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A Mössbauer, Magnetic, and Electronic Structural Study of Two Iron Squarate Complexes

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The squarate dianion $C_4O_4^{2-}$ forms two complexes with iron. The first, $FeC_4O_4(H_2O)_2$, is a high-spin pseudooctahedral iron(II) complex as indicated by its optical and infrared spectra. Magnetic susceptibility and Mössbauer effect studies reveal that this complex is paramagnetic from 1.3 to 300 K. The second, $Fe(OH)C_4O_4(H_2O)_3$, is best formulated as a dihydroxy-bridged iron(III) dimer of stoichiometry $[Fe(OH)C_4O_4(H_2O)_2]_2 \cdot 2H_2O$. Low-temperature magnetic susceptibility results indicate strong intramolecular antiferromagnetic exchange coupling with $S_1 = S_2 = 5/2$, $g = 2.00$, and $J = -7.0$ cm^{-1} . The zero applied field Mössbauer effect spectrum of this compound exhibits no internal hyperfine field even at 1.3 K, a temperature which is ca. 50 K below its ordering temperature. This behavior indicates that at 1.3 K it is undergoing fast spin-spin magnetic relaxation as a result of the strong antiferromagnetic coupling between the two iron(III) ions. This conclusion is supported by an applied field Mössbauer effect study which indicates an induced field of ca. 4 kOe in a 6 T applied field.

The crystal structure and the phase transition observed in 3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$, commonly referred to as squaric acid, have been widely studied.¹⁻⁶ Since the pioneering work by West and Niu,⁷ there have been numerous studies of the metal complexes formed by $C_4O_4^{2-}$, the squarate ion. The formation of various metal complexes in aqueous solution has been studied by Walton and his co-workers.⁸ The thermodynamics of complex formation of $C_4O_4^{2-}$ with various lanthanides have been determined by Orebaugh and Choppin,⁹ and those of the complex formation with nickel ion and vanadyl ion determined by Alexandersson and Vannerberg.¹⁰ Stevens, in a unique application, has used the formation of squarate complex for the detection of traces of iron, uranium, and various other metal ions by microscopy.¹¹

More detailed studies of the squarate complexes with aluminum, gallium, and indium¹² and with tantalum¹³ are also available. An excellent study by Gerstein and Habenschuss of the X-ray structure¹⁴ and magnetic^{14,15} properties of $NiC_4O_4(H_2O)_2$ has revealed an unexpected polymeric solid-state structure and very low temperature ferromagnetic ordering behavior. The magnetic properties of a dimeric vanadium(III) complex¹⁶ and a copper complex¹⁷ have also been reported. Tsuchiya et al.¹⁸ have described an unusual solid-state thermal conversion of $[Cr(NH_3)_6][Al(C_4O_4)_3]$ into $Al[Cr(C_4O_4)_3]$. In addition the thermal stability of several squarate complexes has been reported.¹⁹

Rather surprisingly, there has been little reported on the solid-state properties of the iron squarate complexes since the early work of West and Niu,⁷ who proposed polymeric structures for the complexes. The purpose of this paper is to report on the magnetic and electronic properties of the iron(II) and dimeric iron(III) complexes with the squarate anion. The goal of this work is to gain a better insight into the relationship of structure to magnetic coupling and the effect of this magnetic coupling on the rate of magnetic relaxation in polynuclear complexes.

Experimental Section

3,4-Dihydroxy-3-cyclobutene-1,2-dione was obtained from the Aldrich Chemical Co. and used as the dipotassium salt without further purification.

The iron(II) complex, $FeC_4O_4(H_2O)_2$, was prepared by the method of West and Niu.⁷ The complex is yellow-green and relatively stable with respect to oxidation if stored in a dry atmosphere. Anal. Calcd for $FeC_4H_4O_6$: Fe, 27.39; C, 23.56; H, 1.98. Found: Fe, 26.95; C, 23.41; H, 2.08.

The iron(III) complex $Fe(OH)C_4O_4(H_2O)_3$ was prepared by the method of West and Niu.⁷ The complex is black-violet and stable.

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Anal. Calcd for $FeC_4H_7O_8$: Fe, 23.37; C, 20.11; H, 2.95. Found: Fe, 23.6; C, 20.45; H, 3.07.

The infrared spectral results were obtained on either a Beckman IR-12 or a Perkin-Elmer 180 spectrometer. Samples were dispersed in KBr and CsI. Electronic spectra were measured on a Cary 14 with the samples milled in a fluorocarbon grease. The magnetic results were determined by the Faraday method by using a balance and calibration procedure which have been described.²⁰ The 78 K and higher temperature Mössbauer spectra were obtained on a Ranger Engineering Corp. constant-acceleration spectrometer. The liquid-helium spectra were obtained by using a Harwell spectrometer and cryostats which placed the sample directly in liquid helium. Both spectrometers utilized a room-temperature rhodium matrix source and were calibrated with natural α -iron foil. The magnetically perturbed spectra were obtained with a British Oxygen Corp. superconducting magnet and cryostat which produced a transverse magnetic field. The Mössbauer spectra were evaluated by using the National Bureau of Standards PARLOR computer program²¹ for the unconstrained fits, FITA²² for the constrained and unconstrained fits, and FITH²³ for the magnetically perturbed spectral fits. The χ values presented below are the sum of the squared difference between the calculated and observed spectrum divided by the number of degrees of freedom. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and the Analytical Section of the Inorganic Chemistry Laboratory, Oxford University, Oxford, England.

