# The Magnetic, Electronic, and Mössbauer Spectral Properties of Several Trinuclear Iron(III) Carboxylate Complexes

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Each of the formate, acetate, monochloroacetate, trichloroacetate, phenylacetate, and benzoate complexes with iron(III), prepared and characterized for study is triangular trinuclear in structure and contains six bridging carboxylate ligands and a central bridging oxygen. Magnetic susceptibility measurements from room temperature to 20 K indicate non-equivalent, antiferromagnetic coupling of the three high-spin iron(III) ions. The Mössbauer spectrum of each of the complexes exhibits quadrupole line asymmetry, which is attributed to the Gol'danskii–Karyagin effect. The i.r. spectrum and electronic spectrum of each complex are reported and discussed in terms of the observed antiferromagnetic coupling.

THE magnetic properties of magnetically intermediate systems have received a good deal of attention in recent publications. The properties of several systems containing two magnetically coupled iron atoms have been reviewed;[1] however, the very interesting system of three magnetically coupled iron atoms has received considerably less attention. Cattrall *et al.*[2] and Prados and Good,[3] have reported the magnetic and Mössbauer spectral properties of several trinuclear iron(III) sulphate complexes. Another example of this type of system is the iron(III) acetate complex which was first reported by Welo.[4] This type of complex was shown to contain three iron(III) atoms at the apices of an equilateral triangle with an oxygen in the centre. Two acetate ligands bridge each pair of iron atoms.[5] The magnetic properties of these systems were first successfully described by Kambe.[6] In a subsequent paper, Earnshaw *et al.*[7] studied the magnetic properties of an extensive series of trinuclear iron(III) carboxylate complexes and concluded that their properties were best understood on the basis of three equivalent iron atoms, each magnetically coupled to the same extent with the other two iron atoms. Further work by Duncan *et al.*[8] indicated that the magnetic properties of a similar series of complexes were best understood on the basis of nonequivalently coupled iron atoms. In each of these cases, the magnetic studies were limited to temperatures above 80 K.

The work reported in this paper was undertaken to clarify the exact nature of the magnetic coupling in a series of trinuclear iron(III) carboxylate complexes. It was anticipated that magnetic measurements down to lower temperatures, approximately 20 K, would provide sufficient additional information to distinguish between equivalently and nonequivalently coupled iron ions in these complexes. The i.r., electronic, and Mössbauer spectral properties were studied in an attempt to correlate these properties with the magnetic coupling.

## EXPERIMENTAL

*Preparation of Compounds.*—All the complexes were prepared with standard reagent chemicals. Each of the complexes (except the formate) was prepared by the method described by Earnshaw *et al.*[7] who used ferric chloride and the sodium salt of the appropriate carboxylic acid. The formate complex was prepared by the method of Duncan *et al.*[8] who used ferric nitrate and 98% formic acid.

TABLE 1

Analysis of compounds

| Compound | Designation | %C | | %H | | %Fe | |
|---|---|---|---|---|---|---|---|
| | | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. |
| $[Fe_3O(HCOO)_6(H_2O)_3]OH,2H_2O$ | Formate | 12·85 | 12·65 | 3·05 | 2·8 | 29·9 | 29·7 |
| $[Fe_3O(H_3CCOO)_6(H_2O)_3]Cl,5H_2O$ | Acetate | 20·1 | 19·8 | 4·8 | 4·65 | | |
| $[Fe_3O(ClH_2CCOO)_6(H_2O)_3]Cl,5H_2O$ | Monochloroacetate | 15·6 | 15·7 | 3·05 | 2·70 | 18·1 | 18·1 |
| $[Fe_3O(Cl_3CCOO)_6(H_2O)_3]Cl,H_2O$ | Trichloroacetate | 11·4 | 11·7 | 0·65 | 0·8 | 13·25 | 13·1 |
| $[Fe_3O(C_8H_7O_2)_6(H_2O)_3]C_8H_7O_2,2H_2O$ | Phenylacetate | 55·15 | 55·3 | 4·85 | 4·7 | 13·75 | 14·2 |
| $[Fe_3O(C_7H_5O_2)_6(H_2O)_3]C_7H_5O_2,6H_2O$ | Benzoate | 49·3 | 48·95 | 4·45 | 4·25 | 14·05 | 14·5 |

The analytical results for each of the compounds are presented in Table 1. The carbon and hydrogen microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. The iron analysis was performed in our laboratory. The acetate, monochloroacetate, and trichloroacetate complexes gave positive tests for the chloride ion, while the remaining complexes gave a negative test.

*Physical Measurements.*—Room-temperature magnetic susceptibility measurements were made on a standard Gouy balance. All low-temperature susceptibility measurements were made on a Faraday balance which has been described.[9,10] The Faraday balance was calibrated with

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[1] B. Jezowska-Trzebiatowska and W. Wojciechowski, ' Transition Metal Chemistry,' Dekker, New York, 1970, vol. 6, p. 1.

[2] R. W. Cattrall, K. S. Murray, and K. I. Peverill, *Inorg. Chem.*, 1971, **10**, 1301.

[3] R. Prados and M. L. Good, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3733.

[4] L. A. Welo, *Phys. Rev.*, 1928, **32**, 320.

[5] B. N. Figgis and G. B. Robertson, *Nature*, 1965, **205**, 694.

