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Magnetic Properties and Mössbauer Spectra of Several Iron(III)-Dicarboxylic Acid Complexes

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Polymeric iron(III) complexes of malonic, succinic, fumaric, and phthalic acids have been prepared and studied by variable-temperature (15-300 K) magnetic susceptibility, ^{57}Fe Mössbauer spectroscopy, and infrared spectroscopy. In addition, properties of iron(III) acetate have been reinvestigated with use of these same techniques. The magnetic susceptibilities of these complexes have been described by a theoretical model which includes, in addition to *intramolecular* exchange terms, a parameter describing *intermolecular* spin-exchange effects. As a consequence of this model it was *not* necessary to assume an isosceles triangular arrangement of the iron(III) ions in these materials in order to explain the magnetic data. Thus, the inclusion of an *intertrimer* exchange parameter, which varies from 2.1 cm^{-1} for the acetate complex to 11.7 cm^{-1} for the *o*-phthalate complex, allowed for a complete description of the temperature dependence of the magnetic susceptibility of these compounds. Mössbauer and infrared spectroscopic studies were utilized to ascertain the correctness of oxidation state and structural assignments.

Complexes of iron(III) with monocarboxylic and dicarboxylic acids were first systematically investigated by Weinland.[2,3] The monocarboxylic acid complexes have subsequently been characterized by others. Although the crystal structure of $[Fe_3O(CH_3COO)_6(H_2O)_3]ClO_4$[4,5] has demonstrated the presence of an equilateral triangle of iron atoms, a variety of assumptions have been involved in attempts to describe the variable-temperature magnetic susceptibility of this and similar complexes. Thus, the data have been modeled on the assumption of an equilateral triangle of ferric ions,[6-9] an isoceles triangle arrangement,[4,10-14] or a higher order spin interaction mechanism.[15,16]

There is very little information in the literature concerning analogous complexes with dicarboxylic acids. In order to determine if such complexes contain the μ_3-oxo-triiron cluster observed for basic iron acetate, we have examined the variable-temperature magnetic susceptibility and Mössbauer spectra of several dicarboxylic acid complexes. As part of this work we have also examined the general applicability of various magnetic models for these materials and as a result have proposed a new model which both reproduces accurately the experimental data and is also consistent with reported structures.

Experimental Section

All chemicals used were reagent grade unless specified. *m*-Phthalic acid (99%) and *p*-phthalic acid (98%) were supplied by Aldrich Chemical Co., Inc. Fumaric acid was supplied by Eastman Kodak Co. Iron wire (reagent grade) as supplied by Merck and Co., Inc., was used as the primary standard for Fe analyses.

Preparation of Complexes. $[Fe_3O(CH_3CO_2)_6(H_2O)_3]ClO_4{\cdot}2H_2O$. μ_3-Oxo-triaquohexakis(acetato)triiron(III) perchlorate dihydrate was prepared by using a modification of the method of Weinland and Hohn.[2] Electrolytic iron metal powder (11.2 g, 0.2 mol) was stirred with 100 mL of water and 51.6 mL (0.6 mol) of 70% $HClO_4$. The mixture was warmed slightly until all of the iron had reacted. A small amount of insoluble matter was removed by centrifugation. After the solution was cooled to 10 °C, an excess (30 mL) of a 15% H_2O_2 solution was added. Complete oxidation of the iron was confirmed with use of the *o*-phenanthroline assay described below.[17] The solution was cooled to 5 °C, and anhydrous sodium acetate (32.8 g, 0.4 mol) was slowly added with stirring. The reaction mixture was placed in a gentle stream of air. After 2 days almost half of the solution had evaporated, leaving large red-brown crystals, yield 7.99 g (30.0%). The crystals were collected, washed with two 25-mL portions of cold water, and blotted with filter paper. The crystals were further dried for 24 h under vacuum at room temperature. Anal. Calcd for $C_{12}H_{28}O_{22}Fe_3Cl$: C, 19.82; Fe, 23.03; H, 3.88. Found: C, 19.84; Fe, 23.12; H, 3.57.

$[Fe_3O(O_2CCH_2CO_2)_3(H_2O)_3]ClO_4{\cdot}3H_2O$. μ_3-Oxo-triaquotris(malonato)triiron(III) perchlorate trihydrate was prepared by suspending malonic acid (5.2 g, 0.05 mol) in 20 mL of water. Sodium bicarbonate (8.4 g, 0.10 mol) was slowly added with stirring. The mixture was warmed slightly to complete the reaction. A small amount of insoluable matter was removed by centrifugation. A solution of $Fe(ClO_4)_3{\cdot}6H_2O$ (23.1 g, 0.05 mol) in 20 mL of water was prepared and slowly added to the sodium malonate solution with vigorous stirring. After the reaction mixture had formed a gel, another 50 mL of water was added and the mixture allowed to stand for 1 h. The precipitate was collected by centrifugation, washed twice with 100-mL portions of 0.05 M $HClO_4$, and 5 more times with 100-mL portions of 0.01 M $HClO_4$. The precipitate was suspended in 100 mL of 0.01 M $HClO_4$ and vacuum-freeze-dried by standard methods; yield 3.68 g (31.6%). Anal. Calcd for $C_9H_{18}O_{23}Fe_3Cl$: C, 15.50; Fe, 24.03; H, 2.60. Found: C, 15.21; Fe, 23.41; H, 2.25.

$[Fe_3O(O_2CCH_2CH_2CO_2)_3(H_2O)_3]ClO_4{\cdot}3H_2O]$. μ_3-Oxo-triaquotris(succinato)triiron(III) perchlorate trihydrate was prepared by suspending succinic acid (5.9 g, 0.05 mol) in 250 mL of water. Sodium bicarbonate (8.4 g, 0.10 mol) was added with stirring. The mixture was warmed slightly to complete the reaction whereupon 70% $HClO_4$ (0.5 mL) was added. A solution of $Fe(ClO_4)_3{\cdot}6H_2O$ (23.1 g, 0.05 mol) in 250 mL of water was prepared and added to the sodium succinate solution with vigorous stirring. The resulting suspension was allowed to stand for 16 h at 4 °C. The precipitate was collected by centrifugation and washed 7 times with 200-mL portions of 0.001 M $HClO_4$ or until no sodium could be detected in the supernate with a flame test. The precipitate was suspended in 150 mL of 0.01 M $HClO_4$ and freeze-dried; yield 7.44 g (61.9%). Anal. Calcd for $C_{12}H_{24}O_{23}Fe_3Cl$: C, 19.49; Fe, 22.66; H, 3.27. Found: C, 19.50; Fe, 22.05; H, 2.62.