Results and Discussion

Habenschuss and Gerstein¹⁴ have determined the single-crystal structure of $NiC_4O_4(H_2O)_2$ and have stated that it is isostructural with $FeC_4O_4(H_2O)_2$. Powder X-ray diffraction results for our sample of $FeC_4O_4(H_2O)_2$ confirm this result. Hence the divalent iron compound has a structure at least very close to that of the nickel complex. In this structure the pseudooctahedral metal ion is coordinated to four different squarate molecules and to two water molecules in the trans positions. Individual squarate anions do not bridge only two metal ions, as proposed earlier,⁷ but rather bridge four different divalent metal ions to form a three-dimensional structure.¹⁴

The infrared spectral bands for $K_2C_4O_4 \cdot H_2O$ and the iron complexes are presented in Table I. The spectrum obtained for $K_2C_4O_4 \cdot H_2O$ is very similar to that reported by Ito and West⁶ except that several additional weak to moderate bands are found. This may be the result of the water present in our sample. The spectrum of $FeC_4O_4(H_2O)_2$ is similar to that of $C_4O_4^{2-}$ with certain shifts as would be expected on coordination. It is difficult to assign the ligand to iron bands, but the band at 425 cm^{-1} is tentatively assigned to ν_{Fe-O} , the iron to squarate vibrational band.

The optical and near-infrared spectrum of $FeC_4O_4(H_2O)_2$ is presented in Figure 1. As would be expected for a

Table I. Infrared Spectral Bands^a

$K_2C_4O_4 \cdot H_2O$	$FeC_4O_4 \cdot (H_2O)_2$	$Fe(OH)C_4O_4 \cdot (H_2O)_3$	assignment ^b
3450 s, b	3400 s, b, sh	3300 s, b	water
3300 s, b	3275 s, b	3050 s, b	water
2210 m	2240 m	2240 m	ν_5, ν_{13} combination
1530 s, b	1520 s, b	1620 s, b	ν_{12}, ν_{CO}
1450 s, b		1490 s, b	
1100 m	1102 s	1105 s	ν_{13}, ν_{CC}
1090 m		1085 s	
		980 m	δ_{FeOH}
880 m		860 m	
750 m	740 m, b	750 s	
680 m		700 s, b	
590 m, b	550 m, b	495 m	
	425 m	430 s	ν_{Fe-O}
348 m	390 m, sh	363 m	ν_{14}, δ_{CO}
		300 m	ν_{Fe-OH_2}
250 s	250 m	280 m	ν_4, δ_{CO}

^a All data were obtained at room temperature and given in wave-numbers. Key: m, medium; s, strong; b, broad; w, weak; sh, shoulder. ^b Assignments are taken in part from ref 6 and 24.

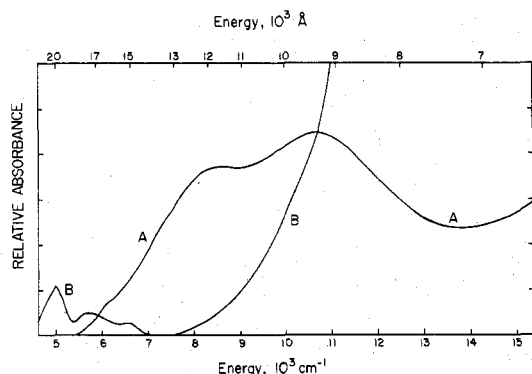


Figure 1. Room-temperature electronic absorption spectrum of (A) $FeC_4O_4(H_2O)_2$ and (B) $Fe(OH)C_4O_4(H_2O)_3$.

pseudooctahedral iron(II) complex with an approximate tetragonal ligand field,¹⁴ the electronic spectrum shows two broad reasonably well-separated bands at ca. 8500 and 10750 cm^{-1} . These bands are respectively assigned to transitions to the $^5B_{1g}$ and the $^5A_{1g}$ states which arise from the reduced symmetry splitting of the 5E_g excited state in octahedral symmetry. The higher energy transition to the $^5A_{1g}$ state at 10750 cm^{-1} is very similar in energy to the absorption observed for $Fe(ClO_4)_2$ in aqueous solution at ca. 10000 cm^{-1} and is in agreement with the ligand field expected for trans axial water molecules. The lower energy transition to the $^5B_{1g}$ state at 8500 cm^{-1} yields a value of Dq for the equatorial squarate ligands of ca. 850 cm^{-1} . This is in excellent agreement with the squarate ligand field potential of 855 cm^{-1} observed¹⁴ in $NiC_4O_4(H_2O)_2$ and of 890 cm^{-1} in $CoC_4O_4(H_2O)_2$.²⁶ The splitting of ca. 3000 cm^{-1} in these two bands is a reflection of the differing σ -bonding characteristics of the squarate anion and water.

