CONTRIBUTION FROM BELL TELEPHONE LABORATORIES, INC.,
MURRAY HILL, NEW JERSEY 07971

Synthesis and Low-Temperature Mössbauer Effect of Several Intermediate-Spin Iron(III) Complexes

BY H. H. WICKMAN AND A. M. TROZZOLO

Received July 10, 1967

A series of pentacoordinate bis(N,N-dialkyldithiocarbamato)iron(III) halides has been prepared in which the ground Fe term is an orbital singlet and spin quartet. The new methods of preparation involve the reactions of the appropriate ferric halide, FeX_3, with (1) the N,N,N′,N′-tetraalkylthiuram disulfide, (2) the sodium dialkyldithiocarbamate, and (3) the tris-(N,N-dialkyldithiocarbamato)iron (III) complexes. These techniques were employed to produce variations in the basic unit, bis(N,N-diethyldithiocarbamato)iron(III) chloride, which shows a magnetic ordering at low temperatures (T_c = 2.5°K). While the paramagnetic character of the ground quartet remains independent of these structural changes, no new magnetically ordered systems were found. However, low-temperature Mössbauer data suggest that the small zero-field splitting of the quartet manifold is markedly affected by the halo constituent of the pentacoordinate complex.

Introduction

While an extensive range of transition metal ion dithiocarbamates is known,[1] considerable interest has been focused on the iron(III) dithiocarbamates. The tris compounds, $Fe^{III}(S_2CNRR')_3$, possess magnetic properties in accord with the predictions of ligand field theory for trivalent iron in a $3d^5$ configuration in octahedral symmetry. Both high-spin ($S = {}^5/_2$) and low-spin ($S = {}^1/_2$) species, together with complexes whose magnetic behavior suggest a thermal equilibrium between these states, have been reported.[2-4]

Recently, a new class of pentacoordinate iron(III) complexes has been synthesized which is of the type $(R_2NCS_2)FeX$, where R is a simple alkyl group and X a halide.[5-8] These compounds have a number of interesting properties, the most important being an orbitally nondegenerate, spin quartet ground term. The evidence for this behavior includes ac and dc magnetic susceptibility, epr, and Mössbauer effect studies.[6,7,9] Most of these compounds are simple paramagnets, although the $((C_2H_5)_2NCS_2)_2FeCl$ derivative has shown a magnetic ordering at low temperatures (T_c = 2.5°K).[9]

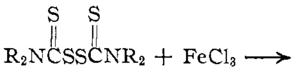
In the following we describe several methods of synthesis and crystal growth of the basic pentacoordinate unit, including alternatives to those previously described in the literature. In particular, we consider those compounds representing the minimal structural changes that are possible, starting from the basic unit, $Fe(S_2CN(C_2H_5)_2)_2Cl$. A methyl group has been added to or subtracted from the alkyl constituent, and a bromide ion has replaced the chloro group. Bulk dc and ac susceptibility data show that with any of these substitutions the magnetic ordering property is lost. However, the paramagnetic character of the ground quartet remains substantially independent of structural changes. The difference in magnetic properties among the compounds appears as a change in sign of the splitting of the lower quartet level on substitution of a bromo for a chloro group; low-temperature Mössbauer effect (ME) data illustrate this effect.

Synthetic Methods

The method of synthesis employed by Martin, White, and Hoskins[6,7] involves the reaction of the tris(N,N-dialkyldithiocarbamato)iron(III) complex (Fe(DTC)$_3$) with the appropriate hydrogen halide in benzene solution.

$$Fe(DTC)_3 + HX \longrightarrow Fe(DTC)_2X + DTCH \qquad (1)$$

The present authors have employed somewhat different approaches to the synthesis of the Fe(DTC)$_2$X. The first was to treat the tetraalkylthiuram disulfide, $R_2N(C{=}S)S_2(C{=}S)NR_2$, with an excess of ferric chloride in chloroform solution



$$R_2N\overset{\overset{S}{\|}}{C}S S\overset{\overset{S}{\|}}{C}NR_2 + FeCl_3 \longrightarrow (DTC)_2FeCl(s) + \text{other products} \qquad \text{(method 1)}$$

The second method involved the treatment of the sodium dialkyldithiocarbamate, NaDTC, with an excess of the appropriate ferric halide in acetone or ethanol solution

$$2NaDTC + FeX_3 \longrightarrow Fe(DTC)_2X + 2NaCl \qquad \text{(method 2)}$$

A third approach, similar to that of Martin, White, and Hoskins,[6] employed the reaction of the tris complex, Fe(DTC)$_3$, with excess ferric halide

$$2Fe(DTC)_3 + FeX_3 \longrightarrow 3Fe(DTC)_2X \qquad \text{(method 3)}$$

Methods 2 and 3 were the most convenient and offer a number of interesting synthetic applications. For example, it was found that the Fe(DTC)$_2$X could be converted to the tris compound by the addition of NaDTC to the solution. This (reversible) transforma-

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[1] G. D. Thom and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., Amsterdam, 1962.

