

line was obtained as an average of ten measurements. From the strongest lines in the powder pattern 17 independent structure factors were calculated. No absorption correction was applied.

Orthorhombic CrOOH proved to be isostructural with InOOH.² The crystal structure of CrOOH is a deformed rutile structure. Oxygen atoms are coordinated with chromium atoms in distorted octahedra. One set of octahedra with chromium at (0, 0, 0) are sharing edges and are stacked along the (0, 0, 1) direction. Another set of octahedra with chromium at (1/2, 1/2, 1/2) are also sharing edges and are stacked along the (0, 0, 1) direction. The two sets of octahedra are sharing corners and are held together by rather short hydrogen bonds.

An R value ($R = \Sigma ||F_o| - k|F_c|| / \Sigma |F_o|$) of 11.0% was obtained on inserting Cr and O atoms in the structure factor calculations using the coordinates of In and O in InOOH. Inserting the Cr atoms only gave an R value of 18.7%. Coordinates and temperature factors were refined by the method of Bhuiya and Stanley.⁸ The structure factors were calculated using the atomic scattering factors from Vol. III of the International Tables of X-Ray Crystallography and the interpolation formula of Bassi.⁹ The refinement yielded an R value of 9.6%.

The crystallographic data obtained are: crystal system, orthorhombic; $a = 4.861$ A, $b = 4.292$ A, $c = 2.960$ A; space group, No. 58, Pnnm; density calculated for two formula units in the unit cell, 4.57 g/cm³; absorption coefficient $\mu = 89$ cm⁻¹ for Mo K α radiation ($\lambda 0.7107$ A).

TABLE I

ATOMIC COORDINATES AND TEMPERATURE FACTORS

Atom	Posi- tions	x	σ_x	y	σ_y	z	B, A^2	$\sigma B, \text{A}^2$
Cr	2(a)	0.0		0.0		0.0	0.4	0.3
O	4(g)	0.361	0.013	0.230	0.020	0.0	8	2

Table I gives atomic coordinates and temperature factors with their standard deviations. Table II gives interatomic distances. The Cr-O distance of 2.0 ± 0.1 A is comparable with the distance of 1.97 ± 0.04 A found in rhombohedral CrOOH.³ The O-O distance of 2.4 ± 0.2 A corresponds to a hydrogen bond. In InOOH a hydrogen bond of 2.58 A was found. Table III gives X-ray data for orthorhombic CrOOH with observed and calculated intensities.

TABLE II

INTERATOMIC DISTANCES l AND STANDARD DEVIATIONS σ_l IN A

	l	σ_l
Cr-O	2.0	0.07
O-O between octahedra	2.4	0.1
O-O within octahedra	2.8	0.1

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TABLE III

X-RAY DIFFRACTION DATA FOR CrOOH

$h k l$	$d_{\text{calcd}}, \text{A}$	I_{obsd}	I_{calcd}	$h k l$	$d_{\text{calcd}}, \text{A}$	I_{obsd}	I_{calcd}
1 1 0	3.217	276	306	0 3 1	1.288	15	15
1 0 1	2.528	74	85	2 0 2	1.264	12	15
0 1 1	2.437	228	172	1 3 1	1.245	2	1
2 0 0	2.430			65	2 3 0	1.233	1
1 1 1	2.178	30	20	0 2 2	1.218	15	10
0 2 0	2.146	35	20	4 0 0	1.215		
2 1 0	2.115	24	14	2 1 2	1.213		
2 1 1	1.721	103	101	3 2 1	1.185	19	20
1 2 1	1.636	139	117	2 3 1	1.138	19	21
2 2 0	1.609	60	44	2 2 2	1.089	37	18
3 1 0	1.516	31	34	4 1 1	1.088		
0 0 2	1.480	20	22	0 4 0	1.073	3	5
3 0 1	1.421	43	35	3 1 2	1.059	29	16
1 3 0	1.372	38	48	4 2 0	1.057		
1 1 2	1.345	31	40				

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Mössbauer Effect in
Iron(III) Dithiocarbamates