The magnetic data for $FeC_4O_4(H_2O)_2$ are presented in Table II and shown in Figure 2. The magnetic moment is ca. 5.50 μ_B and essentially constant between 80 and 300 K. These values are reasonable for a high-spin iron(II) complex in a pseudooctahedral oxygen environment.²⁷ Below ca. 80 K the moment begins to drop slowly to a value of 5.06 μ_B at 20.4 K. Although this may be an indication of the onset of antiferromagnetic ordering in this polymeric material, it is more likely a result of the reduced symmetry of the complex. Figgis et al.²⁸ have calculated the magnetic moment expected for a high-spin d^6 configuration as a function of temperature, spin-orbit coupling, electron delocalization, and reduced symmetry ligand field. The solid line in Figure 2 is the

Table II. Magnetic Susceptibility Data

compound	T, K	$10^6 \chi_M^c$, cgsu	μ_{eff}, μ_B
$FeC_4O_4(H_2O)_2^a$	296.5	12 760	5.50
	262.0	14 440	5.50
	243.5	15 650	5.52
	222.5	17 060	5.51
	182.0	20 780	5.50
	160.0	23 640	5.50
	143.0	26 550	5.51
	118.0	31 940	5.49
	100.3	37 710	5.50
	84.7	44 490	5.49
	67.1	55 630	5.46
	52.8	69 030	5.40
	40.8	86 770	5.32
	33.6	102 400	5.25
	20.4	157 000	5.06
$Fe(OH)C_4O_4(H_2O)_3^b$	295.0	11 880	5.29
	247.5	13 490	5.17
	221.5	14 640	5.09
	202.0	15 320	4.97
	178.5	16 500	4.86
	157.5	17 660	4.72
	143.0	18 730	4.63
	109.5	20 970	4.28
	88.2	22 100	3.95
	63.5	22 890	3.41
	50.5	22 900	3.04
	38.6	22 560	2.64
	23.8	21 570	2.03
	20.2	21 150	1.85

^a Mol wt = 203.92. $\chi_M^c = -58 \times 10^{-6}$. ^b Mol wt = 238.95. $\chi_M^c = -84 \times 10^{-6}$.

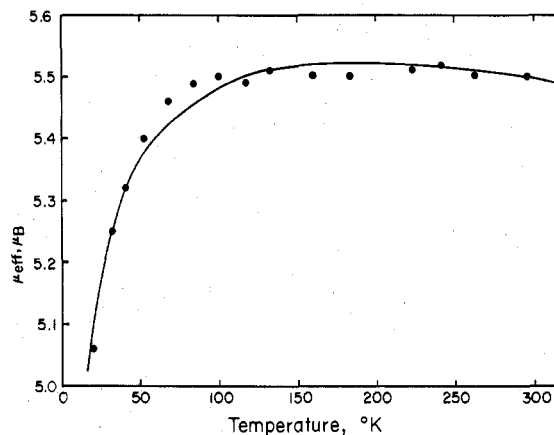


Figure 2. Temperature dependence of the magnetic moment for $FeC_4O_4(H_2O)_2$. The solid line represents a calculated dependence for a tetragonally distorted octahedral complex (see text).

calculated magnetic moment obtained for an electron delocalization factor, k , of 0.96, a spin-orbit coupling constant λ , of -92 cm^{-1} , and a tetragonal distortion parameter, Δ , of $+360 \text{ cm}^{-1}$, indicating an orbitally nondegenerate $^5B_{2g}$ ground state. Unfortunately, this model is far from unique²⁹ and hence the exact values of the parameters probably have limited significance. The results do, however, indicate that the observed temperature dependence is reasonable and that it is not necessary to propose any magnetic coupling to understand the results. This is not surprising because the $C_4O_4^{2-}$ ion is known to provide a poor pathway for superexchange of electron spin.^{14,17}

The Mössbauer effect spectrum of $FeC_4O_4(H_2O)_2$ at 4.2 K is shown in Figure 3 and the spectral parameters are presented in Table III. All of the zero-field parameters were determined by an unconstrained fitting procedure (see Experimental Section). In all instances the line widths and areas

Table III. Mössbauer Effect Parameters^a

compound	T, K	H, T	ΔE_Q	δ	$\Gamma_{1/2}$	$A_{2/1}$	χ^2	comments
$\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$	room temp	0	2.26	1.24	0.27	1.00	0.82	unconstrained
	195	0	2.53	1.30	0.29	1.00	1.21	unconstrained
	78	0	2.78	1.35	0.29	1.01	1.56	unconstrained
	4.2	0	2.78	1.41	0.30	0.94	1.02	unconstrained
	4.2	6	2.74	1.39	0.30		0.75	FITH fit 1 ^b
	4.2	6	2.71	1.39	0.20		0.36	FITH fit 2 ^b
	1.3	0	2.76	1.41	0.30	0.93	1.36	unconstrained
$\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$	room temp	0		0.42	0.40		0.663	unconstrained
		0	0.13	0.42	0.34	1.00	0.666	constrained ^c
	78	0	0.52	0.52	0.35		0.720	unconstrained
		0	0.13	0.52	0.28	1.00	0.689	constrained ^c
	4.2	0		0.57	0.36		0.812	unconstrained
		0	0.14	0.57	0.28	1.00	1.106	constrained ^c
	4.2	6	0.14	0.53	0.28		1.036	FITH
	1.35	0	0.56	0.56	0.41		1.450	unconstrained
		0	0.16	0.56	0.32	1.00	1.512	constrained ^c

^a Data in mm/s relative to natural α -iron foil. $A_{2/1}$ is the area ratio of line 2 to 1. ^b See text. ^c Constrained to two lines of equivalent area and line width.

