2-pyridyl radical, as suggested by Symons,[24] then the agreement for both the N and H hyperfine coupling constants is much better. The observed spectrum shows three protons with a coupling constant of 4.3 G[23] and a nitrogen coupling constant of 29.7 G.[19] Examination of the calculated proton coupling constants for the pyridine cation, shown in Table I, reveals no correlation of the calculated and observed spectra. Further, the calculated nitrogen coupling constant for the cation is 52.5 G, which also does not agree with the observed 30 G. However, when we consider the 2-pyridyl calculation, the agreement of the nitrogen coupling constant is much better. Also, when we consider our failure to calculate the coupling constant of the *para* proton of the phenyl radical, we reach the conclusion that our value for the 5-H coupling constant should be about 2–4 G. Using this value, a reproduction of our calculated spectra for the 2-pyridyl radical agrees well with the spectrum observed by Tsuji, *et al.*,[23] since many of the lines due to proton coupling are calculated to be so close that they would not be resolved. Hence we conclude that the radical obtained on irradiation of pyridine is the 2-pyridyl radical as suggested by Symons,[24] rather than the pyridine cation.

The extended Hückel method seems to give surprisingly good results when applied to the calculation of epr hyperfine coupling constants, and the range of the applicability seems large. It appears to be a useful tool in the difficult task of determining the structure of radicals. Trends in the wave functions appear to be significant but their absolute magnitudes do not. The neglect of spin polarization sets a limit on the accuracy with which we can calculate spin densities, and we have taken this into consideration in the conclusions we have drawn. We do not ordinarily know from experiment the sign of the coupling constant; we cannot calculate a negative spin density, and in some cases where we calculate a small value for A this could turn out to be negative. We are currently attempting to improve the calculation by including spin polarization. Preliminary results indicate spin polarization is very important for protons bonded to atoms containing a large fraction of the unpaired spin density.[25] For example, the α-proton coupling constant in the vinyl radical is probably negative. Consequently, we can draw no conclusions[2,3] that depend on the magnitude of a coupling constant directly bonded to a carbon atom containing most of the unpaired spin density.

The success in calculating nitrogen hyperfine coupling constants suggests that this is not as difficult a problem as one might suppose. Further, this method can possibly be extended to calculate ^{13}C and ^{19}F hyperfine splittings.

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Studies of Some Binuclear, Oxygen-Bridged Complexes of Iron(III). New Iron(III)–2,2′,2″-Terpyridine Complexes

W. M. Reiff,[1a] W. A. Baker, Jr.,[1a,b] and N. E. Erickson[1c]

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York, 13210, and the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973.
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Abstract: Three complexes of iron(III) with the tridentate ligand 2,2,′2″-terpyridine have been isolated and characterized. One is a simple, high-spin octahedral complex, $[Fe(terpy)Cl_3]$, while another, $[Fe(terpy)_2](ClO_4)_3$, is a low-spin octahedral complex. The third, $[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$, is a binuclear complex exhibiting properties similar to those of the related 1,10-phenanthroline, 2,2′-bipyridine, and N,N′-ethylenebis(salicylideneiminate) binuclear species. The magnetic behavior and the Mössbauer, electronic, and infrared spectra of the binuclear terpyridine complex are reported and compared with those of other similar systems. The possibility of a quartet ($S = {}^3/_2$) *vs.* a sextet ($S = {}^5/_2$) spin state for the iron is discussed.

Complexes of Fe(II) with 2,2′,2″-terpyridine (hereafter terpyridine or terpy) having one or two terpyridines per iron are known. The mono complexes having the general formula $[Fe(terpy)X_2]$ ($X^- = Br^-, SCN^-, I^-$) have been shown on the basis of X-ray, magnetic, and spectroscopic studies[2,3] to have a distorted square-pyramidal structure. The bis complexes are low spin and have a distorted octahedral configuration. Mössbauer spectra of the bis complexes show an unusually large (for low-spin Fe(II)) quadrupole splitting (ΔE_q)[3,4] similar to that observed for the $[Fe(CN)_5NO]^{2-}$ ion.[5] The generally accepted explanation for the large values of ΔE_q observed for these systems is that there exists considerable anisotropic covalent bonding involving the t_{2g} orbitals. In the

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Table I. Analytical Data

Complex	Calculated, %					Found, %				
	C	H	N	Fe	Cl	C	H	N	Fe	Cl
$[Fe(terpy)Cl_3]$	45.55	2.81	10.63	14.1	26.95	45.07	3.20	10.64	13.8	27.30
$[Fe(terpy)_2](ClO_4)_3$	43.90	2.71	10.24	6.80		43.90	2.62	10.31	6.65	
$[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$	41.88	2.82	16.29	12.98		41.78	3.09	16.30	13.09	
$[Fe_2(phen)_4OCl_2]Cl_2 \cdot 5H_2O$	53.35	3.93	10.37			53.17	3.52	10.21		
$[Fe_2(phen)_4O](NO_3)_4 \cdot 3H_2O$	50.10	3.56	14.62			49.85	3.34	14.61		
$[Fe_2(bipy)_4O](SO_4)_2 \cdot 3.5H_2O$	47.68	3.91	11.12	11.09		47.77	3.70	11.15	10.57	
$[(Fe(salen)py)_2O]$	61.62	4.69	10.27			62.10	5.12	10.01		
$[(Fe(salen))_2O]$	58.20	4.28	8.49			59.01	4.45	8.79		
$[(Fe(salen))_2O] \cdot CH_2Cl_2$	53.18	4.07	7.52			53.27	3.89	7.50		

terpyridine complexes, this is presumably due to the difference in metal–ligand bonding between the center and outer rings of the ligand.