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According to ligand field theory, the magnetic moments of d^4 , d^5 , d^6 , and d^7 transition metal complexes depend on the relative values of the mean spin-pairing energy π and the strength of the cubic ligand field parameter Δ . Thus, in the case of Fe^{III} ($3d^5$ configuration) the magnetic moment is about 5.9 BM in high-spin complexes (weak ligand fields) and 2.9 BM in low-spin or spin-paired complexes (strong ligand fields).²

Cambi and co-workers²⁻⁶ have investigated the magnetic properties of some iron(III) tris(dithiocarbamates) $[\text{Fe}^{\text{III}}(\text{DTC})_3]$ and found magnetic moments between 2.3 and 5.9 BM depending on the substituents in the DTC ligands; furthermore, measurements between 84 and 300°K showed that the magnetic moments increased with temperature. More

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TABLE I
PARAMETERS OF MÖSSBAUER SPECTRA OF IRON(III) TRIS(DITHIOCARBAMATES) $[\text{Fe}^{\text{III}}(\text{R}_2\text{NCS}_2)_3]$ AT ROOM TEMPERATURE USING A Co^{57} -Cr SOURCE

Substituent in ligand	Line 1, cm/sec (± 0.002)	Line 2, cm/sec (± 0.002)	ΔE_Q , cm/sec (± 0.005)	Center ^a shift, cm/sec (± 0.003)	Isomer shift, ^b cm/sec (± 0.003)	μ , BM
Butyl	0.055	0.064	0.009	0.060	0.051	5.32
Ethyl	0.045	0.070	0.025	0.057	0.048	4.24
Methyl	0.040	0.067	0.027	0.054	0.045	4.17
Benzyl	0.028	0.083	0.055	0.055	0.046	4.02
Isopropyl	0.020	0.085	0.065	0.052	0.043	2.62

^a With respect to Co^{57} -Cr source. ^b With respect to $\text{K}_4\text{Fe}(\text{CN})_6$ standard absorber.

recently White, *et al.*,^{7,8} have reinvestigated the magnetic properties of these compounds and have also extended their work to include spectral, conductivity, and molecular weight determinations. From their results, which are in general agreement with the earlier work of Cambi, they conclude that the unusual magnetic properties of $\text{Fe}^{\text{III}}(\text{DTC})_3$ are due to a thermal equilibrium between its low- and high-spin forms. This situation arises because π and Δ are of the same order of magnitude and the energy difference between the low- and high-spin states is sufficiently small so that in most of the $\text{Fe}^{\text{III}}(\text{DTC})_3$ complexes investigated both states are populated. At low temperatures only the spin-paired state is occupied because it lies lowest.

The results of White, *et al.*, prompted us to undertake a Mössbauer-effect study of these compounds. Several authors⁹⁻¹¹ have pointed out that there are intrinsic differences in the electronic properties of low- and high-spin complexes which give rise to differences in the isomer shift and the quadrupole splittings (ΔE_Q) of the Mössbauer-effect spectra. The thermal equilibrium between the two forms in $\text{Fe}^{\text{III}}(\text{DTC})_3$ offers the possibility of testing some of these ideas by comparing their Mössbauer-effect characteristics under the same conditions.

During the course of the present work Wickman and Trozzolo¹² reported Mössbauer-effect data on $\text{Fe}^{\text{III}}(\text{N,N-dimethyl-DTC})_3$ and $\text{Fe}^{\text{III}}(\text{N,N-diisopropyl-DTC})_3$ between 1.8 and 300°K which show interesting electronic relaxation phenomena at low temperatures but give no evidence of the thermal equilibrium postulated by White, *et al.* More recently, however, they have attributed their spectra to complexes of the type $\text{ClFe}(\text{DTC})_2$.¹³

Experimental Section

Preparation of Samples.—The $\text{Fe}^{\text{III}}(\text{DTC})_3$ complexes were prepared with both natural iron and 92% enriched Fe^{57} following the general method described by White, *et al.*,⁷ from ferric hydroxide, carbon disulfide, and the corresponding secondary

amine. The dimethyl complex was also prepared following the alternative preparation from ferric chloride and $\text{Na}(\text{N,N-dimethyl-DTC})$ but the product proved to be a mixture of two compounds: one, brown, identical with that prepared by the above method and the other, green, which was deficient in DTC ligand; by addition of excess NaDTC the green compound was converted to the brown one.

