Inorg. Chem. **1986**, *25*, 2786–2790

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The Second Isomer of Dichloro(2,2′-bipyridine)iron(II): Syntheses and Spectroscopic and Magnetic Characterizations of Three Related Dichloro(α-diimine)iron(II) Complexes Containing Five-Coordinate, High-Spin Iron(II)

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Received June 21, 1985

The second or orange isomer of Fe(bpy)Cl_2 (bpy = 2,2′-bipyridine) has now been isolated by a new procedure and more completely characterized than before. Studies using Mössbauer and far-infrared spectroscopy reveal that this isomer has five-coordinate, high-spin Fe(II) sites and both terminal chlorine atoms and bridging chlorine atoms. Magnetic susceptibility studies show that magnetic exchange in the orange isomer is extremely weak, allowing two single-ion effects (zero-field splitting and slow paramagnetic relaxation) to become evident at $T < 12$ K. The above results lead to a *proposed* molecular structure: a chain of five-coordinate Fe(II) centers and single chloro bridges. The syntheses and the characteristics of two FeLCl_2 analogues of the orange Fe(bpy)Cl_2 isomer (L = 4,4′-$(C_6H_5)_2$- and 4,4′-$(CH_3)_2$bpy) are discussed briefly.

Introduction

Two isomers of Fe(bpy)Cl_2 (bpy = 2,2′-bipyridine) have been identified so far. The *red*, polymeric, pseudooctahedral isomer has been studied intensively in this laboratory for a number of years.[1,2] During this investigation, a second form of Fe(bpy)Cl_2 was at first detected but not isolated.[1] Sato and Tominaga[3,4] are, so are as we know, the first researchers to isolate and begin characterizing the second form, the *orange* isomer, but they described it incorrectly as a monomeric, pseudotetrahedral complex.

We now report (a) a new synthesis and a more complete characterization of the orange isomer of Fe(bpy)Cl_2, (b) a new synthesis of the related orange Fe(4,4′-Me_2bpy)Cl_2 compound (Me = CH_3 = methyl), and (c) the synthesis and the preliminary characterization of the red-orange Fe(4,4′-Ph_2bpy)Cl_2 compound (Ph = C_6H_5 = phenyl). In addition, we propose for these three compounds and the Fe(5,5′-Me_2bpy)Cl_2 compound discussed[1,2] earlier a single fundamental molecular structure: a chain of five-coordinate Fe(II) centers and single chloro bridges.

Experimental Section

Syntheses. The orange isomer of Fe(bpy)Cl_2 was synthesized under an atmosphere of nitrogen gas to ensure that the Fe(II) cation was not oxidized during the reaction. Nitrogen gas was bubbled through $\sim$60 mL of concentrated hydrochloric acid for $\sim$15 min to drive off dissolved oxygen. Then the deoxygenated acid was combined with $\sim$1.81 g ($\sim$32.4 mmol) of Fe powder. Dissolving the iron efficiently required mild heating ($t \simeq 80$ °C) and gentle stirring. Once all of the Fe powder was dissolved, increased heating ($t \simeq 100$ °C) and more vigorous stirring were used to drive off the excess hydrochloric acid and to take the solution *almost* to dryness. The heating and the stirring were stopped while the resulting pale green ferrous chloride powder (probably $FeCl_2 \cdot 4H_2O$) was still slightly damp. The heat left in the reaction vessel then was enough to finish drying the powder without charring it. After being allowed to cool to room temperature, the freshly prepared ferrous chloride was dissolved with mild heating ($t \simeq 60$ °C) and gentle stirring in $\sim$60 mL of absolute ethanol, which had been deoxygenated with nitrogen gas. Once the pale green ferrous chloride powder was entirely dissolved in ethanol, heating and stirring were continued, and a deoxygenated solution of $\sim$0.511 g ($\sim$3.27 mmol) of 2,2′-bipyridine in $\sim$60 mL of absolute ethanol was added slowly (during approximately 10 min). The 1/10 bpy/Fe molar ratio was used to favor the formation of the mono-2,2′-bipyridine complex Fe(bpy)Cl_2 over the bis or tris complex. As soon as a few milliliters of the transparent, colorless bpy/ethanol solution had been combined with the clear, light green $FeCl_2$/ethanol solution, the color of the reaction mixture became bright red. As the addition of the bpy/ethanol solution proceeded, the reaction mixture gradually changed from a bright red, transparent solution to a red-orange, very clouded mixture. After all of the bpy/ethanol solution had been added, heating and stirring were continued for another 3–5 min to be sure that the reaction was completed. Then the heating and the stirring were stopped, and the reaction mixture was allowed to cool to room temperature. The product, a red-orange precipitate, was collected on a 30-mL, 30 M sintered-glass funnel by suction filtration and was washed first with two 25-mL portions of ethanol (with 2–3 drops of concentrated hydrochloric acid in each portion) and second with two 30-mL portions of pure ethanol. Drying the precipitate for $\sim$15 h under vacuum ($\sim$10 torr) at room temperature ($t \simeq 23$ °C) produced an orange powder. Anal. Calcd for the orange isomer of Fe(bpy)Cl_2, $C_{10}H_8Cl_2FeN_2$: C, 42.45; H, 2.85; N, 9.90. Found (Galbraith Laboratories, Knoxville, TN 37921): C, 42.61; H, 2.95; N, 9.80. The observed yield was 80% of the theoretical yield.