Prior to the present investigation, attempts to isolate pure terpyridine complexes of Fe(III) have been generally unsuccessful[6a] although Ford-Smith and Sutin[6b] reported the preparation of $[Fe(terpy)_2](ClO_4)_3$. We can find no other reports of such complexes in the literature. Direct addition of terpyridine to Fe(III) salts results in rapid reduction and formation of $[Fe(terpy)_2]^{2+}$. This is to be contrasted with the behavior of bipyridine and phenanthroline which upon direct reaction with Fe(III) salts form stable binuclear complexes.[6a,7] Mononuclear complexes of Fe(III) and the latter two ligands can be isolated by oxidation of the corresponding Fe(II) complexes, and we have applied this method to the preparation of terpyridine complexes. Oxidation of $[Fe(terpy)_2]^{2+}$ followed by saturation of the solution with a given anion yields for most anions the corresponding Fe(II) complex but, when the anion is one of the weakly reducing anions Cl^-, ClO_4^-, or NO_3^-, an Fe(III)–terpyridine complex is obtained, although it is of a different nature in each case. The chloride yields a yellow complex of empirical formula $Fe(terpy)Cl_3$, the perchlorate a simple light green mononuclear complex, $[Fe(terpy)_2](ClO_4)_3$, and the nitrate an orange-red binuclear complex, $[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$. It is the purpose of this article to discuss these three complexes and to present data on other binuclear complexes of Fe(III) which bear on their molecular geometry and electronic structure.

Experimental Section

Materials. All metal salts used were reagent grade. The various ligands were used as obtained from the suppliers, G. F. Smith, Co. and Matheson Coleman and Bell.

Preparations. The three Fe(III)–terpyridine complexes were all prepared in a similar manner. In this procedure, 75 ml of 0.025 *M* $[Fe(terpy)_2]SO_4$ in water was oxidized by a mixture of excess PbO_2 and 10 ml of 0.2 *N* H_2SO_4. The resulting green $[Fe(terpy)_2]^{3+}$ solution was then filtered and cooled in an ice bath after which 5–10 ml of a saturated water solution of the sodium salt of the appropriate anion was added to effect precipitation. The solution was then filtered and the precipitate dried under vacuum. The entire preparation was carried out in the dark to minimize the possibility of reduction.

The two complexes $[Fe_2(phen)_4OCl_2]OCl_2 \cdot 5H_2O$ and $[Fe_2(phen)_4O](NO_3)_4 \cdot 3H_2O$ were prepared by the method given by Gaines.[7]

The complex $[Fe_2(bipy)_4O](SO_4)_2 \cdot 3.5H_2O$ was prepared by a modification of the procedure used for the phenanthroline complexes. In this procedure, $Fe_2(SO_4)_3$ was stirred in warm water with bipyridine (4:1 molar ratio of ligand to salt) until all solids had dissolved. The warm solution was then filtered and the filtrate allowed to stand for 1 hr, after which a light brown precipitate formed. The precipitate, which was the desired product, was isolated, washed with water, and dried under vacuum.

Complexes of N,N′-ethylenebis(salicylideneiminate) (hereafter called salen), $[(Fe(salen))_2O]$, and $[(Fe(salen))_2O] \cdot CH_2Cl_2$ were prepared by methods recently described.[8] The pyridine adduct was prepared by crystallization of the CH_2Cl_2 adduct from pyridine. The product was dried under vacuum only briefly since extensive pumping removes pyridine.

Analytical data for all complexes reported are given in Table I.

Magnetic Measurements. Magnetic data were obtained using both Gouy and Faraday balances. The calibrant used was $HgCo(NCS)_4$. A description of the Faraday balance as well as the diamagnetic corrections used have been given previously.[9]

Spectra. Visible and near-infrared spectra were obtained using a Cary Model 14 spectrophotometer. Reflectance spectra were obtained using the standard integrating sphere reflectance attachment. Spectra were also obtained at room and liquid nitrogen temperatures on samples mulled with Kel-F stopcock grease. An Air Products Co. Cryo-Tip apparatus was used for the low temperatures.

Infrared spectra were obtained using a Perkin-Elmer 521 grating spectrophotometer. The samples were in the form of KBr disks or Nujol mulls.

Mössbauer spectra were obtained using an Austin Science Associates constant-acceleration spectrometer. Data were stored in an RIDL 400 channel analyzer. The data were displayed on an oscilloscope from which readings were taken. No curve fitting of the data has been performed.

X-Ray Powder Data. All powder data were obtained using a General Electric XRD powder camera and Ni-filtered Cu Kα radiation. No corrections for film shrinkage were made.

Conductivity Measurements. Conductivities were measured on an Industrial Instruments, Inc., Model RC 16B1 bridge with a standard Pt electrode cell and 0.001 *M* solutions.