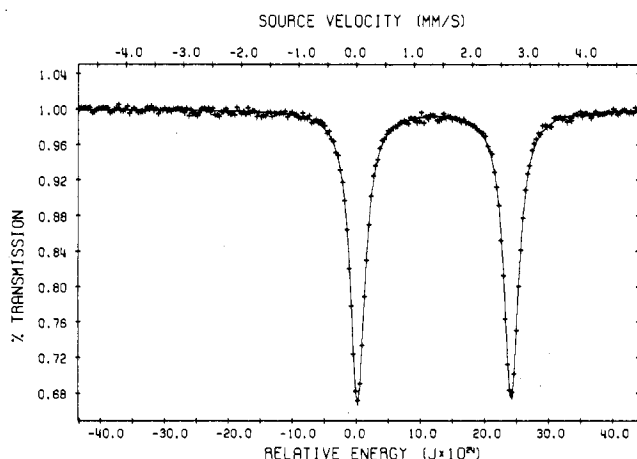


Figure 3. Mössbauer effect spectrum of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ at 4.2 K.

of the two quadrupole-split lines were found to be equivalent. The values of δ , the Mössbauer effect isomer shift, are reasonable for the high-spin iron(II) ion in an oxygen environment. In fact the magnitude and temperature dependence of the isomer shift are almost identical with those observed in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (e.g., 1.26 mm/s at room temperature and 1.39 mm/s at 5 K).^{30,31} The values of ΔE_Q , the quadrupole interaction, are also reasonable for high-spin iron(II) in a tetragonal ligand field. The observed increase in ΔE_Q with decreasing temperature is expected in reduced symmetry.³² An approximate calculation of ΔE_Q as a function of temperature (for the 78 K and above data) with the model of Ingalls³² and Gibb³³ indicates a value of the distortion parameter,³² Δ , of between +300 and +400 cm^{-1} depending upon the value of the covalency factor and the nuclear quadrupole moment used. This is in surprisingly good agreement with the value of +360 cm^{-1} obtained from the magnetic data and indicates an orbitally degenerate $^5\text{B}_{2g}$ ground state (at least if the complex approximates tetragonal symmetry).

Gerstein and Habenschuss¹⁵ have reported that $\text{NiC}_4\text{O}_4(\text{H}_2\text{O})_2$ undergoes a transition to a ferromagnetically ordered state at temperatures of the order of 1.6–2.1 K. The exact ordering temperature appears to depend upon the type of clathrated solvent molecule present in this very open solid-state structure. Because $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ is isomorphous to the nickel compound, a similar ordering might occur. However, at temperatures down to 1.3 K our sample remains paramagnetic as indicated by a two-line Mössbauer spectrum which is identical with that shown in Figure 3. Specific

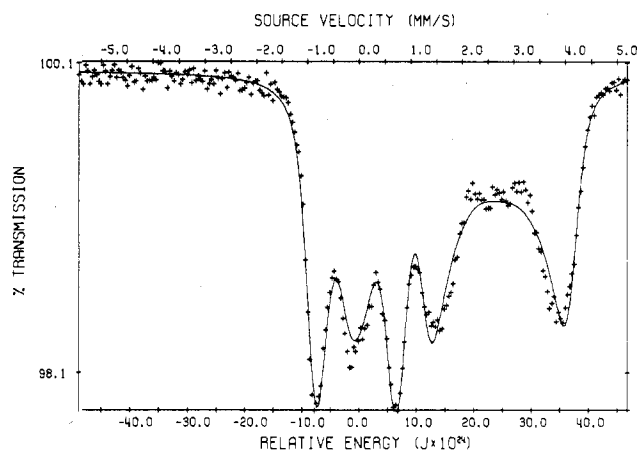


Figure 4. Mössbauer effect spectrum of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ obtained at 4.2 K in a 6 T transverse applied magnetic field. The line is theoretical fit 1 discussed in the text.

parameters are given in Table III. The elemental analysis for our sample of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ eliminates the possibility of significant clathrated water. This may account for the failure of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ to order above 1.3 K. The failure of this compound to order provides further indication that $\text{C}_4\text{O}_4^{2-}$ is not an effective pathway for superexchange (see below).