The orange Fe(4,4′-Me_2bpy)Cl_2 compound was synthesized in solution by the same procedure. Anal. Calcd for $C_{12}H_{12}Cl_2FeN_2$: C, 46.35; H, 3.89; N, 9.01. Found: C, 46.33; H, 3.90; N, 9.09.

Fe(4,4′-Ph_2bpy)Cl_2 was made in the same way except that the ligand 4,4′-Ph_2bpy was dissolved in ethyl ether rather than absolute ethanol. The color of the product is red-orange. Anal. Calcd for $C_{22}H_{16}Cl_2FeN_2$: C, 60.73; H, 3.71; N, 6.44. Found: C, 60.54; H, 3.62; N, 6.26.

Far-Infrared Spectroscopy. The sample was an FeLCl_2/Nujol mull. Each spectrum was recorded at room temperature ($t \simeq 23$ °C) on a Perkin-Elmer Model 567 spectrophotometer purged with nitrogen gas. The calibrant was polystyrene film; the calibration mark was the sharp peak at 906.9 cm^{-1}.

Mössbauer Spectroscopy. Our procedure for controlled-temperature, zero-field Mössbauer spectroscopy has been published[5] previously. The chemical-shift calibrant was natural iron foil.

Faraday Balance Measurements. Our procedure for measuring magnetic susceptibilities at set temperatures by means of a Faraday balance has been described[6] before. The calibrant was $HgCo(NCS)_4$.[7] The correction for the diamagnetism of FeLCl_2 (L = 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, or 4,4′-diphenyl-2,2′-bipyridine) was calculated from Pascal's constants: −13 for Fe^{2+}, −26 for Cl^-, −105 for 2,2′-bipyridine, −129 for 4,4′-dimethyl-2,2′-bipyridine, and −96 for 4,4′-diphenyl-2,2′-bipyridine (the units for all of these constants are 10^{-6} emu/mol).[8] We assumed that 4,4′-dimethyl-2,2′-bipyridine has the diamagnetism of 2,2′-bipyridine plus two carbon atoms and four hydrogen atoms and that 4,4′-diphenyl-2,2′-bipyridine has the diamagnetism of 2,2′-bipyridine plus two benzene rings minus four hydrogen atoms.

Results

Far-Infrared Spectra. The far-infrared spectrum that we recorded for the orange Fe(bpy)Cl_2 isomer synthesized in solution is essentially a duplicate of the spectrum that Sato and Tominaga recorded[3] for the orange Fe(bpy)Cl_2 isomer prepared by thermolysis of $[Fe(bpy)_3]Cl_2$ as a solid in a flowing stream of nitrogen gas. Furthermore, both spectra are very similar to the spectra

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Table I. Mössbauer Results for Related $FeLCl_2$ Compounds

compd	T, K	δ,ᵃ mm/s	ΔE_Q,ᵃ mm/s	chromophore
$Fe(py)_2Cl_2$[b]	296	1.08	0.57	*trans*-FeN_2Cl_4
	78	1.21	1.25	
red $Fe(bpy)Cl_2$[c]	300	1.04	1.10	*cis*-FeN_2Cl_4
	78	1.17	1.73	
orange $Fe(bpy)Cl_2$[d]	296	0.93	3.56	*cis*-FeN_2Cl_2Cl'
	78	1.01	3.68	
	19	1.05	3.77	
	10	1.01	3.77	
$Fe(4,4'\text{-}Me_2bpy)Cl_2$[d]	296	0.92	3.55	*cis*-FeN_2Cl_2Cl'
	78	1.04	3.78	
	8.8	1.04	3.94	
$Fe(4,4'\text{-}Ph_2bpy)Cl_2$	296	0.93	3.68	*cis*-FeN_2Cl_2Cl'
	80	0.94	3.77	
	4.1	1.08	3.92	
	1.5	1.08	3.96	
$Fe(5,5'\text{-}Me_2bpy)Cl_2$[c]	300	0.93	3.51	*cis*-FeN_2Cl_2Cl'
	78	1.06	3.72	
$Fe(2,2'\text{-}biq)Cl_2$[e]	300	0.78	2.76	*cis*-FeN_2Cl_2
	78	0.88	2.85	
$Fe(2,9\text{-}dmp)Cl_2$[c]	300	0.80	2.66	*cis*-FeN_2Cl_2
	78	0.91	2.77	
$Fe(phen)Cl_2$[f]	296	1.03	1.46	*cis*-FeN_2Cl_4
	78	1.15	2.16	

[a] Relative to natural iron foil. [b] Reference 37; py = pyridine. [c] Reference 1. [d] Prepared in solution. [e] Reference 16. [f] See also ref 11 and 12.