Results and Discussion

$[Fe(terpy)Cl_3]$. Addition of chloride ion to an acidic solution of $Fe(terpy)_2{}^{3+}$ results in precipitation of the hitherto unreported $[Fe(terpy)Cl_3]$. There is little doubt that this complex is a simple, mononuclear, high-spin Fe(III) complex. The magnetic moment is 5.85 BM and independent of temperature as predicted for a $^6A_1$ ground state. The Mössbauer data (Table III) are normal for high-spin Fe(III).[10] Further, there are no discernible d–d bands in the electronic spectrum, a result which is expected for a $^6A_1$ ground state since all possible transitions would be spin forbidden.

Evidence that the three Cl^- ions are coordinated comes from the infrared spectrum (Table V). The four bands in the 300–400-cm^{-1} region are assigned as

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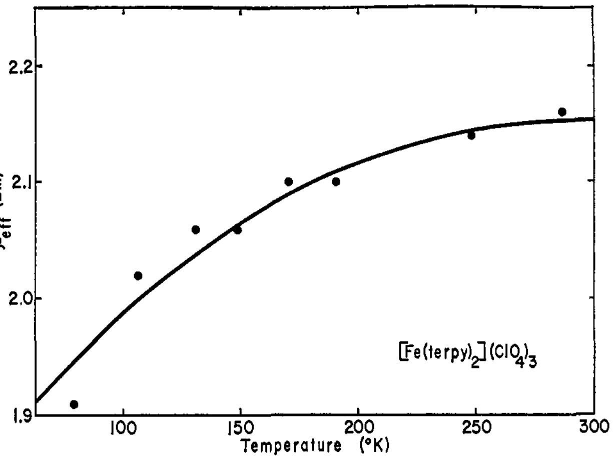

Figure 1. Magnetic moment (BM) *vs.* T (°K) for [Fe(terpy)$_2$]-(ClO$_4$)$_3$. The solid line is that calculated assuming $\Delta = -1750$ cm^{-1}, $\lambda = -350$ cm^{-1}, and $\kappa = 0.8$.

Table II. Magnetic Data

Compound	Temp, °K	μ_{eff}, BM	$\chi_g \times 10^6$, cgs	$\chi_M' \times 10^6$, cgs[a,b]
[Fe(terpy)Cl$_3$]	290	5.78[c]	35.53	14,270
[Fe(terpy)$_2$](ClO$_4$)$_3$	286.5	2.16	1.97	2,010
	247.7	2.14	2.29	2,280
	190.3	2.10	3.00	2,870
	170.6	2.10	3.40	3,200
	148.9	2.06	3.80	3,520
	130.8	2.06	4.38	4,000
	106.8	2.02	5.31	4,770
	78.5	1.91	6.53	5,770
[Fe$_2$(terpy)$_2$O](NO$_3$)$_4$·H$_2$O	296.7	1.83	2.73	1,390
	252.4	1.67	2.66	1,350
	215.4	1.50	2.52	1,290
	184.3	1.38	2.46	1,270
	152.9	1.19	2.17	1,140
	127.2	1.01	1.82	990
	102.0	0.83	1.45	830
	81.2	0.65	0.98	630
[Fe$_2$(phen)$_4$OCl$_2$]Cl$_2$·5H$_2$O	292.1	1.83	1.98	1,420
	89.2	0.64	0.38	560
[Fe$_2$(phen)$_4$O](NO$_3$)$_4$·3H$_2$O	291.9	1.74	1.67	1,290
	78.0	0.49	0.09	380
[Fe$_2$(bipy)$_4$O](SO$_4$)$_2$·3.5H$_2$O	292.5	1.86	2.36	1,470
	233.8	1.61	2.18	1,380
	180.1	1.36	1.97	1,280
	148.3	1.17	1.72	1,150
	127.5	1.06	1.49	1,040
	110.8	0.90	1.22	900
	102.8	0.83	0.96	820
	90.4	0.72	0.46	710
	71.4	0.51	0.31	460
[(Fe(salen)py)$_2$O]	291.4	2.04	3.80	1,760
[(Fe(salen))$_2$O]	293.7	1.94	4.40	1,590
	78.0	0.48	0.70	370

[a] The molar susceptibility after correction for diamagnetism. [b] Diamagnetic corrections ($\times 10^6$ cgs): Fe^{3+}, 13; Cl$^-$, 23; NO$_3^-$, 19; ClO$_4^-$, 32; SO$_4^{2-}$, 40; H$_2$O, 13; bipy, 105; phen, 128. All were taken from B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 403. Values of 138 and 46 were used for salen and pyridine, respectively, and were obtained using constitutive corrections given in the same source. For terpyridine, a value of 148 was used from R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962). The value for the bridging oxygen was estimated to be 6. [c] The moment remains constant down to 78°K.