[6] K. Kambe, *J. Phys. Soc. Japan*, 1950, **5**, 48.

[7] A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc.* (*A*), 1966, 1656.

[8] J. F. Duncan, C. R. Kanekar, and K. F. Mok, *J. Chem. Soc.* (*A*), 1969, 480.

[9] W. M. Reiff, G. J. Long, and W. A. Baker, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 6347.

[10] G. J. Long, Ph.D. Dissertation, Syracuse University, 1968.

$CoHg(NCS)_4$, and the sample temperature was measured with a platinum resistance thermometer. All magnetic moments were measured at three field strengths. None of the compounds exhibited any field dependence in the magnetic moment. The Mössbauer spectral results were obtained with an Austin Science Associates, constant-acceleration spectrometer. The spectrometer was calibrated by using natural iron foil, and the source was maintained at room temperature for all measurements. The National Bureau of Standards Parlor computer program [11] was used to evaluate the spectral results. The error limits for the results presented in Table 4 are calculated from the variance of the final computer iteration.[11]

The electronic spectra were recorded on a Cary 14 spectrophotometer. The solids were mulled with Kel-F No. 90 grease and placed between quartz plates for spectral measurements. The low-temperature results were obtained by using an Air Products Corp. model AC-2 Cryotip refrigerator. I.r. spectral results were obtained by using a Perkin-Elmer 521 spectrometer and a Beckman IR-12 spectrometer.

## RESULTS AND DISCUSSION

The *X*-ray powder diffraction pattern for the iron acetate complex is identical to the pattern obtained for the analogous chromium complex. A previous single-crystal study [5] has shown that the chromium complex contains three metal atoms at the apices of an equilateral triangle with an oxygen atom in the centre. Two acetate ligands bridge each pair of metal atoms. The pattern for the monochloroacetate complex is similar (but not identical) to the patterns for the iron and chromium acetate complexes indicating that this solid most likely belongs to the same space group as the acetate complexes but has a larger unit-cell size. There are no similarities in the patterns for the other four complexes. This is not surprising because they contain different anions and carboxylate ligands of greatly varying size.

On the evidence of the *X*-ray data, the analytical data, and the magnetic and spectral data to be presented below, the authors have concluded, for the purpose of further discussion, that each of the complexes contains the trinuclear iron oxygen moiety and bridging carboxylate ligands. It does not, however, necessarily follow that in each of the complexes the three iron atoms are equivalent. Verification of this conclusion must, of course, await a detailed crystallographic study of each of the complexes.

*Magnetic Properties*.—The magnetic properties of the compounds were studied over a temperature range of 20 to 300 K, and the results are presented in Table 2. For each complex, either two or three samples were prepared and their room temperature magnetic moments measured. The room temperature moments were reproduced to ±0·05. The results reveal that the room temperature moments are significantly reduced from the value expected for the high-spin iron(III) ion. The moments also decrease continuously with decreasing temperature.

These magnetic results are ideally suited for evaluation with the theoretical model of trinuclear magnetic coupling proposed by Kambe [6] and discussed in detail by Martin.[12] In this model, the effects of nearest-neighbour, isotropic, spin–spin coupling are evaluated by using the Hamiltonian

$$H = -2J[(\mathbf{S}_1 \cdot \mathbf{S}_2) + (\mathbf{S}_2 \cdot \mathbf{S}_3)] - 2J'(\mathbf{S}_3 \cdot \mathbf{S}_1)$$

where $\mathbf{S}_i$ is the spin of the $i$th iron atom, and $J$ and $J'$ are the isotopic exchange integrals. This expression assumes equivalent coupling between iron atoms 1 and 2 and atoms 2 and 3. In the special case where $J = J'$, the three iron atoms are all equivalently coupled. All subsequent results are based upon this Hamiltonian.*

TABLE 2

Magnetic data

Temperature (K) followed by $\mu_{eff}$

Formate: ($M$/Fc = 186·92, $\chi^c$ = 76); 292·5, 3·23; 268·0, 3·14; 248·0, 3·06; 223·5, 2·95; 204·0, 2·86; 168·5, 2·67; 146·5, 2·54; 126·5, 2·41; 102·0, 2·21; 88·7, 2·08; 73·2, 1·92; 48·9, 1·60; 26·9, 1·23; 21·1, 1·16

Acetate: ($M$/Fe = 239·13, $\chi^c$ = 118); 292·0, 3·23; 274·0, 3·15; 253·5, 3·07; 233·0, 2·98; 212·0, 2·88; 198·5, 2·77; 164·0, 2·63; 143·0, 2·50; 113·5, 2·27; 87·7, 2·03; 67·6, 1·79; 49·4, 1·53; 33·1, 1·35; 22·9, 1·09; 20·5, 1·10

Monochloroacetate: ($M$/Fe = 308·03, $\chi^c$ = 104); 296·5, 3·30; 267·0, 3·19; 247·0, 3·10; 232·0, 3·02; 213·0, 2·94; 196·5, 2·85; 180·5, 2·77; 161·0, 2·65; 141·5, 2·51; 123·0, 2·37; 105·5, 2·23; 84·5, 2·01; 69·9, 1·83; 50·5, 1·56; 32·5, 1·26; 26·8, 1·18; 22·4, 1·15; 19·7, 1·12

