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# A Novel Series of Five-Coordinated Iron(III) Complexes with the Square-Pyramidal Configuration and Spin, $S = {}^3/_2$

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*Received June 6, 1966*

A simple method has been devised for synthesizing a novel series of complex compounds of the general formula $[Fe^{III}X(S_2CNR_2)_2]$, X being a halogen and R an alkyl group. The magnetic moments of these new compounds lie close to that expected for a system with the central metal ion in $dsp^3$ hybridization, three unpaired electrons and no orbital contribution being observed. The compounds are monomeric, both in the solid state and solution, which excludes the possibility that this rare magnetic condition for iron(III) arises from intermolecular exchange interactions. The Fe–Cl, Fe–Br, and Fe–S stretching modes in the infrared spectrum are located at 309, 225, and *ca.* 353 $cm^{-1}$, respectively. The electronic and the esr spectra are briefly reported. The measured values, $g_{\|} = 2.1$ and $g_{\perp} = 4.08$, are consistent with a ${}^4A_2$ ground state with the tetragonal field depressing the Kramers doublet $S_z = \pm{}^1/_2$ below the associated $S_z = \pm{}^3/_2$ level. A probable ordering for the energies of the 3d orbitals $3d_{xy} < 3d_{xz}, 3d_{yz} < 3d_{z^2} < 3d_{x^2-y^2}$ is suggested.

## Introduction

The magnetic behavior of simple mononuclear iron(III) complexes is, generally, uncomplicated. Nearly all the known compounds exhibit either one unpaired electron with a doublet ground state ($S = {}^1/_2$), *e.g.*, $[Fe^{III}(CN)_6]^{3-}$, in which case $\mu_{eff}$ is temperature dependent, following approximately a Kotani-type curve,[1] or, alternatively, five unpaired electrons with a sextet ground state ($S = {}^5/_2$) as in $[Fe^{III}(H_2O)_6]^{3+}$ and $[Fe^{III}Cl_4]^-$, the compounds of this type having $\mu_{eff} = 5.92$ BM independent of temperature. The symmetry adopted by such iron(III) complexes is high, being either octahedral or tetrahedral. In these systems, a ground state with three unpaired electrons ($S = {}^3/_2$) is specifically excluded by ligand field theory.[2]

The spin condition of an octahedral complex is determined by the balance between the strength of the ligand field $\Delta$ and the magnitudes of the Coulomb and exchange energies. Deviations from the normal low-spin and high-spin behavior described above can arise for octahedral complexes of iron(III) when the ligand field strength is of the same order as the mean pairing energy $\pi$ for the $d^5$ configuration.[3,4] For example, the curious magnetic behavior of the dialkyldithiocarbamate complexes of iron(III), which was first observed by Cambi and his school,[5] involves two states in thermal equilibrium. These have been shown to be ${}^2T_2$ and ${}^6A_1$, and there is no evidence for any appreciable thermal population of the intermediate ${}^4T_1$ level.[4]

During the course of these detailed studies, we succeeded in synthesizing a completely new class of iron(III) complex in which the symmetry is so lowered that a quartet state becomes the favored ground state. These novel compounds are the five-covalent monohalogeno bis(dialkyldithiocarbamato) derivatives of tervalent iron.

Five-covalent complexes of transition metals are not particularly common. One of the first well-characterized examples was the compound $[Co(NO)(S_2CN(C_2H_5)_2)_2]$ discovered by Cambi, *et al.*[6] Alderman, Owston, and Rowe determined the crystal structure of this complex and showed that the orientation of the bonds is that of a square pyramid with the central cobalt atom elevated above the base of the pyramid.[7]

This stereochemistry is slightly at variance with the original theoretical predictions of Daudel and Bucher, who envisaged that $dsp^3$ hybridization in such complexes should lead to a bond distribution with the metal atom lying in the basal plane.[8] In fact, in the majority of known structures of five-covalent transition metal complexes, the metal ion is displaced toward the center of the coordination polyhedron. Recently, this uncommon stereochemistry has been reported[9] for the N-β-diethylaminoethyl-5-chlorosalicylaldimine derivatives of nickel(II) and cobalt(II), and for monoperchloratotetrakis(diphenylmethylarsine oxide)cobalt(II) perchlorate.[10] The measured displacements of the metal atoms above the basal planes are: $Co(NO)(S_2CN(C_2H_5)_2)_2$, 0.54 A;[7] $Ni(5\text{-}Cl\text{-}salen\text{-}N(C_2H_5)_2)_2$, 0.36 A;[9] $Co(OAsCH_3(C_6H_5)_2)_4(ClO_4)_2$, 0.32 A;[10] $VO(acac)_2$, 0.56 A;[11] $Zn(disal)H_2O$, 0.34 A;[12] and $FeCl(S_2CN(C_2H_5)_2)_2$, 0.63 A.[13]

In addition to these mononuclear compounds, a number of divalent copper complexes have crystal structures which involve dimeric or polymeric aggregates of an approximately square-pyramidal nature. Not infrequently the copper atom is found to lie above the basal plane. Vanadyl acetylacetonate provides

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(1) M. Kotani, *J. Phys. Soc. Japan*, **4**, 293 (1949).