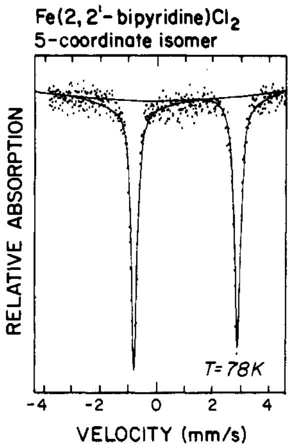

Figure 1. Zero-field Mössbauer spectrum of the orange isomer of $Fe(bpy)Cl_2$ at $T \simeq 78$ K. Smooth curves represent the Lorentzian fit.

that Reiff and co-workers published[1,2] for two $FeLCl_2$ compounds made from $[FeL_3]Cl_2$ (L = 4,4′-Me_2- or 5,5′-Me_2bpy) in the solid state by vacuum thermolysis. Each of these four spectra clearly exhibits two distinct Fe–Cl stretching frequencies: $\bar{\nu} \simeq 320$ cm^{-1} and $\bar{\nu} \simeq 250$ cm^{-1}.

Mössbauer Spectra. The chemical shift δ and the quadrupole splitting ΔE_Q of the zero-field Mössbauer spectrum that we recorded for the orange $Fe(bpy)Cl_2$ isomer synthesized in solution (Table I and Figurel) are —at either $T \simeq 296$ K or $T \simeq 78$ K—almost the same as the values that have been reported[1,3,4] for this isomer generated by thermolysis of $[Fe(bpy)_3]Cl_2$ as a solid. The chemical shift and the quadrupole splitting determined for the orange $Fe(4,4'\text{-}Me_2bpy)Cl_2$ compound prepared in solution (Table I) are nearly identical with the values obtained for the $Fe(4,4'\text{-}Me_2bpy)Cl_2$ compound made[1,2] by vacuum thermolysis of $[Fe(4,4'\text{-}Me_2bpy)_3]Cl_2$ in the solid state.

The chemical shift δ for either the orange $Fe(bpy)Cl_2$ isomer or a related $FeLCl_2$ compound (L = 4,4′-Me_2-, 4,4′-Ph_2-, or 5,5′-Me_2bpy) at $T > 77$ K (Table I) is in the range expected for a high-spin Fe(II) cation surrounded by a mixture of aromatic imine nitrogen atoms and halide anions, but the quadrupole splitting ΔE_Q is among the largest splittings observed for such Fe(II) complexes.[9]

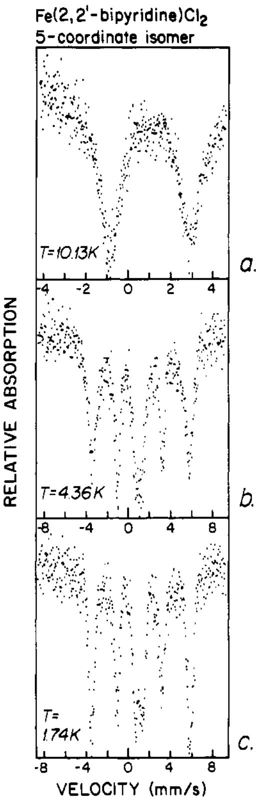

Figure 2. Zero-field Mössbauer spectra of the orange $Fe(bpy)Cl_2$ isomer at $T < 12$ K.

The magnetic hyperfine splitting seen in the zero-field Mössbauer spectra of the orange $Fe(bpy)Cl_2$ isomer (Figure 2) or the related $Fe(5,5'\text{-}Me_2\text{-}$ or $4,4'\text{-}Me_2bpy)Cl_2$ complex[1,2,10] at $T < 12$ K is *gradual*; that is, the magnitude of the internal magnetic field H_n increases slightly with cooling over a large range of temperatures ($\Delta T \simeq 10$ K). In contrast, the hyperfine splitting exhibited by the red, pseudooctahedral $Fe(bpy)Cl_2$ isomer for $T < 4$ K or the analogous red $Fe(phen)Cl_2$ compound (phen = 1,10-phenanthroline) at $T < 5$ K is *abrupt*: the magnitude of the internal field increases dramatically with cooling over a small range of temperatures ($\Delta T < 1$ K).[1,2,11,12] The abrupt transition seen for either of the red $FeLCl_2$ compounds (L = phen, bpy) signifies that the splitting is caused by cooperative, long-range, three-dimensional ordering.[1,2,11,12] The gradual change from a sharp, symmetric, quadrupole-split doublet to a fully resolved, Zeeman-split, six-line spectrum for $Fe(5,5'\text{-}Me_2\text{-}$ or $4,4'\text{-}Me_2bpy)Cl_2$ or the orange $Fe(bpy)Cl_2$ isomer indicates that the hyperfine splitting is due to slow paramagnetic relaxation.[1,2,10,13-16]