Trichloroacetate: ($M$/Fe = 421·80, $\chi^c$ = 203); 293·0, 3·29; 275·0; 3·23; 249·5, 3·14; 230·5, 3·07; 211·5, 2·98; 189·5, 2·90; 168·0, 2·81; 144·5, 2·70; 124·0, 2·59; 101·0, 2·47; 79·7, 2·34; 59·9, 2·18; 40·7, 1·97; 27·8, 1·88; 23·4, 1·86

Phenylacetate: ($M$/Fe = 406·52, $\chi^c$ = 217); 294·0, 3·49; 273·5, 3·41; 252·0, 3·32; 230·5, 3·24; 210·5, 3·16; 188·5, 3·05; 164·5, 2·93; 142·5, 2·81; 120·0, 2·67; 102·0, 2·55; 81·5, 2·38; 60·0, 2·17; 35·7, 1·88; 20·8, 1·68

Benzoate: ($M$/Fe = 397·81, $\chi^c$ = 204); 298·0, 3·39; 266·5, 3·31; 245·5, 3·23; 226·5, 3·16; 200·0, 3·04; 178·5, 2·92; 154·5, 2·82; 134·5, 2·72; 113·5, 2·58; 89·5, 2·41; 70·2, 2·24; 47·3, 2·01; 25·8, 1·79; 20·8, 1·77

The experimental results presented in Table 2 have been evaluated in two different ways. In the first, equivalent coupling is assumed ($J = J'$), and the value of $J$ is varied to optimize the agreement between the theoretical and experimental magnetic moments. In the second method, $J$ and $J'$ are allowed to vary independently to optimize the agreement. In each case, the value of $g$, the Lande splitting factor, is set equal to 2·00, which is the value expected [13] for high-spin iron(III) complexes which do not contribute orbital angular momentum to the total moment. The resulting 'best fit' parameters [10] are presented in Table 3. From these

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* This Hamiltonian was used by Earnshaw *et al.*[7] Duncan *et al.*[8] used a different Hamiltonian, and a direct comparison of the $J$ and $J'$ values presented in this paper and in the work of Duncan *et al.* is not possible. The values can, however, be related by simple expressions.

[11] J. R. DeVoe, ed. *Nat. Bur. Standards* (*U.S.*), *Tech. Note*, *No.* 404, 1966, 108.

[12] R. L. Martin, 'New Pathways in Inorganic Chemistry,' ed. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, London, 1968, p. 175.

[13] B. N. Figgis, 'Introduction to Ligand Fields,' Interscience Publishers, New York, 1966.

results, it is seen that the compounds may be divided into two groups. For the formate, acetate, and monochloroacetate complexes, a reasonable (but not perfect) agreement is found between the experimental moments and the calculated moments if one assumes equivalent coupling between the three iron atoms. For the remaining three complexes, no such agreement can be found, and one is forced to vary $J$ and $J'$ independently to obtain any reasonable agreement between the experimental and theoretical values. The typical agreement found in the two groups is illustrated in Figures 1 and 2. Essentially the same figures would result for the remaining complexes in each group. In all cases, essentially perfect agreement is found between the experimental and theoretical values if $J$ and $J'$ are treated independently.

TABLE 3

Best fit parameters obtained from magnetic data [a]

| Compound | $-J$ | $-J'$ | $\alpha$ [b] | $-J$ [c] |
|---|---|---|---|---|
| Formate [d] | 27·7 | 36·1 | 0·75 | 27·9 |
| Acetate [d] | 28·2 | 34·6 | 0·81 | 28·7 |
| Monochloroacetate [d] | 30·5 | 25·7 | 1·19 | 27·6 |
| Trichloroacetate | 25·1 | 42·7 | 0·59 | *e* |
| Phenylacetate | 21·0 | 33·3 | 0·63 | *e* |
| Benzoate | 29·6 | 20·2 | 1·46 | *e* |

[a] $g = 2{\cdot}00$, $J$ and $J'$ in cm$^{-1}$. [b] $\alpha = J/J'$. [c] For $J = J'$. [d] ' Second best ' fit also obtained (see text): Formate, $J = -32{\cdot}2$, $J' = -25{\cdot}9$; Acetate, $J = -31{\cdot}8$, $J' = -26{\cdot}8$; monochloroacetate, $J = -27{\cdot}0$, $J' = -33{\cdot}4$. [e] No reasonable fit possible.

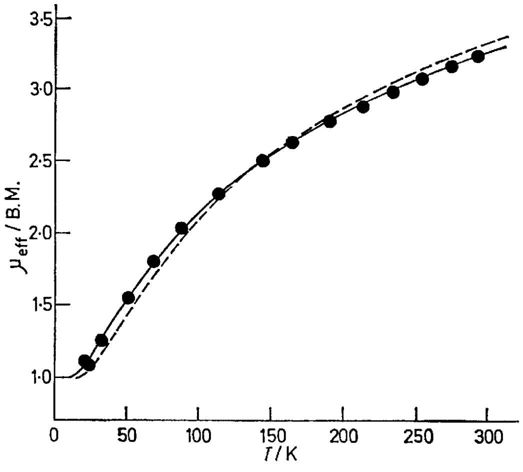

FIGURE 1 Plot of $\mu_{eff}$ *vs.* temperature for the acetate complex. ● experimental points, —— best fit for $J \neq J'$, – – – – best fit for $J = J'$ (value given in Table 3)