(2) J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 1 (1956).

(3) A. H. White, R. Roper, E. Kokot, 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) L. Cambi and L. Szego, *Ber.*, **66**, 656 (1933).

(6) L. Cambi and A. Cagnasso, *Atti Accad. Nazl. Lincei*, **13**, 404 (1931).

(7) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

(8) R. Daudel and A. Bucher, *J. Chim. Phys.*, **42**, 6 (1945).

(9) L. Sacconi, P. L. Oriolo, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(10) P. Pauling, G. B. Robertson, and G. A. Rodley, *Nature*, **207**, 73 (1965).

(11) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).

(12) D. Hall and F. H. Moore, *Proc. Chem. Soc.*, 256 (1960).

(13) B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 627 (1966).

perhaps the most common example of five-covalent stereochemistry of this type.[11]

Cambi, *et al.*, have prepared various nitroso dithiocarbamates which are likely to be of similar type. $[Fe(NO)(S_2CNR_2)_2]$ complexes are well known,[14] and it is not difficult to visualize the replacement of the nitric oxide ligand by a negative ligand such as halide ion. Such a complex, to fulfill the requirements of Daudel and Bucher, would involve either the use of the metal $d_{z^2}$ orbital if the stereochemistry is trigonal bipyramidal, or the $d_{x^2-y^2}$ orbital if the environment is square-pyramidal. In both cases the configuration should give three unpaired electron spins in the ground state. No simple five-covalent iron(III) complex appears to be known in the solid state. However, Griffith[15] has confirmed that the esr spectrum of monochloro(phthalocyaninato)iron(III) is consistent with a square-pyramidal stereochemistry. We report here a very simple method for preparing a series of complexes with the general formula $[Fe^{III}X(S_2CNR_2)]_2$, where X is Cl, Br, or I and R is a suitable organic substituent such as an alkyl or aryl group. Compounds which are representative of this series are described (a) in cases where R is held constant (*e.g.*, R = ethyl) and X is varied and (b) where X is held constant (*e.g.*, X = chloride) and R is varied. These complexes have been characterized chemically and their five-coordinated nature established by the methods of molecular weight determination by cryoscopy, magnetochemistry, and crystal structure determination. In addition, electronic, esr, and infrared absorption spectra have been recorded.

## Experimental Section

**Materials.**—The tris(N,N-dialkyldithiocarbamato)iron(III) compounds $[Fe(S_2CNR_2)_3]$ were prepared and purified as described elsewhere.[8] The derivatives $[Fe^{III}X(S_2CNR_2)_2]$ were synthesized from the parent compounds by the following method.

The tris(dialkyldithiocarbamato)iron(III) derivative is dissolved in benzene and shaken vigorously with the minimum quantity of concentrated aqueous hydrohalic acid. Precipitation of the black, crystalline compounds in high purity occurs almost immediately. If an excess of hydrohalic acid is used, unnecessary moisture is introduced which is both difficult to remove and tends to hydrolyze the monohalogeno compound; it also tends to promote further reaction, particularly in the case of HBr, to form the salt $(R_2NH_2)^+(FeBr_4)^-$ or its analogs. The monohalogeno compound is separated by filtration and is dried over phosphorus(V) oxide as rapidly as possible *in vacuo*. If necessary, the compounds may be recrystallized from a suitable mixed solvent chosen from acetone, chloroform, carbon tetrachloride, and benzene; the compounds are soluble in the first two solvents and insoluble in the latter pair. Care must be taken to avoid hydrolysis by hydroxylic media such as water or alcohol.

The following representative compounds have been prepared and studied in some detail. Melting points are given where possible although decomposition frequently occurs before the melting point, *i.e.*, the monohalogeno complexes are rather less stable thermally than the parent tris-dialkyldithiocarbamato complexes.

