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# Magnetic Susceptibility and Mössbauer Effect Studies of Some Anionic Iron(IV) Dithio Chelates

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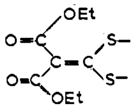
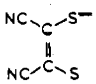
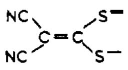
Three spin triplet iron(IV) complexes, the tris compound $Fe(S_2C_2(CN)_2)_3^{2-}$ and the mixed chelates $Fe(S_2C_2(CN)_2)_2(S_2C{:}C(CN)_2)_2^{2-}$ and $Fe(S_2C_2(CN)_2)_2(S_2C{:}C(COOC_2H_5)_2)^{2-}$, have been studied by magnetic susceptibility measurements and Mössbauer spectroscopy in the absence and in the presence of an external magnetic field. The moments of these compounds at room temperature correspond to the spin-only value for two unpaired electrons in a $t_{2g}^4$ configuration. At temperatures below 20 K their magnetic moments decrease drastically. A least-squares fit of the susceptibility data gives values of $D$ between 10 and 17 $cm^{-1}$ for the three compounds. The Mössbauer spectra feature well-defined quadrupole doublets which are temperature independent between 300 and 4.2 K. Application of an external magnetic field shows the sign of the electric field gradient of the tris compound to be positive and of the mixed chelates negative. The data are consistent with a trigonal distortion which together with spin–orbit coupling leaves an orbital singlet ground state. The magnitude of the observed quadrupole splitting is influenced by donation of charge to bonding orbitals.

## Introduction

Outstanding among the properties of the *N*,*N*-dialkyldithiocarbamate ligands, $(R_2dtc)^-$, or the 1,1-dicarboethoxyethylene-2,2-dithiolate dianion, $(DED)^{2-}$, I, is their ability to promote high oxidation states in various metal ions.[2-4] In particular, these 1,1-dithio ligands form iron complexes featuring the metal in the uncommon oxidation state 4+.[3,6-8] Another sulfur chelate that appears equally effective in stabilizing iron in the 4+ oxidation state is the 1,2-dicyano-1,2-ethylenedithiolate dianion, $(MNT)^{2-}$, II. Thus, the tris compound $(Ph_4As)_2[Fe(MNT)_3]$,[9] **1**, and the mixed chelate $(Ph_4P)_2[Fe(MNT)_2(i\text{-}MNT)]$,[10] **2**, where *i*-MNT is the 1,1-dicyanoethylene-2,2-dithiolate dianion, III, have compositions indicative of the presence of iron(IV) centers.


I = DED


II = MNT


III = i-MNT

The room-temperature magnetic moments of 3.0 $\mu_B$ for **1**[9] and 2.85 $\mu_B$ for **2**[10] are very similar to those obtained from the iron(IV) dithiocarbamates[6,7] and from $(BzPh_3P)_2[Fe(DED)_3]$.[2] The moments correspond to two unpaired electrons and indicate an octahedrally coordinated iron in a $t_{2g}^4$ configuration. However, there are other conceivable descriptions of the electronic structure of these dithiolene complexes. One such description could involve localization of one of the two electrons in an iron orbital and the other in a molecular orbital mainly of ligand character. This is equivalent to saying that the redox reaction

$$[Fe(t_{2g}^5)(MNT)]^{3-} \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} [Fe(t_{2g}^5)(\cdot MNT)]^{2-}$$

is centered on the ligand system leading to a coordinate radical anion (·MNT) while the iron ion remains probably unchanged in a trivalent low-spin configuration. The existence of the MNT ligand in the form of a radical anion has been postulated in the analogous $[V(MNT)]^{3-}$ complex on the basis of ESR results.[11] The complexes could also be described as iron(II) systems, in an $S = 1$ state, resulting from interligand oxidation of two MNT units. Structural data available for compound **1** support a dithiolato formulation of the MNT ligand and therefore a formal 4+ oxidation state for iron.[12]

Mössbauer spectroscopy can easily distinguish between the different oxidation states of iron. In addition, as in the more familiar cases of Fe(III) and Fe(II) compounds, Mössbauer data can be used to determine electronic parameters which characterize the state of the iron ion. Detailed magnetic susceptibility measurements over a wide range of temperatures furnish similarly parallel and supplementary information. To this aim, we report here the results of detailed Mössbauer and magnetic susceptibility measurements for compounds **1** and **2** and also for the related new mixed chelate $(Ph_4P)_2[Fe(MNT)_2(DED)]$, **3**.

