through alumina. Pressures of CO reported are corrected for temperature difference. Run 1 (Table III) was sealed *in vacuo* (0.1 mm). Samples for run 2 were prepared by sealing the tubes under 0.84 atm of CO at −78°; the pressure calculated at 50.8° is 1.4 atm. Samples for run 3 were sealed under 0.59 atm of CO at −196°; the pressure calculated at 50.8° is 2.5 atm.

The samples were immersed in a constant-temperature bath at 50.87 ± 0.02°. For run 1, the sealed tubes were shaken to achieve equilibration of CO between the gas phase and solution. Rates were slower by a factor of 2 in the absence of shaking. The reaction was quenched at −78° and samples stored at −25° until the scale-expanded (5 times) ir spectrum could be obtained on the PE 267. Examination of the ir spectra indicated **2a** was the product. Rates are based on a single run of at least five points.

Kinetic Studies of the Reaction of 1a with ETPO. Samples were prepared in degassed chloroform in sealed tubes. The samples were immersed in a constant-temperature bath at 50.87 ± 0.02°. The reaction was quenched at −78° and samples stored at −25° until the high-resolution Fourier transform ir spectrum could be obtained. The disappearance of the band at 2120 cm^{-1} of **1a** was used to determine the rate. Examination of the ir spectrum of the samples indicated **1b** was the sole product in runs 1–4 (Table IV).

Acknowledgment. We thank Mr. Terry Burkhardt for obtaining Varian XL-100 nmr spectra. Financial support from the National Science Foundation (Grants No. GP-32160 and GP-41259X) is gratefully acknowledged.

Registry No. 1a, 53897-19-1; **1b**, 53897-17-9; **2a**, 53897-12-4; **2b**, 53897-18-0; **3**, 53897-20-4; NaMn(CO)$_5$, 13859-41-1; *o*-carbomethoxybenzoyl chloride, 4397-55-1; *o*-isopropylbenzoyl chloride, 53881-34-8.

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Magnetic Ordering of Mono(diimine)iron(II) Chlorides. Fe(2,2'-bipy)Cl$_2$ and Fe(5,5'-(CH$_3$)$_2$-2,2'-bipy)Cl$_2$

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The temperature and magnetic field dependences of the Mössbauer spectra of Fe(2,2'-bipy)Cl$_2$ (prepared in solution) show the compound to be a ferromagnet with a Curie temperature of ~4 K, V_{zz} positive, and H_{hf} = −60 kOe. A similar study of the methyl-substituted derivative Fe(5,5'-(CH$_3$)$_2$-2,2'-bipy)Cl$_2$ (prepared by vacuum thermolysis) indicates this complex to be a slowly relaxing paramagnet over the range ~11–2 K with V_{zz} positive and H_{hf} = −211 kOe. These results correlate with susceptibility studies and far- and near-infrared spectra which show Fe(2,2'-bipy)Cl$_2$ to be a chain polymer containing six-coordinate iron(II) while the dimethyl derivative is probably a dimer for which the iron coordination number is 5. When Fe(2,2'-bipy)Cl$_2$ is prepared by low-temperature vacuum thermolysis of [Fe(2,2'-bipy)$_3$]Cl$_2$, the resulting system does not order sharply as in the case of the solution preparation but otherwise appears to have the same structure. Mössbauer spectra show that high-temperature thermolysis results in partial breaking of the chloro bridging of polymeric Fe(2,2'-bipy)Cl$_2$ to give a system of the same empirical formula but with a lower coordination number for the iron atoms.

I. Introduction

Ferromagnetic ordering in transition metal–organic ligand systems is not common. However, in a recent susceptibility study,[1] Fe(phen)Cl$_2$ was observed to order ferromagnetically with a Curie temperature T_c = 8 ± 2 K, a Curie–Weiss constant C = 3.8 emu/mol, and a paramagnetic Curie temperature Θ = +12 K. In this paper we use Mössbauer spectroscopy to consider the effects of replacing the phenanthroline ligand by other diimines, specifically as in Fe(2,2'-bipy)Cl$_2$ and the methyl-substituted derivative Fe(5,5'-(CH$_3$)$_2$-2,2'-bipy)Cl$_2$, and to measure T_c precisely. At the present time, the techniques involved in the preparation of these systems do not lend themselves to the formation of appropriate single crystals for direct X-ray structure determination or other single-crystal studies and the measurements reported here refer to powder materials. As we will show below, the addition of the methyl substituents considerably alters the magnetic properties. The Fe(2,2'-bipy)Cl$_2$ is ferromagnetic and structurally similar[2] to the Fe(phen)Cl$_2$. The Fe(5,5'-(CH$_3$)$_2$-2,2'-bipy)Cl$_2$ is paramagnetic and has a different structure. We present spectroscopic data from which we infer that the ferromagnetic materials have a chloro-bridged polymeric chain structure, while the paramagnetic compound has a dimeric structure with five-coordinate iron sites. The effects of preparative technique and thermal annealing on the magnetic ordering of Fe(2,2'-bipy)Cl$_2$ and Fe(phen)Cl$_2$ are also briefly discussed.

II. Experimental Section

Both Fe(phen)Cl$_2$ and Fe(2,2'-bipy)Cl$_2$ were prepared in solution using the method of Dwyer.[3] In this preparation, the complex is rapidly precipitated when a warm aqueous hydrochloric acid solution containing a tenfold excess of ferrous chloride is decanted directly onto the finely ground solid ligand. Attempts to grow single crystals of these complexes by conventional solution methods result in disproportionation of the mono(diimine) complex to more stable species such as [Fe(2,2'-bipy)$_3$]$^{2+}$.

It is also possible to prepare Fe(2,2'-bipy)Cl$_2$ by (10 hr) vacuum (~10 μ) thermolysis[4] of [Fe(2,2'-bipy)$_3$]Cl$_2$ at 145° with subsequent loss of 2 mol of ligand. The X-ray powder patterns as well as near-infrared and visible electronic spectra of the foregoing solution and thermolysis preparations of Fe(2,2'-bipy)Cl$_2$ are identical. This and Mössbauer spectra at 300 and 78 K suggest that the systems are isomorphous and have essentially the same molecular structure.