In order to determine the sign of the quadrupole interaction, the Mössbauer spectrum of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ was measured at 4.2 K in a 6 T transverse applied magnetic field. The experimental points shown in Figure 4 give the resulting spectrum. The spectrum indicates that the high-velocity line is split into a doublet while the low-velocity line yields a triplet. This splitting pattern indicates^{32,34,35} a positive principal component for the electric field gradient tensor. Further, if one assumes an axially symmetric EFG about the water-iron-water axis, then an orbitally nondegenerate $^5\text{B}_{1g}$ electronic ground state is indicated. This would of course correspond to the d_{xy} orbital as the lowest energy orbital and would be consistent with the results presented above.

In an attempt to better understand the electronic properties of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ the applied field Mössbauer spectrum has been evaluated by using the effective Hamiltonian

$$H = \beta \mathbf{H}_{\text{ap}} \cdot \mathbf{g} \cdot \mathbf{S} + [QV_{zz}/4][I_z^2 - 5/4 + \eta/3(I_x^2 - I_y^2)] + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - g_N \beta_N \mathbf{I} \cdot \mathbf{H}_{\text{ap}}$$

where the symbols have their usual meaning.^{23,24} The evaluation was carried out by using the FITH computer program

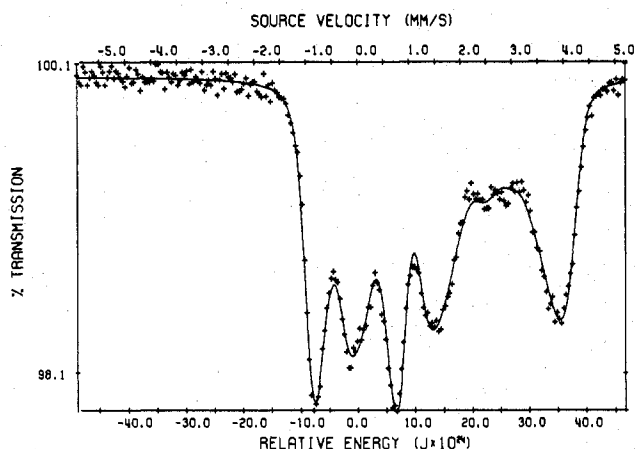
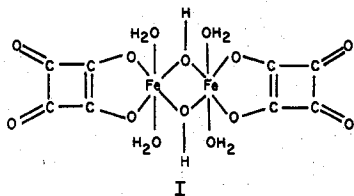


Figure 5. Mössbauer effect spectrum of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ obtained at 4.2 K in a 6 T transverse applied magnetic field. The line is theoretical fit 2 discussed in the text.

of Lang and Dale.²³ Unfortunately the approach is not unique in its fit to the experimental spectrum, and two different fits were found. The first, poorer but perhaps more reasonable, fit is shown by the solid line in Figure 4. The Mössbauer parameters are listed as FITH fit 1 in Table III. In this solution, where the g tensor was constrained to axial symmetry and η was constrained to zero, $g_1 = g_2 = 1.80$, $g_3 = 2.73$, $A_1 = 0.89$, $A_2 = 1.67$, and $A_3 = 2.00$. Only a negligible improvement in the fit was obtained if the constraints were removed. In this case the g and A values seem reasonable, but the fit is certainly far from exact. The second, better fit is illustrated in Figure 5. In this instance the parameters listed in Table III as FITH fit 2, and $g_1 = 1.43$, $g_2 = 0.45$, $g_3 = 4.52$, $A_1 = 0.89$, $A_2 = 0.69$, $A_3 = -0.49$, and $\eta = 0.33$ were obtained. No constraints were applied. Although in this instance the fit to the experimental spectrum is very good, the anisotropy in the g and A tensors is less satisfactory.³⁴ In the absence of additional experimental data, obtained for instance on single crystals, it is difficult to eliminate either of the fits. Fit 1 does, however, seem more satisfactory in view of the expected structure of the compound.¹⁴

The stoichiometry of the iron(III) squarate complex is found to be best represented by $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ where the iron to hydroxide ratio is 1:1. A study³⁶ of the DTGA for this complex indicates two different types of water in the ratio of approximately 1:2. On the basis of magnetic data (see below) and in agreement with previous studies,^{7,16} we formulate this material as a dimer, I, with stoichiometry $[\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$ and with two bridging hydroxy groups between the trivalent iron atoms.



The infrared spectral results for this dimeric complex are presented in Table I. Because the dimeric structure contains two bridging hydroxy groups, one might expect to observe the ν_{OH} vibrational band at rather lower energies than is normally observed.³⁷⁻³⁹ Unfortunately the region of the infrared spectra exhibiting this vibrational band is dominated by the water bands which in $\text{K}_2\text{C}_4\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ extend from ca. 3600 cm^{-1} to ca. 2800 cm^{-1} . The infrared spectrum of $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ exhibits these same broad bands which preclude a definitive identification of the ν_{OH} band. $\text{Fe}(\text{O}-$