$[Fe_3O(O_2CCHCHCO_2)_3(H_2O)_3](O_2CCHCHCO_2)_{0.25}(ClO_4)_{0.50}{\cdot}2H_2O$. μ_3-Oxo-triaquotris(fumarato)triiron(III) fumarate perchlorate

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(1) IBM Corp., East Fishkill Facility, Hopewell Junction, NY, 12533.
(2) Weinland, R. F.; Hohn, A. *Z. Anorg. Chem.* **1926**, *152*, 1.
(3) Meyer, R. J., Ed. "Gmelins Handbuch der Anorganischen Chemie, Eisen"; Verlag Chemie: Weinheim/Bergstr., Germany, 1930.
(4) Orgel, L. E. *Nature (London)* **1960**, *187*, 504.
(5) Anzenhofer, K.; De Boer, J. J. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 286.
(6) Earnshaw, A.; Figgis, B. N.; Lewis, J. *J. Chem. Soc. A* **1966**, 1656.
(7) Wucher, J.; Gijsman, H. *Physica (Amsterdam)* **1954**, *20*, 361.
(8) Schriempf, J. T.; Freidberg, S. A. *J. Chem. Phys.* **1964**, *40*, 296.
(9) Zelentsov, V. V.; Zhemchuznikova, T. A.; Yablokov, Yu. V.; Yakubov, Kh. M. *Dokl. Chem. (Engl. Transl.)* **1974**, *216*, 526.
(10) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48.
(11) Duncan, J. F.; Kanekar, C. R.; Mok, K. F. *J. Chem. Soc. A* **1969**, 480.
(12) Long, G. J.; Robinson, W. T.; Tappmeyer, W. P.; Bridges, D. L. *J. Chem. Soc., Dalton Trans.* **1973**, 573.
(13) Martin, R. L. In "New Pathways in Inorganic Chemistry"; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: London, 1968; p 175 ff.
(14) Marathe, V. B.; Date, S. K.; Jawaderkar, V. L.; Thakur, N. V. *Proc. Nucl. Phys. Solid State Phys. Symp.* **1972**, *17*, 639.
(15) Uryu, N.; Friedberg, S. A. *Phys. Rev. A* **1965**, *140*, 1803.
(16) Rakitin, Yu. V.; Zhemchuznikova, T. A.; Zelentsov, V. V. *Inorg. Chim. Acta* **1977**, *23*, 145.
(17) Willard, H.; Merritt, L., Jr.; Dean, J. "Instrumental Analysis"; Van Nostrand: New York, 1969; pp 104-105.

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dihydrate was prepared by suspending fumaric acid (5.42 g, 0.0467 mol) in 500 mL of water. Sodium hydroxide (3.73 g, 0.0934 mol) was added and the mixture stirred until all the fumaric acid had dissolved. A solution of $Fe(ClO_4)_3{\cdot}6H_2O$ (18.49 g, 0.04 mol) in 200 mL of water was added to the sodium fumarate solution. The mixture was allowed to stand for 30 min and the precipitate collected by centrifugation. The precipitate was washed 8 times with 200-mL portions of water. It was suspended in 100 mL of water and freeze-dried; yield 6.81 g (63.3%). Anal. Calcd for $C_{13}H_{17}O_{21}Fe_3$: C, 22.50; Fe, 24.14; H, 1.80; Cl, 2.55. Found: C, 22.50; Fe, 23.92; H, 2.17; Cl, 1.91.

[Fe$_3$O(*o*-phthalate)$_3$(H$_2$O)$_3$](*o*-phthalate)$_{0.5}$·2H$_2$O. μ_3-Oxo-triaquotris(*o*-phthalato)triiron(III) *o*-phthalate dihydrate was prepared by suspending phthalic anhydride (10.4 g, 0.07 mol) in 400 mL of water. Sodium hydroxide (5.6 g, 0.14 mol) was added and the mixture was stirred and heated to complete the reaction. The solution was filtered and cooled to 5 °C. A solution of $FeCl_3{\cdot}6H_2O$ (16.2 g, 0.06 mol in 400 mL of water) was prepared, centrifuged to remove some insoluble material, and cooled to 5 °C. The $FeCl_3$ solution was added slowly to the sodium phthalate solution, and the reaction mixture was allowed to stand for 16 h at 4 °C. The precipitate was collected by centrifugation and washed exhaustively with water at room temperature until the supernate gave no precipitate when tested with 0.1 M silver nitrate. The precipitate was suspended in 150 mL of water and freeze-dried; yield 12.2 g (72.0%). Anal. Calcd for $C_{28}H_{24}O_{20}Fe_3$: C, 39.66; Fe, 19.76; H, 2.85. Found: C, 39.72; Fe, 19.35; H, 2.58.

[Fe$_3$O(*m*-phthalate)$_3$(H$_2$O)$_3$](*m*-phthalate)$_{0.45}$(ClO$_4$)$_{0.1}$·H$_2$O. μ_3-Oxo-triaquotris(*m*-phthalato)triiron(III) *m*-phthalate perchlorate hydrate was prepared by suspending *m*-phthalic acid (9.69 g, 0.07 mol) in 300 mL of water. Sodium bicarbonate (11.8 g, 0.14 mol) was added slowly, and the mixture was stirred until all dissolved and then filtered. A solution of $Fe(ClO_4)_3{\cdot}6H_2O$ (23.11 g, 0.05 mol) in 300 mL of water was slowly added to the sodium phthalate solution with stirring over a 45-min period. The product was collected by centrifugation, suspended in 600 mL of water, and allowed to stand for 16 h at 4 °C. The precipitate was washed exhaustively with water until no sodium could be detected in the supernate with a flame test. The precipitate was suspended in 150 mL of water and freeze-dried; yield 10.7 g (63.4%). Anal. Calcd for $C_{27.6}Cl_{0.1}H_{21.8}O_{19.2}Fe_3$: C, 39.85; Fe, 20.10; H, 2.64; Cl, 0.42. Found: C, 39.73; Fe, 19.33; H, 2.52; Cl, 0.61.

Attempts to synthesize the *p*-phthalic acid complex failed. No product which retained a constant C:Fe ratio could be isolated after repeated synthetic attempts.

Physical Measurements. Magnetic susceptibilities were determined on polycrystalline samples with use of a conventional Faraday balance calibrated with $Hg[Co(NCS)_4]$.[18] This balance employed a Model CS-202 Displex cryogenic refrigerator with a model APD-E temperature controller manufactured by Air Products and Chemicals, Inc., Allentown, PA. Vibrations caused by the Displex expander were dampened by separating the piston from the remainder of the system with an air-tight PVC membrane. Noise levels caused by vibration were reduced to deflections of less than 10 μg. Corrections for ligand diamagnetism were calculated from a table of Pascal's constants.[19] Experimental values of the magnetic susceptibilities and effective magnetic moments were fitted to theoretical expressions with a computer routine which employed the Simplex minimization algorithm.[20,21] The goodness of fit criteria, including the standard error of estimate,[22] and the χ^2 test (eq 1, where $\bar{\chi}_M$ = molar susceptibility, n = number of data points, and k = number of parameters) were applied to curve fits obtained in this manner.

$$\chi^2 = \sum_{i=1}^{n}\{[\bar{\chi}_M(\text{obsd}) - \bar{\chi}_M(\text{calcd})]^2/\bar{\chi}_M(\text{calcd})\}/(n-k) \qquad (1)$$

Mössbauer spectra were obtained on a spectrometer described earlier.[23] The source was ^{57}Co(Pd) which was maintained at room temperature. A 25-μm α-Fe foil (430 μg of ^{57}Fe/cm^2) was used to calibrate the velocity scale. Mössbauer spectra were computer fit on the assumption that Lorentzian line shapes are superimposed upon a parabolic base line. All samples were finely ground, dispersed in Vaseline, and held in place within a lead block between Fe-free Mylar tape. Low-temperature spectra were obtained with use of the Displex cryogenic refrigerator coupled to a special, helium-gas-filled shroud, Model DMX-20, supplied by Air Products and Chemicals, Inc.