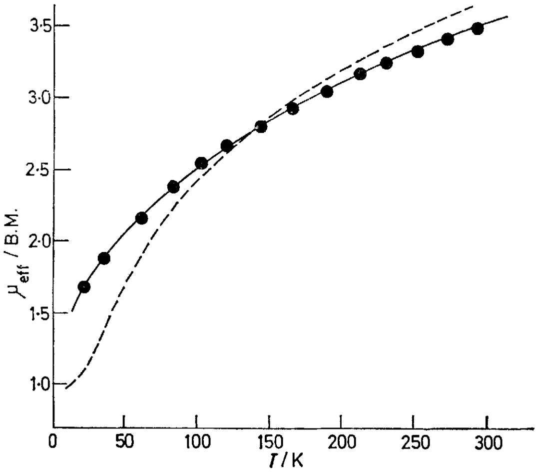

FIGURE 2 Plot of $\mu_{eff}$ *vs.* temperature for the phenylacetate complex. ● Experimental points, —— best fit for $J \neq J'$, – – – – best fit for $J = J'$ (values given in Table 3)

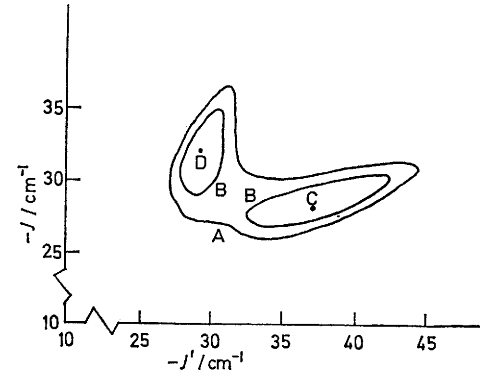

FIGURE 3 Best fit contour map for the acetate complex A, $\mu_{eff} = \pm 0{\cdot}10$ B.M.; B, $\mu_{eff} = \pm 0{\cdot}05$ B.M.; C, best fit; D, second best fit

A more extensive evaluation of the magnitude of $J$ and $J'$ for the acetate complex was made to determine whether the experimental data were sufficient to distinguish between equivalent and nonequivalent spin–spin, coupled iron atoms. The results of this analysis are presented in Figure 3. This figure is like a contour map. Any set of values for $J$ and $J'$ located inside contour line A will reproduce the experimental magnetic moments to ±0·10; inside contour line B to ±0·05. From these results, it is apparent that if the experimental magnetic moments are valid to *ca.* ±0·05 then the coupling is best described as nonequivalent. If the experimental moments are valid to ±0·10 or more, then the equivalently coupled model is sufficient to describe the spin–spin magnetic coupling. Because the room temperature magnetic moment is reproducible to *ca.* ±0·05, the authors believe that the nonequivalently coupled model is justified. A similar argument can be made for the nonequivalently coupled model for the formate and monochloroacetate complexes. It is interesting to note that Figure 3 shows two maxima in the quality of fit for the acetate complex. The same ' second best ' fit maximum (see Table 3) was also observed for the formate and monochloroacetate complexes.

The effect of the variation of $g$ from a value of 2·00 for the acetate complex was also studied. In order to improve significantly the agreement between the equivalently coupled model and the experimental results, a value of $g$ of the order of 1·60 is required. A reduction of this magnitude in $g$ would not be expected for a high-spin iron(III) complex.[13] The authors believe that, until better $g$ values are available from e.s.r. data, the value of 2·00 is the most reasonable value to use in the evaluation of the magnetic results.

A careful study of the trends in $J$ and $J'$ presented in Table 3 is disappointing because it does not reveal any distinct correlation between the values of $J$ and $J'$ and the chemical nature of the carboxylate ligand. There does appear to be some correlation between the size of the carboxylate ligand and the absolute value of the difference between $J$ and $J'$. This trend is not, however, observed in the ratio of $J$ and $J'$ and may simply be coincidental. It would appear that perhaps some nonchemical factor influences the magnetic coupling. This factor could be of a crystallographic nature or may result from inclusion of impurities in certain of the complexes. It is almost impossible to estimate the effect of impurities on these results; however, the authors believe that the impurity problem has been minimized in this work. This belief is based upon the reproducibility of the room temperature value of $\mu_{eff}$ from sample to sample, upon the lack of any field dependence in $\mu_{eff}$ at low temperature, upon the Mössbauer spectral data presented below, and upon the i.r. spectra for the compounds.

An alternative reason for the lack of any correlation may be the use of an over-simplified Hamiltonian. The inclusion of second-order coupling terms or ' molecular ' coupling terms in the equivalently coupled Hamiltonian would no doubt lead to better agreement between the theoretically calculated values and the experimental results. However, the physical significance of such terms is far from well established and hence, they have not been included. Perhaps a model including molecular orbital angular momentum should be used.

*Mössbauer Spectral Properties*.—The Mössbauer spectrum of each of the complexes has been measured at room and liquid nitrogen temperatures. The resulting spectral and lineshape parameters are presented in Table 4. The error limits for the values of $\Delta E_Q$ and $\delta$ are better than or equal to $\pm$0·03 mm s$^{-1}$. The error limits for the linewidth values are *ca.* $\pm$0·01 mm s$^{-1}$. The area and intensity ratios are found to be reproducible to *ca.* $\pm$0·02. A typical spectrum is presented in Figure 4. The isomer shift values, $\delta$, presented in Table 4 are of the magnitude expected for high-spin iron(III) complexes[14] and show as expected a slight decrease with decreasing temperature. These values are surprisingly constant from one carboxylate to the next and indicate that a change in the carboxylate group—with its varying electron withdrawing power—has little effect upon the *s*-electron density at the surface of the iron nucleus.