Analyses were carried out by Dr. W. Zimmerman of the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

(1) **Monochlorobis(N,N-dimethyldithiocarbamato)iron(III) (Mp 300°).**—*Anal.* Calcd for $C_6H_{12}N_2S_4ClFe$: C, 21.72; H, 3.65; N, 8.45; S, 38.66; Cl, 10.8; Fe, 16.83. Found: C, 22.98; H, 3.88; N, 8.49; S, 37.19; Cl, 11.4; Fe, 16.3.

(2) **Monochlorobis(N,N-diethyldithiocarbamato)iron(III) (Mp 250–255°).**—*Anal.* Calcd for $C_{10}H_{20}N_2S_4ClFe$: C, 30.98; H, 5.20; N, 7.22; S, 33.06; Cl, 9.14; Fe, 14.40. Found: C, 31.42; H, 5.26; N, 7.19; S, 32.80; Cl, 9.57; Fe, 14.7.

(3) **Monobromobis(N,N-diethyldithiocarbamato)iron(III) (Mp 230–235°).**—*Anal.* Calcd for $C_{10}H_{20}N_2S_4BrFe$: C, 27.80; H, 4.66; N, 6.48; S, 29.66; Br, 18.48; Fe, 12.91. Found: C, 28.21; H, 4.86; N, 7.09; S, 29.61; Br, 18.6; Fe, 13.26.

(4) **Monoiodobis(N,N-diethyldithiocarbamato)iron(III) (Mp 220–225°).**—*Anal.* Calcd for $C_{10}H_{20}N_2S_4IFe$: C, 25.07; H, 4.21; N, 5.84; S, 26.75; I, 26.47; Fe, 11.65. Found: C, 25.65; H, 4.22; N, 5.62; S, 26.15; I, 27.2; Fe, 11.3.

(5) **Monochlorobis(N,N-diisopropyldithiocarbamato)iron(III) (Mp 300°).**—*Anal.* Calcd for $C_{14}H_{28}N_2S_4ClFe$: C, 37.87; H, 6.36; N, 6.31; S, 28.89; Cl, 7.99; Fe, 12.58. Found: C, 37.69; H, 6.46; N, 7.21; S, 28.69; Cl, 9.10; Fe, 12.37.

(6) **Monochlorobis(N,N-di-*sec*-butyldithiocarbamato)iron(III) (Mp 190–194°).**—*Anal.* Calcd for $C_{18}H_{26}N_2S_4ClFe$: C, 43.24; H, 7.26; N, 5.60; S, 25.64; Fe, 11.17. Found: C, 43.52; H, 7.17; N, 7.43; S, 25.89; Fe, 11.17.

## Results

**Molecular Weight Determinations.**—In general, the monohalogeno complexes are soluble only in a range of solvents with intermediate dielectric constant, such as acetone, nitrobenzene, and chloroform. Since benzene is unsuitable, nitrobenzene, distilled from calcium hydride to remove all moisture and calibrated with azobenzene, was chosen as the most appropriate solvent. The determinations were carried out in the cryometer described by Martin and Winter,[16] carefully purified solute samples being used. The values obtained for $[Fe^{III}Cl(S_2CN(C_2H_5)_2)_2]$ and $[Fe^{III}Br(S_2CN(C_2H_5)_2)_2]$ unambiguously confirm their monomeric nature in this solvent. $[Fe^{III}Cl(S_2CN(C_2H_5)_2)_2]$: calcd for monomer, 388; found, 386 ± 10 ($1.5 \times 10^{-2}$ *M*). $[Fe^{III}Br(S_2CN(C_2H_5)_2)_2]$: calcd for monomer, 432; found, 420 ± 10 ($1.5 \times 10^{-2}$ *M*); 432 ± 10 ($3.0 \times 10^{-2}$ *M*).

For the complex, $[Fe^{III}Cl(S_2CN(i\text{-}C_3H_7)_2)_2]$, a low value of 320 was obtained in $1.5 \times 10^{-2}$ *M* solution in nitrobenzene (calcd for monomer, 444). Furthermore, the molecular weight exhibits an apparent dependence on concentration both in nitrobenzene and nitromethane. These solutions are electrolytes. The possible existence of an equilibrium of the type $[FeL_2Cl] \rightleftharpoons FeL_2^+ + Cl^-$ where L is the dialkyldithiocarbamate ligand is suggested. Similar results are obtained for the iodo complex $[Fe^{III}I(S_2CN(C_2H_5)_2)_2]$, but in this case the more labile nature of the complex which involves an $Fe^{III}$–I bond makes it extremely susceptible to hydrolysis.