[2] L. Cambi and L. Szego, *Ber.*, **66**, 656 (1933).

[3] A. H. White, E. Kokot, R. Roper, H. Waterman, and R. L. Martin, *Australian J. Chem.*, **17**, 294 (1964).

[4] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.* (London), **A280**, 235 (1964).

[5] H. H. Wickman and A. M. Trozzolo, *Phys. Rev. Letters*, **15**, 156 (1965); *Erratum, ibid.*, **16**, 162 (1966).

[6] B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 677 (1966).

[7] R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

[8] E. Frank and C. Abeledo, *ibid.*, **5**, 1453 (1966).

[9] H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt, *Phys. Rev.*, **155**, 563 (1967).

tion is easily visible owing to the brown color of the tris complexes *vs.* the green bis complexes[8]

$$\mathrm{Fe(DTC)_2X + NaDTC \longrightarrow Fe(DTC)_3 + NaX} \quad (2)$$

With this approach, it should be possible to synthesize mixed complexes of the type $(R_2NCS_2)_2Fe(S_2CNR'_2)$ as well as $(R_2NCS_2)(R'_2NCS_2)FeX$. In addition, method 2 is attractive in view of the ready availability of sodium dithiocarbamates, as it offers a direct path to the $Fe(DTC)_2X$ without recourse to isolation of the intermediate $Fe(DTC)_3$ compounds.

The details of the chemical preparations and analyses follow.

Monochlorobis(N,N-dimethyldithiocarbamato)iron(III) (Method 1).—Tetramethylthiuram disulfide (2.5 g) and ferric chloride (1.3 g) were stirred in acetone (50 ml). A greenish black solution formed upon mixing and a black solid precipitated. Absolute alcohol (10 ml) was added and the reaction mixture was allowed to stand for 3 hr at 20°. The precipitate was filtered and washed with acetone. The very fine black crystals when examined with a polarized light microscope exhibited strong pleochroism (red ↔ green). *Anal.* Calcd for $C_6H_{12}N_2S_4ClFe$: C, 21.75; H, 3.65; N, 8.45; S, 38.70; Cl, 10.70; Fe, 16.85. Found: C, 22.17; H, 3.92; N, 8.43; S, 36.62; Cl, 10.94; Fe, 17.81.

Monochlorobis(N,N-diethyldithiocarbamato)iron(III) (Method 2).—Sodium N,N-diethyldithiocarbamate (3.0 g) was treated with anhydrous ferric chloride (2.0 g) in absolute alcohol (75 ml). The greenish black complex precipitated immediately and was filtered, dried, and recrystallized from chloroform. *Anal.* Calcd for $C_{10}H_{20}N_2S_4ClFe$: C, 30.97; H, 5.20; N, 7.22; S, 33.07; Cl, 9.14; Fe, 14.40. Found: C, 30.96; H, 5.40; N, 7.15; S, 32.81; Cl, 9.03; Fe, 13.50.

Monochlorobis(N,N-diisopropyldithiocarbamato)iron(III) (Method 2).—A solution of sodium N,N-diisopropyl dithiocarbamate (3.0 g) in acetone (100 ml) was *added to* ferric chloride (3.0 g) in acetone (50 ml). The resulting black solution was allowed to stand for 4 hr. The black glistening crystals were filtered, washed with acetone, and dried. *Anal.* Calcd for $C_{14}H_{28}N_2S_4ClFe$: C, 37.88; H, 6.36; N, 6.31; S, 28.89; Cl, 7.99; Fe, 12.58. Found: C, 37.63; H, 6.46; N, 6.58; S, 28.65; Cl, 8.17; Fe, 12.84.

Monobromobis(N,N-diethyldithiocarbamato)iron(III). (Method 2).—This compound was prepared in the same manner as the monochloro derivative, except that ferric bromide was used in place of ferric chloride. *Anal.* Calcd for $C_{10}H_{20}N_2S_4BrFe$: C, 27.80; H, 4.67; N, 6.48; S, 29.70; Br, 17.50; Fe, 12.93. Found: C, 28.36; H, 4.83; N, 6.64; S, 29.33; Br, 18.18; Fe, 12.51.

No striking instabilities of the freshly precipitated material were observed. However, in the presence of moisture or alcohols a (reversible) conversion to the tris form occurs. The bis-dimethyl derivative was virtually insoluble after formation and we could find no useful solvent for this material.