## Experimental Section

The ligands $Na_2MNT$,[9] $K_2(i\text{-}MNT)$,[13] and $K_2DED$[13] were prepared according to previously published methods. Complex **1** was prepared as described in the literature.[9] The mixed chelates **2** and **3** are easily prepared as follows. To an acetone extract of the disodium salt $(Fe(MNT)_2)_2Na_2$, prepared by reacting the required amounts of $FeCl_3{\cdot}6H_2O$ and $Na_2MNT$ in aqueous solution, $K_2(i\text{-}MNT)$ or $K_2(DED)$ in a small amount of water was added followed by the corresponding quantity of $Ph_4PCl$ in alcohol. The crystals which were formed on standing for 2–4 h were collected, washed with water and alcohol, and dried in air. They were recrystallized from acetone–propan-2-ol in air. Analyses for C, H, and N, performed at the Analytical Services Laboratory of "Demokritos", gave the following results. Anal. Calcd for **1**: C, 57.96; H, 3.24; N, 6.79. Found: C, 58.46; H, 3.26; N, 6.66. Calcd for **2**: C, 62.40; H, 3.5; N, 7.3. Found: C, 62.77; H, 3.41; N, 7.00. Calcd for **3**: C, 61.55; H, 4.00; N, 4.48. Found: C, 61.58; H, 3.98; N, 4.35. The possibility of having mixtures in the mixed chelates was excluded from their Mössbauer spectra which showed the presence of only one iron compound. A mixture of $[Fe(MNT)_3]^{2-}$ with $[Fe(i\text{-}MNT)_3]^{3-}$ or with $[Fe(DED)]^{2-}$ would give a three- or four-line spectrum, respectively, since each of these compounds has a different Mössbauer spectrum.[8]

**Physical Measurements.** Mössbauer spectra were recorded with a conventional constant-acceleration spectrometer coupled with a multichannel analyzer operating in the time mode. The source was $^{57}Co$ in a Rh matrix. The system was calibrated with an iron foil absorber. Relative errors were less than ±0.01 mm/s. The parameters were obtained by a least-squares computer fit of the data. Magnetic susceptibilities were measured by application of the Faraday method, using $HgCo(NCS)_4$ as a calibrant. Measurements were performed at six different field strengths, viz., 3.50, 5.55, 8.60, 10.90, 12.00, and 13.00 kG in the temperature range 1–300 K. Temperature measurements were accurate to ±0.02 K. The accuracy of the measurements of the susceptibilities of the complexes was ±1% or better. The diamagnetic corrections were −535, −530, and $-613 \times 10^{-6}$ cgsu for compounds **1**, **2**, and **3**.

## Results and Discussion

**Magnetic Susceptibility.** The magnetic susceptibilities corrected for diamagnetism are shown in Table I. Figure 1 is a graph of the $\chi_M^{-1}$ as a function of temperature for compound **1**. It is clear that the susceptibility obeys the Curie–Weiss law, $\chi = C/(T - \Theta)$, between 15 and 300 K, while below 15 K a non-Curie–Weiss response is observed. Compounds **2** and **3** behave in a similar way. Above 15 K a linear least-squares fit of $\chi_M^{-1}$ vs. $T$ yielded the values of the

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Table I. Magnetic Susceptibility and Effective Magnetic Moments of the Complexes[a]