Table I. Mössbauer Data for the Dicarboxylic Acid Complexes

complex	T, K	width^a peak I	peak II	δ, mm/s	ΔE_Q, mm/s
acetate	295	0.33	0.29	0.42	0.58
acetate	21	0.53	0.43	0.53	0.74
malonate	295	0.36	0.40	0.41	0.58
malonate	21	0.42	0.44	0.52	0.72
succinate	295	0.43	0.40	0.42	0.67
succinate	22	0.45	0.46	0.53	0.81
o-phthalate	295	0.57	0.54	0.41	0.81
o-phthalate	22	0.63	0.67	0.52	0.82
m-phthalate	295	0.59	0.55	0.42	0.79
m-phthalate	22	0.62	0.62	0.53	0.93
fumarate	295	0.59	0.61	0.42	0.79
fumarate	20	0.66	0.71	0.51	0.88

[a] Full width at half-maximum intensity (in mm/s)

Infrared spectra were obtained on a Beckman IR-20A spectrophotometer with KBr pressed pellets. Optical spectra were recorded on a Cary Model 14 recording spectrophotometer. Iron was determined according to a modification of the method of Cheng et al.[24] Samples containing 10–25 mg of iron were digested in 1 mL of boiling nitric acid. After the solutions were cooled, they were mixed with 30 mL of a buffer solution which was 1 M in sodium acetate and 2 M in monochloracetic acid (pH 2.8). They were titrated with 1 × 10^{-2} M EDTA with use of Tiron (4,5-dihydroxy-*m*-benzenedisulfonic acid, disodium salt) as the indicator. Reagent grade iron wire (99.8% Fe minimum) was used as a primary standard. Iron was also determined with *o*-phenanthroline according to the method of Willard et al.[17] C, H, and Cl analyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, NC.

Results and Discussion

For convenience the following abbreviations are used: acetate complex = $[Fe_3O(CH_3COO)_6(H_2O)_3]ClO_4{\cdot}2H_2O$; malonate complex = $[Fe_3O(O_2CCH_2CO_2)_3(H_2O)_3]ClO_4{\cdot}3H_2O$; succinate complex = $[Fe_3O(O_2CCH_2CH_2CO_2)_3(H_2O)_3]ClO_4{\cdot}3H_2O$; fumarate complex = $[Fe_3O(O_2CCHCHCO_2)_3(H_2O)_3](O_2CCHCHCO_2)_{0.25}(ClO_4)_{0.5}{\cdot}2H_2O$; *o*-phthalate complex = [Fe$_3$O(*o*-phthalate)$_3$(H$_2$O)$_3$](*o*-phthalate)$_{0.5}$·2H$_2$O; *m*-phthalate complex = [Fe$_3$O(*m*-phthalate)$_3$(H$_2$O)$_3$](*m*-phthalate)$_{0.45}$(ClO$_4$)$_{0.1}$·H$_2$O.

Because of their nearly total insolubility in all solvents examined, all of the dicarboxylic acid complexes prepared here are believed to be polymeric. By contrast, iron complexes with monocarboxylic acids are reported to be soluble.[2,3] The polymeric behavior of these materials is undoubtedly a consequence of the bifunctionality of the dicarboxylic acids. It is likely that the dicarboxylic acids form essentially the same μ_3-oxo-triiron structure which has been observed[4,5,25–27] for the monocarboxylic acid complexes. However, steric constraints made it unlikely that these dicarboxylic acids are capable of intratrimer chelation of both carboxylate groups. Consequently these dicarboxylic acids are expected to function as intertrimer ligand bridges, as is shown schematically for a fragment of the malonate complex in Figure 1. The polymeric three-dimensional structures which will result from the bridging of all dicarboxylates may be rather complex and cannot be easily

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(18) Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

(19) Mabbs, F. E.; Machin, D. S. "Magnetism and Transition Metal Complexes"; Wiley: New York, 1973; p 5.

(20) Deming, S. N.; Morgan, S. L. *Anal. Chem.* **1973**, *45*, 278A.

(21) Dean, W. K.; Heald, K. J.; Deming, S. N. *Science (Washington, D.C.)* **1975**, *189*, 805.

(22) Ginsberg, A. P.; Martin, R. L.; Brookes, R. W.; Sherwood, R. C. *Inorg. Chem.* **1972**, *11*, 2884.

(23) Allen, C. W.; Brown, D. B. *Inorg. Chem.* **1974**, *13*, 2020.

(24) Cheng, K. L.; Bray, R. H.; Kurz, T. *Anal. Chem.* **1953**, *25*, 347.

(25) Blake, A. B.; Fraser, L. R. *J. Chem. Soc., Dalton Trans.* **1975**, 193.

(26) Thundathil, R. V.; Holt, E. M.; Holt, S. L.; Watson, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 1818.

(27) Mereiter, K.; Vollenkle, H. *Acta Crystallogr., Sect. B* **1978**, *B34*, 378.

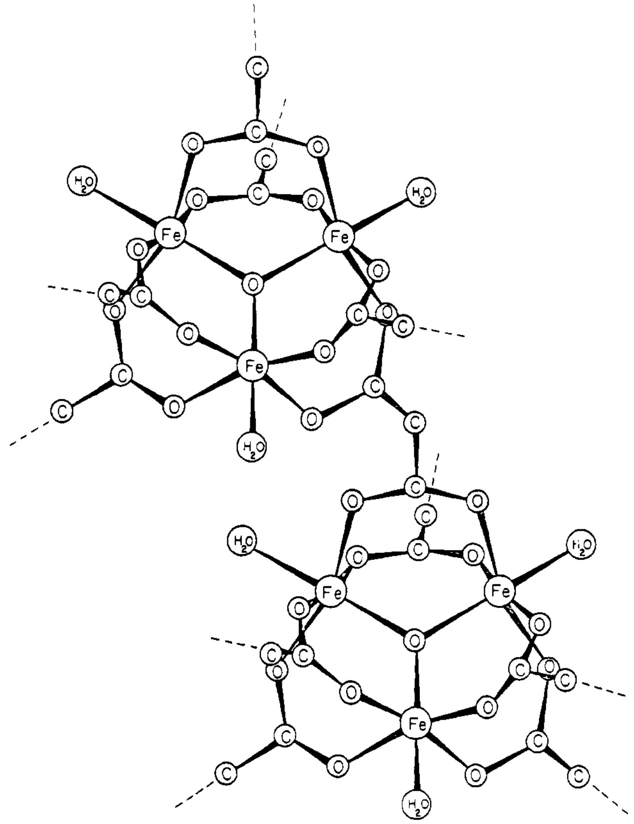

Figure 1. Proposed structure for the malonate complex. Two trimer centers are linked by a single malonic acid unit. Dotted lines indicate possibilities for attachment to other trimer centers.

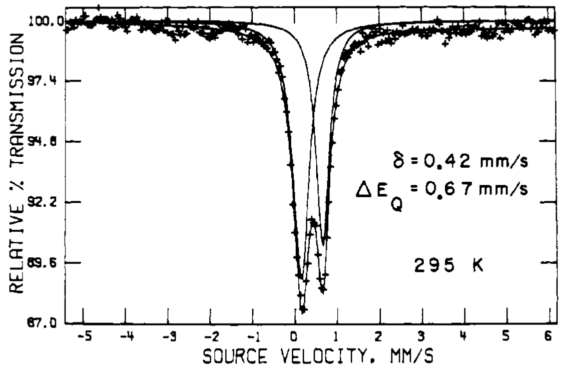

Figure 2. Mössbauer spectrum of the succinate complex at 295 K. The solid curves represent fits to two lines with parameters given in Table I.

predicted in the absence of single-crystal X-ray diffraction data.