To obtain single crystals for epr work some experimentation with crystal-growing techniques was performed. With the exception noted above, the bis derivatives are quite soluble in chloroform, while only slightly soluble in toluene. We found that excellent single crystals could be grown starting from a saturated 50:50 (by volume) solution of chloroform and toluene. Slow evaporation (3–5 weeks) produced crystals 2–3 mm × 1–3 mm with a thickness of ~0.5 mm. Each homolog showed a slightly different growth habit. The ethylchloro and ethylbromo derivatives approximated rectangular prisms while the diisopropyl derivative was parallelogram shaped. Analyses, performed before and after recrystallization from the solvent mixture, showed a variable solvent content in the crystals. Those specimens used in epr work tended to deteriorate within 1 week after removal from the mother liquor. Our general experience here indicates that single-crystal measurements are most reliably performed on freshly grown crystals. Single crystals of lesser quality may also be obtained from chloroform or acetone solutions.

The crystal structure of the $Fe(S_2CN(C_2H_5)_2)_2Cl$ complex has been reported by Hoskins, Martin, and White.[6] The structural formula and local iron environment of this derivative are shown in Figure 1. The chemical similarities of all of the related complexes prepared to date indicate that the iron environment is qualitatively similar in different species. The point group symmetry at the iron(III) is therefore assumed to be C_{2v} and the ligand fields have rhombic symmetry.

Low-Temperature Mössbauer Experiments

The Mössbauer effect in the four derivatives mentioned above have been observed with sample temperatures from 300 to 1.2°K. At temperatures in the range 2–10°K, rather complex relaxation effects have been observed in the chloro derivatives;[5,9] a full discussion of these spectra will be given elsewhere. With the exception of $Fe(S_2CN(C_2H_5)_2)_2Cl$, the samples showed no magnetic orderings. These results were also confirmed by dc susceptibility data to 1.4°K and by ac susceptibility data to 0.3°K. The four homologs and their effective moments, derived from dc susceptibility data, are listed in Table I.[10] The moments show no marked dissimilarities and are in good agreement with the theoretical effective moment of 3.88 BM predicted for $S = {}^3/_2$ and $g = 2.00$.

Information concerning the magnetic hyperfine interactions within the quartet level is best derived from low-temperature data where relaxation effects are minimal. In Figure 2 we give the Mössbauer absorption, at 1.2°K, of (a) $Fe(S_2CN(C_2H_5)_2)_2Br$, (b) $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$, (c) $Fe(S_2CN(C_2H_5)_2)_2Cl$, and (d) $Fe(S_2CN(CH_3)_2)_2Cl$. The nuclear parameters consistent with these data may be found in Table II. The prominent features of the spectra are summarized as follows.

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[10] The dc and ac susceptibility data were kindly supplied by H. J. Willams and G. W. Hull, who employed techniques described in ref 9.

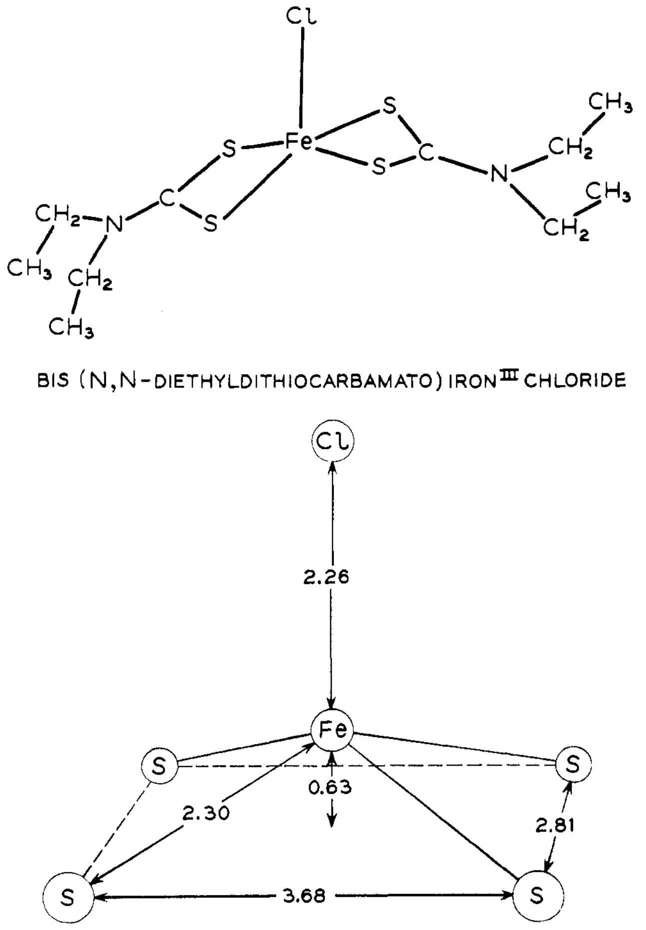

Figure 1.—Structural formula and local iron symmetry in $Fe(S_2CN(C_2H_5)_2)_2Cl$, after Hoskins, Martin, and White.[6]