Elemental chemical analysis were performed on the natural iron complexes only because the Fe^{57} samples were prepared in too small quantities. To ensure the identity of the respective Fe^{57} and natural iron samples, infrared and visible spectra were taken on both series of complexes. Infrared spectra of Nujol mulls were run between 2 and 15 μ with a Beckman IR5 spectrometer, and visible spectra of chloroform solutions were recorded between 350 and 750 $m\mu$ with a Perkin-Elmer 137UV spectrometer. Chemical analysis gave the following results. *Anal.* Calcd for $\text{Fe}^{\text{III}}(\text{N,N-dimethyl-DTC})_3$: C, 26.0; H, 4.4; N, 10.1; S, 46.2; Fe, 13.4. Found: C, 27.5; H, 4.6; N, 10.5; S, 46.7; Fe, 12.7. Calcd for $\text{Fe}^{\text{III}}(\text{N,N-diethyl-DTC})_3$: C, 36.0; H, 6.0; N, 8.4; S, 38.4; Fe, 11.2. Found: C, 35.3; H, 6.3; N, 7.8; S, 37.3; Fe, 11.6. Calcd for $\text{Fe}^{\text{III}}(\text{N,N-diisopropyl-DTC})_3$: C, 43.1; H, 7.2; N, 7.2; S, 32.9; Fe, 9.6. Found: C, 43.4; H, 7.2; N, 7.0; S, 33.1; Fe, 9.2. Calcd for $\text{Fe}^{\text{III}}(\text{N,N-dibutyl-DTC})_3$: C, 48.6; H, 8.1; N, 6.3; S, 28.8; Fe, 8.40. Found: C, 48.1; H, 8.2; N, 5.8; S, 27.2; Fe, 8.9. Calcd for $\text{Fe}^{\text{III}}(\text{N,N-dibenzyl-DTC})_3$: C, 61.8; H, 4.9; N, 4.9; S, 22.1; Fe, 6.5. Found: C, 61.1; H, 4.9; N, 4.4; S, 20.1; Fe, 6.5.

Results and Discussion

The Mössbauer-effect spectra of $\text{Fe}^{\text{III}}(\text{DTC})_3$ absorbers containing 92% enriched Fe^{57} were taken with a constant acceleration apparatus similar to that described by Cohen, *et al.*¹⁴ Measurements were made at room temperature using a Co^{57} -Cr source. Spectra for the methyl and isopropyl complexes are shown in Figures 1 and 2. Results for all the $\text{Fe}^{\text{III}}(\text{DTC})_3$ complexes thus far investigated are summarized in Table I together with the room-temperature magnetic moments (μ) measured by White, *et al.*⁷

While the separation between the two observed lines ranges from 0.009 cm/sec in the butyl complex to 0.065 cm/sec in the isopropyl one, the center of gravity shift remains fairly constant at about 0.045 cm/sec (with respect to ferrocyanide). This latter value agrees well with previously reported¹⁵ isomer shifts of slightly covalent ferric compounds. These spectra can therefore be interpreted as two lines arising from a quadrupole-split Mössbauer-effect transition in slightly covalent ferric compounds. Moreover, the variations in quadru-

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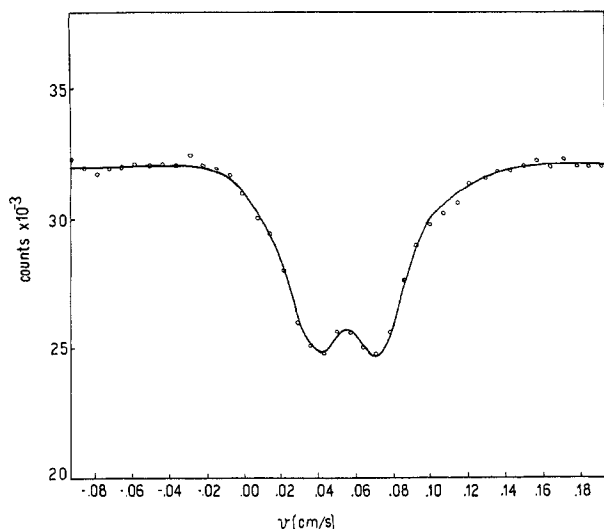


Figure 1.—Mössbauer spectra of iron(III) tris(dimethyldithiocarbamate) at room temperature.