Mössbauer Spectra. The Mössbauer spectrum of the succinate complex at 295 K is shown in Figure 2. The spectrum consists of two absorptions with $\delta = 0.42$ mm/s and $\Delta E_Q = 0.67$ mm/s. The spectrum of this complex at 20 K and the spectra of the other complexes are all quite similar. Table I summarizes the Mössbauer parameters for the dicarboxylic acid complexes. Isomer shifts for the complexes are relatively constant at 0.41–0.42 mm/s at 295 K. These values increase to 0.51–0.53 mm/s at 20 K. The values of ΔE_Q exhibit much greater variability. In general, the aliphatic complexes (acetate, malonate, succinate) have a smaller ΔE_Q than the unsaturated complexes (*o*-phthalate, *m*-phthalate, fumarate) at both 20 and 295 K. The magnitudes of the quadrupole splitting may thus be inversely correlated with the ligand "flexibility", the more rigid dicarboxylates leading to a greater distortion of the octahedral microsymmetry at iron. Quadrupole splittings for all of the complexes, except *o*-phthalate, increase with decreasing temperatures. The values observed for both δ and ΔE_Q are characteristic of high-spin iron(III) complexes.[28]

The line widths reported in Table I are given as full peak width at half-maximum intensity. For the iron(III) succinate complex shown in Figure 1, the width is 0.43 mm/s at 295 K. This is considerably larger than the peak width of the iron foil calibration spectra (0.30 mm/s). Broad lines were also observed for the other complexes (Table I). Several factors could contribute to the observed line broadening in these complexes. Some type of relaxation effect might be present in these strongly coupled spin systems (vide infra), and in fact such an explanation has been invoked.[14] However, if relaxation were the cause of the broad lines, a much greater temperature dependence to the Mössbauer parameters would be expected. Furthermore, a similar effect might be expected for the monocarboxylate complexes, yet the acetate complex exhibits a normal line width at room temperature. We believe that the broad lines are a consequence of iron being present in a variety of slightly different environments, which in turn is a consequence of the polymeric structure of these complexes. These different environments can arise in two ways. First, these polymers are likely to be of fairly low-molecular weight, and consequently edge effects may be significant, the environment of various trimers varying with location. Second, the terminus of these polymers is likely to be a monomeric iron complex with carboxylate and aquo ligands, rather than a trimer. As discussed above, the steric restraint upon intratrimer chelation for the dicarboxylates mitigates against all iron being present in the μ_3-oxo-triiron cluster. Rather, the terminal sites are likely to consist of dangling carboxylate functions, in many cases coordinated to iron. This explanation is consistent with the observation, from magnetic susceptibility data, that as much as 15% of a monomeric component may be present in these materials.

Magnetic Susceptibility Studies. The magnetic susceptibilities and effective magnetic moments as a function of temperature for the six complexes are given in Tables II–VII.[29] (The method used to derive the calculated values in these tables will be discussed below.) Since one of the purposes of this work was to evaluate the various models for the magnetism of these complexes, a suitable criterion for comparison between theory and experiment had to be selected. When the comparisons of the different models presented here are made, it becomes clear that comparisons involving μ, the magnetic moment, are not satisfactory. Figure 3 shows attempts to fit the magnetic moments for the iron(III) acetate complex to several models. It can be seen that there are no appreciable visual differences between the observed points and the calculated curves for any of the different models. Details of these magnetic models and their significance are discussed below. Following the example of Mabbs and Machin[19] and Thundathil and Holt,[30] the average molar susceptibility, $\bar{\chi}_M$, was used as the criterion for comparison in the studies presented here. It can be seen in Figure 4, which contains data for the acetate complex, that the different models do vary considerably in their ability to describe the data. The molar susceptibility is a much more sensitive parameter than the magnetic moment for describing the magnetic behavior. Mabbs and Machin[19] warn that use of the magnetic moment will result in a smoothing out of the variations of the susceptibility with temperature. In this work all judgments (both qualitative and quantitative) concerning

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(28) Bancroft, G. M. "Mössbauer Spectroscopy, An Introduction for Inorganic Chemists and Geochemists"; McGraw-Hill: Maidenhead, England, 1973; pp 53–57.

(29) Supplementary material.

(30) Thundathil, R.; Holt, S. L. *Inorg. Chem.* **1976**, *15*, 745.

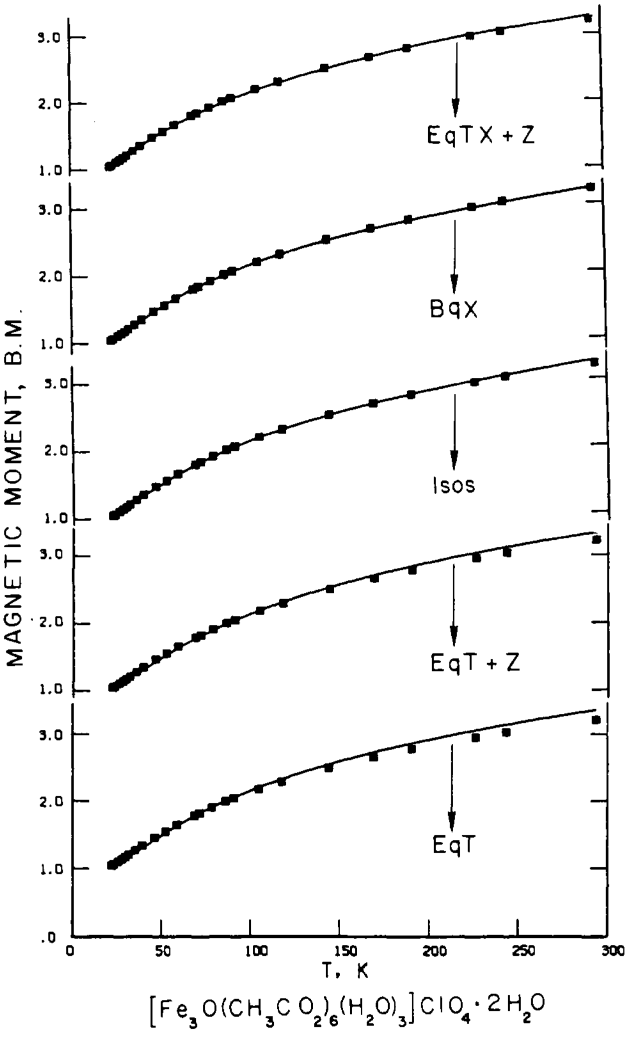

Figure 3. Magnetic moment vs. temperature for the acetate complex for five of the magnetic models. (Abbreviations are defined in text.) Solid lines are calculated curves, and points are the observed values.

the quality of the curve fits were made with use of the molar susceptibility.

A total of seven different models were considered in these attempts to account for the magnetic susceptibility behavior of these complexes. The models investigated were the equilateral triangle (EqT), equilateral triangle plus a monomeric component (EqT + Z), isosceles triangle (ISOS), biquadratic exchange (BqX), biquadratic exchange plus a monomeric component (BqX + Z), equilaterial triangle with intertrimer exchange (EqTX), and equilateral triangle with intertrimer exchange plus monomeric component (EqTX + Z). Theoretical equations for the molar susceptibility were derived for each model and fit to the data with use of the Simplex minimization algorithm.[20,21] In order to avoid the problem of convergence upon a false minimum, we attempted several curve fits for each data set, starting with different initial estimates for the fitting parameters. If the Simplex routines converged on more than a single minimum, the solution with the lowest value in the χ^2 test (eq 1) was selected as the best solution. The value of g was fixed at 2.00 in all cases.