| $(PPh_4)_2[Fe(MNT)_3]$<br>TIP[b] = $-10 \times 10^{-6}$ cgsu<br>$\Theta = -0.64$ K<br>$C = 1.00$ emu/mol | | | $(PPh_4)_2[Fe(MNT)_2(i\text{-}MNT)]$<br>TIP[b] = $-8 \times 10^{-6}$ cgsu<br>$\Theta = -1.61$ K<br>$C = 0.94$ emu/mol | | | $(PPh_4)_2[Fe(MNT)_2(DED)]$<br>TIP[b] = $-100 \times 10^{-6}$ cgsu<br>$\Theta = -7.14$ K<br>$C = 1.20$ emu/mol | | |
|---|---|---|---|---|---|---|---|---|
| temp, K | $\chi_M$, $10^{-6}$ cgsu | $\mu_{eff}$, $\mu_B$ | temp, K | $\chi_M$, $10^{-6}$ cgsu | $\mu_{eff}$, $\mu_B$ | temp, K | $\chi_M$, $10^{-6}$ cgsu | $\mu_{eff}$, $\mu_B$ |
| 0.99 | 131 620 | 1.020 | 4.20 | 95 947 | 1.795 | 4.20 | 95 897 | 1.795 |
| 1.19 | 131 992 | 1.121 | 4.68 | 94 667 | 1.882 | 5.34 | 92 253 | 1.985 |
| 1.54 | 131 893 | 1.275 | 5.92 | 90 749 | 2.073 | 6.60 | 87 365 | 2.148 |
| 1.80 | 131 863 | 1.378 | 8.66 | 77 777 | 2.321 | 8.41 | 80 559 | 2.328 |
| 2.00 | 131 955 | 1.453 | 11.49 | 66 704 | 2.476 | 10.93 | 71 141 | 2.494 |
| 2.42 | 131 980 | 1.598 | 15.12 | 54 716 | 2.572 | 15.14 | 57 920 | 2.683 |
| 2.69 | 132 054 | 1.685 | 17.99 | 47 543 | 2.616 | 21.04 | 45 825 | 2.776 |
| 4.20 | 127 891 | 2.073 | 29.46 | 29 816 | 2.650 | 24.63 | 39 805 | 2.800 |
| 6.11 | 115 438 | 2.375 | 35.01 | 25 521 | 2.674 | 28.67 | 34 620 | 2.817 |
| 9.15 | 92 828 | 2.606 | 41.15 | 21 761 | 2.676 | 37.69 | 27 109 | 2.859 |
| 13.97 | 66 657 | 2.730 | 49.08 | 18 389 | 2.687 | 43.32 | 23 845 | 2.875 |
| 15.76 | 60 498 | 2.762 | 53.17 | 16 993 | 2.688 | 56.03 | 18 853 | 2.906 |
| 22.87 | 42 449 | 2.787 | 70.00 | 13 133 | 2.712 | 66.10 | 16 149 | 2.922 |
| 32.63 | 29 933 | 2.795 | 77.58 | 11 294 | 2.720 | 77.55 | 13 916 | 2.937 |
| 38.47 | 25 470 | 2.798 | 90.54 | 10 198 | 2.719 | 81.54 | 13 214 | 2.935 |
| 47.06 | 20 826 | 2.800 | 99.40 | 9 310 | 2.721 | 101.09 | 10 614 | 2.941 |
| 59.05 | 16 833 | 2.820 | 115.06 | 7 984 | 2.717 | 127.04 | 8 545 | 2.950 |
| 68.62 | 14 628 | 2.833 | 133.03 | 6 994 | 2.731 | 150.03 | 7 345 | 2.968 |
| 77.58 | 12 889 | 2.828 | 149.07 | 6 201 | 2.725 | 184.22 | 6 033 | 2.981 |
| 100.04 | 9 954 | 2.827 | 170.15 | 5 471 | 2.729 | 212.11 | 5 346 | 3.011 |
| 159.82 | 6 241 | 2.824 | 205.55 | 4 543 | 2.733 | 247.84 | 4 573 | 3.010 |
| 214.50 | 4 652 | 2.825 | 244.21 | 3 830 | 2.735 | 267.85 | 4 285 | 3.029 |
| 270.13 | 3 685 | 2.822 | 276.84 | 3 387 | 2.738 | 290.37 | 4 017 | 3.053 |
| 293.95 | 3 399 | 2.827 | 299.73 | 2 133 | 2.740 | 307.63 | 3 750 | 3.038 |

[a] Data refer to measurements at 8.60 kG; they are corrected for diamagnetism and in compound 3 for TIP. [b] This is a high-temperature TIP; the reported value is the mean average for temperatures higher than 70 K.