Fe–Cl bands. This agrees with the results of Clark,[11] who found that increasing coordination decreases the M–Cl frequency. Since the Fe–Cl stretch in FeCl$_4^-$ is found[11] at 378 cm^{-1}, the energies we observe are reasonable for such an assignment. Further, there is a distinct similarity between the spectrum in the 300–400-cm^{-1} range of [Fe(terpy)Cl$_3$] and that of [Ru(py)$_3$-Cl$_3$] which is known to have the three Cl$^-$ ions coordinated to the metal.[12]

[Fe(terpy)$_2$](ClO$_4$)$_3$. In contrast to the system discussed above, the addition of ClO$_4^-$ to an aqueous acidic solution of Fe(terpy)$_2^{3+}$ results in precipitation of a compound which can only be formulated as [Fe-(terpy)$_2$](ClO$_4$)$_3$.[6b] The observed properties of this complex can best be described by considering it to be a distorted octahedral low-spin Fe(III) species. The magnetic data in Figure 1 and Table II show that the ground state is a spin doublet. We have assumed that there is an axial distortion to the ligand field and used the theory developed by Figgis[13] to account for the observed results. In this treatment, there are three parameters which affect the results: Δ, the splitting of the $^2T_{2g}$ ground state due to the axial field component; λ, the spin–orbit coupling constant; and κ, a parameter which allows for reduction of orbital angular momentum due to electron delocalization. The best fit of the experimental data is shown in Figure 1. It should be emphasized that no particular significance should be placed on the precise values of the parameters which give the best fit. The total variation in moment is not great enough, and the experimental data are not accurate enough to indicate other than the general magnitude of the values. Although the best fit as shown corresponds to a negative value of Δ, there are other sets of parameters with a positive Δ which are within the probable error in the measurements. A negative value indicates that the splitting of the $^2T_{2g}$ state is such that the orbital doublet is lower than the orbital singlet. This is opposite to what is found[14] for Fe(phen)$_3{}^{3+}$ and Fe(bipy)$_3{}^{3+}$. Whether or not it is reasonable to expect a difference in the order of the levels for terpy as compared to phen is hard to say. Measurements to lower temperatures would presumably resolve the question, and we hope to do this in the near future. It should be noted that the Mössbauer data (see below) suggest an orbital singlet ground state.

The Mössbauer data for this compound are quite interesting. The low value of the isomer shift (Table III) is normal for low-spin Fe(III),[10] but the quadrupole

Table III. Mössbauer Data[a]

Compound	Isomer shift (δ) Room temp	Isomer shift (δ) 77°K	Quadrupole splitting (ΔE_q) Room temp	Quadrupole splitting (ΔE_q) 77°K
[Fe(terpy)Cl$_3$]	0.34	0.46	0.55	0.54
[Fe(terpy)$_2$](ClO$_4$)$_3$	−0.01	0.07	3.09	3.43
[Fe$_2$(terpy)$_2$O](NO$_3$)$_4$·H$_2$O	0.44	0.59	1.93	2.35
[Fe$_2$(phen)$_4$OCl$_2$]Cl$_2$·5H$_2$O	0.42	0.49	1.70	1.68
[Fe$_2$(phen)$_4$O](NO$_3$)$_4$·3H$_2$O	0.37	0.46	1.39	1.49
[Fe$_2$(bipy)$_4$O](SO$_4$)$_2$·3.5H$_2$O	0.38	0.48	1.33	1.51
[(Fe(salen)py)$_2$O]	0.36	0.44	0.92	0.88
[(Fe(salen))$_2$O]	0.32	0.46	0.72	0.78
[(Fe(salen))$_2$O.CH$_2$Cl$_2$]	0.35	0.46	0.78	0.78

[a] All data in mm/sec relative to natural iron foil.

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splitting is larger by almost a factor of 2 than any we have seen reported. For example, the corresponding bipyridine complex shows a ΔE_q of only 1.76 mm/sec.[10] We have tried to account for both the magnitude and temperature dependence of ΔE_q using current theoretical models, but the agreement is poor. In particular, the theory of Golding[15] for low-spin Fe(III) was examined, since the theory is specifically concerned with systems having low-symmetry field components. The observed values of ΔE_q are much larger than the predicted values[15] for low-spin Fe(III), and, although other treatments[16] give predicted values of the order of that observed for $[Fe(terpy)_2](ClO_4)_3$, the predicted temperature dependence is much less than that observed.

About all that can be said, therefore, is that qualitatively the large ΔE_q is probably due to an additive effect of a valence contribution from the "hole" in the t_{2g} subshell and a lattice contribution due to the asymmetry of the ligands. In fact, if one assumes that the lattice contribution is the same as that found in $Fe(terpy)_2{}^{2+}$, 1.14 mm/sec, then the remainder, 1.95 mm/sec, is about the same as that found for the analogous bipyridine complex[10] which has an orbital singlet ground state and falls into the range predicted for low-spin Fe(III) for a valence contribution only.[15] It is also worth noting that the idea that the lattice gradient adds rather than subtracts from the valence gradient is contrary to what is usually assumed for Fe(II),[17a] although it has been reported[17b] that in $FeSiF_6 \cdot 6H_2O$ the valence and lattice field gradient contributions are additive.

The assumption that $[Fe(terpy)_2](ClO_4)_3$ is a simple six-coordinate complex is also supported by its electronic and infrared spectra. There are no observable d–d bands due to the onset of ligand and charge-transfer bands at 14,000 cm^{-1}, and any spin-allowed d–d bands would be of appreciably higher energy. The infrared spectrum is typical of coordinated terpyridine and ionic perchlorate.[18]