TABLE 4

Mössbauer spectral parameters

| Compound | $T$/K | $\Delta E_Q$ mm s$^{-1}$ | $\delta$[a] mm s$^{-1}$ | Linewidth[b] mm s$^{-1}$ | | Area ratio[c] | Intensity ratio[c] |
|---|---|---|---|---|---|---|---|
| Formate | RT | 0·45 | 0·42 | 0·32 | 0·32 | 1·15 | 1·12 |
| | 78 | 0·50 | 0·48 | 0·37 | 0·38 | 1·05 | 1·02 |
| Acetate | RT | 0·55 | 0·42 | 0·31 | 0·32 | 1·17 | 1·15 |
| | 78 | 0·61 | 0·55 | 0·32 | 0·34 | 1·08 | 1·00 |
| Monochloro-acetate | RT | 0·48 | 0·42 | 0·32 | 0·30 | 1·18 | 1·17 |
| | 78 | 0·53 | 0·53 | 0·34 | 0·34 | 1·08 | 1·08 |
| Trichloro-acetate | RT | 0·72 | 0·43 | 0·31 | 0·33 | 1·18 | 1·04 |
| | 78 | 0·71 | 0·54 | 0·36 | 0·38 | 1·08 | 1·02 |
| Phenylacetate | RT | 0·60 | 0·42 | 0·37 | 0·35 | 1·13 | 1·22 |
| | 78 | 0·63 | 0·53 | 0·36 | 0·36 | 1·06 | 1·10 |
| Benzoate | RT | 0·48 | 0·42 | 0·35 | 0·36 | 1·19 | 1·14 |
| | 78 | 0·45 | 0·53 | 0·38 | 0·40 | 1·13 | 1·06 |

[a] Relative to natural iron foil. [b] Full width at half maximum. [c] Ratio of the lower energy absorption band to the higher energy absorption band.

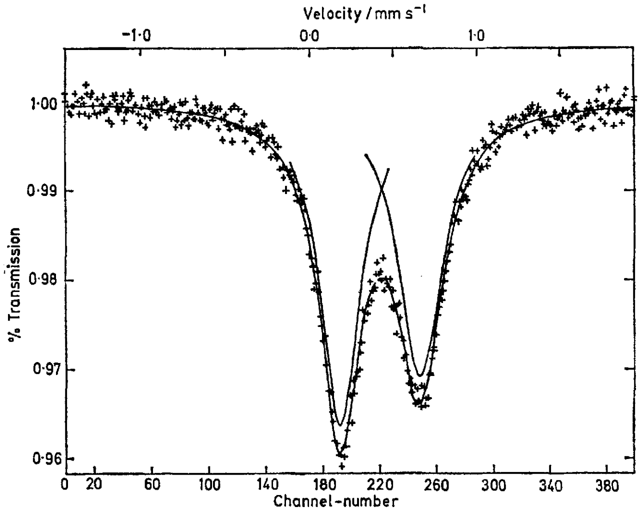

FIGURE 4 Room temperature Mössbauer spectrum of the Cl acetate complex

The magnitude of the quadrupole splitting, $\Delta E_Q$, reported in Table 4 is also that which is expected[12] for high-spin iron(III) complexes. It should be noted that the quadrupole splitting for the trichloroacetate and phenylacetate complexes is slightly higher than for the remaining complexes indicating that these bulky carboxylate groups produce a slightly larger electric field gradient at the iron nucleus. Duncan *et al.*[8] have reported room temperature values of $\delta$ and $\Delta E_Q$ for several similar complexes. The present results agree well with their results. It should be noted that the linewidth of the quadrupole split lines is considerably larger than expected for all equivalent iron atoms. The observed linewidth for the iron foil used in calibration is, for example, *ca.* 0·24 mm s$^{-1}$. These broadened linewidths would be expected if the three iron atoms are nonequivalent as indicated by the magnetic results.

The most interesting aspect of the Mössbauer spectrum of each of these complexes is the asymmetry observed in the intensity of the quadrupole split lines. This asymmetry is apparent in Figure 4, and numerical data for the area ratio and intensity ratio are included in Table 4. The presence of an impurity with a single line coincident with one of the two quadrupole split lines could account for the observed asymmetry; however, the asymmetry is reproducible from one sample preparation to the next and decreases with decreasing temperature. The

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[14] E. Fluck, ' Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Gol'danskii and R. H. Herber, Academic Press, New York, 1968, p. 268.

magnitude of the line asymmetry at room temperature for the acetate and formate complexes was found to be independent of sample orientation and of sample particle size to within the error limits of the measurement of the line asymmetry. As a further check against crystallite orientation, an acetone solution of the acetate complex was evaporated on paper (Gelman ITLC type SG) coated with silica gel. This technique for the elimination of particle orientation has been suggested by Collins *et al.*[15] The spectrum of the resulting sample, exhibited essentially the same line intensity asymmetry. It would therefore appear that the observed asymmetry cannot be a result of crystallite orientation or sample impurity.