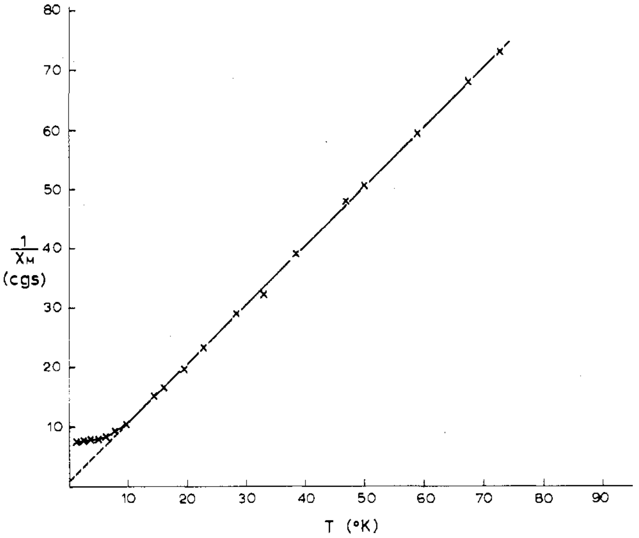

**Figure 1.** Temperature dependence of the reciprocal molar susceptibility for compound **1**.

Curie constant $C$ and the paramagnetic Curie temperature $\Theta$ listed also in Table I. Using these values and the relation $\chi_M = C/(T - \Theta) + \text{TIP}$, where TIP represents the high-temperature term in the susceptibility which is independent of temperature, we have obtained from a nonlinear least-squares-fitting procedure the values of TIP shown in Table I. For compounds **2** and **3** these values are very small and hence we have not made any TIP corrections in the experimentally determined $C$ and $\Theta$ values. However, since for compounds **3** the high-temperature TIP is of the order of 100 $\times$ $10^{-6}$ cgsu, the susceptibility data, $\mu_{eff}$, $C$, and $\Theta$, were properly corrected. These corrected values are reported in Table I.

From the magnetic moments (Table I) it is seen that for temperatures greater than 30 K the values of $\mu_{eff}$ for all three compounds are close to the spin-only value of 2.83 $\mu_B$ for two unpaired electrons. This, plus the fact that the susceptibility data conform to the Curie law, implies that the ground state is an orbital singlet level.[14] A low-symmetry component in the ligand field, having possibly its origin with Jahn–Teller distortion, is expected to remove the orbital degeneracy of the octahedral $^3T_{1g}$ term (Figure 2) yielding orbital singlet $^3A_1$ and doublet $^3E$ states. Spin–orbit coupling effects remove further the spin degeneracy in these states, and for the $^3A_1$ state a spin singlet state and a spin doublet state with $M_s$ values 0 and ±1 are obtained. Finally, the effect of a magnetic field is to split further the $|\pm1\rangle$ state. The magnetic properties can now be understood in terms of the energy levels at the right-hand side of this energy diagram. As the temperature approaches zero the $M_s = 0$ level will be the only one occupied and the moment will tend to zero. At higher temperatures a thermal distribution over the three levels will confer to the moment a certain value. The variation of the $\mu_{eff}$ with temperature for compound **1** is illustrated in Figure 3. It is clear that the moment falls off sharply below 15 K indicating that the lowest lying state is the $M_s = 0$ level. Similar plots were obtained for the other compounds. This type of thermal behavior of the magnetic moment is characteristic of a $t_{2g}{}^4$ ion in an octahedral field perturbed by an axial field and by spin–orbit coupling.[15]

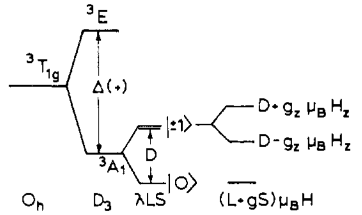

**Figure 2.** Schematic representation showing the splitting of the octahedral $^3T_{1g}$ term under the action of a trigonal-field component, spin–orbit coupling, and an external magnetic field.

Another possibility would be that the parameter $\Delta$ is negative leading to an $^3E$ ground state which through spin–orbit coupling leaves two low-lying spin singlet, nonmagnetic

**Table II.** Spin Hamiltonian Parameters Derived from Susceptibility Data

| compd | $D$, $cm^{-1}$ | $E$, $cm^{-1}$ | $g_x$ | $g_y$ | $g_z$ | $\Delta$,[a] $cm^{-1}$ |
|---|---|---|---|---|---|---|
| 1 $(PPh_4)_2[Fe(MNT)_3]$ | 10.0 | 1 | 2.01 | 2.01 | 1.99 | 3060 |
| 2 $(PPh_4)_2[Fe(MNT)_2(i\text{-}MNT)]$ | 15.0 | 1 | 2.04 | 2.04 | 1.96 | 2040 |
| 3 $(PPh_4)_2[Fe(MNT)_2(DED)]$ | 17.0 | 1 | 2.10 | 2.10 | 1.98 | 1800 |

[a] Approximate values.