Molecular weight data are not available for the dimethyl derivative. Dimethyl-substituted dithiocarbamate complexes are generally characterized by low solubility, in spite of being monomeric. The five-covalent complexes are apparently no exception.

**Magnetic Behavior. (i) In Solution.**—The magnetic properties of several of these complexes were examined at room temperature in solutions of chloroform. The Gouy method was employed as was de-

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[14] L. Cambi and A. Cagnasso, *Atti Accad. Nazl. Lincei*, **13**, 254 (1931).

[15] J. S. Griffith, *Discussions Faraday Soc.*, **26**, 81 (1958).

[16] R. L. Martin and G. Winter, *J. Chem. Soc.*, 2947 (1961).

scribed for the tris(N,N-dialkyldithiocarbamato)iron(III) complexes.[3] The results are given in Table I.

Table I

Magnetic Moments of $[FeX(S_2CN(C_2H_5)_2)_2]$ in Solution

| Compound | T, °K | Concn, M | $10^6\chi_M$, cm$^3$ mole$^{-1}$ | $\mu_{eff}$, BM |
|---|---|---|---|---|
| $[Fe^{III}Cl(S_2CN(C_2H_5)_2)_2]$ | 298 | 0.031 | 6268 | 3.88 |
| $[Fe^{III}Br(S_2CN(C_2H_5)_2)_2]$ | 298 | 0.036 | 6331 | 3.87 |
| $[Fe^{III}I(S_2CN(C_2H_5)_2)_2]$ | 298 | 0.042 | 5960 | 3.79 |

(ii) **In the Solid Phase.**—The temperature dependence of the magnetic behavior of the polycrystalline solids was determined by the Gouy method using an apparatus similar to that described by Colton.[17] The compound $Hg[Co(CNS)_4]$ was adopted as the calibrant.[18] Experimental values were measured at several temperatures in order to verify the temperature dependence of $\mu_{eff}$. Values for the diamagnetic correction term, Δ, are estimated following the Pascal constants and constitutive corrections summarized by Figgis and Lewis.[19] No allowance is made for the temperature-independent paramagnetism of the ferric ion. The data are collected in Table II.

Table II

Magnetic Data, $\chi_M$ and $\mu_{eff}$, for the Compounds $[FeX(S_2CNR_2)_2]$

$[FeCl(S_2CN(CH_3)_2)_2]$ ($\Delta = -166 \times 10^{-6}$)

| Temp, °K | 109.0 | 131.8 | 166.0 | 181.0 | 213.1 | 250.8 | 279.8 |
|---|---|---|---|---|---|---|---|
| $10^6\chi_M$, cm$^3$ mole$^{-1}$ | 17,580 | 14,540 | 11,640 | 10,590 | 9040 | 7740 | 6980 |
| $\mu_{eff}$, BM | 3.93 | 3.93 | 3.95 | 3.93 | 3.94 | 3.96 | 3.97 |

$[FeCl(S_2CN(C_2H_5)_2)_2]$ ($\Delta = -212 \times 10^{-6}$)

| Temp, °K | 130.9 | 158.3 | 185.4 | 215.0 | 252.0 | 298.2 |
|---|---|---|---|---|---|---|
| $10^6\chi_M$, cm$^3$ mole$^{-1}$ | 14,780 | 12,210 | 10,420 | 9250 | 7990 | 6670 |
| $\mu_{eff}$, BM | 3.95 | 3.95 | 3.95 | 4.00 | 4.03 | 4.00 |

$[FeBr(S_2CN(C_2H_5)_2)_2]$ ($\Delta = -224 \times 10^{-6}$)

| Temp, °K | 133.8 | 173.8 | 213.5 | 250.1 | 287.8 |
|---|---|---|---|---|---|
| $10^6\chi_M$, cm$^3$ mole$^{-1}$ | 14,479 | 11,314 | 9282 | 8050 | 7069 |
| $\mu_{eff}$, BM | 3.95 | 3.98 | 3.99 | 4.02 | 4.05 |

$[FeI(S_2CN(C_2H_5)_2)_2]$ ($\Delta = -240 \times 10^{6}$)

| Temp, °K | 133.0 | 172.7 | 213.8 | 254.6 | 292.7 |
|---|---|---|---|---|---|
| $10^6\chi_M$, cm$^3$ mole$^{-1}$ | 13,270 | 10,380 | 8430 | 7180 | 6390 |
| $\mu_{eff}$, BM | 3.77 | 3.77 | 3.81 | 3.84 | 3.88 |