Karyagin has discussed[16] the intensity asymmetry in quadrupole split lines in noncubic polycrystalline solids. The asymmetry results from the anisotropy of the recoil-free fraction of the iron nucleus in the reduced symmetry site and is predicted to decrease with decreasing temperature.[17] Furthermore, the linewidth of the component lines is expected to remain the same (at a given temperature) while the integrated areas of the two lines should differ. For the carboxylate complexes under study, the linewidths of the two quadrupole split components (Table 4) are in most cases equivalent (at a given temperature) to within the error limits of the linewidth measurement. In addition, the asymmetry of the line intensity (area ratio) decreases with decreasing temperature. Hence, it would appear that the line intensity asymmetry is consistent with that expected from the Gol'danskii–Karyagin effect. Indeed, one might expect the recoil-free fraction for these complexes to be anisotropic because the strength of the bonding of the iron to the central oxygen and water molecule in the axial positions would be expected to be different from the bonding to the four carboxylate oxygen atoms in the equatorial positions.[5]

The effect of magnetic relaxation upon the asymmetry of quadrupole split Mössbauer absorption bands has been discussed in detail by Blume[18] and by Blume and Tjon.[19] By treating magnetic relaxation as a fluctuating internal magnetic field, these authors concluded that asymmetric quadrupole absorptions will result if the fluctuation rate is of the same magnitude as the precessional frequency of the Mössbauer nucleus in the internal field. For iron with a $^6S$ free-ion ground state, magnetic relaxation will occur mainly *via* spin–spin relaxation, and spin–lattice relaxation can in general be ignored.[20] If electronic spin–spin relaxation is the primary relaxation mechanism, the line asymmetry will depend upon the concentration of paramagnetic ions and will be essentially independent of temperature. In addition, the linewidths of the asymmetric quadrupole split lines are not expected to be the same in the presence of magnetic relaxation.[18] Although the possibility of magnetic relaxation cannot be completely eliminated, it would appear that the observed results are more consistent with the Gol'danskii–Karyagin effect.

*Electronic Spectral Properties.*—The near i.r. and visible electronic spectrum for each of these complexes has been measured in the solid state and in solution. The results are presented in Table 5 and in Figures 5 and 6.

TABLE 5

Electronic spectral results

| Compound | Solvent | $H_2O$ | Band assignments[a] $^6A_{1g}\rightarrow{}^4T_{1g}$ | $^6A_{1g}\rightarrow{}^4A_{2g}$ |
|---|---|---|---|---|
| Formate | Mull | 6950 | 10,400 | ~14,800, sh |
| | Water | | 11,100 (3·1) | |
| | Formic acid | | 10,250 (5·0) | ~15,000 (2·0), sh |
| Acetate | Mull | 6950 | 10,250 | ~15,400, sh |
| | Mull[b] | | 10,250 | 15,700 |
| | Water | | 10,700 (4·6) | |
| | Acetic acid | | 10,400 (6·4) | ~15,300 (2·8), sh |
| Monochloroacetate | Mull | 7000 | 10,250 | ~15,500, sh |
| | Mull[b] | 7000 | 10,300 | ~16,000, sh |
| | Water | | 10,900 (3·4) | |
| Trichloroacetate | Mull | 7050 | 10,200 | |
| Phenylacetate | Mull | 7000 | 10,300 | ~15,400, sh |
| | Chloroform | | 10,300 (7·5) | |
| Benzoate | Mull | 7100 | 10,500 | ~14,900, sh |
| | Chloroform | | 10,700 (19·8[c]) | |

[a] All band assignments are in cm$^{-1}$. Molar extinction coefficients per metal ion are given in parentheses. [b] At *ca.* 80 K. [c] Concentration dependent.

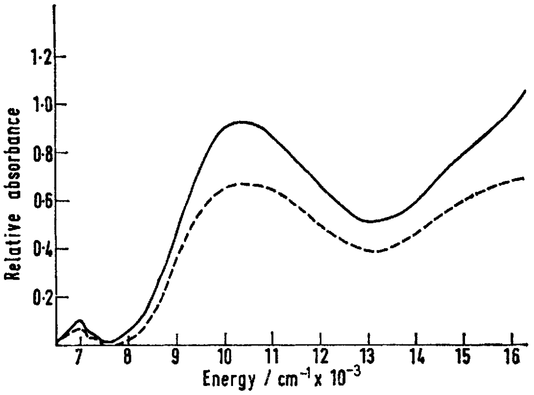

FIGURE 5 Mull electronic spectrum of the monochloroacetate complex on the same mull at room temperature (——) and *ca.* 80 K (- - - -)

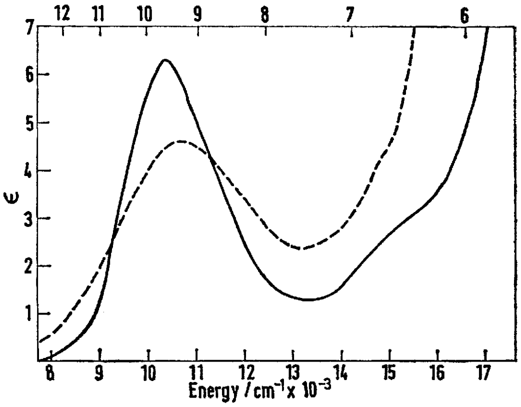

Figure 6 Solution electronic spectrum of the acetate complex in acetic acid and water; (- - - -) $H_2O$, (——) acetic acid

The electronic spectral properties of iron(III) carboxylate complexes have received little attention. Dubicki and Martin,[21] have reported the diffuse reflectance spectra of the iron(III) complexes formed with formate, acetate, and monochloroacetate ligands. The present results are in excellent agreement with their results. Baillie *et al.*[22] have studied the electronic spectral properties of several metal trifluoroacetate complexes. The spectrum of Fe(trifluoroacetate)$_3$ is very similar to the results reported in Table 5.