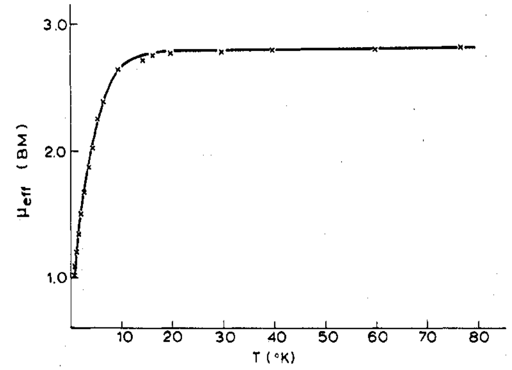

**Figure 3.** Temperature variation of the effective magnetic moment for compound **1**.

states.[15] However, in this case we would expect a marked temperature dependence of the magnetic moment in the high-temperature region ($T > 50$ K). To demonstrate this dependence we have calculated effective magnetic moments as a function of the parameters $\Delta$ and $\lambda$, where $\lambda$ is the one-electron spin–orbit parameter, using the expressions given by Kamimura.[15] The results of these calculations are shown in Figure 4 for $\Delta = +2000\ cm^{-1}$ (solid curve) and $-2000\ cm^{-1}$ (broken curve) and $\lambda = -380\ cm^{-1}$. It is seen that the magnitude of the magnetic moment and its thermal variation are different in each case. A similar behavior is also borne out from the tabulated results of Figgis et al., who have studied the magnetic properties of the $^3T_1$ ground term under the perturbation of an axial ligand field component, spin–oribt coupling, and the orbital reduction factor $\kappa$.[16] In general, the magnetic results in the present work are consistent with an $^3A_1$ ground state and a positive value of $\Delta$.

**Table III.** Mössbauer Results

| | 297 K | | 77 K | | 4.2 K | | |
|---|---|---|---|---|---|---|---|
| compd | $\delta$,[a] mm/s | QS, mm/s | $\delta$,[a] mm/s | QS, mm/s | $\delta$,[a] mm/s | QS, mm/s | sign of $V_{zz}$ |
| 1 $(PPh_4)_2[Fe(MNT)_3]$ | 0.012 | 1.53 | 0.105 | 1.59 | 0.114 | 1.61 | + |
| 2 $(PPh_4)_2[Fe(MNT)_2\text{-}(i\text{-}MNT)]$ | 0.012 | 1.58 | 0.123 | 1.63 | 0.133 | 1.64 | – |
| 3 $(PPh_4)_2[Fe(MNT)_2\text{-}(DED)]$ | 0.023 | 1.75 | 0.110 | 1.82 | 0.125 | 1.83 | – |

[a] Relative to iron at room temperature.

The temperature dependence of the bulk susceptibility of the powdered samples was treated using the equation

$$\chi_M = \frac{N\beta^2}{3\left(1 + \exp\left(-\frac{D+E}{kT}\right) + \exp\left(-\frac{D-E}{kT}\right)\right)} \left[\frac{g_z^{\,2}}{E}\left(\exp\left(-\frac{D-E}{kT}\right) - \exp\left(-\frac{D+E}{kT}\right)\right) + \frac{2g_x^{\,2}}{D+E} \times \left(1 - \exp\left(-\frac{D+E}{kT}\right)\right) + \frac{2g_y^{\,2}}{D-E}\left(1 - \exp\left(-\frac{D-E}{kT}\right)\right)\right]$$

in which $D$ and $E$ are the zero-field splitting parameters and the other symbols have their usual significance. This equation was derived by Birker et al.[17] taking into account the energy levels arising from the $^3A_1$ state. It was subsequently used by Oosterhuis et al.[7] and by Reiff et al.[18] to treat the susceptibility data of $[Fe(Et_2dtc)_3]BF_4$ and of some spin triplet iron(II) compounds. The curve superimposed on the data points in Figure 3 is a least-squares fit to the temperature dependence of the magnetic moment for compound **1**. The best values of $D$, $E$, $g_x$, $g_y$, and $g_z$ obtained for all three compounds are listed in Table II. Perturbation theory relates $D$ to $\Delta$ by the expression $\Delta = \lambda^2/4D$.[7] Assuming $\lambda$ to be about $-350\ cm^{-1}$, as in the case of the iron(IV) dithiocarbamates,[8] the above equation gave the approximate values of $\Delta$ listed also in Table II. In the present work the values of $\Delta$ are much higher than in the other known $Fe^{IV}S_6$ systems, namely, the various $[Fe(R_2dtc)]^+(BF_4)^-$ or $-(ClO_4)^-$ and the $(BzPh_3P)_2[Fe(DED)_3]$

