The solution of phenanthrenesodium was poured into a dropping funnel under argon and slowly added to a THF solution of Cr(CO)₆ (0.3 g, 0.00136 mole) at room temperature. The green radical anion was immediately discharged upon addition to the chromium hexacarbonyl–THF solution which became yellow. Slowly the solution became dark red-brown. There was little if any gas evolved. Removal of excess THF yielded a rust-red solid. The phenanthrene was recovered quantitatively by washing the rust-red solid with dry benzene. Infrared spectra of this rust-red solid in perfluorokerosene and nmr spectra gave no evidence for phenanthrene.

E. Reaction of Cr(CO)₆ with Trimesitylboron Sodium. A solution of trimesitylboron (1.002 g, 0.00272 mole) was allowed to react with a fourfold excess of sodium for 12 hr. The deep blue trimesitylboron sodium was poured completely into a dropping funnel and then added to chromium hexacarbonyl (0.3 g, 0.00136 mole) in THF. The solution became bright yellow to yelloworange. Dry benzene was used to quantitatively removed trimesitylboron from the reaction mixture after THF had been removed.

F. Reaction of [Cr(CO)₅Br]⁻ [38] with Sodium and Potassium Amalgam. A yellow THF solution of [(C₂H₅)₄N][Cr(CO)₅Br] (0.3 g, 0.000746 mole) was treated with sodium amalgam (0.15 g of sodium, 0.00655 g-atom, in 1.1 ml of mercury) at room temperature for 5 hr. No gas evolution was observed. A white-yellow solid formed at 15 min of reaction. The reaction mixture was decanted from the amalgam which was decomposed with water and then titrated with standard acid. A titration indicated that 0.001 equiv of sodium had been used.

The same reaction with potassium amalgam (0.0585 g of potassium, 0.00149 g-atom, in 0.5 ml of mercury) gave a green solid; the evolution of gas was observed throughout the 3-hr reaction. The remaining amalgam was decomposed and the solution titrated with standard acid. The titration indicated that 0.00126 equiv of sodium had been used. Chromium hexacarbonyl was also observed in the vacuum trap after removal of solvent from the reaction mixture.

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On the Nature of the Spin States in Some Binuclear Iron(III) Complexes

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Abstract: Detailed magnetic, Mössbauer, and spectroscopic studies have been made on a number of binuclear Fe(III) complexes in an effort to determine the spin state for the Fe(III) ions. The over-all data are most consistent with a spin of $^5/_2$ for each iron. An explanation is offered for the presence of a relatively intense electronic absorption band in most of the complexes.

There has been recently a large amount of interest in binuclear complexes of Fe(III),[3-6] especially those showing intramolecular antiferromagnetic exchange coupling between the Fe(III) ions. It is now generally agreed that for those species showing strong coupling (that is, effective moments at 300° of <2.0 per iron) there exists a linear or near-linear oxygen bridge between the two iron atoms. The presence of an oxygen bridge is supported by infrared data,[3-5] and the near-linear nature of the bridge has been established by X-ray data for the two different compounds, a complex of N,N'-ethylenebis(salicylideneiminate) (hereafter, salen)[4] and a complex reported by Curry and Busch[7] of the macrocyclic ligand 2,13-dimethyl-3,6,9-12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (hereafter, B) which has been studied by Fleischer and Hawkinson[8] and shown to be seven-coordinate.

