed to be an intermediate for breakup of the $[((EDTA)Fe)_2O]^{4-}$ dimer,[2b] since it presumably involves a strained seven-coordinate structure. Nevertheless, in our case it appears stable as long as the solution is maintained below pH 6, only a few percent of monomeric, possibly low-spin species being detected in these conditions (Figure 4). At higher pH's, the mononuclear complex becomes predominant, though the relatively low concentration of the samples (see Experimental Section) makes it difficult to assert whether the binuclear dihydroxy-bridged derivative is still present in a reduced amount.

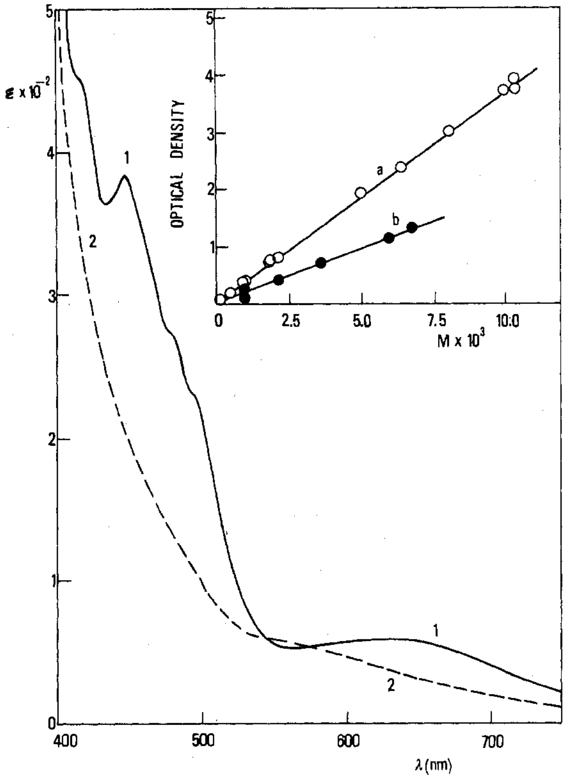


Figure 5. Visible electronic spectrum of aqueous solution of $[(Fe(bmen))_2O(H_2O)_2]^{4+}$ (pH 4.5; curve 1) as compared to the spectrum of the low-spin mononuclear $[Fe(bmen)(H_2O)OH]^{2+}$ ions (curve 2). Insert: Beer's law plot for $[(Fe(bmen))_2O(H_2O)_2]^{4+}$ (a) and $[(Fe(bmen))_2O(OH)_2]^{2+}$ (b). All measurements were normalized for a 1-cm cell, λ 450 nm; molarity based on half the molecular weight of the dimer.

The relevance of these results is that the sole trans dimeric compound happens to undergo a dissociative process in solution, which takes place through a dihydroxo bridging intermediate only at pH values around the $pK_{a,2}$ of the complex.

Electronic Spectra. The electronic spectral data of the cis compound at pH 4.5 and 7.3 are summarized in Table I and a typical absorption spectrum in the visible region is illustrated in Figure 5. $[(Fe(bmen))_2O(H_2O)_2]^{4+}$ ions show visible ligand field bands which are intense even compared to those of a parent mononuclear low-spin derivative,[12] i.e., $[Fe(bmen)OH(H_2O)]^{2+}$ (Figure 5). This intensity enhancement can be ascribed to the breakdown of spin forbiddeness of the transitions,[16] owing to a cooperative mechanism of simultaneous pair electronic (SPE) excitations.[2c,13] It is usually found in materials where a strong coupling interaction between neighboring ions occurs. The assignment of the transitions from a spin sextet ground state leads to calculated energies which agree satisfactorily with the experimental ones (Table I), the SPE bands being very likely masked by the intense charge-transfer or ligand-localized bands. All of these features, together with the finding that Beer's law is obeyed within the wide range of concentration explored at both pH 4.5 and 7.3 (insert of Figure 5), confirm the idea that the approximately linear Fe–O–Fe structural unit[2c,5] of the binuclear cis complex remains practically unperturbed by pH variations.