TABLE I
MAGNETIC SUSCEPTIBILITIES OF REPRESENTATIVE PENTACOORDINATE IRON COMPLEXES

Complex	Effective moment, BM	Magnetic ordering
$Fe(S_2CN(CH_3)_2)_2Cl$	3.94	No
$Fe(S_2CN(C_2H_5)_2)_2Cl$	4.01	Yes
$Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$	3.93	No
$Fe(S_2CN(C_2H_5)_2)_2Br$	3.96	No

(a) **$Fe(S_2CN(C_2H_5)_2)_2Br$.**—A simple quadrupole doublet is observed from 300 to 1.2°K. No appreciable temperature dependence was found; at 1.2°K the splitting is 0.288 ± 0.004 cm/sec.

(b) **$Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$.**—A typical multiline pattern is found. The data are consistent with a paramagnetic hyperfine field H_{eff} together with a large electric field gradient (EFG) with the major axis perpendicular to the direction of H_{eff}. In Table II, θ and φ are conventional spherical polar coordinates defining the orientation of the EFG tensor with respect to H_{eff}.

(c) **$Fe(S_2CN(C_2H_5)_2)_2Cl$.**—This spectrum is quite similar to that of (b). In the latter case, however, the sample is paramagnetic, while here the material is ferromagnetically ordered, $T_c = 2.5$°K. The parameters characterizing the data are given in Table II; the similarity of these parameters with those of the paramagnetic homolog (b) is striking. The data reported here give the polycrystalline absorption in the ordered state at 1.2°K. In the earlier work, the absorber was composed of somewhat larger crystallites which have a tendency to pack in such a way that a

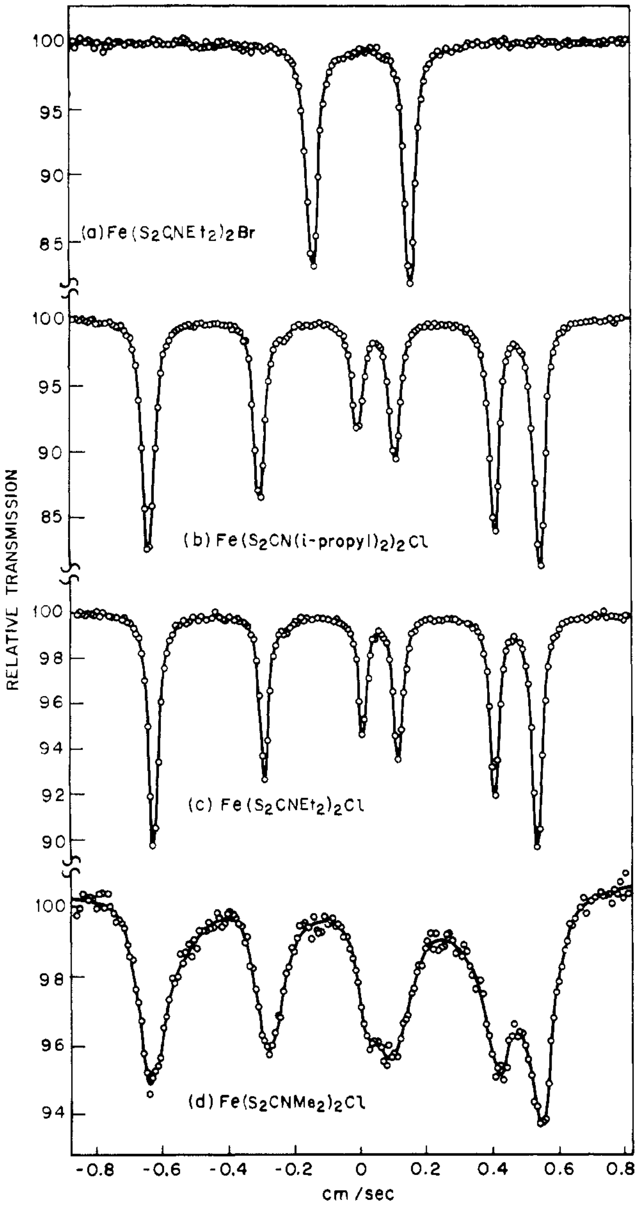

Figure 2.—Mössbauer effect at 1.2°K in polycrystalline absorbers of (a) $Fe(S_2CN(C_2H_5)_2)_2Br$, (b) $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$, (c) $Fe(S_2CN(C_2H_5)_2)_2Cl$, and (d) $Fe(S_2CN(CH_3)_2)_2Cl$.