The separation of either lines 2 and 4 or lines 3 and 5 in a fully resolved, six-line spectrum can be used[17] to determine the magnitude $|H_n|$ of the internal hyperfine field for a compound ex-

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Table II. Magnetization Results for Related $FeLCl_2$ Compounds

compd	Θ, K	C, (emu·K)/mol	μ_{eff},[a] μ_B	μ_{296},[a] μ_B
$Fe(phen)Cl_2$[b]	+10.0	3.71	5.45	5.55
red $Fe(bpy)Cl_2$[c]	+10.8	3.51	5.29	5.41
orange $Fe(bpy)Cl_2$[d]	−1.68	3.41	5.22	5.21
$Fe(4,4'-Me_2bpy)Cl_2$[d]	−0.334	3.54	5.32	5.32
$Fe(5,5'-Me_2bpy)Cl_2$[e]	~0	4.3	5.8	
$Fe(4,4'-Ph_2bpy)Cl_2$	−9.25	3.35	5.18	5.16

[a] $\mu_{eff} = 2.828C^{1/2}$. $\mu_{296} = (\chi_M'T)^{1/2}$, where χ_M' is the corrected molar magnetic susceptibility of the compound at $T \simeq 296$ K. The spin-only moment $\mu_{so} = 4.90$ μ_B for the high-spin d^6 configuration. [b] Reference 11. [c] Redetermined for this report; see ref 1 and 2 for results of earlier measurements. [d] Prepared in solution. [e] Reference 2.

hibiting combined Zeeman-splitting and quadrupole-splitting interactions for the case of $H_n \gg \Delta E_Q$. Either separation corresponds to the Zeeman splitting of the ground state ($I = {}^1/_2$) for the ^{57}Fe nucleus since the two transitions in one pair (lines 2 and 4) or the other (lines 3 and 5) have the same terminus in the manifold of the $I = {}^3/_2$ excited state. The average of the separation between transitions 2 and 4 and the separation between transitions 3 and 5 for the orange $Fe(bpy)Cl_2$ isomer at $T \simeq 1.7$ K (Figure 2c) is 2.470 ± 0.034 mm/s. Dividing this quantity by the conversion factor 0.011 88 (mm/s)/kG yields $|H_n| = 208 \pm 3$ kG as the limiting magnitude ($T \rightarrow 0$ K) of the internal magnetic field for the orange isomer of $Fe(bpy)Cl_2$. This field is nearly equal to the field in the related $Fe(5,5'-Me_2bpy)Cl_2$ complex ($|H_n| \simeq 211$ kG).[1]

The zero-field Mössbauer spectra of $Fe(4,4'-Ph_2bpy)Cl_2$ are remarkably different from the spectra of the related $FeLCl_2$ complexes (L = bpy and 4,4'-Me_2- and 5,5'-Me_2bpy). No hyperfine splitting is detected for $Fe(4,4'-Ph_2bpy)Cl_2$ at 296 K $\geq T \geq 1.5$ K (Table I). This difference has a precedent. Slowly relaxing paramagnetism is observed in $FeA_2{\cdot}2H_2O$ at $T > 1.6$ K when the anion A is either 2,4-pentanedionate or 1,1,1-trifluoro-2,4-pentanedionate; rapid relaxation is seen at these temperatures when A is 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate.[18] Additional studies of $Fe(4,4'-Ph_2bpy)Cl_2$ are planned, particularly experiments using Mössbauer spectroscopy at $T < 1.5$ K and in an applied magnetic field $H_0 > 25$ kG.

Faraday Balance Measurements. The orange $Fe(bpy)Cl_2$ isomer and the related $FeLCl_2$ compounds (L = 5,5'-Me_2-, 4,4'-Me_2-, and 4,4'-Ph_2bpy) like the red $Fe(bpy)Cl_2$ isomer are high-spin Fe(II) complexes. Both μ_{296} and μ_{eff} for each of these complexes (Table II) are greater than the spin-only moment μ_{so} of the high-spin arrangement of d^6 electrons ($\mu_{so} = 4.90$ μ_B for four unpaired electrons).