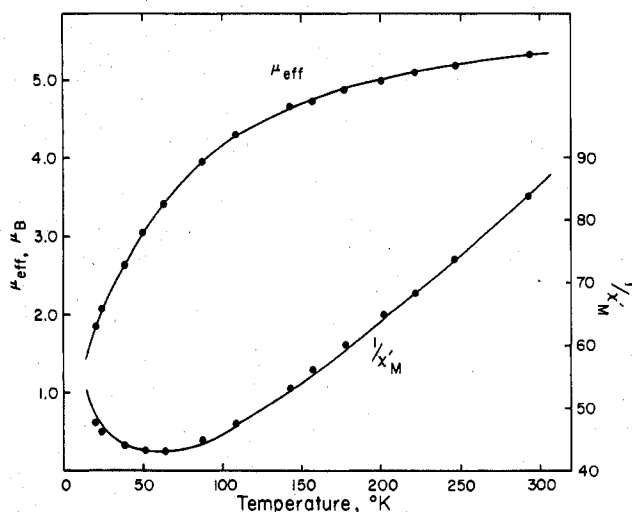


Figure 6. Temperature dependence of the magnetic moment and inverse susceptibility for $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$. The solid line is the theoretical dependence calculated for $S_1 = S_2 = 5/2$, $g = 2.00$, and $J = -7.0\text{ cm}^{-1}$ (see text).

$\text{H})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ does exhibit a band at 980 cm^{-1} which is not found either in $\text{K}_2\text{C}_4\text{O}_4 \cdot \text{H}_2\text{O}$ or in $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$. This band is assigned to a bridging hydroxy deformation mode. A similar band at 950 cm^{-1} was observed by Thich et al.³⁸ In addition a band at 430 cm^{-1} is tentatively assigned to the ν_{FeO} iron(III)-squate vibrational band. This assignment is tentative because the band is expected at higher energy in the Fe(III) complex than in the Fe(II) complex. In addition, a band at 495 cm^{-1} is observed in the Fe(III) complex which could represent the iron-squate vibrational band. This band, however, seems to be related to the 590-cm^{-1} band in $\text{K}_2\text{C}_4\text{O}_4 \cdot \text{H}_2\text{O}$ and the 550-cm^{-1} band in $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$.

The optical spectrum of $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ is shown in Figure 1. It shows three weak bands at 5000 , 5700 , and 6600 cm^{-1} which are most likely associated with water or are vibrational overtone absorption bands. In addition a very strong broad absorption is found at 19200 cm^{-1} . This band is probably a ligand to metal charge-transfer band.

The magnetic susceptibility and moment of $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ are presented in Table II and are plotted as a function of temperature in Figure 6. The magnetic moment steadily decreases from $5.29\text{ }\mu_{\text{B}}$ at room temperature to $1.85\text{ }\mu_{\text{B}}$ at 20.2 K . A maximum in the magnetic susceptibility is observed at ca. 50 K . This behavior is indicative of antiferromagnetic coupling between iron(III) ions and supports the dimeric formulation I. The temperature dependence of the magnetic moment for this antiferromagnetic coupled Fe(III) dimer has been calculated by using the Heisenberg-Dirac-VanVleck expressions.^{40,41} The best fit to the experimental results is found for $S_1 = S_2 = 5/2$, $g = 2.00$, and $J = -7.0\text{ cm}^{-1}$. This fit is represented by the solid lines in Figure 6. The magnitude of J , the magnetic spin-coupling constant, further supports the presence of the hydroxy-bridging ligands. The possibility of exchange through a bridging squarate anion seems unlikely in view of the magnetic properties of $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$ discussed above and of $\text{NiC}_4\text{O}_4(\text{H}_2\text{O})_2$ in which magnetic ordering is observed only below ca. 2 K . The same conclusion has been reached in the study of both a copper and a nickel squarate bridged dimer⁴² and has been justified theoretically by Hoffmann and his co-workers.⁴³ The possibility of exchange through an oxo bridge seems unlikely because they usually exhibit rather strong antiferromagnetic coupling with J values^{44,45} of ca. -80 to -100 cm^{-1} . The observed value of J does, however, agree well with the value of -11.4 cm^{-1} observed³⁸ for μ -dihydroxo-bis[2,6-

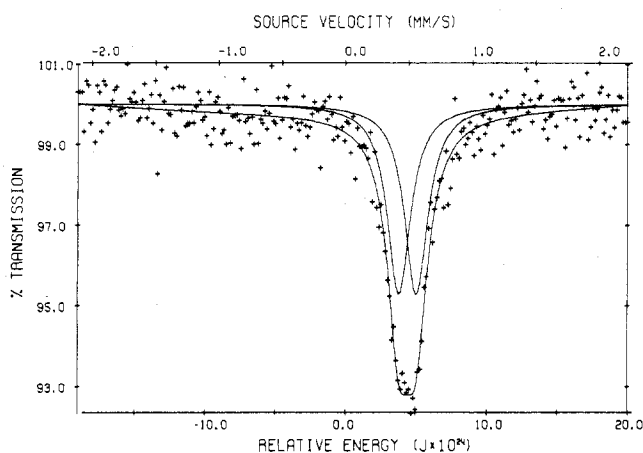


Figure 7. Mössbauer effect spectrum of $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ at 4.2 K. The solid line is a constrained fit to a quadrupole doublet (see text).

pyridinedicarboxylatoquoiron(III)] and the value of -7.3 cm^{-1} observed³⁸ for μ -dihydroxo-bis[4-hydroxo-2,6-pyridinedicarboxylatoquoiron(III)] tetrahydrate. The single-crystal X-ray structures of these two compounds reveal hydroxy bridging ligands. The hydroxy bridging thus seems well supported by the magnetic results. Further conformation will probably require a single-crystal structural analysis.