Binuclear Complexes. Tables I–V contain data obtained on seven binuclear complexes. Of these, $[Fe(terpy)_2O](NO_3)_4 \cdot H_2O$ and the complete magnetic data for $[Fe_2(bipy)_4O](SO_4)_2 \cdot 3.5H_2O$ are reported for the first time while the others have been studied by a number of workers.[19–21] There is little doubt that the terpy and bipy complexes should be formulated as binuclear species having an oxygen bridge as is generally accepted for the other compounds.[19,20] The presence of an infrared band in the region 800–900 cm^{-1} seems to be indicative of such a bridge, and all of the binuclear bipyridines, phenanthroline, and terpyridine complexes show such a band. These data are given in Table V. In agreement with Lewis, *et al.*,[19] we found the infrared spectra of the salen complexes too complex to establish the existence of such a band. The infrared spectra of the terpyridine complex also indicate the presence of bonded as well as ionic nitrate ions (Table V). The splitting of the ν_3 band and the appearance of ν_1 are indicative of coordinated nitrate. Unfortunately, previous infrared studies of the nitrate ion[22] have indicated that it is difficult to distinguish between mono- and bidentate coordinated nitrate. Thus each iron could be five-coordinate, having in addition to the bridge oxygen and the terpyridine a monodentate nitrate, or six-coordinate with a bidentate nitrate. There is no evidence from infrared data of coordinated sulfate in the bipyridine complex. Along this line, conductivity data in methanol of a number of these complexes support the conclusion previously reached[20] that there are two coordinated Cl$^-$ ions in $[Fe_2(phen)_4OCl_2]Cl_2 \cdot 5H_2O$, although the data in aqueous solution suggest that they are ionized in water. The accuracy of these data is reduced somewhat by hydrolysis and reduction, although we believe the measurements were made rapidly enough to minimize such effects.

Table IV. Molar Conductivities

Compound	Aqueous soln	CH_3OH soln
$[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$	439	. . .
$[Fe_2(phen)_4OCl_2]Cl_2 \cdot 5H_2O$	457	147
$[Fe_2(phen)_4O](NO_3)_4 \cdot 3H_2O$	492	278
$[Cr(en)_3]Br_3$	397	. . .
$[Fe(en)_3]Cl_3$	. . .	199

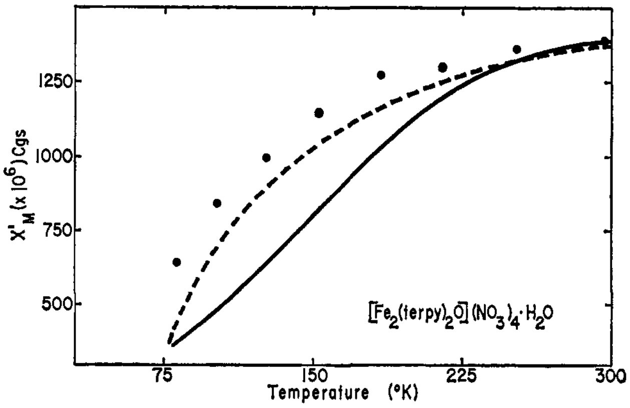

Figure 2. Magnetic data for $[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$: (• • •) experimental data; (----) calculated for $S = {}^5/_2$, $g = 2$, $J = -105$ cm^{-1}, and $N(\alpha) = 0$; (———) calculated for $S = {}^1/_2$, $g = 2.8$, $J = -190$ cm^{-1}, and $N(\alpha) = 3.25 \times 10^{-6}$ cgs.

Magnetic data over a range of temperature for both the terpyridine and bipyridine complexes are given in Table II. Room-temperature and 77°K data are given for some of the other binuclear species for comparison. It is obvious that the general behavior for all of them is similar. Plots of the magnetic data for the two complexes are given in Figures 2 and 3. The data support the idea that the complexes are best represented as two interacting $S = {}^5/_2$ (or, as will be discussed later, $S = {}^3/_2$) centers. Also shown in Figures 2 and 3 are calculated curves.[23] The best-fit parameters used for the calculations are indicated in the captions. It is clear that the data are more consistent with $S = {}^5/_2$

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Table V. Infrared Spectra and Band Assignments

Compound	Band energy, cm^{-1}, and intensity[a]	Assignment[b]
$[Fe(terpy)Cl_3]$	348 (w, sh), 343 (s, br), 330 (w, sh), 309 (m)	Fe–Cl stretch
$[Fe(terpy)_2](ClO_4)_3$	1075 (s, br), 915 (w), 615 (s)	Ionic ClO_4^- (ν_3, ν_4, ν_1)
$[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$	1375 (s), 830 (w)	Ionic NO_3^- (ν_3, ν_2)
	1495 (s), 1295 (s, br), 1039 (m), 808 (w)	Covalent NO_3^- (ν_3, ν_3, ν_1, ν_2)
	870 (s, br)	Fe–O–Fe
$[Fe_2(phen)_4OCl_2]Cl_2 \cdot 5H_2O$	835 (s, br)	Fe–O–Fe
$[Fe_2(phen)_4O](NO_3)_4 \cdot 3H_2O$	1360 (s, br)	Ionic NO_3^- (ν_3)
	820	Fe–O–Fe
$[Fe_2(bipy)_4O](SO_4)_2 \cdot 3.5H_2O$	808 (s)	Fe–O–Fe

[a] s = strong, m = medium, w = weak, br = broad, sh = shoulder. [b] The designations ν_1 are those given in ref 18.