The magnetic moment at room temperature μ_{296} reported in Table II and the magnetic moments plotted in Figure 3b were calculated by means of the expression $\mu(T) = 2.828(\chi_M'T)^{1/2}$, in which χ_M' is the corrected molar magnetic susceptibility of the compound at a particular temperature T. The effective magnetic moment μ_{eff} given in Table II was computed through a different expression, $\mu_{eff} = 2.828\,C^{1/2}$, where C is the Curie constant in the Curie–Weiss law $\chi_M' = C/(T - \Theta)$. Both the Curie constant C and the paramagnetic Curie temperature Θ (Table II) were obtained from a least-squares fit of the *reciprocal form* $1/\chi_M' = (T - \Theta)/C$ of the Curie–Weiss law to the reciprocal corrected molar magnetic susceptibility vs. temperature results. For greater reliability, the data for the fit were obtained from a large sample (~15 mg) of each compound in 10 applied magnetic fields (1.7 kG $\leq H_0 \leq$ 5.1 kG) and at temperatures between 70 and 310 K, that is, at temperatures where the magnetic behavior of a complex such as the complexes considered here is normally expected to conform to a Curie–Weiss law.

The paramagnetic Curie temperature Θ for either the orange $Fe(bpy)Cl_2$ isomer or the $Fe(4,4'-Me_2$- or $5,5'-Me_2bpy)Cl_2$ complex (Table II) is almost zero, suggesting that the magnetic exchange or superexchange in each of these complexes at temperatures 300 K $\geq T \geq$ 70 K is very weak. In contrast, the paramagnetic Curie temperature for either the red pseudooctahedral $Fe(bpy)Cl_2$ isomer or the analogous $Fe(phen)Cl_2$ compound is positive and large (>+10 K), indicating that a strong ferromagnetic correlation exists within either complex.[1,2,11,12]

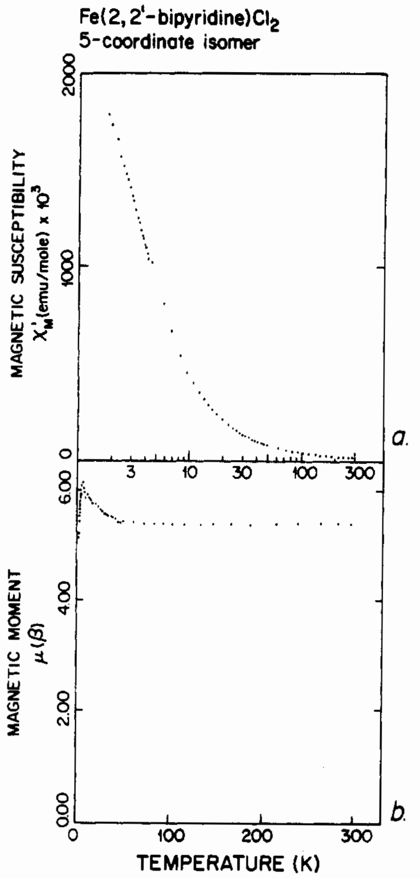

Figure 3. Plots of (a) χ_M' vs. log T and (b) μ vs. T for the orange $Fe(bpy)Cl_2$ isomer in applied field $H_0 = 5.1$ kG.

Even more striking is the difference between the magnetic moment vs. temperature (μ vs. T) curves for the two isomers of $Fe(bpy)Cl_2$. The magnetic moment μ of the red isomer[2] climbs from $\mu \simeq 5.4$ μ_B at $T \simeq 296$ K through $\mu \simeq 5.9$ μ_B at 53 K to a maximum of $\mu > 8$ μ_B at $T \simeq 5$ K (as part of a new study of the red isomer, we recently confirmed the results for 300 K $> T >$ 50 K by repeating the measurements at these temperatures). The moments for the red isomer are certainly too large for a high-spin Fe(II) complex, even one with the usual orbital contribution. The magnetic behavior of the red isomer of $Fe(bpy)Cl_2$ is indeed quite similar to the behavior of the red $Fe(phen)Cl_2$ compound: one-dimensional, ferromagnetic interactions at higher temperatures (70 K $< T <$ 140 K) and cooperative, long-range, three-dimensional, ferromagnetic ordering at lower temperatures (3 K $< T_{Curie} <$ 8 K).[1,2,11,12] In contrast, the magnetic moment of either the orange $Fe(bpy)Cl_2$ isomer or the related $Fe(4,4'-Me_2$-, $5,5'-Me_2$-, or $4,4'-Ph_2bpy)Cl_2$ compound at 300 K $\geq T \geq$ 50 K remains almost constant at 5.0 $\mu_B \leq \mu \leq$ 5.2 μ_B. These moments are typical of a high-spin Fe(II) complex with both a spin contribution and a classic orbital contribution but without strong magnetic exchange or superexchange.