TABLE II
NUCLEAR SPIN-HAMILTONIAN PARAMETERS WHICH REPRODUCE THE MÖSSBAUER SPECTRA OF FIGURE 2

Complex	Nuclear hyperfine data
(a) $Fe(S_2CN(C_2H_5)_2)_2Br$	ΔE (1.2°K) = 0.288 ± 0.004 cm/sec $= eqQ/2\sqrt{1+(\eta^2/3)}$
(b) $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$	$H_{eff} = 334 \pm 5$ koersteds, $eqQ/2 = 0.268 \pm 0.003$ cm/sec, $\eta = 0.16 \pm 0.01$, $\varphi = 0$, $\theta = 90°$
(c) $Fe(S_2CN(C_2H_5)_2)_2Cl$	$H_{eff} = 333 \pm 5$ koersteds, $eqQ/2 = 0.268 \pm 0.004$ cm/sec, $\eta = 0.15 \pm 0.01$, $\varphi = 0$, $\theta = 90°$
(d) $Fe(S_2CN(CH_3)_2)_2Cl$	$H_{eff} = 338 \pm 10$ koersteds, $eqQ/2 \cong 0.266$ cm/sec, $\eta \cong 0.15$, $\varphi = 0$, $\theta = 90°$

geometrically polarized absorber was produced. The relative intensities of Figure 2c and those in ref 9 (Figure 4) are slightly different for this reason.

(d) **$Fe(S_2CN(CH_3)_2)_2Cl$.**—In this system a modestly well-defined magnetic hfs is observed. The material is paramagnetic and the broadening of the lines arises from electronic relaxation among the electronic levels. The estimated field, H_{eff}, and EFG are similar to those in (b) and (c). The shorter relaxation times are probably due to decreased iron–iron separations in this compound, which is the smallest homolog studied.

Discussion

The ground electronic term in the present series of complexes is an orbital singlet and spin quartet. The magnetic properties of the iron ion are therefore to good approximation ascribed entirely to the four levels of the $S = {}^3/_2$ manifold. The interpretation of the Mössbauer magnetic hfs requires knowledge of the magnetic interaction between the quartet levels and nucleus. In orbitally nondegenerate iron states, such as Fe^{3+} (^6S), or the present case, the interaction with the nucleus is primarily due to the isotropic contact interaction arising from core polarization. The standard procedure under these circumstances is to characterize first the electronic levels with a spin Hamiltonian, $S = {}^3/_2$, and then perturb these levels with the isotropic hyperfine interaction. The spin-Hamiltonian parameters for one of the paramagnetic homologs have been determined from epr data and we begin by summarizing these results.

Single-crystal epr data have been reported for the $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$ derivative.[11] These results may be described by the spin Hamiltonian, appropriate to rhombic symmetry

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D\left(S_z^2 - \frac{1}{3}S(S + 1)\right) + E(S_x^2 - S_y^2) \tag{3}$$

with $S = {}^3/_2$ and $g = 2.00$. The experimentally determined parameters D and $\lambda = E/D$ were 4.0 ± 0.5°K and 0.036 ± 0.003, respectively. In the absence of an external field, the quartet manifold is split into two Kramers doublets spaced by $|2D\sqrt{1 + \lambda^2}|$. For simplicity in the following discussion, we will assume that $\lambda = 0$ (*i.e.*, $E = 0$), so that the two doublets are $|M_S = \pm{}^3/_2\rangle$ and $|M_S = \pm{}^1/_2\rangle$. When D is negative, the $|M_S = \pm{}^3/_2\rangle$ level is lower lying, and positive D reverses the ordering, as shown in Figure 3. At low temperature, $T \cong 1\text{°K} < |2D|$, only the ground doublet will be responsible for the Mössbauer magnetic hfs.

Owing to a combination of (i) intrinsically different effective hyperfine interactions and (ii) markedly different relaxation rates, quite specific Mössbauer patterns are expected, depending on whether the $|\pm{}^3/_2\rangle$ or $|\pm{}^1/_2\rangle$ level is lowest lying, *i.e.*, whether D is negative or positive. For example, it is well known that under similar low-temperature circumstances in high-spin Fe^{3+} (^6S) ions with an $|S = {}^5/_2, M_S = \pm{}^1/_2\rangle$ level lowest lying, effective paramagnetic relaxation times and local perturbing fields preclude well-defined paramagnetic hfs.[12] In this fast relaxation limit one is left with a quadrupole doublet described by the nuclear spin Hamiltonian for the excited Fe^{57} level

$$\mathcal{H}_Q = \frac{eqQ}{4}\left\{I_z^2 - \frac{5}{4} + \frac{\eta}{3}(I_x^2 - I_y^2)\right\} \tag{4}$$

Completely analogous arguments apply to the present case of the $|S = {}^3/_2, M_S = \pm{}^1/_2\rangle$ doublet; again a simple quadrupole splitting is expected when this is the ground doublet. No accurate description of the origin of the large EFG in these complexes is presently available; we return to this point below.