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(2) To whom correspondence should be addressed.
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(5) A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *ibid.,* 1561 (1967).
(6) L. N. Mulay and N. L. Hoffman, *Inorg. Nucl. Chem. Letters,* **2,** 189 (1966).
(7) J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.,* **86,** 592 (1964).
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On the basis of differences in Mössbauer and electronic spectral data for a series of binuclear Fe(III) complexes of 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), 2,2',2''-terpyridine (terpy), and salen, we previously suggested[3] that the bipy, phen, and terpy system were best formulated as two interacting $S = \,^3/_2$ systems, while the salen complexes appeared to be $S = \,^5/_2$ systems. In particular, the former group of binuclear species exhibit quadrupole splittings in their Mössbauer spectra which are unusually large compared to those normally found for $S = \,^5/_2$ Fe(III). The same group of compounds shows an electronic absorption around 10,000 cm⁻¹ with a molar extinction coefficient of ∼7, a value unusually large for the spin-forbidden bands usually observed in high-spin Fe(III). The salen complexes on the other hand exhibit small quadrupole splittings and show no electronic absorption attributable to d–d transitions. The correlation between the quadrupole splittings and the existence of the electronic band, both of which are somewhat unexpected for $S = \,^5/_2$ systems, thus are circumstantial evidence in favor of an $S = \,^3/_2$ state for the polyimine complexes, although the evidence is much less than conclusive.

We therefore decided to study further these systems in an effort to obtain more data relevant to the question of the spin state of the iron. First we wanted to measure the magnetic behavior down to lower tempera-

Table I. Magnetic Data[a]

Compound	Temp, °K	$\chi_g \times 10^6$ cgs	$\chi_M' \times 10^6$ cgs[b]	μ_{eff}, BM	Compound	Temp, °K	$\chi_g \times 10^6$ cgs	$\chi_M' \times 10^6$ cgs[b]	μ_{eff}, BM
[Fe(salen)Cl]₂	296	32.88	11,930	5.32	[Fe(phen)₂]₂OCl₄·5H₂O	293	1.82	1,340	1.78
	245	37.75	13,670	5.17		254	1.72	1,280	1.62
	202	42.25	15,280	4.98		226	1.65	1,240	1.50
	158	48.20	17,410	4.68		187	1.49	1,170	1.32
	122	53.40	19,270	4.35		152	1.34	1,070	1.15
	84	58.07	20,940	3.75		135	1.11	952	1.02
	57	57.45	20,720	3.07		110	0.74	752	0.82
	39	55.19	19,910	2.49		89	0.38	558	0.63
	29	52.62	18,990	2.11		70	0.00	352	0.45
	22	50.08	18,080	1.76		58	−0.19	249	0.34
[(FeBH₂O)₂O](ClO₄)₄	289	2.43	1,620	1.94		45	−0.10	296	0.33
	252	2.37	1,590	1.80		32	0.05	378	0.31
	220	2.20	1,490	1.62		21	0.70	728	0.35
	186	2.08	1,430	1.46	[Fe(terpy)]₂O(NO₃)₄·H₂O	297	2.61	1,390	1.83
	150	1.87	1,310	1.22		252	2.54	1,360	1.66
	122	1.51	1,110	1.04		215	2.40	1,300	1.50
	99	1.09	876	0.83		184	2.35	1,280	1.38
	78	0.62	617	0.62		153	2.07	1,150	1.19
	61	0.38	484	0.49		127	1.73	1,000	1.01
	46	0.12	343	0.36		102	1.38	843	0.83
	28	0.16	364	0.29		81	0.93	641	0.65
	22	0.30	442	0.28		61	0.68	528	0.51
	20	0.74	686	0.33		46	0.60	492	0.43
[Fe(bipy)₂]₂O(SO₄)₂·3.5H₂O	290	2.39	1,490	1.86		39	0.77	568	0.42
	243	2.16	1,370	1.63		33	0.88	619	0.41
	201	2.01	1,300	1.44		26	1.14	735	0.39
	159	1.83	1,210	1.24		23	1.39	848	0.40
	125	1.45	1,020	1.00	[Fe(salen)₂]₂O	297	4.14	1,520	1.91
	103	1.07	824	0.83		252	4.01	1,480	1.73
	90	0.85	713	0.72		212	3.76	1,400	1.55
	71	0.34	458	0.51		169	3.31	1,250	1.31
	59	0.13	350	0.41		130	2.70	1,040	1.05
	49	−0.09	240	0.31		98	1.93	792	0.79
	38	−0.22	173	0.23		68	0.66	372	0.45
	31	−0.01	279	0.26		48	0.07	177	0.26
	28	0.16	366	0.29		33	−0.04	140	0.19
	24	0.37	471	0.30		24	−0.11	119	0.15
	22	0.52	547	0.31		22	0.13	196	0.19
						21	0.19	216	0.19