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Table I. Analytical Data

Compd	% calcd			% obsd^c		
	C	H	N	C	H	N
$Fe(2,2'\text{-bipy})Cl_2$^{a}	42.42	2.86	9.91	42.26	2.86	10.10
$Fe(2,2'\text{-bipy})Cl_2$^{b}	42.42	2.86	9.91	42.52	2.84	9.53
$Fe(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$^{b}	46.31	3.90	9.01	46.36	3.86	8.69
$Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$^{b}	46.31	3.90	9.01	45.81	3.87	8.35
$Fe(2,9\text{-}(CH_3)_2\text{phen})Cl_2$^{a}	50.16	3.62	8.37	49.97	3.56	8.37
$Zn(2,2'\text{-bipy})Cl_2$^{a}	41.07	2.76	9.58	41.21	2.78	9.76
$Zn(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$^{a}	44.97	3.77	8.74	44.97	3.66	7.86

^{a} Prepared in solution. ^{b} Prepared by vacuum thermolysis. ^{c} Error in analysis ~0.1%.

Table II. Mössbauer Data

Compd	Temp, K	δ,^{a} mm/sec	ΔE, mm/sec
$Fe(2,2'\text{-bipy})Cl_2$^{c}	300	1.04	1.10
	198	1.10	1.32
	78	1.17	1.73
	4.2^b	1.03	1.65
$Fe(2,2'\text{-bipy})Cl_2$^{d}	300	1.04	1.10
	78	1.15	1.72
	4.2	1.17	1.73
$Fe(2,2'\text{-bipy})Cl_2$^{e}	300	1.03	1.10
Inner doublet	78	1.15	1.68
Outer doublet	300	0.93	3.55
	78	1.04	3.69
$Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$	300	0.93	3.51
	78	1.06	3.72
$Fe(2,9\text{-}(CH_3)_2\text{-phen})Cl_2$	300	0.80	2.66
	78	0.91	2.77
	4.2	0.93	2.76

^{a} Relative to iron metal; error in δ and ΔE ±0.02 mm/sec. ^{b} Source and absorber at 4.2 K. ^{c} Prepared in solution. ^{d} Prepared by thermolysis. ^{e} Prolonged thermolysis.

However, as will be discussed below, the Mössbauer spectra of these preparations of $Fe(2,2'\text{-bipy})Cl_2$ do differ at $T \leq 4.2$ K. The complex $Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$ could only be prepared by vacuum thermolysis (10 μ, 160°) of the corresponding tris-chelate system. Corresponding zinc complexes were prepared by the addition of an ethanol solution of the ligand to heated ethanol solution containing a fivefold molar excess of zinc chloride. Analytical data for the compounds are given in Table I and were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn. 37921, and Chemalytics, Inc., Tempe, Ariz. 85281.

Far-infrared spectra were determined on a Perkin-Elmer Model 180 spectrophotometer using mineral oil mulls on thin polyethylene strips. Near-infrared and visible spectra were obtained on a Cary Model 14 spectrophotometer using fluorocarbon grease mulls on uv grade quartz or those for undispersed powder samples were obtained using the Cary Model 1411 diffuse-reflectance attachment. The X-ray powder patterns were obtained using a General Electric XRD-5 diffractometer. The Mössbauer spectra were determined on constant-acceleration devices previously described.[4] The γ-ray source was cobalt-57 (100 mCi) on copper or rhodium matrices.

The temperature dependence of Mössbauer spectra was studied using a standard stainless steel cryostat with an accompanying set point temperature controller. The sensors used were germanium resistors and control was nominally ±0.01 K. Mössbauer spectra in magnetic fields were obtained at 300 K using a Varian Model 4000 electromagnet (transverse geometry for the γ ray and applied field) and at 4.2 K with a Nb_3Sn superconducting solenoid (longitudinal geometry). The Mössbauer spectra were simulated using programs previously described.[5]

III. Results

A. Mössbauer Spectroscopy. 1. $Fe(2,2'\text{-bipy})Cl_2$. The Mössbauer spectrum of the $Fe(2,2'\text{-bipy})Cl_2$ consists of a single quadrupole doublet from 300 down to 4.2 K (see Table II). As the temperature is decreased below 4.2 K, the spectrum is observed to split into magnetic hyperfine components (Figure 1), indicating the onset of long-range magnetic order with a transition temperature 3.8 K < T_c < 4.2 K. At 1.5 K, the spectrum is compatible with the following parameters: quadrupole splitting $\Delta E = +1.7$ mm/sec, asymmetry parameter $\eta \leq 0.3$, hyperfine field $H_{hf} = -60$ kOe, and the angle between the principal component of the electric field gradient tensor and the magnetic hyperfine field $\beta \approx 60°$. The positive sign of the electric quadrupole interaction was checked by observation of the Mössbauer spectrum in an external magnetic field at room temperature where the compound is a rapidly relaxing paramagnet. The low-temperature parameters are very similar to those derived[2] from the low-temperature spectrum[1] of $Fe(phen)Cl_2$ (ΔE = 2.03 mm/sec, H_{hf} = −75 kOe, β = 60°) indicating that the environment of the Fe atom is very similar in the two complexes.