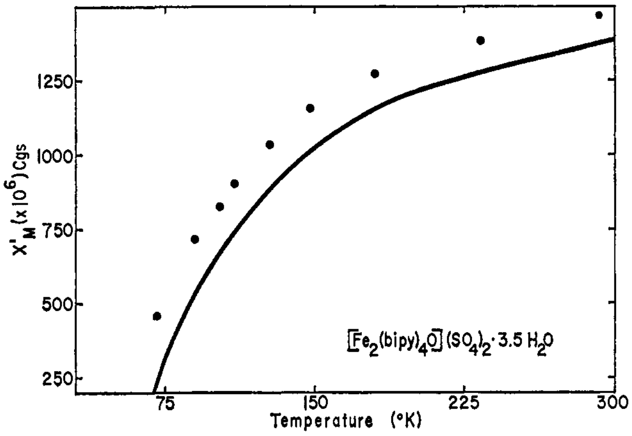

Figure 3. Magnetic data for $[Fe_2(bipy)_4O](SO_4)_2 \cdot 3.5H_2O$: (•••) experimental data; (———) calculated for $S = {}^5/_2$, $g = 2$, $J = -105$ cm^{-1}, and $N(\alpha) = 0$.

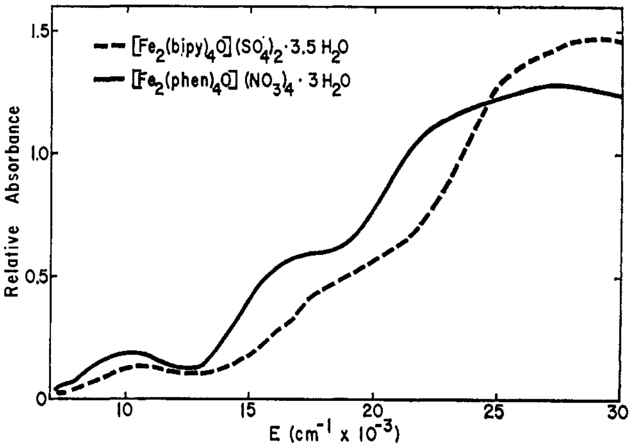

Figure 4. Reflectance spectra of $[Fe_2(bipy)_4O](SO_4)_2 \cdot 3.5H_2O$ (--------) and $[Fe_2(phen)_4O](NO_3)_4 \cdot 3H_2O$ (———).

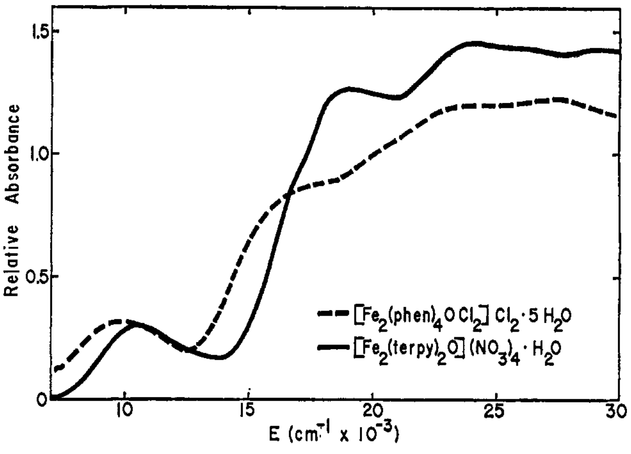

Figure 5. Reflectance spectra of $[Fe_2(terpy)_2O](NO_3)_4 \cdot H_2O$ (———) and $[Fe_2(phen)_4OCl_2]Cl_2 \cdot 5H_2O$ (-------).

than $S = {}^1/_2$. In fact, the general temperature dependence of the susceptibility is reproduced quite well using $S = {}^5/_2$. We wish to point out that the calculated curves for $S = {}^5/_2$ assume no TIP (temperature-independent paramagnetism), which is to be expected,[19] yet the addition of about 100×10^{-6} cgs as a TIP contribution would improve the fit. This will be discussed in more detail in the next section.

The Nature of the Spin State in Binuclear Complexes. Most of the early work on the binuclear complexes of Fe(III) assumed that the iron was in an $S = {}^1/_2$ state, but recently opinion has shifted in favor of the $S = {}^5/_2$ state.[20] The magnetic data we have obtained certainly support the belief that the possibility of interacting $S = {}^1/_2$ states can be ruled out. We wish to suggest, however, that, at least in certain complexes, the evidence is compatible with and may favor an $S = {}^3/_2$ state for each iron. It has been pointed out[22] that magnetic measurements over the normally studied range (77–300°K) cannot distinguish between two interacting $S = {}^3/_2$ or $S = {}^5/_2$ centers because with reasonable values of J, the exchange integral, only states with the lower values of S', the total spin, will be populated. Since they are identical for the two cases up to $S' = 3$, the magnetic behavior will be nearly identical. One difference would be that no TIP would be expected if $S = {}^5/_2$ but would be expected if $S = {}^3/_2$. As previously mentioned, the calculated curves in Figures 2 and 3 are without a TIP contribution. The addition of some small amount of TIP would, as can obviously be seen, improve the agreement. Although we do obtain analytically and magnetically reproducible samples, there is probably some small amount of paramagnetic monomer present in the products measured,[20,21] so the better agreement including TIP cannot be taken as conclusive but only as indicating that the fit is as good with it as without. Measurements to lower temperatures might be of some usefulness.