[a] All data per iron atom. [b] The diamagnetic corrections used are given in the Experimental Section and in ref 3.

tures than were previously used (80°). Since little or no temperature-independent paramagnetism (TIP, second-order Zeeman) contribution would be expected for an $S = \frac{5}{2}$ system while a contribution of several hundred ($\times 10^{-6}$ cgs) might be expected if $S = \frac{3}{2}$, the minimum value of the susceptibility obtained, especially if a constant value were obtained as the temperature was lowered, would be significant. The wide range of temperatures would also allow a more accurate evaluation of g and J. Second, we were interested in looking at the Mössbauer spectra of some binuclear complexes, which from the magnetic data were definitely $S = \frac{5}{2}$ systems, in order to test the assumption that all such complexes would show small quadrupole splittings. Fortunately, Gerloch, et al.,[9] recently reported a number of complexes of salen and its derivatives which exhibit such behavior. Among them was the complex [Fe(salen)Cl]₂ which is a binuclear species[10] in which an oxygen of the salen forms a bridge between the two iron atoms. The Fe–O–Fe angle is about 90°. This complex can be recrystallized from CH₂NO₂, yielding what is apparently a normal five-coordinate high-spin mononuclear complex.[9,10] Third, we wanted to ob-

serve the electronic spectra of some additional binuclear species in order to determine if a large quadrupole splitting was always observed in systems showing anomalously intense d–d bands. If this were the case, the argument for these complexes being $S = \frac{3}{2}$ systems would be reinforced. It is the purpose of this paper to present the results of these investigations.

Experimental Section

Preparation of Complexes. With the exception of the complexes [Fe(salen)Cl]₂ and [(FeBH₂O)₂O](ClO₄)₄, preparations and analytical data for the substances studied have been given previously.[3] The preparation of [Fe(salen)Cl]₂ followed that given by Gerloch, et al.[9] Anal. Calcd for FeC₁₆H₁₄N₂O₂Cl: C, 53.73; H, 3.95; N, 7.83. Found: C, 53.58; H, 3.75; N, 7.72. The complex of the macrocyclic ligand, [(FeBH₂O)₂O](ClO₄)₄, was prepared according to the procedure given by Curry and Busch.[7] Anal. Calcd for Fe₂C₃₀H₅₀N₁₀O₁₉Cl₄: C, 32.51; H, 4.55; N, 12.64. Found: C, 32.84; H, 4.55; N, 12.83.

Physical Measurements. Mössbauer, infrared, and electronic spectra were obtained using instrumentation previously described.[3] Magnetic measurements were made using a Faraday balance.[11] All measurements were made at three field strengths, and no field dependence was observed except where noted in the discussion. Corrections to the molar susceptibilities for diamagnetic constituents were made using values given in ref 3 and a value of 161×10^{-6} for the macrocyclic ligand, B, as given in ref 7.

(9) M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, J. Chem. Soc., A, 112 (1968).

(10) M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, Nature, 212, 809 (1966).