Magnetic Models. The equilateral triangle model (EqT) requires that all the interacting ions in a complex be identical and be at the corners of an equilateral triangle. The Hamiltonian for this system is

$$\mathcal{H} = -2J[(S_1\cdot S_2) + (S_2\cdot S_3) + (S_1\cdot S_3)] \qquad (2)$$

where J = exchange integral and S = spin operator. Details of this model have been reported.[19] The quality of the fit of the observed magnetic susceptibility to the theoretical expression for the susceptibility of the equilateral triangle model improves significantly with the addition of a term which allows for the presence of some monomeric component (possibly an impurity).[31] This component is assumed to be due to Fe^{3+} and to follow the Curie law, so its susceptibility was expressed as $4.376/T$. The contribution of this component was added to the expression for the molar susceptibility for the equilateral triangle model to give a model (EqT + Z), with one additional parameter, the percent of monomeric component.

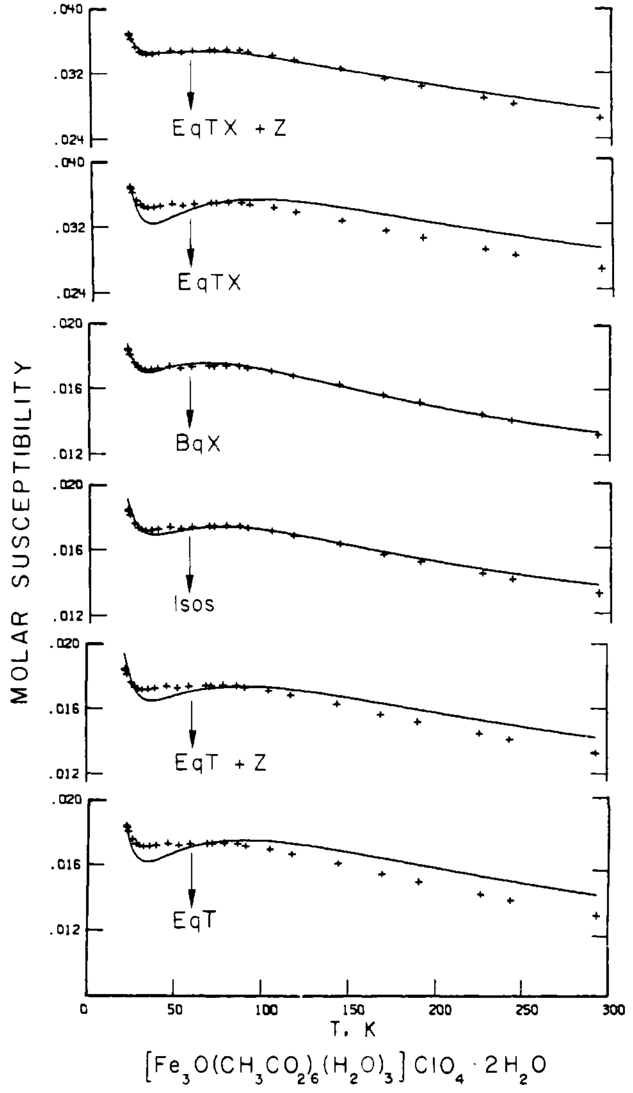

Figure 4. Molar susceptibility vs. temperature for the acetate complex for the six magnetic models. (Abbreviations are defined in text.) Solid lines are calculated curves, and points are the observed values.

The theoretical expression for the isosceles triangle was derived with use of using the Hamiltonian reported earlier[12] (eq 3). When $J = J'$, the equation reduces to the equilateral

$$\mathcal{H} = -2J[(S_1\cdot S_2) + (S_2\cdot S_3)] - 2J'(S_3\cdot S_1) \qquad (3)$$

triangle case. The working expression for the isosceles triangle model is given in eq 4.[29] If higher order terms involving the spin operators are added to the exchange Hamiltonian, the result is the biquadratic exchange model (BqX). This model has been used in the past to describe the variable-temperature magnetic susceptibilities of chromium(III) and iron(III) dimers. Hatfield[32] gives for the energy of the spin state for the

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(31) Wollman, R. G.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 926.

(32) Hatfield, W. E. In "Theory and Applications of Molecular Paramagnetism"; Boudreau, E. A., Mulay, L. N., Eds.; Wiley: New York, 1976; pp 362-366.

biquadratic exchange model expression 5, where S' = sum of

$$E(S') = -J_{12}[S'(S'+1) - 2S(S+1)] - j_{12}\{{}^1\!/_2[S'(S'+1) - 2S(S+1)]\}^2 \quad (5)$$

the spins (${}^{15}/_2, {}^{13}/_2, ..., {}^{1}/_2$) and S = spin on the individual ion (${}^{5}/_2$). When eq 5 is substituted into the Van Vleck equation,[19] the result is the working expression for magnetic susceptibility within the biquadratic exchange model (eq 6).[29] Inclusion of an additional term describing a monomeric component following the Curie law to the BqX susceptibility equation leads to the BqX + Z model. The method is analogous to that of the EqT + Z model.

We propose that an additional model exists which is both compatible with the known properties of μ_3-oxo-triiron carboxylates and also reproduces faithfully the magnetic behavior of these materials. This model is based on the equilateral triangle model but allows for intertrimer as well as intratrimer exchange (EqTX). The Hamiltonian for this model is

$$\mathcal{H} = -2J[(S_1 \cdot S_2) + (S_2 \cdot S_3) + (S_1 \cdot S_3)] - j(S'_1 \cdot S'_2) \quad (7)$$

the same Hamiltonian as employed in the equilateral triangle model except for one additional term allowing for spin coupling between the two trimer centers. The derivation of the molar susceptibility equation is identical with that of the equilateral triangle model except for

$$S^* = S'_1 + S'_2, S'_1 + S'_2 - 1, \ldots, S'_1 - S'_2 \quad (8)$$

where S^* = 15, 14, ..., 0. This new spin quantum number, S^*, provides for spin coupling between the two trimer centers. The resulting expression for the molar susceptibility is complex (eq 9),[29] containing 72 terms (some of which are zero) in both the numerator and denominator. Each term contains an exponent in $J/4kT$ and $j/4kT$, where J is the intratrimer exchange integral and j the intertrimer exchange integral. If j = 0, the equation reduces to the equilateral triangle model. For given values of J and g, the effect of the intertrimer exchange is to decrease the Curie tail at low temperature. In particular, larger values of j tend to flatten the susceptibility vs. temperature curve. This effect is shown for a range of j values in Figure 5.[29]

Because intercluster-exchange interactions will occur with all of the neighboring trimers, a molecular field approximation would provide a more exact model for the system. However, in systems such as the iron(III) carboxylates, with weak intertrimer interactions, the molecular field approximation is essentially equivalent to a sum of pairwise interactions. Thus, the intercluster-exchange model discussed above gives results comparable to those expected from the molecular field approximation yet retains the essentially molecular nature of the system. For these reasons, though, no specific interpretation should be inferred for the absolute magnitude of the values of j. Nonetheless, comparison of relative values of j for different materials does provide a meaningful indication of the relative importance of intercluster-exchange interactions.

Comparison of Magnetic Models. In order to assess the ability of each model to describe the magnetic susceptibility of the acetate complex, we performed a study in which a single set of data was fit to the expression for the theoretical molar susceptibility with use of each of the models. Figure 4 depicts the experimental data for the acetate complex and calculated curves for the EqT, EqT + Z, ISOS, BqX, and EqTX + Z models. Each calculated curve fit is for the same data. The observed and calculated susceptibilities are given in Table VIII.[29] The curve fitting parameters including J, j, and Z are listed in Table IX.

It becomes apparent from an examination of Figure 4 that the equilateral triangle (EqT) model does not adequately describe the magnetic susceptibility. The addition of a term due to a monomeric component in the EqT + Z model improves the quality of the fit only slightly as evidenced by the values of χ and the standard error in Table IX. The EqT model required $J = -27.0$ cm^{-1} while the EqT + Z model required $J = -27.8$ cm^{-1} with a 99.8% fraction of trimer (Z = 0.998).