$[FeCl(S_2CN(sec\text{-}C_4H_9)_2)_2]$ ($\Delta = -308 \times 10^{6}$)

| Temp, °K | 88.2 | 103.2 | 121.6 | 139.1 | 157.7 | 176.2 | 201.2 | 231.4 | 255.7 | 300.3 |
|---|---|---|---|---|---|---|---|---|---|---|
| $10^6\chi_M$, cm$^3$ mole$^{-1}$ | 21,840 | 18,380 | 15,690 | 13,760 | 12,110 | 10,940 | 9670 | 8444 | 7670 | 6811 |
| $\mu_{eff}$, BM | 3.94 | 3.91 | 3.92 | 3.93 | 3.92 | 3.94 | 3.96 | 3.97 | 3.98 | 4.06 |

**X-Ray Crystal Structure.**—This has recently been reported elsewhere for the compound $[Fe^{III}Cl(CS_2N(C_2H_5)_2)_2]$ by Hoskins, Martin, and White.[13] The molecule has been shown to have the geometry depicted in Figure 1.

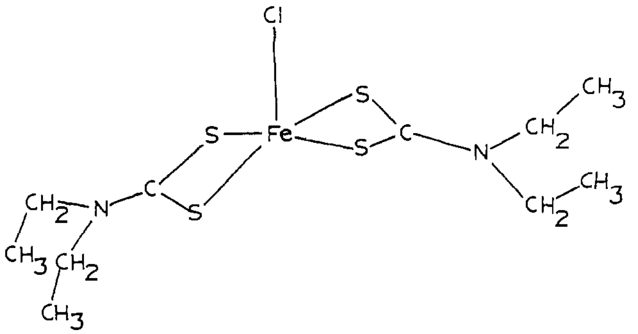

Figure 1.—Molecular structure[13] of $[FeCl(S_2CN(C_2H_5)_2)_2]$.

The Fe–Cl (2.27 A) and Fe–S(2.32 A) bond lengths are normal. The four sulfur atoms are coplanar and the Fe–Cl atoms lie on an axis at right angles to the $S_4$ plane. An important feature of the structure is the coplanarity of each of the two $FeS_2CNC_2$ skeletons even though the dihedral angle between the two planes is 50°. As a consequence the central Fe atom is 0.63 A above the $S_4$ plane.

**Infrared Absorption Spectra.**—These have been recorded in the region 2000–200 cm$^{-1}$ in KBr disks and Nujol mulls, a Perkin-Elmer Model 421 recording spectrophotometer being used. The infrared spectra in the low-wavenumber region of some representative compounds are reproduced in Figures 2 and 3.

**Electronic Absorption Spectra.**—These were recorded for several compounds in chloroform solution in the region 5000–40,000 cm$^{-1}$, a Unicam S.P. 700 recording spectrophotometer being used. Typical spectra are reproduced in Figure 4. Positions of the absorption maxima and their intensities are listed in Table III.

Because of the richness of the spectrum, some shoulders appear rather weak and even doubtful. They are marked accordingly. In the near-infrared region, chloroform is not an ideal solvent and, unfortunately, the complexes have only limited solubility in carbon tetrachloride. The complex $[Fe^{III}Cl(S_2CN(n\text{-}C_5\text{-}$

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(17) R. Colton, United Kingdom Atomic Energy Authority Report R 4186, 1963.

(18) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(19) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960, p 400.

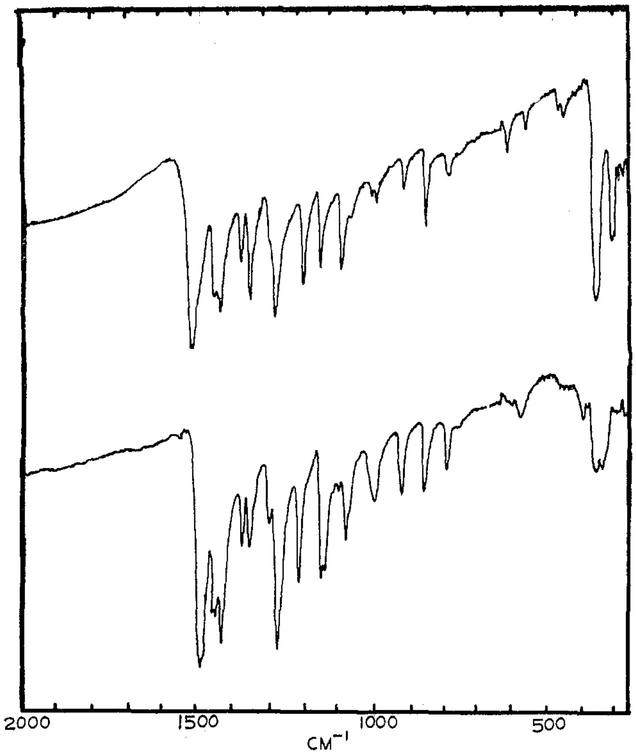

Figure 2.—Infrared spectra (KBr disks: 250–2000 cm$^{-1}$) of [$FeCl(S_2CN(C_2H_5)_2)_2$] (upper) and [$Fe(S_2CN(C_2H_5)_2)_3$] (lower).