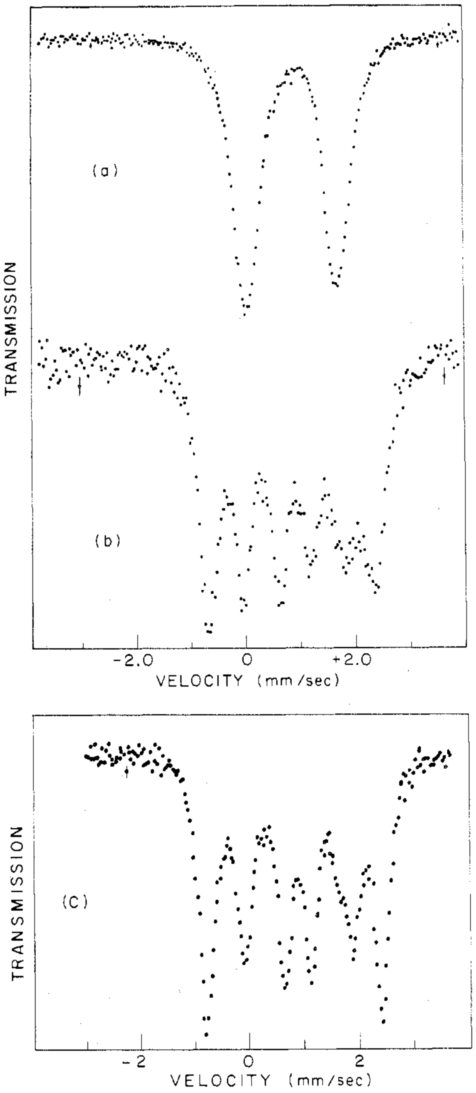

Figure 1. Mössbauer spectrum of $Fe(2,2'\text{-bipy})Cl_2$ in zero field at (a) 4.2 K and (b) 3.6 K, just above and below T_c, respectively, and (c) 1.5 K.

Application of a small external magnetic field at 4.2 K (*i.e.*, just above T_c) induces magnetic hyperfine structure in $Fe(2,2'\text{-bipy})Cl_2$. This is evidenced by the appearance of a spectrum generally similar to that observed below T_c in zero field. For example an external field of 5 kOe at 4.2 K results in a magnetic field of ~50 kOe at the nucleus. Increasing the external field to 35 kOe causes alignment of the spin moments and magnetic hyperfine interaction along the field direction indicating that the moments are ferromagnetically aligned. As expected the intensity of the $\Delta m_I = 0$ lines decreases. However they do not go to zero suggesting that the

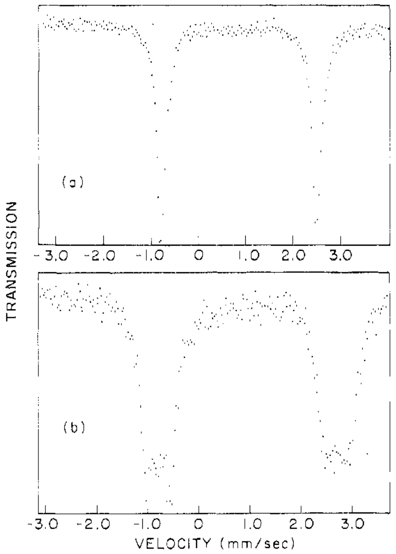

Figure 2. Mössbauer spectrum of Fe(5,5′-$(CH_3)_2$-2,2′-bipy)Cl_2 at (a) 300 K, $H = 0$, and (b) 300 K, H(transverse) = 20 kOe. For ^{57}Fe, the appearance of the apparent triplet at lower energy implies that the sign of the principal component of the electric field gradient is positive.

system is not completely saturated at these fields. This is not surprising for ferrous iron where anisotropy and zero-field splitting effects can compete with the Zeeman splitting and exchange fields and thus reduce moment polarization by an external field. In addition the total field at the nucleus decreases in larger applied fields indicating that the magnetic hyperfine interaction has a negative sign.

Magnetic susceptibility data obtained[2] as a function of temperature are very similar to those obtained for the Fe(phen)Cl_2, *i.e.*, Curie–Weiss behavior with a large positive intercept and ferromagnetic ordering near 4.2 K.

2. Fe(5,5′-$(CH_3)_2$bipy)Cl_2. The Mössbauer spectrum of the Fe(5,5′-$(CH_3)_2$bipy)Cl_2 consists of a single quadrupole from 300 to 12 K (see Table II). Measurements in an external magnetic field at room temperature show (Figure 2) the typical triplet–doublet pattern corresponding to V_{zz} positive. Below 12 K in zero external field, one observes a *gradual* transformation to a Zeeman split spectrum with decreasing temperature (Figure 3) characteristic of slow-paramagnetic relaxation, rather than long-range order. The lowest temperature spectrum is compatible with the following parameters: $\Delta E = +3.5$mm/sec, $\eta \leq 0.3$, $H_{hf} = -211$ kOe, and $\beta \approx 55°$. The sign of H_{hf} was checked by measurements in an external magnetic field at 4.2 K. The temperature dependence of the Mössbauer spectrum and the low-temperature parameters suggest that this compound does not order magnetically above 2.2 K and that the iron site is considerably different from the site in Fe(phen)Cl_2 and Fe(2,2′-bipy)Cl_2. The magnetic susceptibility data[2] also reflect such a difference in that the dimethyl compound shows Curie–Weiss behavior down to 4.2 K with $\Theta \approx 0$.

B. Structural Studies. Several molecular structures are possible for the empirical formulas Fe(2,2′-bipy)Cl_2 and Fe(5,5′-$(CH_3)_2$-2,2′-bipy)Cl_2. These include (a) a pseudotetrahedral monomer, (b) a chloro-bridged polymer, and (c) a five-coordinate dimer having both terminal and bridging chlorines. However, we will show that only the latter two are consistent with the X-ray and spectroscopic data we present below.

The simplest possible formulation of these compounds is the monomeric pseudotetrahedral. However, we have determined their X-ray diffraction patterns and compared them to those of the known pseudotetrahedral zinc analogs.[8] They are not similar, indicating that the systems are not isomorphous. Moreover, the single intense broad band expected in the optical spectrum between 6000 and 7000 cm^{-1} corresponding to the $^5E \rightarrow {}^5T_2$ transition of a tetrahedral FeN_2Cl_2 chromophore is not observed in either case. Finally, we can compare the systems under discussion to Fe(2,9-$(CH_3)_2$phen)Cl_2 whose Mössbauer parameters are also given in Table II. This complex is isomorphous[9] to the tetrahedral zinc analog whose single-crystal structure has been determined.[10] It appears to be magnetically dilute exhibiting neither ordering nor slow paramagnetic relaxation. We find that the latter tetrahedral system does exhibit the expected $^5E \rightarrow {}^5T_2$ transition as a broad intense band centered at 6800 cm^{-1} and there are no bands attributable to d–d transitions at higher energies. All of these observations lead us confidently to eliminate tetrahedral monomers from consideration.