The band assignments presented in Table 5 appear reasonable [13] for high-spin iron(III) complexes in a pseudo-octahedral environment. The value of *Dq* is estimated to be *ca.* 1100 cm$^{-1}$. A more extensive evaluation of the various crystal-field parameters is not possible because of the paucity of *d–d* transitions. The spectrum of each of these complexes in a mull above 17,000 cm$^{-1}$ did not reveal the presence of the higher energy bands reported previously.[21] The molar extinction coefficients reported in Table 5 appear to be rather large for formally spin-forbidden transitions; however, a similar high intensity band has been reported [9,23] in a series of binuclear iron(III) complexes. Ferguson *et al.*[24] have noted a similar phenomenon in their study of the electronic spectral bands in several Mn$^{II}$ complexes. They concluded that the high band intensities could be attributed to magnetic interactions between pairs of manganese ions. A similar mechanism could account for the high molar extinction coefficients observed in the carboxylate complexes. If this is the case, the band intensity would be expected to show a temperature dependence. Indeed, the spectrum presented in Figure 5 on the same mull at two temperatures indicates that the intensity of the band at *ca.* 10,000 cm$^{-1}$ decreases with decreasing temperature. The authors are currently studying the temperature dependence of the intensities of the observed bands from room temperature to 20 K.

*Infrared Spectral Properties.*—The i.r. spectrum of each of the complexes has been measured and the results are presented in Table 6. The i.r. spectra of the acetate complex and sodium acetate are shown in Figure 7 for comparison. The i.r. spectra of sodium acetate and sodium formate have been studied in detail by Ito and Bernstein [25] and their assignments have been used in Table 6. The assignments for the acetate and formate complexes generally follow from a comparison with the spectra of the sodium salts. The i.r. and Raman spectrum of the acetate complex has previously been reported by Griffith.[26] A careful comparison of the results presented for the acetate complex with those presented by Griffith reveals several experimental discrepancies which cannot be explained by the authors. Griffith has performed calculations using the approach of Clarke and Woodward [27] to determine the approximate locations of the symmetric and asymmetric $\nu(M_3O)$ vibrations. He has concluded that for a $D_{3h}$ complex $\nu_{sym}(Fe_3O)$ should be found near 160 cm$^{-1}$ and $\nu_{asym}(Fe_3O)$ should be in the 500—600 cm$^{-1}$ region. Griffith could not locate the $\nu_{asym}(Fe_3O)$ absorption line in the acetate complex. The present work, however, reveals a broad moderate intensity absorption at 520 cm$^{-1}$ which the authors attribute to the $\nu_{asym}(Fe_3O)$ vibration. The exact origin of the additional bands located between 300 and 400 cm$^{-1}$ in the acetate and formate complexes is not certain but these bands appear to be associated with metal ligand bonding and may be the $\delta(Fe_3O)$ and $\nu_{sym}(Fe_3O)$ vibrational bands. More extensive i.r. and Raman studies will be required to assign reliably these lines. The origin of the sharp line at 1352 cm$^{-1}$ in the acetate complex is at present uncertain. Johnson *et al.*[28] have discussed the relationship between the separation of the symmetric and asymmetric $\nu$(COO) vibrational bands and the nature of the acetate coordination. For a bridging acetate ion, the separation is expected to remain the same as in free ionic acetate. The results in Table 6 indicate that the separation is 145 cm$^{-1}$ for the acetate complex and 164 cm$^{-1}$ for sodium acetate. This agreement is consistent with the proposed bridging nature of the acetate ligand. Unfortunately, the i.r. spectra of the monochloroacetate, trichloroacetate, phenylacetate, and benzoate complexes are so

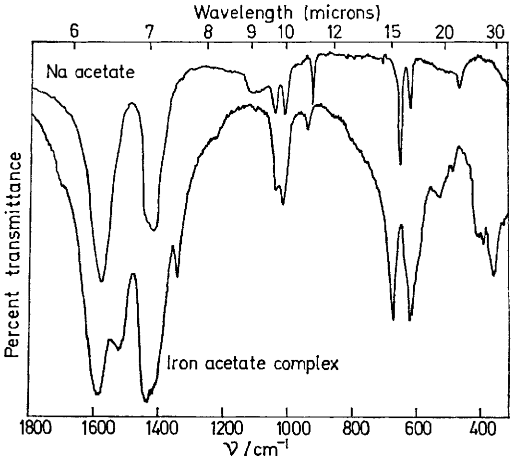

FIGURE 7 Infrared spectrum of the acetate complex and sodium acetate obtained in a KBr pellet

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complex that it is almost impossible to make any specific assignments of the bands observed in these complexes. The experimentally observed results are presented in Table 6.