On the other hand, when the $|S = {}^3/_2, M_S = \pm{}^3/_2\rangle$ level lies lowest, effective relaxation times τ_e are long ($\tau_e \gg \omega_L^{-1}$) at low temperatures, and a well-defined effective magnetic field is expected.[13] The resulting Mössbauer pattern is described by the nuclear spin Hamiltonian (for the excited state of Fe^{57}, $I = {}^3/_2$)

$$\mathcal{H} = g_I\beta_N H_{eff} I_z + \frac{eqQ}{4}\left\{I_{z'}^2 - \frac{5}{4} + \frac{\eta}{3}(I_{x'}^2 - I_{y'}^2)\right\} \tag{5}$$

the EFG tensor is expressed with respect to its principal axis system. The combined electric and magnetic interactions in this case lead to a multiline pattern of, normally, six or more lines. Experimental data given below and appropriate to the case have been analyzed using a computer program whose outputs are polycrystalline absorption patterns for the Hamiltonian of eq 6. The general methods used to compute the spectra have been described earlier,[13,14] and in the present case all of the pertinent matrix elements have been given in closed form by Matthias, Schneider, and Steffen.[15] In the latter authors' work, the spherical polar coordinates φ and θ are denoted α and β, respectively. Except for this notational change, the data of Figure 2 were analyzed with the conventions of ref 15 and are summarized in Table II.

As mentioned earlier, the ground term in the $S = {}^3/_2$ complexes is an orbital singlet, so the hyperfine field arises from the core polarization interaction

$$\mathcal{H}_C = a\,\vec{I}\cdot\vec{S} \tag{6}$$

with $S = {}^3/_2$. In the ground doublet, $|M_S = \pm{}^3/_2\rangle$, $\mathcal{H}_C$ is given by

$$\mathcal{H}_C = aI_z\langle S_z\rangle \tag{7}$$

where $\langle S_z\rangle = \pm{}^3/_2$. Comparing eq 7 and 5 we find $H_{eff} = \pm{}^3/_2(a/g_I\beta_N)$; it is easily shown that both "polarities" yield the same Mössbauer pattern. By analogy with high-spin Fe^{3+} (^6S) ions the core polarization term a is assumed negative.

The description just given suffices to interpret the observed Mössbauer data in the paramagnetic com-

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(11) H. H. Wickman and F. R. Merritt, *Chem. Phys. Letters*, **1**, 117 (1967).

(12) G. K. Wertheim and J. P. Remeika, *Phys. Letters*, **10**, 14 (1964).

(13) H. H. Wickman, M. P. Klein, and D. A. Shirley, *Phys. Rev.*, **152**, 345 (1966).

(14) H. H. Wickman and G. K. Wertheim, *ibid.*, **148**, 211 (1966).

(15) E. Matthias, W. Schneider, and R. M. Steffen, *Arkiv Fysik*, **24**, 97 (1963).

plexes, $Fe(S_2CN(CH_3)_2)_2Cl$, $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$, and $Fe(S_2CN(C_2H_5)_2)_2Br$. In the former two complexes the ME shows a many-line pattern, a well-defined magnetic field (within the limit of relaxation broadening), and we conclude that the spin-Hamiltonian parameter D is negative in these cases. This result is, of course, consistent with the epr data in the diisopropyl derivative. The similarity of the spectra of (b) and (d) suggest that the zero-field splittings in these two complexes do not differ greatly. On the other hand, the quadrupole doublet in the $Fe(S_2CN(C_2H_5)_2)_2Br$ strongly suggests that D is positive; the $|S = {}^3/_2, M_S = \pm{}^1/_2\rangle$ level is lowest lying.

The Mössbauer data, while consistent with positive D in $Fe(S_2CN(C_2H_5)_2)Br$, do not establish this result in a completely unambiguous fashion. For example, if the zero-field splitting was extremely small, $|D|/k \leq 1.2°K$, one would expect fast relaxation and only a quadrupole doublet, independent of the sign of D. In the most general case then, there are two possible explanations for the doublet of Figure 2a: (i) very small $|D|$ or (ii) comparatively large $|D|$ and $D > 0$. In principle, these two possibilities may be distinguished by a simple single-crystal epr experiment at relatively large fields and low temperatures. In case (i) the small zero field splitting would not be expected to affect greatly the isotropic $g = 2.0$ resonance of the spin quartet level, especially for large external fields. In case (ii) a resonance with $g_{max} \sim 4.0$, similar to that of $Fe(S_2CN(i\text{-}C_3H_7)_2)Cl$, is expected. Unlike the latter case where the resonant doublet is an excited doublet, the epr signal would be strongest at lowest temperature for $D > 0$. Epr experiments (24 Gc) at 4.2 and 1.4°K were therefore performed using a single crystal of $Fe(S_2CN(C_2H_5)_2)_2Br$. The magnetic symmetry axes of the crystal were not known prior to the experiment. The sample showed a single strong resonance whose intensity increased with decreasing temperature and which was characterized by $g_{max} = 4.0 \pm 0.2$ and $g_{min} = 2.7 \pm 0.3$. No resonance near $g = 2$ was found. This result argues for case (ii): a large ($\geq 2°K$) and positive sign of D. The halo constituent therefore appears crucial in determining the sign of the zero-field splittings of the $S = {}^3/_2$ manifold.