In Table III and Figures 4–7 we present some data which are relevant to the question of the nature of the spin state. From the data in Table III it can be seen that the isomer shifts of all the binuclear complexes are similar, although the value for the terpyridine complex is slightly larger than the rest. The quadrupole splittings are quite different, however. The terpyridine complex has a ΔE_q of 2.35 mm/sec, the bipyridine and phenanthroline species have some-

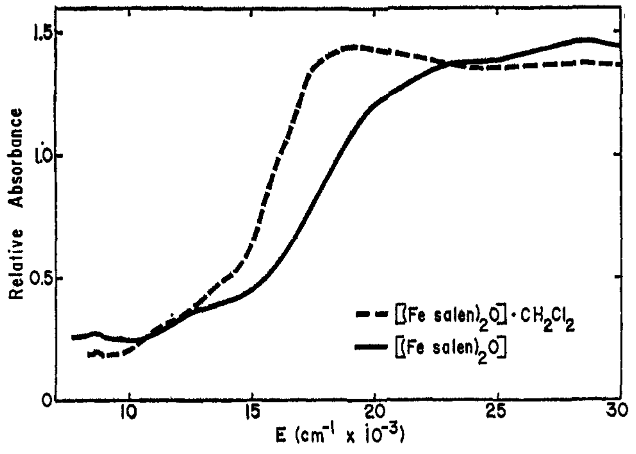

Figure 6. Reflectance spectra of [(Fe(salen))$_2$O] (———) and [(Fe(salen))$_2$O]·CH$_2$Cl$_2$ (---------).

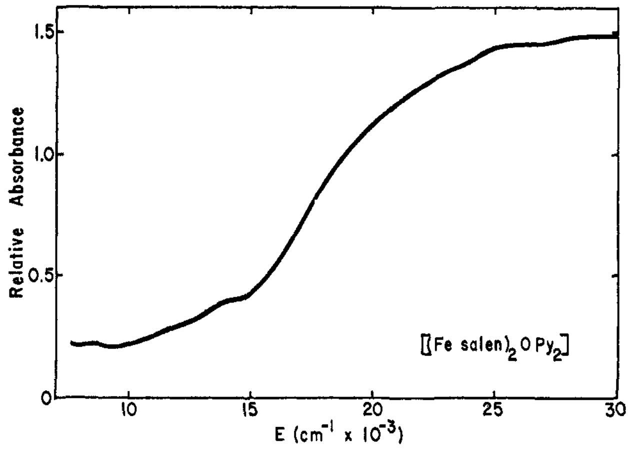

Figure 7. Reflectance spectrum of [(Fe(salen)py)$_2$O].

what smaller values in the range 1.5–1.7, and the salen complexes have even smaller values of 0.7–0.9 mm/sec. For Fe(III) in an $S = {}^5/_2$ state, one expects a small ΔE_q since any field gradient must come from a "lattice" contribution, there being no "valence" gradient. The observed values indeed are generally somewhat less than 1.0 mm/sec.[15] One compound, NH$_4$FeF$_4$, presumed to be $S = {}^5/_2$ Fe(III), has been observed[24] to have a ΔE_q of 1.5 mm/sec, but no other examples with splittings that high are known.

On the other hand, Martin and White[25] have recently reported a five-coordinate Fe(III) complex, monochlorobis(N,N-diethyldithiocarbamato)iron(III), [Fe(DEDTC)$_2$Cl], which has an $S = {}^3/_2$ ground state and which has an isomer shift of 0.38 mm/sec and a quadrupole splitting of 2.54 mm/sec.[26] Therefore the Mössbauer ΔE_q data for the phenanthroline, bipyridine, and especially terpyridine species are unusual for Fe(III) in an $S = {}^5/_2$ state but might indeed be reasonable for an $S = {}^3/_2$ state where there may exist an electric field gradient due to the d-electron distribution and therefore the possibility of large quadrupole splittings. It is worth noting, however, that the 3d orbital filling scheme proposed[25] for [Fe(DEDTC)$_2$Cl], $(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^1$, actually gives a vanishing 3d field-gradient contribution.

The data for the salen complexes, however, are not abnormal for an $S = {}^5/_2$ state, since the quadrupole splittings are distinctly lower. Further, the small difference in splitting between the simple salen complex which is assumed to be five-coordinate[19] and the pyridine adduct which is six-coordinate is also consistent with an $S = {}^5/_2$ state. The fact that ΔE_q for the pyridine adduct is different from that of the simple salen complex while the CH$_2$Cl$_2$ adduct has the same value as the simple complex may be taken in support of the contention[19] that the CH$_2$Cl$_2$ is not coordinated to the iron.

In Figures 4–7 are presented reflectance spectra of the seven binuclear complexes. There is similarity in all the spectra in that there are intense charge-transfer bands above 15,000 cm^{-1}. The interesting feature of the spectra for this discussion is that in the polyimine systems there is a weaker band around 10,000 cm^{-1} which is not observable in the salen complexes. The reflectance spectra are presented here because they show the weaker band most clearly, but the spectra have also been observed in solution and as mulls in Kel-F grease and all are essentially identical. The molar extinction coefficients as obtained from the solution spectra is ~6, and, at least in the mull spectra, less intense at 77°K than at room temperature. All of this is clearly indicative of d–d transitions. The possibility that the band is due to an impurity can be ruled out with reasonable certainty. The most likely impurities are monomeric Fe(III) species.[21] None of these is likely to have a band in that region of the spectrum intense enough to show up, and appreciable amounts of impurities are ruled out by the analytical, Mössbauer, and magnetic data. The possibility that it is due to Fe(II) impurities was checked by adding small amounts of NH$_2$OH·HCl. Such addition resulted in reduction of the intensity of the band and eventually its complete disappearance.