(11) J. S. Judge and W. A. Baker, Jr., Inorg. Chim. Acta, 1, 68 (1967). A more detailed description will be published soon.
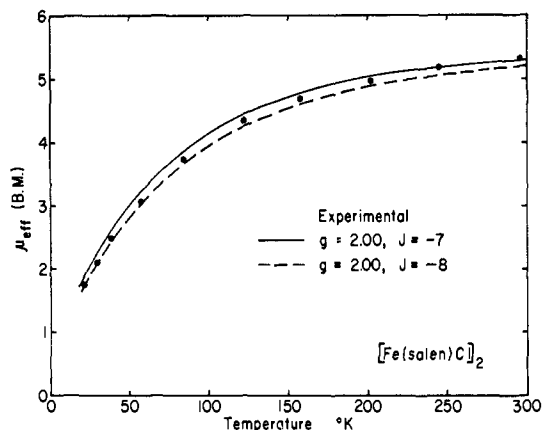
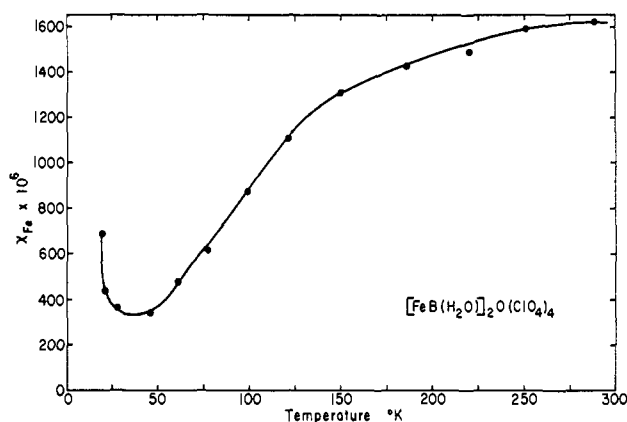Figure 1. Plot of μ_{eff} vs. T for [Fe(salen)Cl]$_2$.

Figure 2. Plot of χ_M' vs. T for [(FeBH$_2$O)$_2$O](ClO$_4$)$_4$.
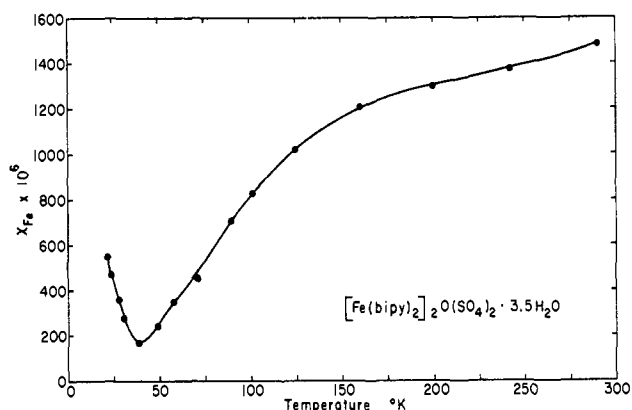
Figure 3. Plot of χ_M' vs. T for [Fe(bipy)$_2$]$_2$O(SO$_4$)$_2 \cdot$ 3.5H$_2$O.

Figure 4. Plot of χ_M' vs. T for [Fe(phen)$_2$]$_2$OCl$_4 \cdot$ 5H$_2$O.
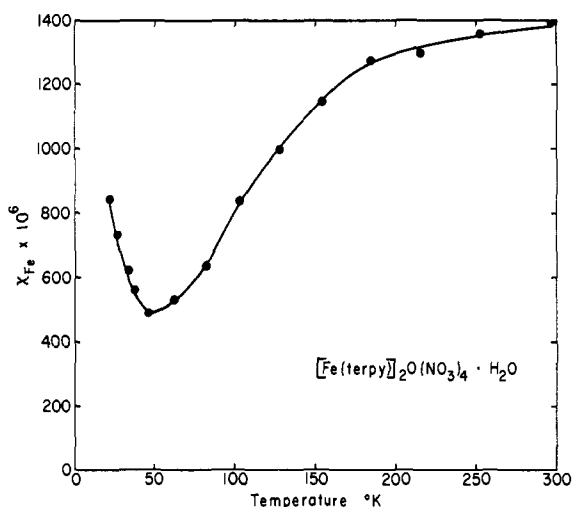
Figure 5. Plot of χ_M' vs. T for [Fe(terpy)]$_2$O(NO$_3$)$_4 \cdot$ H$_2$O.