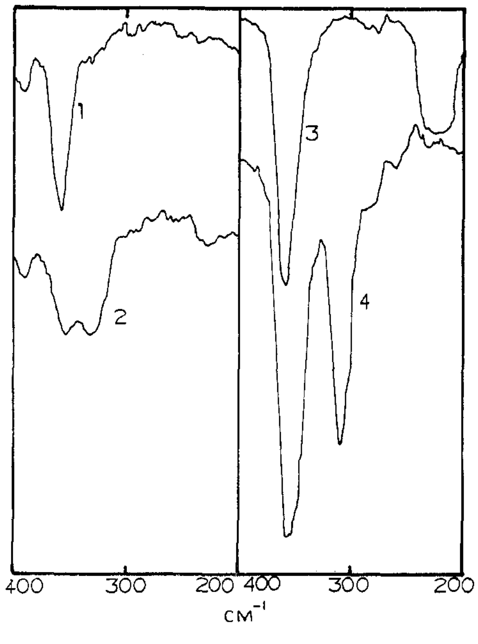

Figure 3.—Infrared spectra (KBr disks: 200–400 cm$^{-1}$) of: 1, [$Co(S_2CN(C_2H_5)_2)_3$]; 2, [$Fe(S_2CN(C_2H_5)_2)_3$]; 3, [$FeBr(S_2CN(C_2H_5)_2)_2$]; 4, [$FeCl(S_2CN(C_2H_5)_2)_2$].

$H_{11})_2)_2$] exhibits a band at 8400 cm$^{-1}$ (log $\epsilon$ 0.62) and possibly another which is largely buried in infrared overtones at 6500 cm$^{-1}$ (log $\epsilon \sim 0.55$). When the other complexes are at all soluble, these two bands seem to be present in the same positions, but it is not possible to measure them accurately.

## Discussion

The present work shows that compounds of the general type $FeX(dtc)_2$ where dtc = $R_2NCS_2$ and X = Cl, Br, and I can be prepared by allowing concentrated aqueous HX to react with the compound $Fe(dtc)_3$ dissolved in benzene. The compounds take the form of lustrous black crystals, which usually melt with decomposition at temperatures higher than 200°. They are soluble in solvents of intermediate polarity such as nitrobenzene, chloroform, and acetone, giving very intensely green solutions in the case of the chloro and bromo complexes while the iodo complexes are almost brown. They are stable in the absence of moist air but in its presence they hydrolyze slowly, the iodo compound readily so, presumably because of the presence of a labile Fe(III)–I bond. Likewise, the iodine atom is readily displaced in the presence of other halide ions. There is some evidence, yet to be fully investigated, which suggests that ionic dissociation in solution occurs with some of these derivatives.