The question thus is how to explain the features of the observed spectra. One possibility is that the phenanthroline, bipyridine, and terpyridine species represent $S = {}^3/_2$ systems while the salen complexes represent $S = {}^5/_2$ systems. It might be expected that if the ground state were a quartet there would be spin-allowed d–d bands in that region. Indeed, Martin has observed[25] what are presumably d–d bands in his quartet system at 6500 and 8400 cm^{-1}. In sextet systems, of course, all d–d bands are spin forbidden and would be expected to be weak. An interpretation of the spectra in terms of an $S = {}^5/_2$ ground state for the salen complexes and $S = {}^3/_2$ for the others is consistent with the differences in Mössbauer data for the two groups.

At the same time, the electronic spectra do not conclusively rule out the possibility that all of the binuclear complexes represent sextet ground-state systems. The 10,000-cm^{-1} band could be assigned as a ${}^6A_1 \rightarrow {}^4T_1$, spin-forbidden transition (using the octahedral notation). It is known that Fe^{3+} in the mineral beryl has a broad and rather intense band at 12,200 cm^{-1} which has been so assigned.[27] If this assignment is correct, then the band should appear at *lower* energies in the polyimine complexes since the excited quartet state *de-*

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creases in energy with respect to the ground $^6A_1$ state as the ligand field strength *increases*. The absence of the band in the salen complexes could then be explained by assuming that the ligand field strength is weaker than in the polyimines and is high enough in energy to be masked by the charge-transfer bands. It does not seem likely that the ligand field strength in the salen complexes would be less than in beryl (six oxides), but the effects of the lower symmetry in the salen complexes cannot be estimated. There is some small additional absorption in the tail of the charge-transfer bands (around 12,000–14,000 cm^{-1}) which could be due to this transition, although, if this is true, the intensity is appreciably less than in the polyimine systems. Further, the similarity in isomer shifts for all of these binuclear complexes to each other and to that found for [Fe(terpy)Cl$_3$] suggests that, to the extent that the isomer shifts in closely related compounds are indicative of spin state, all of them are $S = {}^5/_2$ systems.

Conclusions

On the basis of the data presented it seems clear that [Fe(terpy)Cl$_3$] and [Fe(terpy)$_2$](ClO$_4$)$_3$ are monomeric high- and low-spin Fe(III) complexes, respectively. The new binuclear complex [Fe$_2$(terpy)$_2$O](NO$_3$)$_4$·H$_2$O and the complex [Fe$_2$(bipy)$_4$O](SO$_4$)$_2$·3.5H$_2$O are analogous to the well-established phenanthroline system. The magnetic as well as the Mössbauer and electronic spectral data presented in this paper can be explained assuming an $S = {}^5/_2$ ground state for each iron. We believe, however, that the data for the phenanthroline, bipyridine, and particularly terpyridine complexes suggest the possibility that the ground state for each iron is a spin quartet, unlike the salen data which are only compatible with a sextet ground state. More work needs to be done on these and on similar systems in order to resolve the problem.

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Nucleophilic Reactivity in Substitution Reactions of Square-Planar Metal Complexes. III. Kinetic Evidence for the Accumulation of a Reaction Intermediate in Nucleophilic Substitutions in Rhodium(I) Complexes

L. Cattalini, R. Ugo, and A. Orio

Contribution from Istituto di Chimica Generale ed Inorganica, University of Padua, Padua, Italy. *Received February 23, 1968*

Abstract: The kinetics of the nucleophilic displacement of the stibine from the complex [Rh(1,5-cyclooctadiene)-Cl(SbR$_3$)] (R = *p*-tolyl) by amines (am) are reported. The reactions occur in two steps, the first corresponding to the rapid formation of a five-coordinated species; the second, which is slower, to its dissociation to give the product [Rh(1,5-cyclooctadiene)Cl(am)]. This is the first direct evidence for the accumulation of a five-coordinate reaction intermediate in square-planar substitution. The effect on the kinetics of changing the chelate olefin, the leaving group, the ligand *cis* to the leaving group, the entering group, and the solvent is also reported and discussed.

Ligand substitution reactions in coordination compounds occur with a variety of mechanisms, depending on the nature of the reagents, the solvent, the coordination number, etc. The behavior of planar complexes of d^8 transition metal ions such as Rh(I), Pt(II), Pd(II), and Au(III) appears to be simple, in the sense that the substrates generally undergo bimolecular substitution with transition states in which both the entering and leaving groups are bonded to the metal.

However, even though the rates of these processes generally follow a first-order dependence on both the concentrations of the substrate and entering reagent, it has been suggested[1,2] that the intimate mechanism is not a synchronous interchange of ligands. Langford and Gray[1] suggest an associative mechanism, with a five-coordinated intermediate that represents the incipient coordination unsaturation of the four-coordinate d^8 system. In the past few years indirect kinetic evidence supporting this point of view has been reported,[3] and the same argument has been used as a possible explanation of the difference in the kinetic behavior of platinum(II) and gold(III) complexes.[4]

In a preliminary communication[5] we reported some

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