Figure 6. Plot of χ_M' vs. T for [Fe(salen)]$_2$O.

Results and Discussion

Magnetic Data. The results of magnetic measurements on six binuclear complexes of Fe(III) are given in Table I and Figures 1–6. It is obvious that the interaction is quite weak in the case of [Fe(salen)Cl]$_2$ (Figure 1). The results presented here agree well with those reported by Gerloch, et al.,[9] over a more limited temperature range. Figure 1 compares the experimental results with curves calculated for $g = 2.00$ and $J = -7$ and -8 cm^{-1}. These are essentially the same values assigned by the other workers, even though their studies went down to only 82°. This indicates that it is in fact possible in certain cases to get good results
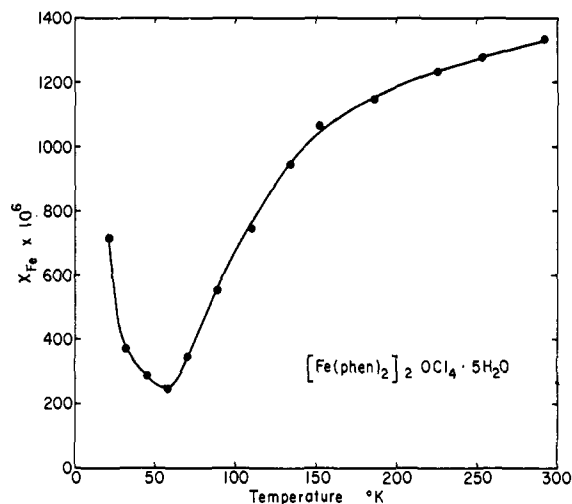
from measurements down to nitrogen temperatures From the data it can be concluded that this complex can only be considered as consisting of two interacting $S = \frac{5}{2}$ centers.

Figures 2–6 show data for five complexes which exhibit strong antiferromagnetic coupling. Data for the bipy, phen, terpy, and salen complexes have been reported[3–5] for temperatures of 80–300°. The complete

magnetic data for the complex of the macrocyclic ligand, B, have to our knowledge not been reported, but Nelson, et al.,[12] did state that the data indicate spin-spin interaction, and the room temperature moment was reported earlier.[7] Nelson, et al., indicate that a maximum in the susceptibility, which is not evident from our data, occurs at 270°.

A maximum in the susceptibility at a temperature that low would be unexpected unless each iron were in an $S = \frac{1}{2}$ state, and the Mössbauer parameters (see later discussion) eliminate this possibility. For an $S = \frac{5}{2}$ system and a J large enough to give the observed values of χ_M', the maximum should occur at much higher temperatures.

The data in Figures 2–6 all follow the same general pattern. The susceptibility drops as the temperature is lowered below room temperature until a minimum is reached around 40–50° and then begins to rise at lower temperatures. The rise may be due to the presence of paramagnetic or ferromagnetic impurities. If the impurity were high-spin Fe(III), only amounts of the order of 0.3% would be required to give the observed results. At the same time, the phenomenon could be a real property of the system. Similar behavior has been observed by Hatfield and Bunger[13] in a number of binuclear copper complexes. There is a very slight field dependence to the susceptibility at temperatures below the minimum in the curve, but this could be due either to the presence of ferromagnetic impurities or to inherent ferromagnetism of the systems.

In an attempt to determine if the rise in susceptibility at low temperatures was due to the presence of impurities, three different samples of $[Fe(phen)_2]_2OCl_4 \cdot 3.5H_2O$ were prepared and their susceptibilities studied. The temperature at which the minimum susceptibility was obtained varied from a low of 34° to a high of 58° for the three samples, and the value of χ_M' at the minimum varied between 249 and 351 $\times$ 10⁻⁶ cgs. What is somewhat puzzling is that there is an inverse relationship between the minimum value of χ_M' and the temperature at which it occurs. That is, the sample with the lowest minimum χ_M' exhibits the minimum at a higher temperature than do the other samples. The susceptibilities at higher temperatures agreed well for the three samples.