The electronic spectral patterns of $[(Fe(tetpy))_2O(H_2O)_2]^{4+}$ ions are, in contrast, complicated by the presence of intense low-energy charge-transfer bands (Figure 6), as are those observed in similar compounds, such as $[Fe_2(bpy)_4O](SO_4)_2$ and $[Fe_2(terpy)_2O](NO_3)_4$.[17] The onset of these bands at around 17 000 cm^{-1} makes it possible to detect as a shoulder only one intense LF band in the visible region (18 200 cm^{-1}), besides a very weak one ($\epsilon \sim 0.5$) at 11 300 cm^{-1}. These bands may be assigned to the spin-forbidden d–d transitions $^6A_1 \rightarrow {}^4T_2$ and $^6A_1 \rightarrow {}^4T_1$, respectively, in agreement with a number of examples reported in the literature.[5,13] On the other hand, the lack of any knowledge on the spectral behavior of well established mononuclear parent derivatives makes it difficult at present to interpret these data in terms of the structural characteristics of the molecule. Furthermore, the lability of this complex at very high ionic strength, which is necessary for performing low-temperature spectra,[13b] prevented use of

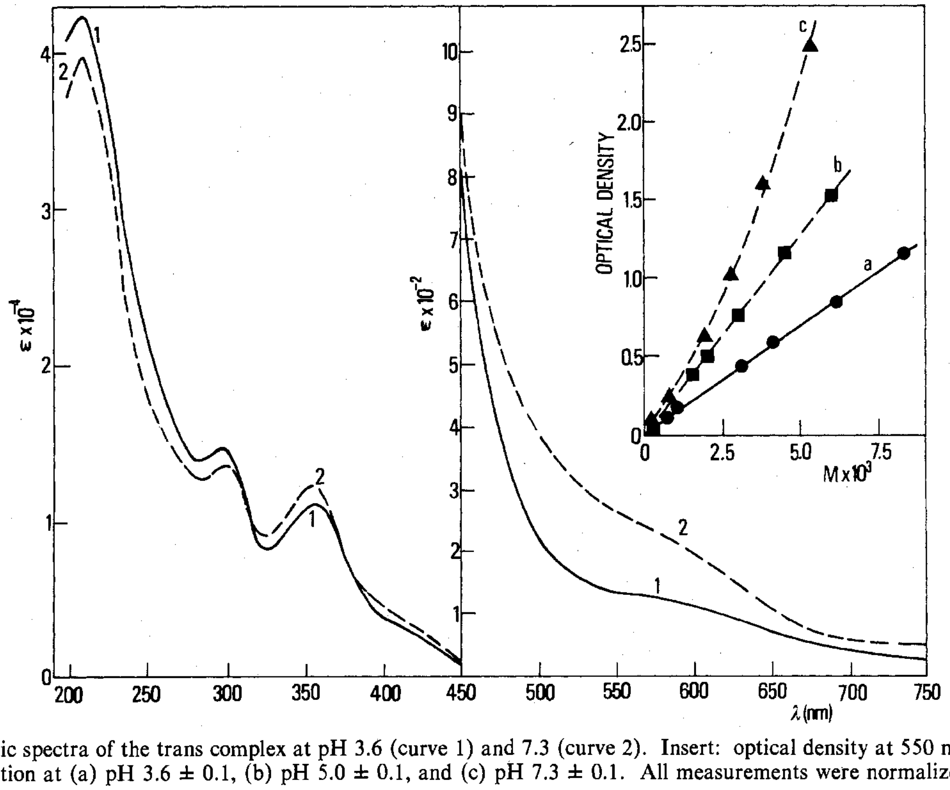


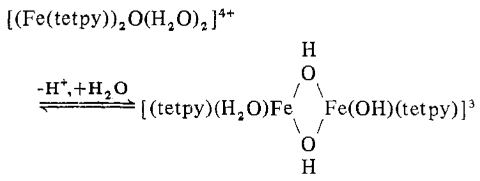
Figure 6. Electronic spectra of the trans complex at pH 3.6 (curve 1) and 7.3 (curve 2). Insert: optical density at 550 nm as a function of complex concentration at (a) pH 3.6 ± 0.1, (b) pH 5.0 ± 0.1, and (c) pH 7.3 ± 0.1. All measurements were normalized for a 1-cm cell.