Table IX. Comparison of the Curve Fitting Parameters of $[Fe_3O(CH_3CO_2)_6(H_2O)_3]ClO_4 \cdot 2H_2O$[a]

model	$10^3\chi$[b]	SE[c]	J, cm^{-1}	j, cm^{-1}	Z
EqT	5.84	7.41×10^{-3}	−27.0		1.000
EqT + Z	4.71	6.02×10^{-4}	−27.8		0.9980
ISOS	2.07	2.70×10^{-3}	−26.3, −29.4		1.000
BqX	1.05	1.38×10^{-4}	−35.6	1.3	1.000
BqX + Z	1.07	1.40×10^{-4}	−35.8	1.3	1.0001
EqTX	8.62	1.55×10^{-3}	−27.0	−0.24	1.000
EqTX + Z	2.14	3.71×10^{-4}	−28.6	3.3	0.9894

[a] g = 2.00. [b] χ is as defined in eq 1. [c] $\mathrm{SE} = \sum_{i=1}^{n} [(\mu_{\mathrm{eff}})_i(\mathrm{obsd}) - (\mu_{\mathrm{eff}})_i(\mathrm{calcd})]/(n-k)$ (see ref 22).

The isosceles triangle model (ISOS) provides a substantial statistical improvement over both the EqT and EqT + Z models. This model succeeds in accounting for the observed temperature dependence to the susceptibility, but its use is incompatible with the structure of this complex. X-ray studies on both this[5] complex and related complexes[25,26] demonstrate an equilateral triangular array of irons. Consequently, no matter how attractive this model may appear on the basis of curve fitting analysis, it must be rejected.

The biquadratic-exchange model used by Rakitin[16] was also applied to the data for the acetate complex and resulted in an excellent mathematical fit to the experimental data. Nonetheless, we conclude that the use of this model is inappropriate. First, the use of higher order exchange terms in similar systems has been investigated in some detail by Gaponenko et al.[33] and has shown to be insufficient to explain the magnetic data. Second, the physical significance of biquadratic exchange is far from clear.[32] Finally, although the agreement between experiment and theory is excellent for the acetate complex, the biquadratic-exchange model does not provide a particularly good fit for the other complexes (vide infra) and leads to values of J which are divergent from those obtained with monocarboxylic acids.

It is seen then that none of the various models which have been proposed in the past are really adequate to describe the magnetism of the iron carboxylates. The equilateral triangle model, which is perfectly reasonable in light of the known structural parameters, does not accurately reproduce the data. By contrast, both the isoceles triangle and biquadratic-exchange models reproduce the data reasonably accurately. As noted above, however, neither of these models has physical significance here, and their application appears to be only an exercise in paramaterization. We believe that the model (EqTX) proposed here provides the most appropriate description of the magnetic properties of the iron(III) carboxylates. This model both retains the known structural features (an equilateral triangle) and also accurately reproduces the data.

It is apparent from Figure 4 that the EqTX model alone is insufficient to describe the variable-temperature magnetic susceptibility data. The solution reached by the EqTX equation is very close to that provided by the EqT model with $J = -27.0$ cm^{-1} for EqT and $J = -27.0$ cm^{-1} for EqTX with the intertrimer exchange parameter $j = -0.24$ cm^{-1}. An additional term must be included to describe the contribution of a monomeric component following the Curie law. When

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(33) Gaponenko, V. A.; Zhikharev, V. A.; Yablokov, Yu. V. *Sov. Phys.—Solid State (Engl. Transl.)* **1972**, *13*, 1875.

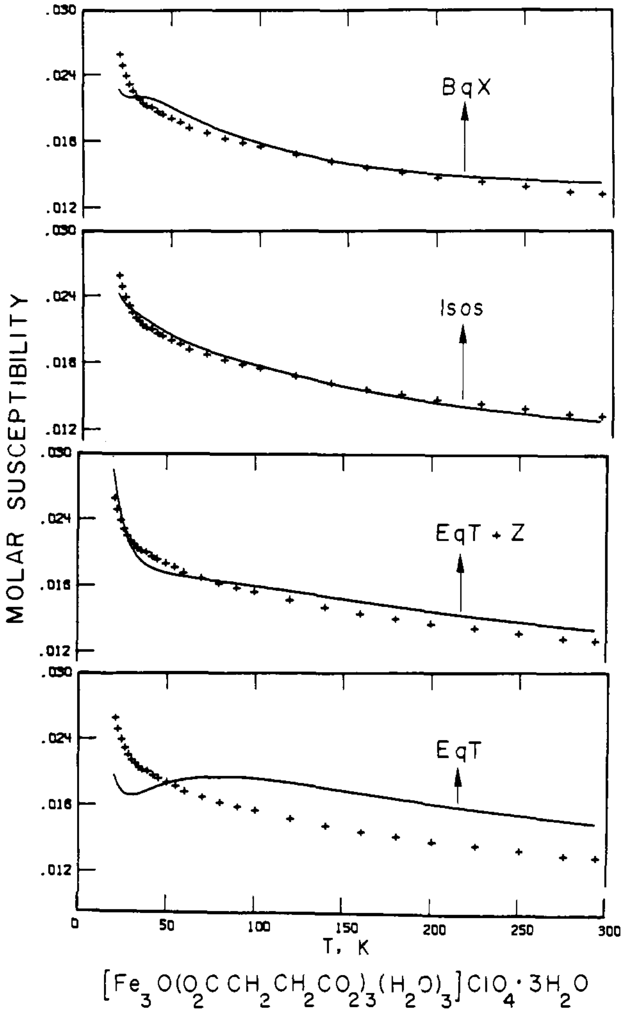

Figure 6. Molar susceptibility vs. temperature for the succinate complex for four of the magnetic models. Solid lines are calculated curves, and points are the observed values.

this term is included, the EqTX + Z model becomes quite satisfactory with J and j equal to −28.6 and 3.3 cm^{-1}, respectively. The value of Z necessary was 0.989 or 98.9% trimer. Because of the form in which the Hamiltonian was written (eq 7), a positive sign for j is indicative of antiferromagnetic coupling between the trimers. This value of Z = 0.989 is not unrealistic for the percent of trimer in this complex. The iron(III) acetate dihydrate was formed from the crystals of iron(III) acetate pentahydrate by vacuum-drying. It was observed that the pentahydrate was not stable for long periods of time because a small amount of a brown material formed on the surface of the crystals. This may be due to some hydrolysis or decomposition of the trimer resulting in a monomeric iron(III) component present in the dihydrate used for the magnetic studies. Although this model does provide a statistically somewhat better fit to the data than do most of the other models, its primary advantage lies in the fact that it is a model with considerable physical significance.

A similar study was undertaken to compare the different models for describing the magnetic data of a dicarboxylic acid complex. The iron(III)–succinic acid complex was selected. Figures 6 and 7 show the results from the six models used to fit the data. It is even clearer here than in the acetate case that intertrimer exchange is necessary to account for all of the features of the susceptibility vs. temperature curve. Tables X and XI contain the data and the results of the curve fitting of this complex.[29] The equilateral triangle model, which gives J = −24.2 cm^{-1}, does not adequately describe the magnetic properties of this complex. The addition of Z to form the EqT + Z model requires J = −30.1 cm^{-1} with Z = 0.986 and does much to improve the quality of the fit, but it does not completely describe all of the features of the curve. The isosceles triangle (ISOS) model is an improvement requiring J = −42.1 and J' = −30.8 cm^{-1} but was rejected for the same reasons as described in the discussion of the acetate complex. These two different values of J and J' imply an unreasonable distortion of the trimer center. The BqX model requires J = −60.7 cm^{-1} and j = +5.3 cm^{-1}. The addition of Z to make the BqX + Z model required J = −48.9 cm^{-1} and j = +3.1 cm^{-1}. Both the BqX and the BqX + Z models were rejected because of the large negative values of J and for the reasons given in the discussion of the acetate complex.