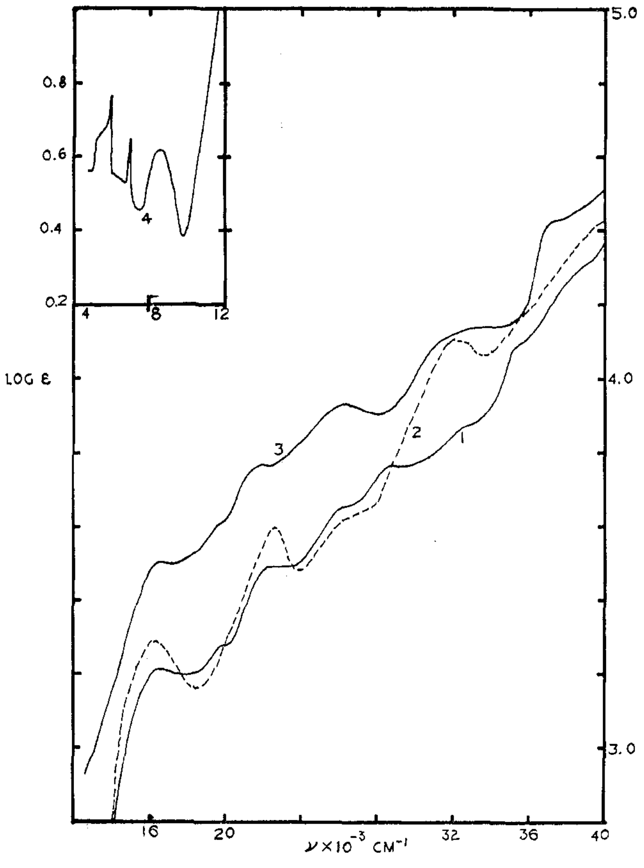

Figure 4.—Electronic absorption spectra of: 1, [$FeBr(S_2CN(C_2H_5)_2)_2$]; 2, [$FeCl(S_2CN(C_2H_5)_2)_2$]; 3, [$FeI(S_2CN(C_2H_5)_2)_2$] in chloroform solution. Spectrum 4 refers to [$FeCl(S_2CN(n\text{-}C_5H_{11})_2)_2$] in carbon tetrachloride solution.

The X-ray crystal structure confirms the monomeric nature of the substance [$Fe^{III}Cl(S_2CN(C_2H_5)_2)_2$] in the solid state.[13] The molecular structure is approximately square-pyramidal with the iron atom lying above the basal plane formed by the four sulfur atoms (*i.e.*, point group $C_{2v}$). The cryoscopic and magnetic data confirm that the molecular structure is also monomeric in solution.

The distortion which raises the metal atom above the $S_4$ plane may originate in a compromise between a condition of maximum $\sigma$ and $\pi$ overlap which requires

TABLE III

ABSORPTION BANDS OF THE MONOHALOGENODIETHYLDITHIOCARBAMATEIRON(III) COMPLEXES IN CHLOROFORM SOLUTION

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $[FeCl(S_2CN(C_2H_5)_2)_2]$ | | | | | |
| $\nu$, cm$^{-1}$ | 16,200 | 20,000 sh?? | 22,200 | 26,000 sh | 28,200 sh? | 30,000 sh | 32,200 | 35,400 sh | 38,000 sh |
| log $\epsilon$ | 3.29 | 3.28 | 3.60 | 3.63 | 3.72 | 3.91 | 4.10 | 4.16 | 4.40 |
| | | | | $[FeBr(S_2CN(C_2H_5)_2)_2]$ | | | | | |
| $\nu$, cm$^{-1}$ | 16,500 | 19,600 sh | 22,300 sh | 25,700 sh | 28,700 sh | 32,500 sh | 35,300 sh | 38,900 sh | |
| log $\epsilon$ | 3.22 | 3.27 | 3.49 | 3.64 | 3.76 | 3.87 | 4.09 | 4.31 | |
| | | | | $[FeI(S_2CN(C_2H_5)_2)_2]$ | | | | | |
| $\nu$, cm$^{-1}$ | 16,500 | 19,600 | 21,800 sh | 23,700 sh | 26,400 | 30,000 sh?? | 33,600 sh | 37,600 sh?? | |
| log $\epsilon$ | 3.50 | 3.60 | 3.76 | 3.81 | 3.93 | 3.96 | 4.14 | 4.21 | |

the metal ion to lie in the plane of the ligands and of steric expediency determined by the repulsive forces between the ligand atoms. The natural displacement of the positively charged metal ion toward the cavity formed by four sulfur and one chlorine atoms should also minimize the electrostatic potential energy of the system.[20-22]

The value of $\mu_{eff} = 3.9$ BM in the solid state is independent of temperature down to 80°K and corresponds to that expected for three unpaired electrons with no orbital contribution. The paramagnetic susceptibility is not altered in solution, which confirms that the intermediate value of the total spin, $S = {}^3/_2$, is a characteristic property of the monomeric species.

Electron spin resonance is observed[23] with a polycrystalline specimen of the compound from which the $g$ values, $g_{||} = 2.1$ and $g_{\perp} = 4.08$, can be deduced. In acetone solution,[23] $g_{av} = 3.54$, which agrees well with the root-mean-square average, $[g_{||}^2/3 + 2g_{\perp}^2/3]^{1/2} = 3.55$. The Fe–Cl axis is taken here as the $z$ axis, so that $g_{||}$ is the $g$ value in this direction; $x$ and $y$ directions pass through the planes which contain the atoms (Fe, Cl, S). The present values are similar to those ($g_{||} = 2$ and $g_{\perp} = 3.8$) observed by Gibson, Ingram, and Schonland[24] for the compound monochlorophthalocyaninatoiron(III), which almost certainly involves a similar square-pyramidal stereochemistry about the central iron atom on account of the rigidity of the phthalocyanine molecule.