spectral data in that temperature region. It is worth noting, however, that acid solutions of this compound strictly follow Beer's law (insert of Figure 6), a result consistent with the observed magnetic stability of the oxy-bridged diaquo or dihydroxy-bridged hydroxoaquo dimer. The opposite is found at pH values around neutrality, where concentration-dependence experiments clearly indicate the occurrence of a monomer–dimer equilibrium.

Discussion

The reported magnetic data strongly suggest that the binuclear complexes under investigation are characterized by an approximately linear Fe–O–Fe unit also in aqueous medium (pH ca. 4).[2c,5,13] Furthermore, they indicate that upon moderate increase of pH (~5) the dimeric trans derivative utilizes dihydroxo bridging in its coordination structure, whose fragmentation occurs only at higher pH values (>6). In contrast, evidence is produced that the oxy-bridged unit of the dimeric cis complex is stable in solution, the antiferromagnetic coupling between the two iron(III) ions being practically insensitive to pH variations.

Two points arise from these results: (1) why the antiferromagnetic interaction in *trans*-$[(\mathrm{Fe(tetpy)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+}$ ions is pH dependent and (2) why this phenomenon occurs solely in this compound. As far as point 1 is concerned, it is reasonable to assume that added $\mathrm{OH^-}$ ions titrate preferentially the coordinated water molecules in the apical sites of the complex, since the protolytic process should be fast enough to predominate over any other reaction.[2b] This hypothesis is consistent with the results obtained with *cis*-$[(\mathrm{Fe(bmen)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+}$ ions. Moreover, $\mathrm{OH^-}$ ions cannot be thought to be directly involved in the formation of the dihydroxy-bridged structural unit because the intramolecular assistance from one proton of coordinated water molecules is very unlikely on both chemical and steric grounds. The most plausible mechanism of formation of the dihydroxy-bridged unit is, therefore, that which sees the assistance of an entering water molecule, in agreement with that proposed in a number of cases.[2b,2] The role played by pH should be primarily that of weakening the strong Fe–O–Fe bonds through the replacement of $\mathrm{H_2O}$ groups by electron-releasing $\mathrm{OH^-}$ ions in the complex. This is expected to facilitate the binding of a solvent molecule, leading to the symmetrical dihydroxy-bridged structure



$$[(\mathrm{Fe(tetpy)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+} \xrightleftharpoons{-\mathrm{H^+},+\mathrm{H_2O}} [(\mathrm{tetpy})(\mathrm{H_2O})\mathrm{Fe}(\mu\text{-}\mathrm{OH})_2\mathrm{Fe(OH)(tetpy)}]^{3}$$

According to molecular models, the trans arrangement of porphyrin-like tetpy around the central metal ions brings about a rather open structure as compared to that of the complex formed by the highly flexible bmen ligand, which was definitely shown to prefer a cis-type geometry.[13,18,19] This would make the oxygen bridge of $[(\mathrm{Fe(tetpy)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+}$ ions more easily accessible to solvent molecules than that of the structurally more compact *cis*-$[(\mathrm{Fe(bmen)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+}$ ions and account for the formation of the dihydroxy-bridged unit. Point 2 is therefore closely related to the proposed mechanism in that the stereochemical environment around the oxy-bridged metal ions is primarily responsible for the different behavior displayed by the two complexes in aqueous solution.