The magnetic moment of the orange $Fe(bpy)Cl_2$ isomer does climb from $\mu \simeq 5.2$ μ_B at $T \simeq 51$ K to a maximum of $\mu \simeq 6.1$ μ_B at $T \simeq 5.9$ K (Figure 3b), but this small rise is not a sign of ferromagnetic ordering. The maximum in the μ vs. T curve occurs at $T < 12$ K, that is, at temperatures for which hyperfine splitting is observed in the zero-field Mössbauer spectra (Figure 2). The corrected molar magnetic susceptibility χ_M' of the orange isomer at $T < 12$ K, however, does not level off (Figure 3a) and does not become both strongly and inversely dependent on the applied field H_0 as the magnetic susceptibility of a ferromagnetically

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ordered compound—Fe(phen)Cl_2, for example—does at $T < T_{\text{Curie}}$.[11,12]

The small maximum seen in the μ vs. T curve recorded from a *powder sample* of the orange Fe(bpy)Cl_2 isomer at $T < 40$ K can be observed when highly anisotropic g factors favor a field-induced orientation of the magnetic moments in a polycrystalline (powder) sample.[19] This oriented-single-crystal behavior is more pronounced if $g_{\parallel} > g_{\perp}$, that is, $\mu_{\parallel} > \mu_{\perp}$ than if $g_{\parallel} < g_{\perp}$ ($\mu_{\parallel} < \mu_{\perp}$). The condition $g_{\parallel} > g_{\perp}$ corresponds (usually[20]) to a zero-field splitting D that is negative. If $D < 0$, the ground spin state is the Kramers $m_s = \pm 2$ doublet, and slow paramagnetic relaxation can occur because transitions between components of the ground $m_s = \pm 2$ state are highly forbidden. The monomeric, pseudotetrahedral Fe(2,9-dmp)$(NCS)_2$ complex (2,9-dmp = 2,9-dimethyl-1,10-phenanthroline) exhibits slow relaxation at $T < 20$ K, and the μ vs. T curve for a powder sample of this compound climbs to a maximum of $\mu = 8.10\ \mu_B$ at $T = 3.01$ K.[16] We emphasize that this magnetic behavior is purely a single-ion effect not involving exchange or ordering.

The slight decrease in the magnetic moment of the orange Fe(bpy)Cl_2 isomer from $\mu \simeq 5.2\ \mu_B$ at 300 K $> T >$ 50 K to $\mu \simeq 5.1\ \mu_B$ at $T \simeq 1.8$ K (Figure 3b) suggests[16,20,21] that the magnitude of the zero-field splitting for this complex is small: $|D| \simeq 2\ \text{cm}^{-1}$. The observation of slow paramagnetic relaxation in this complex (Figure 2) indicates that the splitting is negative: $D \simeq -2\ \text{cm}^{-1}$.

Discussion

The stretching frequencies for the M–Cl bonds in monomeric, pseudotetrahedral complexes such as Fe(2,9-dmp)Cl_2, β-Co(bpy)Cl_2, and Zn(bpy)Cl_2 are observed near $\tilde{\nu} \simeq 330\ \text{cm}^{-1}$ in the far-infrared spectra of these compounds.[1,22-25] The M–Cl stretching frequencies for polymeric, pseudooctahedral complexes such as Fe(phen)Cl_2, Mn(bpy)Cl_2, α-Co(bpy)Cl_2, and the red isomer of Fe(bpy)Cl_2 are seen near $\tilde{\nu} \simeq 260\ \text{cm}^{-1}$.[1,2,23,26] The far-infrared spectrum of either the orange Fe(bpy)Cl_2 isomer or the related Fe(4,4′-Me_2- or 5,5′-Me_2bpy)Cl_2 compound clearly indicates that each of these complexes has not only the terminal chlorine atoms of Zn(bpy)Cl_2 and Fe(2,9-dmp)Cl_2 but also the bridging chlorine atoms of α-Co(bpy)Cl_2 and the red Fe(bpy)Cl_2 isomer.

The chemical shift ($\delta \simeq 0.92$ mm/s) of either the orange Fe(bpy)Cl_2 isomer or any one of the related FeLCl_2 complexes (L = 5,5′-Me_2-, 4,4′-Me_2-, and 4,4′-Ph_2bpy) at $T \simeq 296$ K is approximately halfway (Table I) between the chemical shift ($\delta \geq 1$ mm/s) of six-coordinate, high-spin Fe(II) in pseudooctahedral complexes—for example, Fe(phen)Cl_2 or the red Fe(bpy)Cl_2 isomer—and the chemical shift ($\delta \simeq 0.8$ mm/s) of four-coordinate, high-spin Fe(II) in pseudotetrahedral complexes—for example, Fe(2,9-dmp)Cl_2 or Fe(2,2′-biq)Cl_2 (2,2′-biq = 2,2′-biquinoline).[1,2,16,22] The chemical shift of dichloro[2,4,6-tris(2-pyridyl)-1,3,5-triazine]iron(II) or Fe(terpy)X_2 (terpy = 2,2′:6′,2″-terpyridine; X = Br or NCS) at $T \simeq 296$ K is $\delta \simeq 0.9$ mm/s, and it has been demonstrated that the molecular structure of each of these three compounds is a monomeric complex with five-coordinate, high-spin Fe(II).[27,28] Moreover, the preceding observations clearly conform to the established systematics of chemical shift vs. coordination number for high-spin Fe(II) compounds.[9]