In spite of the fact that the susceptibility undergoes the sharp rise near 50° which precludes our evaluating the magnitude of the TIP, the low-temperature data do allow us to draw certain conclusions. We can now set an upper limit on the size of the TIP. This varies from 120 to 430 $\times$ 10⁻⁶ cgs, thus demonstrating that assignments[6] of the parameters involving larger values of the TIP cannot be correct. A second important point is that with the above limitation on the TIP, it is impossible to fit the data (above the minimum) with g values greater than 2.1. This is true if we assume that the sharp rise at low temperatures is due to a paramagnetic impurity and subtract out a Curie law type portion or if we assume a more temperature-dependent type of impurity and correct accordingly. Making either of these types of corrections, the only reasonable fits of the data are obtained with $g < 2.1$ and $J \sim -100$

cm⁻¹. Values of g near 2.0 can be taken as circumstantial evidence against formulating the complexes as involving $S = \frac{3}{2}$ states, since known examples of Fe(III) in a quartet state exhibit large g values.[14,15] It must be noted, however, that the systems studied here could have a lower symmetry which would tend to lower the g value.

Spectral Data. The Mössbauer data for the compounds for which data have not previously been given are shown in Table II. These data are quite relevant

Table II. Mössbauer Data

Compound	Temp, °C	ΔE_Q, mm/sec[a]	δ, mm/sec[a]
[Fe(salen)Cl]₂	Room	1.40	0.40
	78	1.40	0.51
Fe(salen)Cl·XCH₃NO₂[b]	Room	1.34	0.35
[(FeBH₂O)₂]O(ClO₄)₄	Room	0.42	0.45
	78	0.52	0.58

[a] Relative to iron foil. [b] Obtained by recrystallization of [Fe(salen)Cl]₂ from CH₃NO₂.

to the question of the spin state of iron in the complexes. The isomer shifts (δ) are normal for Fe(III), and the quadrupole splitting (ΔE_Q) of $[(FeBH_2O)_2]O(ClO_4)_4$ is in the range normally found for high-spin Fe(III). The ΔE_Q values for [Fe(salen)Cl]₂, however, are quite large, and yet the magnetic data clearly show the compound to be an $S = \frac{5}{2}$ system. This indicates that it is possible to get large ΔE_Q values due to "lattice" effects in high-spin Fe(III). Since the ΔE_Q values reported here for the salen complex approach in magnitude the corresponding values for the phen and bipy binuclear systems,[3] they weaken the arguments in support of the latter compounds being $S = \frac{3}{2}$ systems. It is certainly fair to say then that the relationship between ΔE_Q and the spin state of iron in a complex is not an obvious one. The use of ΔE_Q values in assigning such a property is of questionable validity until such time as more data are available. While the isomer shift might be more useful in this regard, the exact way in which it can be used as an indicator of spin is still uncertain.

Table II also gives Mössbauer data on the mononuclear salen complex which is indicated from X-ray data[10] to be five-coordinate. There is little change in the quadrupole splitting or the isomer shift as compared to the binuclear complex. The slight change substantiates the idea that the intermolecular bonding in the binuclear species is weak.

The argument in favor of $S = \frac{3}{2}$ is even further weakened when one considers the electronic spectrum of $[(FeBH_2O)_2]O(ClO_4)_4$. This complex has a band at 11,400 cm⁻¹ with $\epsilon \sim 4$. This band resembles closely that observed in the polyimine binuclear systems, the existence of which was one of the reasons for suggesting the possibility of quartet spin states. Since there is no reason for believing that the macrocyclic complex is other than high spin, it appears that relatively intense bands are indeed possible in such systems.