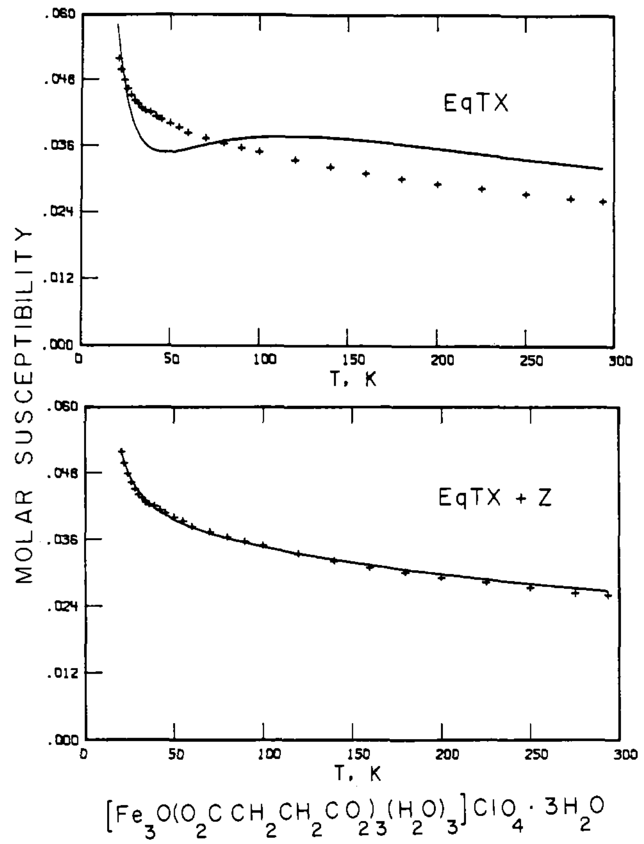

Figure 7. Molar susceptibility vs. temperature for the succinate complex for the EqTX and EqTX + Z models. Solid lines are calculated curves, and points are the observed values.

The EqTX model, with J = −25.2 cm^{-1} and j = −7.2 cm^{-1}, did not adequately describe the data for the iron(III) succinate complex, (Figure 7). However, the addition of a monomeric component following the Curie law, the EqTX + Z model, gave an excellent fit with J = −31.5 cm^{-1}, j = +6.1 cm^{-1}, and Z = 0.961. These numbers are reasonable, and the resulting curve reproduced all the features of the experimental curve within the uncertainty of the determinations.

The variable-temperature magnetic susceptibility data for the acetate, malonate, succinate, fumarate, *o*-phthalate, and *m*-phthalate complexes are given in Tables II–VII.[29] The data for all these compounds were fitted to the EqTX + Z model, and susceptibilities calculated by using the EqTX + Z model are included in Tables II–VII.

The results of the curve fitting for all six complexes are presented in Table XII. The calculated values of J for these compounds are relatively constant ranging from −30.0 to −37.3 cm^{-1}. These values of J are similar to those obtained for the monocarboxylic acid analogues by other investigators and suggest the presence of the Fe_3O center in these dicarboxylic acid complexes. The most likely pathway for spin-exchange interactions between the ferric ions is through the central

Table XII. Comparison of Magnetic Parameters for the Iron(III) Complexes

complex	J^a	j^a	Z
acetate	−29.0	+2.1	0.989
malonate	−31.4	+2.5	0.974
succinate	−31.5	+6.1	0.961
o-phthalate	−37.3	+11.7	0.858
m-phthalate	−36.2	+9.3	0.838
fumarate	−35.0	+9.0	0.855

[a] All values of J and j in cm^{-1}.

oxygen, since the X-ray structures cited earlier show the ferric ions are too far apart for direct interaction. It seems plausible that the t_{2g} orbitals of the ferric ions interact with the pπ orbitals on the central oxygen and that superexchange interactions occur via this route.

The intertrimer exchange parameter, j, ranged from +2.0 cm^{-1} for acetate to +11.7 cm^{-1} for *o*-phthalate. The trend in j values suggests larger antiferromagnetic interactions between trimer centers for compounds containing unsaturated carbon linkages. The presence of an extended π-orbital system in certain of the dicarboxylic acid complexes would lead to greater interaction between trimer centers, consistent with what is observed. Thus, the *o*-phthalic, *m*-phthalic, and fumaric acid complexes have the highest values of j, whereas the aliphatic acid complexes (malonic and succinic acid) have lower values of j. The only monocarboxylic acid complex studied, the acetic acid complex, had the lowest value of the intetrimer exchange integral. Although this complex does not contain trimer centers linked by ligand bridges, it nonetheless gives a nonzero j = +2.0 cm^{-1}. This slightly positive value of j may indicate some weak magnetic exchange occurring through the hydrogen-bonding network.

The fraction of trimer, Z, was the greatest for the acetate complex, with somewhat smaller values for the malonate and succinate complexes (see Table XII). The lowest values of Z were observed for fumarate, *o*-phthalate, and *m*-phthalate, the most sterically constrained ligands. This result is consistent with the results of Mössbauer spectral measurements. As mentioned previously, complexes of the sterically constrained dicarboxylic acids gave Mössbauer spectra with relatively broad lines, presumably as the result of iron being present in a variety of similar, but not identical, environments. This parallel between the magnetic and Mössbauer results serves to justify the use of the Curie law term in the description of the susceptibilities.

Replicate preparations and measurement of the susceptibilities for several of these materials indicated that the results were highly reproducible. In particular, values of J and Z are probably accurate to ±1.5 cm^{-1} and ±0.005, respectively. The construction of error analysis contour maps in J, Z, and j space demonstrates that the quality of the data fits are markedly less sensitive to j, the uncertainty being ±2 cm^{-1}. Consequently, absolute values of j should be treated with some caution. However, the trends in j, and the necessity for a model which incorporates intertrimer exchange, are clear.

Infrared Studies. The infrared spectra for the iron(III)-dicarboxylic acid complexes are given in Figure 8. The spectral data including band assignments are listed in Tables XIII–XVII.[29] Infrared bands were assigned by using the conventions of Nakamoto.[34]

The most prominent features of the infrared spectra of these complexes are the absorptions due to the symmetric and asymmetric stretching of the coordinated carboxyl groups. These are broad, very intense and well-defined bands located at about 1450 and 1600 cm^{-1}, respectively. Their positions and intensities are similar to those reported for other metal-coordinated acetates.[14,35] Three prominent bands due to absorption by the perchlorate anion are found in the 1100-cm^{-1} region for the acetate, malonate, and succinate complexes with weak bands observed in the spectra of the fumarate and *m*-phthalate complexes. Assignments were made according to the data of Ross.[36] Additional absorptions due to the perchlorate anion and carboxyl groups were found in the 600–660-cm^{-1} region. Long et al.[12] have assigned a weak band appearing at 520 cm^{-1} in the acetate complex to the asymmetric vibration of the Fe_3O moiety. A band of similar shape and intensity was observed in the spectrum of the acetate complex prepared in this study. However, this band could not be located with complete certainty in the spectra of the dicarboxylic acid complexes.