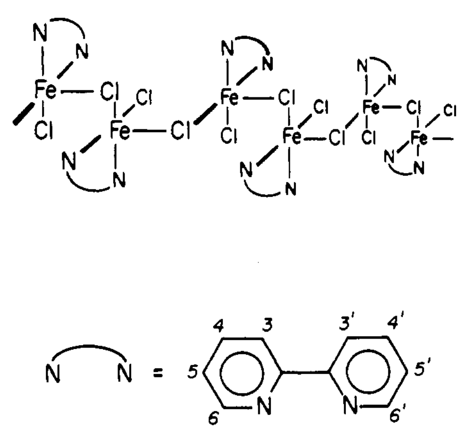

Figure 4. Schematic of chainlike molecular structure *proposed* for the orange Fe(bpy)Cl_2 isomer and related Fe(5,5′-Me_2-, 4,4′-Me_2-, and 4,4′-Ph_2bpy)Cl_2 complexes.

We *propose* the following molecular structure for the orange isomer of Fe(bpy)Cl_2 and for the only isomer obtained so far for FeLCl_2 (L = 5,5′-Me_2-, 4,4′-Me_2-, or 4,4′-Ph_2bpy): a chain of five-coordinate Fe(II) centers and single chloro bridges (Figure 4). The second chloride anion in the empirical formula FeLCl_2 is terminal; the two nitrogen atoms of the α-diimine ligand L are cis-coordinated to the Fe(II) cation.

The *cis*-$Fe^{II}N_2Cl_2Cl'$ chromophore in the proposed structure probably has a configuration that is between the extremes of a trigonal bipyramid and a square pyramid. The near-infrared–visible spectrum[1,2] of Fe(5,5′-Me_2- or 4,4′-Me_2bpy)Cl_2 is much more consistent with our proposed chromophore than with the pseudotetrahedral *cis*-$Fe^{II}N_2Cl_2$ chromophore that Sato and Tominaga[3] put forward. In addition, the very large quadrupole splitting ($\Delta E_Q > 3.5$ mm/s) of the orange Fe(bpy)Cl_2 isomer or a related FeLCl_2 compound (L = 5,5′-Me_2-, 4,4′-Me_2-, or 4,4′-Ph_2bpy) at 300 K $\geq T \geq$ 1.5 K (Table I) is more compatible with our proposed structure than with a monomeric, pseudotetrahedral complex such as Fe(2,9-dmp)Cl_2 or Fe(2,2′-biq)Cl_2 (3.0 mm/s $> \Delta E_Q$; Table I).[9,20]

The single chloro bridge between two adjacent high-spin Fe(II) centers in the molecular structure that we propose (Figure 4) is consistent with magnetic exchange that is so weak that single-ion effects such as zero-field splitting (Figure 3) and slow paramagnetic relaxation (Figure 2) are dominant. The single chloro bridge apparently produces a chain with a solid-state configuration in which metal–metal distances, bond angles, and bond lengths are unfavorable to magnetic correlations.

The weakness of the magnetic exchange in either the orange Fe(bpy)Cl_2 isomer or any one of the three related FeLCl_2 compounds (L = 5,5′-Me_2-, 4,4′-Me_2-, and 4,4′-Ph_2bpy) eliminates from consideration another molecular structure that is possible for an Fe(α-diimine)Cl_2 complex with five-coordinate Fe(II) sites, terminal chlorine atoms, and bridging chlorine atoms. This alternative structure, a dimer of two five-coordinate metal centers joined by twin chloro bridges, has been found in $[NiLCl_2]_2$ (L = 2,9-dmp or 2,2′-biq) and $[Mn(2,2'\text{-biq})Cl_2]_2$.[1,2,29-31] The dimeric $[Mn(2,2'\text{-biq})Cl_2]_2$ complex exhibits[31] ferromagnetic ex-

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change, and $[Ni(2,9\text{-dmp})Cl_2]_2$ and $[Ni(2,2'\text{-biq})Cl_2]_2$ show[32,33] antiferromagnetic exchange, but not one of the $FeLCl_2$ compounds with five-coordinate Fe(II) sites displays the magnetic exchange expected for strongly coupled paramagnetic metal ions.

Strong ferromagnetic exchange has been detected in the red $Fe(bpy)Cl_2$ isomer and in similar, polymeric, pseudooctahedral complexes such as $Fe(phen)Cl_2$, $Mn(bpy)Cl_2$, and α-$Co(bpy)Cl_2$.[34] X-ray crystallographic analysis of a single crystal of α-$Co(bpy)Cl_2$ has revealed[35] that the molecular structure of this compound is a stepped, zigzag, chain in which each Co(II) center is linked to the next by twin chloro bridges (this structure can be generated from Figure 4 if the Fe centers are changed to Co centers and the terminal chlorine atoms are made into bridging atoms). The far-infrared spectra of $Fe(phen)Cl_2$, $Mn(bpy)Cl_2$, the red $Fe(bpy)Cl_2$ isomer, and α-$Co(bpy)Cl_2$[1,2,23,26] indicate that these compounds are isomorphous to each other. The strong ferromagnetic exchange observed in these four compounds suggests that they have very similar molecular structures. The twin chloro bridges produce a chain with bond lengths and bond angles that are favorable to strong magnetic exchange.