The question of why what are presumably spin-forbidden d–d band have intensities an order of mag-

(12) S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.*, 2, 641 (1966).

(13) W. E. Hatfield and F. L. Bunger, *Inorg. Chem.*, 5, 1161 (1966).

(14) R. L. Martin and A. H. White, *ibid.*, 6, 712 (1967).

(15) D. J. E. Ingram and J. E. Bennett, *Discussions Faraday Soc.*, 19, 140 (1955).

nitude larger than are usually observed still remains. The answer may be related to some observations of Ferguson, *et al.*,[16] made while studying intensities of electronic bands in some Mn(II) compounds of the type $KMnF_3$. They observed that certain of the bands had abnormally high intensities which they attributed to magnetic interactions between pairs of manganese ions linked by a fluoride ion. They conclude that such "pair spectra" may have intensities one or two orders of magnitude greater than single-ion spectra. If such a mechanism is operative in the binuclear iron systems, then there is no need to propose spin states that would allow spin-allowed bands in order to account for the observed results.

There is one observation that we have made regarding the Mössbauer spectra of these compounds which we feel is worth noting. If one looks at published spectra of simple high-spin Fe(III) complexes, in most cases where quadrupole splitting is observed there is a distinct and often rather large difference between the intensities of the two components of the doublets.[17] The line width is also in most cases several times the natural width. We have observed the same effect in our mononuclear Fe(III) complexes. However, all of the linear-bridged binuclear species have line widths less than twice the natural width, and the two components of the doublet are of equal or nearly equal intensity. On the other hand, the spectrum of the binuclear [Fe(salen)Cl]$_2$ as well as the presumed mononuclear product obtained from the recrystallization of the former from CH_2NO_2 shows broader lines, and one component is only 60% as intense as the other. Whether or not the differences are related to the extent of spin coupling we do not know. We have no explanation for the phenomenon but only point it out as an observation.

(16) J. Ferguson, H. J. Guggenheim, and Y. Tanabe, *J. Phys. Soc. Japan*, 21, 692 (1966), and references therein.

(17) See, for example, J. J. Spijkerman, L. H. Hall, and J. L. Lambert, *J. Am. Chem. Soc.*, 90, 2039 (1968), for data and a discussion of possible explanations.

Finally, we wish to mention some infrared data on these binuclear species. A band in most of these complexes between 795 and 870 cm^{-1} has been assigned to the Fe–O–Fe linkage,[3-5,12] but this band was not directly observable in [Fe(salen)]$_2$O due to salen bands in the region. We have been able to locate this band in the salen complex by looking at the infrared spectra at 78°. At the lower temperature, the band assigned as the Fe–O–Fe stretch shifts to higher energies by 10–20 cm^{-1} while the other bands shift at most 1–2 cm^{-1}. The Fe–O–Fe band also increases in intensity relative to the other bands. In the spectrum of [Fe(salen)]$_2$O there is a band at 807 cm^{-1} that shifts to 817 cm^{-1} at 78°. Comparison of this spectrum with that of [Fe(salen)Cl]$_2$ also supports the assignment. The increase in energy of the Fe–O–Fe band on cooling might suggest that the exchange integral J also changes with temperature, although the magnetic data indicates that the change cannot be large.

Conclusions

On the basis of the data presented here, we now conclude that, contrary to our previous suggestion, there is no convincing reason for postulating the existence of quartet ground states for the binuclear Fe(III) complexes. The observation of a ΔE_Q value of 1.40 mm/sec for [Fe(salen)Cl]$_2$, which is certainly an $S = {}^5/_2$ system, along with the presence of the relatively intense d–d band in [(FeBH$_2$O)$_2$O](ClO$_4$)$_4$ negates to some extent the arguments previously made[3] in support of $S = {}^3/_2$ and reinforces the interpretation based on the assumption that the iron atoms exhibit $S = {}^5/_2$ states.