The Mössbauer effect spectral parameters for $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ are presented in Table III, and the 4.2 K spectrum is shown in Figure 7. All of the unperturbed Mössbauer spectra are similar in that they exhibit a rather broad featureless absorption band. This broad band can be fit either to a single line or to a quadrupole split doublet with essentially the same χ value. The fit to a quadrupole doublet was constrained to two lines of equivalent area and line width. Essentially the same results were obtained when these constraints were removed. The absorption is probably best represented as a quadrupole-split doublet with ΔE_Q of ca. 0.13 mm/s (see Table III), and this fit is represented by the solid lines in Figure 7. Both the isomer shift δ and the quadrupole interaction ΔE_Q for this compound are exactly what might be expected of the iron(III) ion in an essentially octahedral six-coordinate oxygen environment. The values observed are almost the same as those found in the rhombohedral modification of $\text{Fe}_2(\text{SO}_4)_3$. For this compound the room-temperature isomer shift is 0.496 mm/s and the quadrupole splitting is 0.15 mm/s.⁴⁶

The magnetic susceptibility studies described above indicate that the antiferromagnetic ordering temperature of dimeric $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ is ca. 50 K (see Figure 6). As a result, an internal hyperfine field would be expected below this temperature. However, the absence of any magnetic ordering in the 4.2 K zero field spectrum (Figure 7) indicates that $\langle S_z \rangle = 0$ at this temperature. The compound exhibits rapid magnetic relaxation and the net hyperfine field at the iron(III) nucleus is averaging to zero on the Mössbauer time scale. This rapid relaxation is no doubt a result of facile spin-spin relaxation which results because the two iron(III) ions are strongly antiferromagnetically coupled.⁴⁷ In other words, the relaxation of a given iron(III) from a magnetic state characterized by S_z to one characterized by S_z' may be accompanied by the change of the second, strongly coupled ion, from $-S_z$ to $-S_z'$. In the absence of an applied field, all of these states are equivalent in energy. In an attempt to slow down this rapid relaxation, we have applied a 6.1 T transverse magnetic field to the sample at 4.2 K. The resulting spectrum is shown in Figure 8 and reveals a six-line spectrum with an internal hyperfine field of 56.7 kOe, a value slightly, but significantly, lower than the applied field. Apparently this

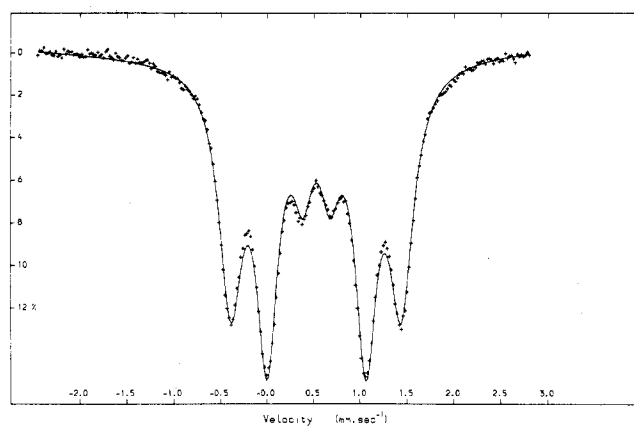


Figure 8. Mössbauer effect spectrum of $\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_3$ at 4.2 K in a 6 T transverse applied magnetic field. The line is the theoretical fit discussed in the text.

magnitude applied field produces only a small reduction in the magnetic relaxation rate. The reduction is, however, large enough to produce an internal hyperfine field of ca. 4 kOe. The observed field is reduced because the Fermi contact term will be opposite in sign to the applied field.⁴⁸ Alternately, but less likely, the internal hyperfine field could be ca. 118 kOe. Surprisingly, the internal hyperfine field is essentially the same at 1.6 K with the same applied field. The applied field spectrum may be fit to a fast relaxing magnetic model with an isotropic g value of 2.00 and with $\eta = 0$. The remaining parameters are given in Table III and the fit is illustrated by the solid line in Figure 8. The higher intensity of the two and five lines is that expected in a transverse applied magnetic field. We are currently studying this compound in detail as a function of applied field and temperature.

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Registry No. $\text{K}_2\text{C}_4\text{O}_4$, 13021-39-1; $\text{FeC}_4\text{O}_4(\text{H}_2\text{O})_2$, 33679-04-8; $[\text{Fe}(\text{OH})\text{C}_4\text{O}_4(\text{H}_2\text{O})_2]_2$, 67424-50-4.