We believe that the red, pseudooctahedral isomer of $Fe(bpy)Cl_2$ is kinetically favored and that the orange isomer, the isomer with five-coordinate Fe(II), is thermodynamically favored. The red form can be obtained by the Broomhead–Dwyer synthesis: a hot, acidic, aqueous solution of $FeCl_2$ is decanted onto a thin layer of finely ground 2,2′-bipyridine, and the reaction mixture is stirred, heated, and concentrated until the red isomer precipitates.[1,36] During some of our recent attempts to prepare the red form in solution, we discovered that if the reaction mixture is stirred and heated too long, the color changes from red to orange. The Mössbauer spectrum of the product isolated from any one of these excesses reveals that both isomers are present in a ratio of approximately one part red to three parts orange. This observation is consistent with our synthesis of the orange form in solution: if a 2,2′-bipyridine/absolute ethanol solution is gradually added with heating and stirring to a freshly prepared $FeCl_2$/ethanol solution (bpy/Fe molar ratio 1/10) and the reaction mixture is heated and stirred further, then just the orange isomer precipitates (see Experimental Section). Furthermore, while careful vacuum thermolysis (10 μm Hg for 10 h) of $[Fe(bpy)_3]Cl_2$ in the solid state at moderate temperatures (145 °C) produces only the red form of $Fe(bpy)Cl_2$, prolonged (>20 h) vacuum thermolysis at higher temperatures (>150 °C) yields an approximately 1/1 mixture of the two isomers.[1]

Conclusions

The spectra and the magnetic behavior recorded for the orange $Fe(bpy)Cl_2$ isomer and related $FeLCl_2$ compounds (L = 5,5′-Me_2-, 4,4′-Me_2-, and 4,4′-Ph_2bpy) are most consistent with our proposed molecular structure: a chain of single chloro bridges and five-coordinate, high-spin Fe(II) sites. The differences between the two isomers of $Fe(bpy)Cl_2$ indicate that a rich variety of molecular structures and chemical and physical properties is to be found among $FeLX_2$ compounds where L = endo bidentate ligand and X = halogen or pseudohalogen.

Acknowledgment. We are very grateful for the financial support of the U.S. National Science Foundation, Division of Materials Research, Solid State Chemistry Program Grants 8016441 and 8313710. We thank Drs. Edward H. Witten and Karoly Lâzâr for executing magnetic susceptibility and Mössbauer spectroscopy measurements of $Fe(4,4'\text{-}Ph_2bpy)Cl_2$, and we thank Brian Rappoli for devising a reliable preparation of this complex.

Registry No. $Fe(bpy)Cl_2$, 32425-36-8; $Fe(4,4'\text{-}Me_2bpy)Cl_2$, 102630-78-4; $Fe(4,4'\text{-}Ph_2bpy)Cl_2$, 102630-79-5.

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Contribution from the Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241
liée par convention à l'Université P. Sabatier, 31400 Toulouse, France

New Route to Bimetallic Imidazolate-Bridged Complexes. 1. Synthesis and Solid-State Properties of a Homodinuclear (Copper–Copper) Complex and Its Heterodinuclear (Copper–Nickel) Homologue. Structure of the Heterodinuclear Complex

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Received October 28, 1985

The synthesis and magnetic properties of the (μ-imidazolato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1−))dicopper(II) perchlorate complex and its heterodinuclear (copper–nickel) homologue are described. The structure of the heterodinuclear complex is reported. It crystallizes in the triclinic space group C_i^1-$P\bar{1}$ with two formula weights in a cell having the dimensions a = 11.227 (2) Å, b = 13.218 (2) Å, c = 8.271 (1) Å, α = 103.34 (1)°, β = 100.27 (1)°, and γ = 76.87 (1)°. $\Delta M_S = 2$ transitions are observed in EPR spectra related to solid samples of both complexes. Their disappearance upon dilution suggests that dipolar interactions between the individual dinuclear units are operative in the solid. Static susceptibility measurements point to an intramolecular exchange interaction ($2J = -43.0$ cm^{-1}) between the two copper(II) ions of the dicopper complex.

Introduction

Binding of imidazole-type molecules to metal complexes is a subject of considerable interest because of the frequent occurrence of imidazole derivatives in biologically important metal complexes. One of the most extensively studied members of this group is the Cu–Zn superoxide dismutase,[1] which has been shown by X-ray crystallography to have an imidazolate bridge between the two metals. Consequently a number of model compounds have been prepared. They involve pairs of either identical or dissimilar metals bridged by a deprotonated imidazole-type molecule.[2–15]

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