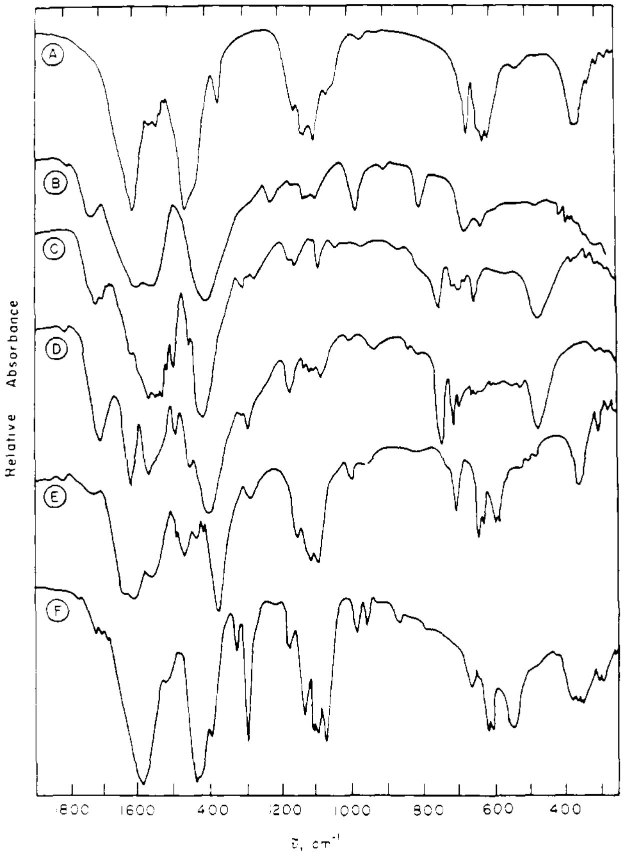

Figure 8. Infrared spectra of the iron(III) complexes, where A = acetate, B = fumarate, C = *o*-phthalate, D = *m*-phthalate, E = malonate, and F = succinate.

The *o*-phthalate, *m*-phthalate, and fumarate complexes all have quite similar infrared spectra. They show absorptions due to symmetric stretching of the carboxyl groups at about 1400 cm^{-1}. They also exhibit other absorptions attributed to C–H, C–C, or C═C vibrations characteristic of the structure of the respective ligands.[37] All three also show a strong absorption due to the asymmetric stretching of the anionic carboxyl group confirming the presence of acid as the anion. The absorptions due to asymmetric stretching of the carboxyl groups at about 1600 cm^{-1} are complex. Both fumarate and *o*-phthalate exhibit a broad, unresolved band. The *m*-phthalate complex shows some resolution into two bands at 1570 and 1620 cm^{-1}. These bands, as in the malonate complex, may reflect an interaction between the coordinated carboxyl groups

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(34) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1970.

(35) Vratny, F.; Rao, C. N. R.; Dilling, M. *Anal. Chem.* **1961**, *33*, 1455.

(36) Ross, S. D. *Spectrochim. Acta* **1962**, *18*, 225.

(37) Gonzalez-Sanchez, F. *Spectrochim. Acta* **1958**, *12*, 17.

of the same ligand through the unsaturated carbon linkages. This interaction is similar to that observed in the infrared spectrum of the malonate complex.

Infrared spectra suggested that the fumarate complex contained a mixture of counterions. Attempts to make the complex either with fumarate or perchlorate as the only anion never resulted in close agreement between the theoretical and calculated C, H, and Fe analyses. Compounds prepared with perchlorate as the only anion presumed present always displayed an infrared spectral band due to asymmetric stretching of anionic carboxyl groups. Compounds prepared with fumarate as the only anion presumed present similarly displayed a band due to perchlorate. Attempts at varying the proportion of the reactants resulted in products with similar C:Fe ratios. Analysis for perchlorate as chloride resulted in 1.9% as Cl. This fit the formulation described in the Experimental Section with 0.25 mol of the fumarate dianion and 0.50 mol of ClO_4 present as the counterions. (A similar mixture of anions was observed for the *m*-phthalate complex.) Although this evidence does indicate certain heterogeneity of the anion in this complex, it is important to remember that the Mössbauer spectra and the magnetic susceptibility data should not be significantly affected by this problem. This problem of heterogeneity of the anion for the fumarate and *m*-phthalate complexes is most likely an unavoidable consequence of the nature of these polymers.

Conclusions. Several dicarboxylic acid complexes of iron(III) have been synthesized as polymers which are insoluble in aqueous solution. During synthesis they formed suspensions which exhibited a sensitivity to variations in pH and ionic strength. After isolation these complexes were stable indefinitely at room temperature provided they were kept in tightly sealed vials in the absence of moisture.

The Mössbauer spectra of these complexes were characteristic of high-spin iron(III)-containing compounds. The observed values of δ, ΔE_Q, and line widths were similar to those reported by other researchers for complexes containing the Fe_3O center. The line widths of the absorption bands were broad, probably caused by ferric ions in slightly different sites. There appeared to be a correlation between ΔE_Q and the nature of the ligands. Complexes of the more sterically constrained ligands (*o*-phthalate, *m*-phthalate, fumarate) have a larger ΔE_Q than observed for the succinate, malonate, and acetate complexes. This suggests that the sterically hindered ligands cause a small distortion in the Fe–O coordination sphere. Unfortunately, the complexes could only be isolated as microcrystalline powders so that X-ray crystal studies to confirm this distortion could not be done.

The inconsistency between the equilateral triangle arrangement of the ferric ions found in the crystal structure of the monocarboxylic acid complexes and the isosceles triangle model required to explain the magnetic data has been resolved. All previously known models are inadequate. A new model EqTX has been proposed. It has the advantage of employing the equilateral triangle arrangement of ferric ions which has been observed, yet describes the magnetic data by allowing some small antiferromagnetic exchange between trimeric centers. Both of these factors are physically real and can be justified by observable physical phenomena.

The EqTX model has recently been applied successfully to metal trimer complexes other than iron by Wrobleski et al.[38] to describe the thermal and magnetic behavior of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl{\cdot}6H_2O$. The magnetic heat capacity data for this complex in the region of 1.1–25 K were used to calculate exchange parameters. These parameters were then successfully applied to the magnetic susceptibility data of this complex. This agreement confirmed the presence of intercluster spin exchange at low temperature.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Registry No. $[Fe_3O(CH_3CO_2)_6(H_2O)_3]ClO_4$, 75732-14-8; $[Fe_3O(O_2CCH_2CO_2)_3(H_2O)_3]ClO_4$, 75732-16-0; $[Fe_3O(O_2CCH_2CH_2CO_2)_3(H_2O)_3]ClO_4$, 75732-18-2; $[Fe_3O(O_2CCHCHCO_2)_3(H_2O)_3](O_2CHCHCO_2)_{0.25}(ClO_4)_{0.50}$, 75751-01-8; $[Fe_3O($*o*-phthalate$)_3(H_2O)_3]($*o*-phthalate$)_{0.5}$, 75751-03-0; $[Fe_3O($*m*-phthalate$)_3(H_2O)_3]($*m*-phthalate$)_{0.45}(ClO_4)_{0.1}$, 75751-05-2.

Supplementary Material Available: Magnetic susceptibility expressions (eq 4, 6, and 9), experimental and calculated magnetic susceptibilities (Tables II–VIII and X), summary of curve-fitting parameters (Table XI), infrared spectral data and assignments (Tables XIII–XVII), and effect of intertrimer exchange parameter on calculated magnetic susceptibilities (Figure 5) (20 pages). Ordering information is given on any current masthead page.

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[38] Wrobleski, J. T.; Dziobkowski, C. T.; Brown, D. B. *Inorg. Chem.*, following paper in this issue.