TABLE 6

Infrared spectral results [a]

Band assignments

| Formate complex | $NaHCO_2$ [b] | Assignment | Acetate complex | $NaH_3C_2O_2$ [b] | Assignment |
|---|---|---|---|---|---|
| ~3400b,s | | $\nu_3(H_2O)$ | 3440b,s | | $\nu_3(H_2O)$ |
| ~3200b,s | | $\nu_1(H_2O)$ | ~3200b,s,sh | | $\nu_1(H_2O)$ |
| 2880w,sh | 2841 | $\nu(CH)$ | 2975w,sh | 2989w | $\nu(CH)$ |
| | | | | 2936w | $\nu(CH)$ |
| | | | 1720w,sh | 1720w [c] | ? |
| 1630b,s | 1567 | $\nu_{asym}(COO)$ | 1595b,s | 1578b,s | $\nu_{asym}(COO)$ |
| 1570m,sh | | $\nu_2(H_2O)$ | 1530b,s | | $\nu_2(H_2O)$ |
| 1388s | 1377 | $\delta(CH)$ or $\rho_r(COO)$ | | 1443 | $\delta(CH_3)$ |
| | | | | 1430 | $\delta(CH_3)$ |
| 1375s | 1366 | $\nu_{sym}(COO)$ | 1450b,s,asym | 1414 | $\nu_{sym}(COO)$ |
| | | | 1352m,sp | | $\nu(COO)$ ? |
| | | | 1240w,sh | | ? |
| 1050m | 1073 | $\pi$(CH or COO) | 1052m,sh | 1042m | $\rho_r(CH_3)$ |
| 830m,sp | | | 1035m,sh | 1009m | $\rho_r(CH_3)$ |
| 764s,sp | 772 | $\delta(OCO)$ | 954m | 924m | $\nu(CC)$ |
| | | | 663s | 646s | $\delta(OCO)$ |
| 605m,b | | | 612s,asym | 615m | $\pi$(CH or COO) |
| | | | 520b,w | | $\nu_{asym}(M_3O)$ |
| | | | 470w | 460w | $\delta(CH)$ or $\rho_r(COO)$ |
| 400m,b | | | 400m | | |
| | | | 380m | | |
| 330m,b | | | 350m | | |

Additional spectral data

Cl acetate: 1620b,s, 1560m,sh, 1435s, 1405m, 1265s, 1148m, 1123s, 1088s, 1045w,sh, 957m, 1034m, 802s, 690b,s, 625m, 512b,m, 385b,m, 315m

$Cl_3$ acetate: 1755m, 1670b,s, 1618b,s, 1545w,sh, 1440m,sh, 1400b,s, 1265w, 977s,sp, 855s, 842s, 750s,sp, 695b,s, 605b,m, 561m, 480b,s, 387s, 335m, 315m, 298m

Phenylacetate: 1680w,sh, 1605b,s, 1589s, 1562s, 1538s, 1501m,sp, 1449m,sp, 1432b,s, 1418b,s, 1340w, 1300m, 1287m, 1200m, 1172b,m, 1077m, 1031m, 950m, 912w, 845m, 762m, 730s, 711s, 640s,sh, 608b,s, 580s, 545m,sh, 468b,m, 395b,s, 320m

Benzoate: 1670w,sh, 1625m,sh, 1604s, 1568s, 1525b,m, 1498m,sp, 1450m,sh, 1415b,s, 1322w, 1313w, 1225b,w, 1181m, 1160w, 1125w, 1172m, 1129m, 1103w, 940w, 841w, 818w, 721s, 688m, 675s, 635b,s, 540b,w, 488b,s, 422w, 400m, 390w, 381w, 331m, 295w, 287m

[a] All results in $cm^{-1}$. Abbreviations: b, broad; s, strong; m, medium; w, weak; sh, shoulder; sp, sharp; sym, symmetric; asym, asymmetric. [b] Data and assignments taken from ref. 25. [c] Not observed in Figure 7 but reported in ref. 25.

## CONCLUSIONS

Several conclusions may be drawn from the preceding results. Of the six carboxylate complexes studied, the magnetic properties of the trichloroacetate, phenylacetate, and benzoate complexes indicate that the observed antiferromagnetic coupling is best described as nonequivalent. More specifically, two of the three pairs of iron atoms in the trinuclear complex are equivalently coupled while the third pair of iron atoms exhibit coupling of a different magnitude. The magnetic properties of the formate, acetate, and monochloroacetate complexes indicate that the three pairs of iron atoms are more nearly equivalently coupled than in the other complexes. However, based upon an analysis of the error limits associated with the magnetic measurements on the acetate complex, the authors have concluded that these complexes also exhibit nonequivalent antiferromagnetic coupling. The Mössbauer spectral studies of the complexes reveal quadrupole split absorption bands of asymmetric intensity. This asymmetry is attributed to the Gol'danskii–Karyagin effect which results from the anisotropy of the recoil-free fraction of the iron nucleus in its reduced symmetry co-ordination site. The electronic absorption spectra of the complexes reveal spin-forbidden absorption bands of rather high intensity. The mechanism by which the transition gains intensity is uncertain but appears to be related to the observed antiferromagnetic coupling within the molecule.

The authors thank Dr. W. A. Baker, jun., and Syracuse University for the use of the Faraday magnetic balance and the National Science Foundation for a grant. A Department of Defense Project Themis Grant, made possible the purchase of components for the Mössbauer spectrometer.

[2/1007 *Received, 5th May,* 1972]