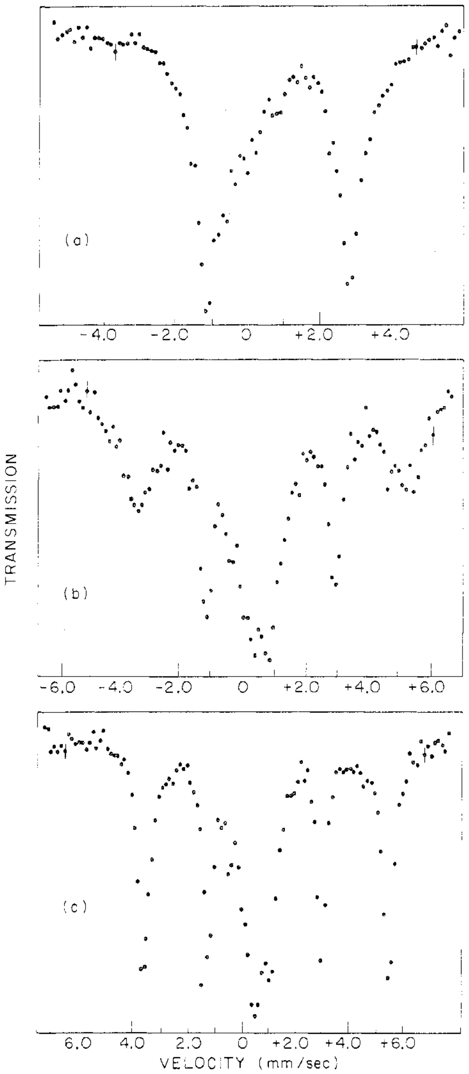

Figure 3. Mössbauer spectrum of Fe(5,5′-$(CH_3)_2$-2,2′-bipy)Cl_2 in zero field at (a) 10 K, (b) 5 K, and (c) 2.2 K.

1. Near-Infrared and Visible Spectra. The formulation of Fe(2,2′-bipy)Cl_2 as a chloro-bridged polymer containing six-coordinate iron(II) (Figure 4) in approximate C_{2v} symmetry is most consistent with the data we present below. Two of the three near-infrared–visible (d–d) transitions expected[11,12] for a high-spin ferrous FeN_2Cl_4 chromophore in C_{2v} symmetry are seen at 6400 and 10,300 cm^{-1} in Figure 5. As mentioned previously, the sign of the quadrupole interaction of Fe(2,2′-bipy)Cl_2 is *positive* and consistent with a d_{xy} ground orbital or $^5B_2$ ground term. We therefore assign the foregoing optical transitions as $^5B_2$ (arising from $^5T_{2g}$ in O_h symmetry) $\rightarrow$ $^5B_1$

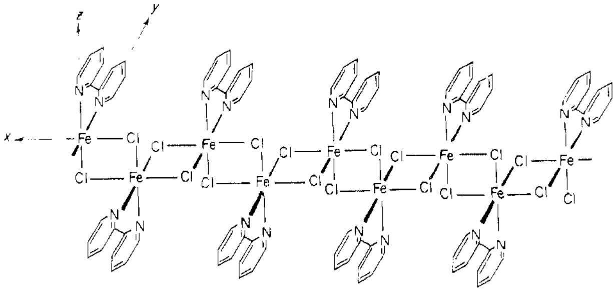

Figure 4. Proposed structure of Fe(2,2'-bipy)Cl_2.

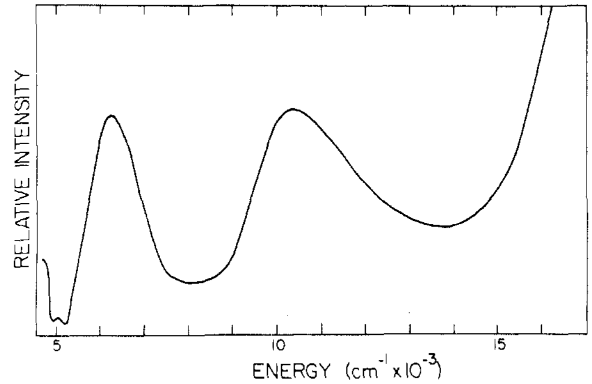

Figure 5. Near-infrared–visible spectrum of Fe(2,2'-bipy)Cl_2 at 300 K.

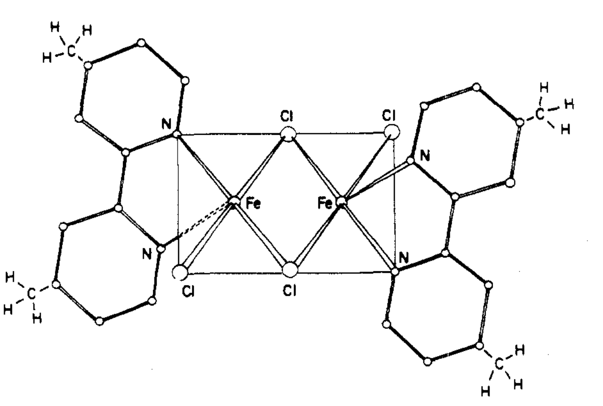

Figure 6. Coordination environment for Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2.

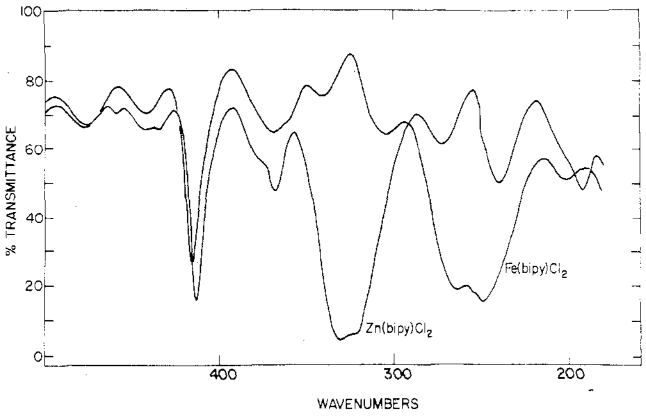

Figure 7. Far-infrared spectra of Zn(2,2'-bipy)Cl_2 and Fe(2,2'-bipy)Cl_2 at 300 K.