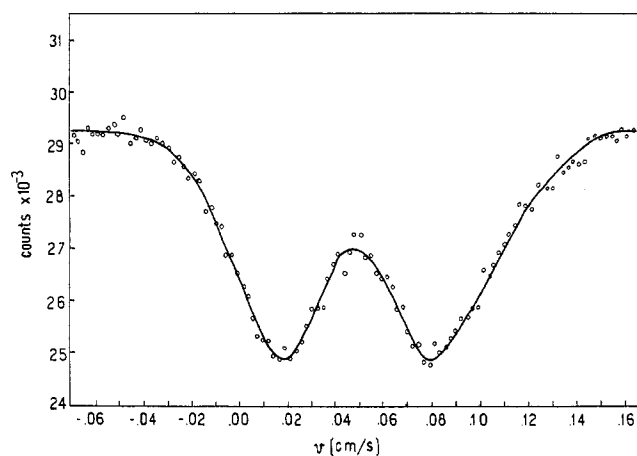


Figure 2.—Mössbauer spectra of iron(III) tris(diisopropyldithiocarbamate) at room temperature.

pole interaction and isomer shift can be correlated with the magnetic properties.

The relationship between magnetic state and quadrupole interaction has been discussed previously by Danon⁹ and by Duncan and Golding.¹¹ Although the complete crystallographic structure of $\text{Fe}^{\text{III}}(\text{DTC})_3$ has not yet been worked out, there are good reasons to believe^{7,8} that each of the bidentate DTC ligands is bonded through its two sulfur atoms so that the resulting point group symmetry at the iron site is D_3 . Under the influence of a ligand field of such symmetry the high-spin d^5 complexes have a spherically symmetric configuration which does not contribute to the electric field gradient (EFG) at the iron nucleus. The low-spin d^5 complexes on the other hand have a nonspherical electron distribution which gives rise to an appreciable EFG at the iron nucleus. Since at 300°K all of these complexes contain an equilibrium between the low- and high-spin states one could expect to find a superposition of the Mössbauer-effect spectra of each of the two forms. The fact that this is not observed indicates that the relaxation time to change from one form to the other is much shorter than the lifetime ($\tau = 1.45$

$\times 10^{-7}$ sec) of the $\text{Fe}^{57} I = 3/2$ state and that the nuclei then "see" an average EFG which depends on the contribution of each form in the equilibrium.

Mössbauer spectra taken on the green methyl complex mentioned above show a quadrupole interaction of the order of 0.26 cm/sec in agreement with the results of Wickman and Trozzolo for $\text{ClFe}(\text{N,N-dimethyl-DTC})_2$.^{12,13}

With the available data it is not easy to interpret the correlation between magnetic moment and isomer shift. One or both of the following mechanisms could be responsible for it.

(i) The isomer shift in the isopropyl complex is smallest because the bonding between the ligands and the iron is more covalent than in the complexes with higher magnetic moments. This higher degree of covalency in the metal-ligand bond is also responsible for a larger Δ and therefore for a smaller population of the high-spin state.

(ii) There is an intrinsic difference in the isomer shift of each of the magnetic forms of a given complex because the bonding between the DTC ligands and the iron ion in the low- or high-spin configurations is qualitatively different (see ref 10). The observed isomer shift would then be a weighted average between those of each form in equilibrium.

An investigation of the temperature dependence (between 4 and 300°K) of the quadrupole interaction and the isomer shift in these complexes is presently in progress.¹⁶ Preliminary results at temperatures down to 4°K confirm the interpretation given here for the correlation between EFG and magnetic moment. When the temperature is decreased, the quadrupole interaction increases as the population of the low-spin state increases and the magnetic moment decreases as observed by White, *et al.*^{7,8} More detailed measurements are necessary to distinguish between the alternative interpretations of the isomer shift data.

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(16) H. H. Wickman, E. Frank, and C. R. Abeledo, to be published.

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Difluorocyanamide¹

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Several recent papers have described reactions of elemental fluorine in aqueous solution to produce prod-

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