The description of the hfs of the $Fe(S_2CN(C_2H_5)_2)_2Cl$ derivative is somewhat different, as this complex undergoes a magnetic transition at 2.5°K.[9] The zero-field splitting in this system has not yet been determined, nor is the mechanism of the collective ordering known in detail. Both dipole and exchange effects undoubtedly contribute to the ordering; we will refer to these interactions collectively as the exchange field, H_{exch}. Depending on the relative strengths of the crystal field and exchange field, rather complicated behavior may occur. As a start, however, we will assume that the zero-field splitting in $Fe(S_2CN(C_2H_5)_2)_2Cl$ is similar to that in the closely related $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$ derivative. Because the ordering occurs at 2.5°K, the magnetic character of the ion is mainly determined by the ground doublet, *i.e.*, the $|M_S = \pm{}^3/_2\rangle$ level. Here the relations $|\langle S_z\rangle| = {}^3/_2$ and $\langle S_x\rangle = \langle S_y\rangle = 0$ are valid. The exchange interaction may then be represented, in the Weiss molecular field approximation, by a field H_{exch} directed along the z axis of the spin Hamiltonian of eq 3.

Under these conditions a relatively simple level scheme is found. As shown in Figure 3, the exchange splitting simply removes the degeneracy of the $|\pm{}^3/_2\rangle$ level. The transition temperature of 2.5°K is a reasonable estimate of the separation of the two levels at the experimental conditions of 1.2°K; the upper-state populations are sufficiently low to be neglected entirely. When relaxation times are long ($\tau_e \gg \omega_L^{-1}$), the $|M_S = +{}^3/_2\rangle$ and $|M_S = -{}^3/_2\rangle$ levels separately contribute identical Mössbauer spectra, and the observed spectrum is a Boltzman sum of these two spectra. The Mössbauer pattern of a polycrystalline absorber is (neglecting polarization of the γ rays) indistinguishable from the magnetic hfs from the unsplit $|M_S = \pm{}^3/_2\rangle$ doublet. (If polarization of the γ rays was observed, the two could often be distinguished; *i.e.*, the transitions in a paramagnetic ion with $\langle S_z\rangle = 0$ are unpolarized.)

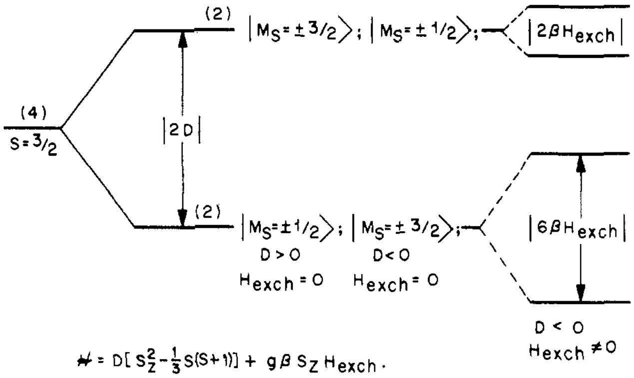

Figure 3.—Representation of crystal field and exchange splitting in the spin quartet state.

The great similarity of the Mössbauer hfs in $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$ and $Fe(S_2CN(C_2H_5)_2)_2Cl$ offers substantial support for a simple exchange splitting of the ground doublet. Deviations from the model would in principle be shown primarily by differences between the observed core polarization fields H_{eff}. The latter parameter is proportional to $\langle S_z\rangle$ in one of the lower two electronic levels of the ion; an exchange field at an angle to the z axis of the electronic spin Hamiltonian would produce a mixing of the $|M_S = \pm{}^3/_2\rangle$ and $|M_S = \pm{}^1/_2\rangle$ levels and thus change $\langle S_z\rangle$ from the value found in the paramagnetic case. In fact, no experimental evidence for such an effect was observed: the field H_{eff} in both the paramagnetic and ferromagnetic samples were essentially the same.