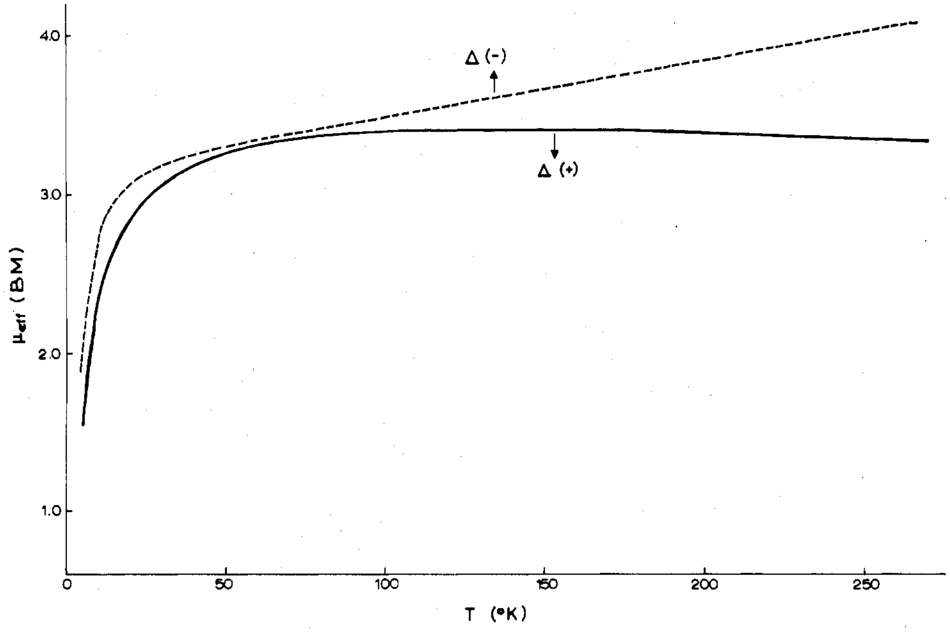

**Figure 4.** Effective magnetic moment vs. temperature. The curves have been calculated on the basis of equations given in ref 14 and by assuming $\lambda = -380\ cm^{-1}$ and $\Delta = 2000\ cm^{-1}$ (solid line) or $\Delta = -2000\ cm^{-1}$ (broken line).

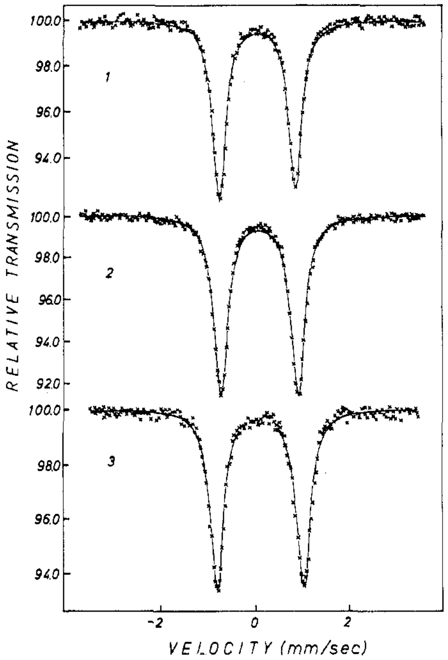

**Figure 5.** Zero-field Mössbauer spectra of complexes **1**, **2**, and **3** at 4.2 K. The full lines are least-squares fits with Lorentzian line shapes.

complexes.[8] The different values are reflected in the different temperature responses of the quadrupole splitting in the several $Fe^{IV}S_6$ complexes as we shall see shortly.

**Mössbauer Spectra.** The Mössbauer results for compounds **1**–**3** are listed in Table III. Characteristic spectra are shown in Figure 5. At zero applied field the spectra between 4.2 and 300 K comprise well-defined quadrupole doublets. The spectrum of compound **1** was recorded at 1.5 K in order to examine the possibility of hyperfine splitting and magnetic ordering. The spectrum remained unchanged with no evidence of paramagnetic relaxation or magnetic ordering.