On the other hand, with increased pH above about 6, magnetic and optical results indicate the occurrence of fragmentation of the dihydroxy-bridged binuclear complex. The pathway for this process may be schematized as

$$[(\mathrm{Fe(tetpy)OH})_2(\mathrm{H_2O})\mathrm{OH}]^{3+} \xrightleftharpoons{-\mathrm{H^+}} [(\mathrm{Fe(tetpy)OH})_2(\mathrm{OH})_2]^{2+}$$
$$\rightleftharpoons 2[\mathrm{Fe(tetpy)(OH)_2}]^{+}$$

Electronic effects rather than steric strains presumably favor the breakup of the postulated seven-coordinate dihydroxy-bridged "dihydroxo" dimer $[(\mathrm{Fe(tetpy)OH})_2(\mathrm{OH})_2]^{2+}$. In fact, only an increased electron density on both iron ions, due to coordinated $\mathrm{OH^-}$ groups arising from the protolysis of the bound water molecules, apparently determines the formation of the mononuclear species.

Independent measurements by electrochemical techniques will be carried out to confirm the proposed mechanism.

Registry No. *cis*-$[(\mathrm{Fe(bmen)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+}$, 61003-07-4; *trans*-$[(\mathrm{Fe(tetpy)})_2\mathrm{O}(\mathrm{H_2O})_2]^{4+}$, 61025-86-3; $[\mathrm{Fe(bmen)(H_2O)OH}]^{2+}$, 59733-64-1; $[(\mathrm{Fe(bmen)})_2\mathrm{O(OH)_2}]^{2+}$, 61025-87-4.

References and Notes

(1) (a) Istituto di Fisica. (b) Istituto di Chimica Fisica. (c) Present address: Facoltà di Scienze, Libera Università di Trento, Trento, Italy.

(2) (a) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712–3720 (1967); (b) H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *ibid.*, **90**, 71–77 (1969); (c) H. B. Gray and H. J. Schugar, *Inorg. Biochem.*, **1**, Chapter 3 (1973), and references cited therein.

(3) D. L. Ehman and D. T. Sawyer, *Inorg. Chem.*, **8**, 900–903 (1969).

(4) V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 3397–3405 (1972).

(5) M. Y. Okamura and I. M. Klotz, *Inorg. Biochem.*, **1**, Chapter 11 (1973).

(6) M. Branca, B. Pispisa, and C. Aurisicchio, *J. Chem. Soc., Dalton Trans.*, 1543–1546 (1976).

(7) M. Cerdonio, C. Cosmelli, F. Mogno, and G. L. Romani, *Proc. Int. Conf. Low Temp. Phys., 14th*, **4**, 258–262 (1975).

(8) M. Cerdonio, C. Cosmelli, G. L. Romani, C. Messana, and C. Gramaccioni, *Rev. Sci. Instrum.*, **47**, 1–5 (1976).

(9) G. S. Kell, *Chem. Phys. Lett.*, **30**, 223–226 (1975).

(10) F. E. Senftle and A. Thorfe, *Nature (London)*, **194**, 673–674 (1962).

(11) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, N.Y., 1969, Chapter 10.

(12) M. Branca, P. Checconi, and B. Pispisa, *J. Chem. Soc., Dalton Trans.*, 481–488 (1976).

(13) (a) H. J. Schugar, G. R. Rossman, J. Thibeault, and H. B. Gray, *Chem. Phys. Lett.*, **6**, 26–29 (1970); (b) H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 2683–2690 (1972).

(14) H. J. Schugar, G. R. Rossman, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 4564–4566 (1969).

(15) C. H. S. Wu, G. R. Rossman, H. B. Gray, G. S. Hammond, and H. J. Schugar, *Inorg. Chem.*, **11**, 990–994 (1972).

(16) L. L. Lohr, Jr., and D. S. McClure, *J. Chem. Phys.*, **49**, 3516–3521 (1968).

(17) W. M. Reiff, W. A. Baker, Jr., and N. E. Erickson, *J. Am. Chem. Soc.*, **90**, 4794–4800 (1968).

(18) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331–1339 (1966).

(19) J. G. Gibson and E. B. McKenzie, *J. Chem. Soc. A*, 1666–1683 (1971).