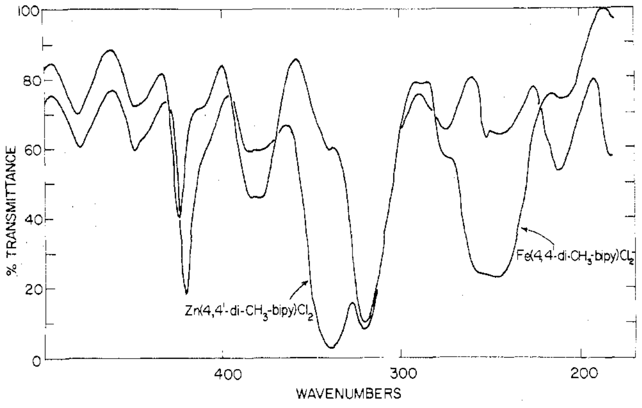

Figure 8. Far-infrared spectra of Zn(4,4'-$(CH_3)_2$-2,2'-bipy)Cl_2 and Fe(4,4'-$(CH_3)_2$-2,2'-bipy)Cl_2 at 300 K.

and $^5B_2 \rightarrow {}^5A_1$. Simple molecular[13,14] orbital considerations based on the symmetry of the complex and position of the ligands in the spectrochemical series also suggest a $^5B_2$ ground term with the $^5B_2 \rightarrow {}^5B_1$ transition at lower energy than the $^5B_2 \rightarrow {}^5A_1$ transition. The latter ordering is of course tentative and must await verification *via* determination of single-crystal polarized spectra. Finally, the $^5B_2 \rightarrow {}^5E$ (arising from $^5T_{2g}$ in O_h) transition represents essentially the low-symmetry splitting of the $^5T_{2g}$ term and is normally at too low an energy to be observed. A similar optical spectrum is observed and transition assignments are made for Fe(phen)Cl_2.[2]

The near-infrared spectrum of Fe(5,5'-$(CH_3)_2$bipy)Cl_2 exhibits one maximum (8900 cm^{-1}) at somewhat lower energy than the highest energy spin-allowed transition of Fe(2,2'-bipy)Cl_2 and the tail of another transition whose maximum is centered somewhere between 4000 and 5000 cm^{-1}. These band positions are most consistent with the five-coordinate (FeN_2Cl_3) chromophore as pictured in Figure 6. Such a structure has a good precedent[15] in the dimer [Ni(2,9-$(CH_3)_2$phen)Cl_2]$_2$ for which X-ray study confirms the five-coordination. The actual structure of Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2 is probably a dimer as indicated by the figure but could also be an extended polymer articulated from such a dimer *via* chloro bridging and having the local coordination environment pictured. Our data do not unequivocally distinguish between the latter possibilities. Sterically a dimer would seem to be most favored. In addition, we have found that for equimolar samples of Fe(2,2'-bipy)Cl_2 and Fe(4,4'-$(CH_3)_2$-2,2'-bipy)Cl_2[16] at 78 K, the respective Mössbauer per cent effects are 7.1% and 3%, consistent with our formulation of the former as the polymer and the latter a dimer.

2. Far-Infrared Spectra. Strong evidence for the proposed structures of Fe(2,2'-bipy)Cl_2 and Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2 which contain six- and five-coordinate iron, respectively, comes from their far-infrared spectra. We present these spectra in Figures 7 and 8 along with those of tetrahedral zinc analogs. The monomeric tetrahedral complexes have essentially C_{2v} symmetry for which there are expected to be four infrared-active metal–ligand bands.[17] Two of these are the terminal metal–chlorine stretches observed at 320 and 330 cm^{-1} for Zn(2,2'-bipy)Cl_2 and 320 and 340 cm^{-1} for Zn(4,4'-$(CH_3)_2$-2,2'-bipy)Cl_2. The assignments agree quite well with previous[18,19] studies of zinc systems. The effect of chloro bridging is obvious. For Fe(2,2'-bipy)Cl_2, the strong absorptions observed between 300 and 350 cm^{-1} in the zinc compound are absent and intense new transitions appear between 250 and 270 cm^{-1} (Figure 7). This shift to lower frequency is expected for bridging. It is however difficult to make an exact assignment for the latter Fe–Cl–Fe vibrations as there is a grating change for the spectrometer in this region and in addition the metal–nitrogen absorption is also observed in this region.[20] It is worthwhile to point out that in a recent study[21] of the physical and chemical properties of Sn(2,2'-bipy)Cl_2, essentially the polymer structure shown in Figure 4 was proposed.

In the case of Fe(4,4'-$(CH_3)_2$-2,2'-bipy)Cl_2 there appear to be both terminal (320 cm^{-1}) and bridging (255 cm^{-1}) chlorine absorptions (Figure 8) consistent with the proposed five-coordinate structure. A similar infrared spectrum is observed for Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2. As a check on our assignments of terminal Fe^{2+}–Cl stretches we have determined the far-infrared spectrum of Fe(2,9-$(CH_3)_2$phen)Cl_2 as well as the corresponding bromide and iodide. These systems are pseudotetrahedral complexes in which nominally two metal–halogen stretches are expected. The foregoing vibrations are observed at 365 and 330 cm^{-1} in the chloride, at 280 and 258 cm^{-1} in the bromide, and as a rather strong broad, band at 241 cm^{-1} in the iodide. The expected shift to lower energy for increased reduced mass of the vibrating system is also observed in Zn(2,9-$(CH_3)_2$phen)Cl_2. In this compound we find the Zn–Cl vibrations to occur at 340 and 323 cm^{-1}.