The large quadrupole splittings in these compounds are not as easily interpreted as the magnetic interactions. Within two Kramers doublets arising from an orbital singlet and spin quartet, there is no temperature dependence of the EFG. That is, the net EFG at the nucleus does not change with the population of the two Kramers doublets. Because of this, no direct determination of the ionic contribution to the EFG from the quartet term is possible. The relatively temperature-independent quadrupole splitting is consistent with the absence of excited electronic terms within a few hundred reciprocal centimeters of the ground state. We have noted previously that the levels of the lowest quartet term in octahedral symmetry, ${}^4T_1$, separately produce no EFG at the nucleus.[10] The lattice contribution to the EFG may be large enough to account for the large splittings, but it seems more likely that an appreciable gradient should arise from the ground quartet term. In this case, the orbital level will be a mixture of states from different octahedral representations. A somewhat larger quadrupole splitting was observed in the bromo derivative than in the chloro complexes; this effect could equally well be accounted for by a change in either the ionic or lattice contribution to the total gradient.

In all of the chloro derivatives the EFG q was positive, with the assumption that eQ is also positive. In earlier work[5] it was shown that at higher temperatures, where the main effect of relaxation is to broaden the quadrupole peaks, the left peak is broadened more than the right peak. This results mainly from the fact that, within the ground Kramers level, the effective field fluctuates along the axis perpendicular to the principal axis of the EFG.[16] For collinear EFG and effective internal field, the right peak would be broadened. This may be seen qualitatively as follows.

Taking the nuclear quantization axis along the z' direction (eq 5), the excited-state nuclear wave functions are (with $\eta = 0$) $|\pm{}^1/_2\rangle$ and $|\pm{}^3/_2\rangle$ and correspond with $q > 0$ to the left- and right-hand peaks in a pure quadrupole pattern when $\langle H_{\text{eff}}\rangle = 0$. These two levels may be described by *effective nuclear g factors* with $I' = {}^1/_2$ in each case. Their magnetic character is described by the respective g' tensors ($g'_x = g'_y = 2g_1$; $g'_z = g_1$) and ($g'_x = g'_y = 0$; $g'_z = 3g_1$). Hence the $|\pm{}^1/_2\rangle$ level will respond more readily to transverse fluctuations of a magnetic field (the present case) while the $|\pm{}^3/_2\rangle$ level is affected first when the effective field fluctuates along an axis parallel to the EFG principal axis. These considerations emphasize the result that it is not, in general, possible to deduce the absolute sign of an EFG from relaxation broadening of a quadrupole doublet without knowledge of the relative orientation of EFG principal axis and the magnetic hyperfine direction.

It should finally be noted that, while the qualitative picture involving effective g values is useful in that it predicts correct features of the spectrum, it is rigorously incorrect in that it assumes a static perturbing field, while, in fact, the fields are of a stochastic nature and models based on these ideas are generally required to give definitive answers relating to origins of broadening in Mössbauer spectra.

Conclusions

Three homologs closely related to magnetically ordered $Fe(S_2CN(C_2H_5)_2)_2Cl$ have not shown collective magnetic properties. However, low-temperature Mössbauer paramagnetic hfs indicates rather similar local iron environments in $Fe(S_2CN(CH_3)_2)_2Cl$ and $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$. It is probable that the weak interactions responsible for the ordering are sufficiently orientation dependent that the present results merely illustrate variable relative orientation of the molecular units. Unfortunately only limited crystallographic information is available for these complexes: the detailed structure of monoclinic $Fe(S_2CN(C_2H_5)_2)_2Cl$ is known,[6] and preliminary X-ray work shows $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$ to be trigonal.

The Mössbauer hfs has also shown that the perturbations within the ground spin quartet are appreciably affected by the halo constituent, but are relatively insensitive to the alkyl constituents in the dithiocarbamato ligands.

In three of the complexes (Table II) a well-defined internal hyperfine field was observed, and the relative orientation of the EFG was determined. It should be noted, however, that the orientation of H_{eff}, with respect to the basic pentacoordinate bonding of the iron, has not been specified. In principle, this can be determined from single-crystal epr measurement in the $Fe(S_2CN(C_2H_5)_2)_2Cl$ derivative; these experiments have so far been frustrated by excessive line widths making the single-crystal resonance quite weak. Low-temperature Mössbauer effect measurements in oriented single crystals, should be able to resolve the point in an unambiguous fashion.

Acknowledgments.—We wish to thank F. R. Merritt for his valuable help in obtaining the epr results related to the present work. The assistance of D. B. McWhan with X-ray studies of the $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$ is greatly appreciated. We also wish to thank R. L. Martin and C. R. Abeledo for a number of interesting discussions of the chemistry of metal–sulfur complexes.

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[16] M. Blume, *Phys. Rev. Letters*, **14**, 96 (1965).