The isomer shifts of the complexes are very close to the values of other low-spin iron(IV) compounds.[8,20,21] In particular, the shifts for compound **1** at various temperatures (Table III) are smaller than the corresponding values of the analogous low-spin iron(III) compound $(Ph_4P)_3[Fe(MNT)_3]$, i.e., 0.29 (300 K), 0.41 (77 K), and 0.43 (4.2 K) relative to the metal iron.[22] The decrease is consistent with the removal of one 3d electron on passing from iron(III) ($d^5$) to iron(IV) ($d^4$). Similarly the shifts are smaller than that of the pseudooctahedral iron(II) ($d^6$), $S = 1$, $Fe(phen)_2F_2{\cdot}4H_2O$ compound which has an isomer shift of 0.24 mm/s at room temperature relative to natural iron.[23] The isomer shift depends directly on the s-electron density at the nuclear site; indirectly it is affected by changing the population of the p or d orbitals since these exert a screening effect on the s orbitals. Accordingly, a $d^4$ configuration in relation to a $d^5$ or $d^6$ configuration is expected to screen less of the s-electron density and to give smaller isomer shifts. In this way the isomer shift data support an iron(IV) formulation or $d^4$ state for all three compounds.

All three complexes possess sizable quadrupole splittings, QS, which remain constant within experimental error between 300 and 4.2 K. Simple crystal field calculations show that the octahedral $^3T_{1g}$ term yields a zero value for the principal component of the electric field tensor, $V_{zz}$. The size, therefore, of the observed quadrupole splitting is in line with the presence of a low-symmetry component in the crystal field which splits the $^3T_{1g}$ state into a singlet $^3A_1$ state and a doublet $^3E$ state (Figure 3). Moreover, the constancy of the quadrupole splitting between 300 and 4.2 K indicates that the separation between $^3A_1$ and $^3E$ is in excess of 1000 $cm^{-1}$. In contrast, the QS of the various $[Fe(R_2dtc)_3]^+$ complexes and of $(BzPh_3P)_2[Fe(DED)_3]$ are temperature dependent owing to the smaller $\Delta$ values which allow contributions to the electric field gradient from the next $^3E$ state.[8] Temperature-independent quadrupole splittings have been observed in the tetragonally distorted iron(IV) complexes of $[Fe(diars)_2X_2](BF_4)_2$ (X = Cl, Br; diars = *o*-phenylenebis(dimethylarsine))[20] and of compound ES derived from cytochrome *c* peroxidase.[21]

In the present complexes the iron ion is surrounded by three bidentate ligands which to a first approximation confer to the molecules a trigonal symmetry. The $^3A_1$ or $^3E$ states in this symmetry are described by different wave functions which are expected to affect differently the magnitude and sign of the $V_{zz}$. In the framework of simple crystal field theory the maximum value of $V_{zz}$ is obtained when the ground state is a singlet and half as much when it is a doublet. The size of the quadrupole splitting of the systems studied at present can be compared with those of the trigonally distorted iron(IV) dithiocarbamates, 2.3–2.5 mm/s, which have orbital singlet ground states.[7] The smaller quadrupole splittings observed in the present molecules indicate that the ground state is either an orbital doublet or a singlet, but in either case extensive covalency effects have caused a significant reduction of the quadrupole splitting. Such reductions in the QS are not uncommon and reflect the extent of $\pi$ interactions.[21] Two such interactions between the iron d orbitals and the MNT molecular orbitals are possible: (1) overlap of the iron $d_{z^2}$ and ligand $\pi_h$ orbitals ($sp^2$-hybridized lone pair on sulfur) and (2) overlap of the iron $d_{xy}$ and $d_{x^2-y^2}$ and ligand $\pi_v$ orbitals (p orbitals perpendicular to the ligand plane). If the ground state is assumed to be $^3A_1$, the $d_{z^2}$ orbital is fully occupied and so the only possible $\pi$ interactions involve flow of charge from the $\pi_v$ ligand orbitals to the partially filled $d_{xy}$ and $d_{x^2-y^2}$ metal orbitals. Transfer of this kind will in part compensate for the high positive charge on the iron ion and will lower the quadrupole splitting to the observed values.