3. Isomer Shift Data. The Mössbauer isomer shift data (Table II) for Fe(2,2'-bipy)Cl_2 and Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2 are certainly consistent with the proposed structures involving six- and five-coordinate iron(II), respectively. An extensive series[22,23] of pseudooctahedral high-spin iron(II) chloride complexes containing imine nitrogen donor ligands has been investigated and the values of the isomer shifts at 300 K (relative to natural iron) are usually close to 1.0 mm/sec. In fact the values of δ for Fe(phen)Cl_2 and Fe(2,2'-bipy)Cl_2 are nearly identical with those[12] of the polymer [Fe$(py)_2Cl_2$] which, as indicated previously, contains six-coordinate iron(II) in the FeN_2Cl_4 chromophore. On the other hand genuine tetrahedral ferrous complexes generally[24,25] exhibit more negative δ values in the range 0.80–0.90 mm/sec at 300 K. Specific examples for the tetrahedral FeN_2Cl_2 chromophore are Fe$(quin)_2Cl_2$[26] (δ = 0.86 mm/sec at 300 K) and Fe(2,9-$(CH_3)_2$phen)Cl_2, Table II. Thus values of $\delta \geq 0.80$ mm/sec as for Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2 and the 4,4'-$(CH_3)_2$ complex are quite reasonable for five-coordination. These compare quite well with those found[27] for monomeric five-coordinate iron(II) compounds such as Fe(2,2',2''-terpy)$(NCS)_2$ or the corresponding bromide. In addition, the large quadrupole splittings of the dimethyl complexes are expected for a low-symmetry, five-coordinate structure.

4. Solution Conductivity Data. Attempts at the determination of molecular weights by conventional solution methods met with solubility problems. The polymeric Fe(2,2'-bipy)Cl_2 and Fe(phen)Cl_2 were as expected for polymers, essentially insoluble in nitromethane and acetonitrile. Heating caused these materials to dissolve and apparently also to dissociate. This is evidenced by the high molar conductivities of the resulting acetonitrile solutions (Λ_m(Fe(phen)Cl_2) = 74 mhos cm^2 mol^{-1}) relative to solutions of the nonelectrolyte Fe(2,9-$(CH_3)_2$phen)Cl_2 (Λ_m = 10.66 mhos cm^2 mol^{-1}) and a 1:1 electrolyte ($(n\text{-Bu})_4$NI (Λ_m = 148 mhos cm^2 mol^{-1}). The complex Fe(5,5'-$(CH_3)_2$-2,2'-bipy)Cl_2 dissolved readily, consistent with a (low molecular weight) dimer. For this compound Λ_m = 83.6 mhos cm^2 mol^{-1}, intermediate to the values for a nonelectrolyte and a 1:1 electrolyte, again suggesting decomposition.

C. Thermal Effects. A polymeric pseudooctahedral form of Co(2,2'-bipy)Cl_2 has been prepared[28] by careful thermolysis of [Co(2,2'-bipy)$_3$]Cl_2 at ~220°. Higher temperature (290°) thermolysis of this polymer results in the breaking of chloro-bridge bonds and formation of a lower coordination number complex of the same empirical formula. Near-infrared and visible mull spectra of the latter compound indicate a monomeric pseudotetrahedral structure. We also observe the phenomenon of scission of chloro-bridge bonds of the polymer using Mössbauer spectroscopy. Figure 9 shows the four transition Mössbauer spectrum of Fe(2,2'-bipy)Cl_2 prepared by prolonged high-temperature (>150°) thermolysis of [Fe(2,2'-bipy)$_3$]Cl_2. *Only the inner quadrupole doublet* is observed when the compound is prepared by careful low-temperature thermolysis. The optical spectrum and X-ray powder pattern of the latter preparation are the same as those of the solution preparation. In addition Mössbauer parameters of this preparation as well as those of the inner doublet of Figure 9 are essentially identical with those for Fe(2,2'-bipy)Cl_2 prepared directly in solution (Table II). The foregoing observations indicate the same basic polymeric structure for Fe(2,2'-bipy)Cl_2 prepared in solution and *via* low-temperature thermolysis. These materials do differ in one important respect. This is that instead of ordering sharply over a small temperature interval (~0.5 K), the Mössbauer spectrum of the thermolysis preparation exhibits gradual Zeeman splitting over a larger interval below 5.0 K and is not completely resolved for temperatures as low as 2.1 K (Figure 10). For the present we can only speculate as to the probable origin of this behavior. One explanation is that Fe(2,2'-bipy)Cl_2 prepared by low-temperature thermolysis contains a small number of broken chloro-bridge bonds thus giving a defect structure in which sharp ferromagnetic ordering is hindered. It is probably more likely that this preparative method results in a greater dis-

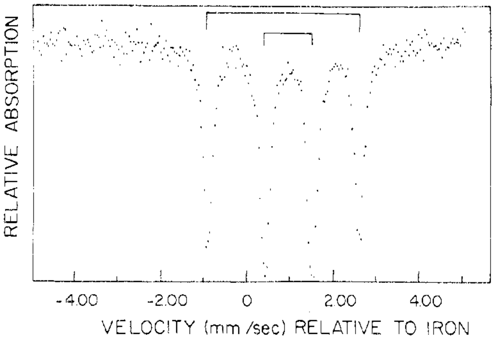

Figure 9. Mössbauer spectrum of Fe(2,2'-bipy)Cl_2 (at 300 K) prepared by prolonged high-temperature thermolysis.

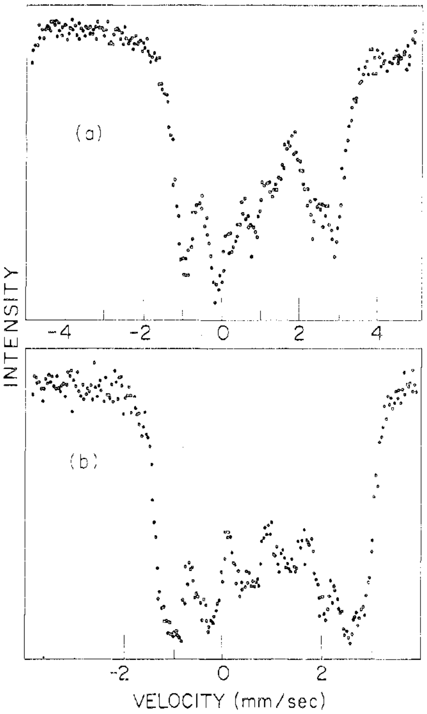

Figure 10. (a) Mössbauer spectrum at 2.1 K of Fe(2,2'-bipy)Cl_2 prepared by low-temperature thermolysis. (b) Mössbauer spectrum at 4.2 K of Fe(phen)Cl_2 prepared in solution and then thermally annealed under vacuum for 2 days at 200°.