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Electronic Spectral and Magnetochemical Studies of Aquo- μ -bis(cyclo-(L-histidyl-L-histidyl))-dicopper(II), a Copper(II) Complex with a Deprotonated Amide Nitrogen Ligand

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The title complex $\text{Cu}_2(\text{C}_{12}\text{H}_{13}\text{N}_6\text{O}_2)_2\text{H}_2\text{O}\cdot 2\text{ClO}_4\cdot 3.5\text{H}_2\text{O}$ (**1**) contains a pseudotetrahedral $\text{Cu}^{\text{II}}\text{N}_4$ unit which is joined by two deprotonated amide bridges to an about square-pyramidal $\text{Cu}^{\text{II}}\text{N}_2\text{O}_3$ unit. Ligation in the former chromophore is supplied by two imidazole and two deprotonated amide nitrogen donor atoms. Mull and single-crystal electronic spectra of **1** reveal a weak and very broad ligand field (LF) absorption at ~ 800 nm, which extends to ~ 1500 nm, and a stronger neighboring absorption at ~ 640 nm. These LF absorptions are mixed; the above spectral features cannot be unambiguously associated with the individual Cu(II) sites. Mull spectra of **1** include broad UV maxima at ~ 360 , ~ 320 , ~ 270 , and ~ 230 nm. Nearly identical UV maxima were observed for a monomeric reference complex of the neutral ligand, $\text{Cu}(\text{C}_{12}\text{H}_{14}\text{N}_6\text{O}_2)_2\cdot 2\text{ClO}_4\cdot 6\text{H}_2\text{O}$ (**2**). Spectral features attributable to $\pi(\text{N}) \rightarrow \text{Cu}(\text{II})$ ligand to metal charge transfer (LMCT) could not be located in the 360–640-nm region. The absorption of the type 1 blue copper proteins at ~ 450 nm is discussed in view of the spectral results reported here. Magnetic susceptibility studies of **1** reveal paramagnetic behavior ($1.90 \pm 0.02 \mu_B$) over the temperature range 286–7.0 K and fix an upper limit of the exchange parameter $|J| < 0.5 \text{ cm}^{-1}$. However, a $|J|$ value $> 0.02 \text{ cm}^{-1}$ is required by the triplet EPR spectrum of **1**; detailed analysis of the spectrum at Q band yielded the parameters $g_{\parallel} = 2.291$, $g_{\perp} = 2.040$, and $D_{\perp} = 0.5354 \text{ cm}^{-1}$. The spectrum of **2** at Q band is that of a monomeric complex having $g_{\perp} = 2.058$, $g_{\parallel} = 2.254$, and a parallel copper hyperfine spacing of 191 G.

The blue (type 1) copper proteins exhibit a characteristic electronic absorption at 610 ± 10 nm ($\epsilon > 3000$) along with weaker neighboring absorptions at ~ 800 and ~ 450 nm. Other workers have suggested that the detailed spectroscopic properties of these proteins may be rationalized in terms of a common, flattened tetrahedral, $\text{Cu}^{\text{II}}\text{N}_2(\text{imidazole})\text{N}^*(\text{deprotonated amide})\text{S}(\text{cysteine})$ chromophore.² Recent studies³ have indicated that the plastocyanins and azurins contain a somewhat different $\text{Cu}^{\text{II}}\text{N}_2(\text{imidazole})\text{S}(\text{cysteine})\text{S}^*(\text{methionine})$ chromophore. Assignment¹ of the absorptions at ~ 610 and ~ 800 nm, respectively, to $\sigma(\text{S}) \rightarrow \text{Cu}(\text{II})$ and $\pi(\text{S}) \rightarrow \text{Cu}(\text{II})$ ligand to metal charge transfer (LMCT) remains consistent with these results and has received support from studies of model, approximately tetrahedral, mercaptoamine complexes.⁴ Assignment of the absorption at ~ 450 nm to $\pi(\text{N}^*) \rightarrow \text{Cu}(\text{II})$ LMCT cannot be correct for the plastocyanins and azurins. An absorption of this type remains possible for stellacyanin, a type 1 copper protein which is free

of methionine residues,³ and of course for simple Cu(II) complexes ligated in part by deprotonated amide nitrogen donors. Spectral studies of probably tetragonal Cu(II) complexes having one or more of these nitrogen donors have not revealed absorptions at ~ 450 nm which may be indicative of $\pi(\text{N}^*) \rightarrow \text{Cu}(\text{II})$.⁵ However, the position of this LMCT band should reflect the ligand field dependency of the copper d vacancy; the intensity of this band will depend upon factors such as the overlap between the π -symmetry orbitals of the Cu(II) and the deprotonated amide nitrogen and the extent of "borrowing" from highly allowed neighboring electronic transitions. Thus, appropriate structural models for detecting biologically relevant $\pi(\text{N}^*) \rightarrow \text{Cu}(\text{II})$ LMCT should maintain an approximately tetrahedral arrangement of donor ligands. The title complex (Figure 1) is an attractive vehicle for such a test.⁶ Cu(B) has a $\text{N}_2(\text{imidazole})\text{N}^*_2$ donor set which approximates a flattened tetrahedron; the dihedral angle, $\text{N}(4)\text{--Cu(B)--N}(5)/\text{N}'(4)\text{--Cu(B)--N}'(5)$, is 51.2° .^{7a} More-