The nature of the ground state can be further deduced from the sign of the $V_{zz}$. This can be determined from the magnetically perturbed Mössbauer spectra obtained in an external magnetic field. The sign of the electric field gradient at the iron nucleus depends on the distribution of all extranuclear charges. The two major contributions come from electrons localized on the metal and from electrons taking part in chemical bonding. For the former contribution a straightforward calculation shows that a negative $V_{zz}$ corresponds to an $^3A_1$ state based on the $t_{2g}^0 = d_{z^2}$ one-electron wave function while a positive $V_{zz}$ corresponds to an $^3E$ state based on the $t_{2g}^+ = (^2/_3)^{1/2}d_{x^2-y^2} - (^1/_3)^{1/2}d_{xz}$ and $t_{2g}^- = (^2/_3)^{1/2}d_{xy} + (^1/_3)^{1/2}d_{yz}$ one-electron wave function. On the other hand, the bonding electrons yield a positive $V_{zz}$ when bonding is stronger in the *xy* plane and a negative $V_{zz}$ when bonding is stronger in the *z* direction. Since in metal–dithiolene complexes the ligand $\pi_v$ or $\pi_h$ molecular orbitals have proper energy and symmetry for bonding interactions with the metal d orbitals,[24] we expect the bonding electrons to have a substantial effect on the sign of $V_{zz}$. The spectra obtained in a magnetic field of 40 or 60 kG applied perpendicularly to the $\gamma$ rays at the indicated temperatures are shown in Figure 6. They exhibit a nearly "diamagnetic" behavior similar to that observed in the iron(IV) dithiocarbamates[5,7] and other iron(IV) complexes.[20,21] The spectra of compounds **2** and **3** consist of a doublet at negative velocity and a triplet at positive velocity, showing that $V_{zz}$ is of negative sign.[25] In contrast, the spectrum of compound **1** features the triplet at negative velocity indicating a positive $V_{zz}$. In the mixed chelates **2** and **3** the negative $V_{zz}$ implies an overwhelming contribution from nonbonding electrons and an $A_1$ state in accord with simple

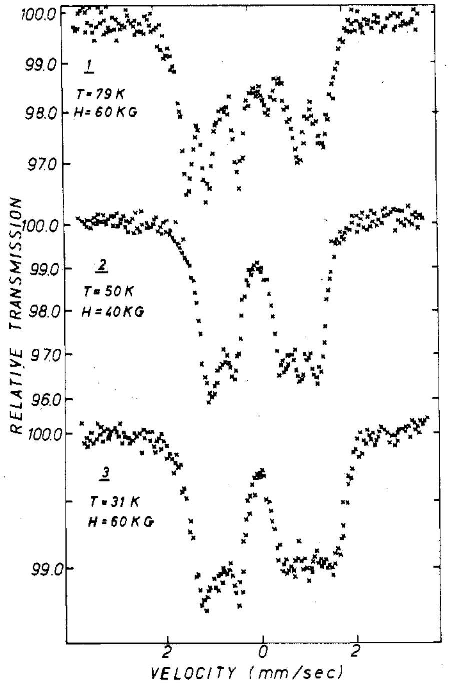

**Figure 6.** Magnetically perturbed Mössbauer spectra of compounds **1**, **2**, and **3**. Transverse magnetic fields and temperatures are as indicated.

crystal field calculations. However, in the case of the tris compound the nature of the ground state cannot be clearly concluded from the sign of $V_{zz}$. Here, according to the crystal field model the positive sign of $V_{zz}$ indicates an $^3E$ state. Yet a singlet $^3A$ state is still possible provided that the **efg** generated by covalency is stronger than that generated by the nonbonding electron. It appears that replacement of one 1,2-dithiolate ligand by one 1,1-dithiolate ligand affects considerably the bonding scheme in these complexes resulting in different signs of $V_{zz}$. In fact it has been noted that the 1,2-dithiolene ligands show more substantial $\pi$ bonding, as evidenced by shorter metal–sulfur bonds, in comparison to 1,1-dithiolates.[26] Ferrous phthalocyanine is another compound which behaves similarly. The ground state in this molecule is a $^3B$ term which on the basis of nonbonding electron configuration gives a negative $V_{zz}$. However, the observed quadrupole interaction is positive due to a prevailing covalence contribution.[27]

In conclusion, the combination of magnetic susceptibility and Mössbauer results shows that the electronic configuration of iron in compounds **1**, **2**, and **3** is $d^4$. A model based on a $d^4$, $S = 1$ assignment with the iron in an octahedral environment perturbed by a trigonal-field component is in line with the susceptibility and Mössbauer results. The trigonal distortion leaves an orbital singlet–spin triplet $^3A_1$ term as the electronic ground state which is separated from the next $^3E$ state by an amount lying between 1800 and 3000 cm$^{-1}$. The magnitude of the QS in each compound implies strong covalency effects which are understandable through charge donation from the ligand $\pi_v$ to the metal $d_{xy}$ and $d_{x^2-y^2}$ orbitals.

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