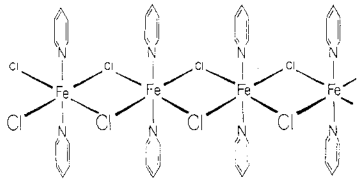

Figure 11. Schematic of the molecular structure of $Fe(py)_2Cl_2$.

tribution of polymer chain lengths and orientations so that the ferromagnetic ordering occurs over a larger temperature range, corresponding to magnetic inhomogeneity. $Fe(phen)Cl_2$ prepared in solution exhibits a well-resolved Zeeman spectrum similar to those found for the corresponding 2,2'-bipyridine compound (Figure 1). However, high-temperature annealing of such a solution preparation results in the broadening of all the Mössbauer transitions (Figure 10). This again may result from a distribution of polymer chain lengths or small defects in the annealed system.

If the low-temperature preparation of $Fe(2,2'\text{-bipy})Cl_2$ is thermolyzed at even higher temperatures, the outer doublet of Figure 9 begins to appear while the intensity of the inner quadrupole doublet decreases. However, continued thermolysis does not result in the complete disappearance of the inner doublet corresponding to the polymer form. The Mössbauer parameters (Table II) of the outer quadrupole doublet are the same as those for $Fe(5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cl_2$ confirming *extensive* cleavage of chloro-bridge bonds and the formation of a lower coordinate species.

IV. Structure and Magnetic Ordering

The observation of ferromagnetism for $Fe(2,2'\text{-bipy})Cl_2$ and $Fe(phen)Cl_2$ is reasonable for the proposed structure, Figure 4. By analogy with other first transition metal series chloro-bridged systems, the intrachain metal–metal distance is probably between 3.4 and 3.7 Å[29] and too great for direct metal–metal interaction to account for all of the magnetic exchange. The interaction must be due in part to "superexchange" through the chloro-bridge groups. Anderson's[30] model of magnetic exchange *via* such bridging groups predicts positive (ferromagnetic) exchange interaction when (a) the metal and bridging atoms lie in the same plane, (b) the bridge angles are ~90°, and (c) the bonding and exchange involve primarily bridge atom p orbitals and metal atom d orbitals. Our proposed structure meets the foregoing conditions. The Goodenough–Kanamori rules[31] also suggest positive exchange interaction for this geometry when the exchange is between metal atoms with more than half-filled t_{2g} manifolds as is the case for the present iron(II) compounds. More recently Ginsberg,[32,33] *et al.*, have used a molecular orbital description to discuss the intramolecular ferromagnetic coupling of some nickel(II) dimers whose bridge geometry is like that proposed here.

In the case of the dimethyl compound, slow paramagnetic relaxation is not unexpected in view of the proposed highly distorted coordination environment. The distortion can result in a substantial quenching of the orbital moment and consequently a long spin–lattice relaxation time.

Other than the fact that the nitrogen atoms of $Fe(2,2'\text{-bipy})Cl_2$ are constrained to be cis, the bridge geometry and magnetic behavior of this compound are expected to be quite similar to those for the polymer $Fe(py)_2Cl_2$, Figure 11. The structure of this latter system is known[12,29] and meets all of the requirements for ferromagnetic exchange. We have recently completed a detailed study of this compound's magnetic susceptibility, field dependence of magnetization, and Mössbauer spectra, and the dominant exchange interaction in the chains is indeed positive.[34] However, the interchain interaction is negative, resulting in an antiferromagnetic ground state. Application[34] of an external magnetic field of sufficient magnitude causes a decoupling of the chains and a transition (metamagnetic) from the antiferromagnetic ground state to a paramagnetic state. Such a transition has also been observed, for example, in anhydrous ferrous chloride[35,36] which has a layer structure with ferromagnetic interactions within the layers and antiferromagnetic interactions between layers.

In $Fe(2,2'\text{-bipy})Cl_2$ and $Fe(phen)Cl_2$ the ground state is ferromagnetic and no magnetic phase transitions are observed in fields from 0 to 200 kOe at temperatures as low as 1.3 K. It may be that the orientation and rigidity of the aromatic rings for $Fe(2,2'\text{-bipy})Cl_2$ (Figure 4) and the analogous phenanthroline complex results in larger *interchain* metal–metal separation with a consequent change in sign of the interchain magnetic interaction to positive. More definitive comments on these interactions must await single-crystal studies.

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Registry No. $Fe(2,2'\text{-bipy})Cl_2$, 40448-08-6; $Fe[5,5'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy}]Cl_2$, 53897-14-6; $Fe[4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy}]Cl_2$, 53897-15-7; $Fe(phen)Cl_2$, 40448-07-5; $Fe[2,9\text{-}(CH_3)_2\text{-phen}]Cl_2$, 53955-80-9; $Zn(2,2'\text{-bipy})Cl_2$, 14491-36-2; $Zn[4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy}]Cl_2$, 53897-16-8.

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Bis[*o*-phenylenebis(dimethylarsine)]iron Complexes with NO, CO, CH_3CN, and Other Small Molecules

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The preparation and characterization of several new *o*-phenylenebis(dimethylarsine) (das) complexes of iron are reported including $[Fe(das)_2(NO)][ClO_4]$, $[Fe(das)_2(NO)Cl][ClO_4]_2$, $[Fe(das)_2(CO)Cl][B(C_6H_5)_4]$, $[Fe(das)_2(CH_3CN)Cl][B(C_6H_5)_4]$, $Fe(das)_2(N_3)_2$, $Fe(das)_2(NCO)_2$, $Fe(das)_2(NO_2)Cl$, and $[Fe(das)_2(NCS)_2]PF_6$. Pmr studies of the diamagnetic six-coordinate complexes show that they all have trans geometry. The pmr spectrum of $[Fe(das)_2(NO)]^+$ in DMSO-d_6, CD_3CN and C_6H_5CN indicates that it is fluxional and has trigonal-bipyramidal geometry. The geometries of the four different nitrosyl complexes *trans*-$[Fe(das)_2(NO)(NCS)]^{2+}$, *trans*-$[Fe(das)_2(NO)(NCS)]^+$, $[Fe(das)_2(NO)]^{2+}$, and $[Fe(das)_2(NO)]^+$ are accounted for by a molecular orbital scheme.

Introduction

Transition metals play a central role in mediating the reactions of many small molecules. Iron compounds are especially important, because they are involved in nitrogen reduction by nitrogenase and by Haber catalysts, in oxygen transport by hemoglobins and myoglobin, and in several important catalysts. However, there is only a limited understanding of the chemical transformations which small molecules undergo while they are attached to iron. The research described below was initiated to elucidate the chemistry of $\{FeXY\}^n$ complexes.[1]

The chemistry of *o*-phenylenebis(dimethylarsine) (das) complexes of iron was first studied by Nyholm,[2] who isolated and characterized $FeX_2(das)_2$ and $FeX_2(das)_2{}^+$. Subsequently, studies of their magnetic properties[3,4] as well as those of an iron(IV) complex showed that all are low spin. The ligand field spectra[5,6] and infrared spectra[7] of *trans*-$[FeX_2(das)_2]^{0,+}$ have also been thoroughly studied and many of their spectral bands assigned. In addition, several nitrosyl derivatives of the $Fe(das)_2$ fragment have been reported previously.[8-10] These prior studies indicated that a series of $Fe(NO)(das)_2$ complexes could be prepared in which the total number of electrons in the $\{FeNO\}^n$ group could easily be varied.

In spite of the large number of $Fe(das)_2$ complexes which have been reported, there has been little systematic investigation of the preparation and chemical reactivity of their complexes with small molecules such as NO, CO, N_2, or CH_3CN. Since das forms complexes with iron in several oxidation states (0, +1, +2, +3, and +4) the $Fe(das)_2$ complexes should be ideal for investigating the chemical and physical consequences of changing the number of electrons in an $\{FeXY\}^n$ group while keeping the other ligands the same. This paper describes the synthesis of a number of such das complexes and demonstrates that the chemical and physical properties of the $\{FeNO\}^n$ group (n = 6–8) do indeed differ dramatically. These $\{FeNO\}^n$ complexes and their properties may serve as a guide to understanding the chemistry of other $\{FeXY\}^n$ groups.

Experimental Section

Reagents and Characterization. The reactions and operations described below were carried out where necessary under oxygen-free nitrogen in Schlenkware[11] using standard inert-atmosphere techniques. All solvents were thoroughly degassed before use. Further purification of solvents and reagents was by standard methods. Nitric oxide was purified by passing it through molecular sieves (Linde 4A) at −78°. The ligand *o*-phenylenebis(dimethylarsine) was prepared according to literature methods.[12] The compounds were analyzed by Huffman Laboratories, Wheatridge, Colo., and Chemalytics, Inc., Tempe, Ariz., and the results are set out in Table I.

The infrared spectra were obtained as Nujol mulls between KBr plates or as KBr pellets using Perkin-Elmer Model 337 and Beckman Model IR-12 infrared spectrophotometers. The nmr spectra were obtained using the Varian Models T60 and HA100 spectrometers equipped with variable-temperature probes. TMS was used as an internal standard. Conductivity measurements were carried out by methods described elsewhere[13] using an International Instruments, Inc., Model RC-16B2 conductivity bridge and a Lab-Line Instruments, Inc., cell.

Preparation of Complexes. Dichlorobis[*o*-phenylenebis(dimethylarsine)]iron(II).[7] A solution of 2.70 g of $FeCl_3 \cdot 6H_2O$ in 100 ml of ethanol was stirred for 2 hr with 0.5 g of iron powder and 2 drops of perchloric acid. The colorless solution was filtered and 4.1 ml of das was added. The yellow slurry was warmed almost to boiling for 30 min and allowed to cool to room temperature. The yellow solid was collected on a frit washed with 50 ml of ethanol and dried *in vacuo*; yield 5.35 g 77%.

Diazidobis[*o*-phenylenebis(dimethylarsine)]iron(II). A solution of 0.50 g of $Fe(das)_2Cl_2$ in 90 ml of methanol was warmed with 0.5 g of sodium azide for 20 min. The green solid was collected and dried *in vacuo*; yield 0.23 g, 45%.

Diisothiocyanatobis[*o*-phenylenebis(dimethylarsine)]iron(II). A solution of 1.0 g of potassium thiocyanate in 20 ml of methanol was added to a warm solution of 0.35 g of $Fe(das)_2Cl_2$ in 40 ml of methanol. After 0.5 hr the solution was cooled, and the purple solid was collected and dried *in vacuo*. The product was recrystallized from chloroform–heptane; yield 0.30 g 81%.

Dicyanatobis[*o*-phenylenebis(dimethylarsine)]iron(II). Solutions of 0.35 g of $Fe(das)_2Cl_2$ in 50 ml of warm methanol and of 0.21 g of potassium cyanate in 40 ml of methanol were mixed and stirred for 1 hr. The green solid was collected by filtration, dried *in vacuo*, and recrystallized from chloroform–heptane; yield 0.15 g, 43%.

Chloronitrobis[*o*-phenylenebis(dimethylarsine)]iron(II). A solution of sodium nitrite (0.15 g) in methanol (10 ml) was added to a warm solution of $Fe(das)_2Cl_2$ (1.00 g) in methanol (50 ml). After stirring for 10 min the brown solid was collected, washed with 5 ml of cold methanol, and dried *in vacuo*; yield 0.82 g, 81%.

Chlorocarbonylbis[*o*-phenylenebis(dimethylarsine)]iron(II) Tetraphenylborate. A methanol solution (100 ml) of $Fe(das)_2Cl_2$ (0.70 g) and sodium tetraphenylborate (0.35 g) were stirred for 24 hr at *ca.* 50° under a carbon monoxide atmosphere. After cooling the solution to room temperature, the yellow crystals which formed were