The temperature dependence of the magnetism confirms that a quartet state lies lowest for [Fe(dtc)$_2$Cl]. The lowest states for [Fe(dtc)$_3$] are those which are classified as $^6A_{1g}$, $^4T_{1g}$, and $^2T_{2g}$ under the octahedral group, but $^4T_{1g}$ cannot lie lowest.[2] However, in the present square-pyramidal compound, $^4T_{1g}$ is split into an orbital singlet ($^4A_2$) and a doublet ($^4E$) under $C_{4v}$ (or into three orbital singlets $^4A_2 + {}^4B_1 + {}^4B_2$ under $C_{2v}$) so that a ground state of intermediate spin $S = {}^3/_2$ is obtained. Griffith[15] has shown an important effect of the tetragonal field in the compound monochlorophthalocyaninatoiron(III) is to depress the Kramers doublet $S_z = \pm{}^1/_2$ relative to the $S_z = \pm{}^3/_2$ Kramers doublet to give a small zero-field splitting of the $^4A_2$ ground state. The resulting ground doublet (using Griffith's determinantal notation)

$$\Psi^+ = \frac{1}{\sqrt{3}}\,[|1^+\ -1^+\ \mu^2 0^-\rangle + |1^+\ -1^-\ \mu^2 0^+\rangle + |1^-\ -1^+\ \mu^2 0^+\rangle]$$

$$\Psi^- = \frac{1}{\sqrt{3}}\,[|1^-\ -1^-\ \mu^2 0^+\rangle + |1^-\ -1^+\ \mu^2 0^-\rangle + |1^+\ -1^-\ \mu^2 0^-\rangle]$$

is characterized by $g_{||} = 2$ and $g_{\perp} = 4$. The experimental values, $g_{||} = 2.1$ and $g_{\perp} = 4.08$, agree well with the calculated values and accordingly are consistent with a relative ordering of the 3d orbitals, $3d_{xy} < 3d_{xz}, 3d_{yz} < 3d_{z^2} < 3d_{x^2-y^2}$, although the degeneracy of the ($3d_{xz}$, $3d_{yz}$) pair may be lifted by interaction with the $\pi$ system of the chelated dithiocarbamate ligand under the $C_{2v}$ symmetry. The resulting configuration of Fe(dtc)$_2$Cl—$[(3d_{xy})^2(3d_{xz},3d_{yz})^2(3d_{z^2})^1(3d_{x^2-y^2})^0]$—is just that which is derived from the valence bond method of Daudel and Bucher[3] with $d_{x^2-y^2}sp^3$ hybridization of the central iron atom. Since the ground state associated with this configuration is not orbitally degenerate ($^4A_2$), the magnetic moment is expected to lie close to the value $\sqrt{15}$ BM as is observed.

The optical spectra of these compounds are rich in absorption bands. The high molar absorbance of the majority of the bands suggests that they have their origin in metal-to-ligand and ligand-to-metal charge-transfer transitions. Ligand–ligand bands are also present. Notable exceptions are the two weak near-infrared bands at 6500 and 8400 cm$^{-1}$, which are likely to have their origin in spin-allowed internal transitions within the d shell. The assignments $(xy) \rightarrow (xz,yz)$ at 6500 cm$^{-1}$ and $(xy) \rightarrow (z^2)$ at 8400 cm$^{-1}$ are possible. Alternatively, both transitions may terminate in $(x^2 - y^2)$ from $(z^2)$ and $(xz,yz)$, respectively. Any attempt to assign these bands is complicated by the likelihood of interaction of the metal and ligand $\pi$ systems lifting the degeneracy of the $3d_{xz}$, $3d_{yz}$ pair.

The infrared spectra contain several features of special interest. Intercomparison of the spectra of the complexes $FeCl(S_2CN(C_2H_5)_2)_2$, $FeBr(S_2CN(C_2H_5)_2)_2$, $Co(S_2CN(C_2H_5)_2)_3$, and $Co(Se_2CN(C_2H_5)_2)_3$ enables the Fe–Cl, Fe–Br, and Fe–S stretching vibrations to be

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assigned to the frequencies 309, 225, and 353 $cm^{-1}$, respectively. The Fe–Cl frequency is rather lower than those observed[25] for the $[FeCl_4]^-$ anion (376 $cm^{-1}$) and the complex cation $[FeCl_2(diarsine)_2]^+$ (373 $cm^{-1}$).[26] Certainly, a $\nu$(Fe–Cl) stretching mode is expected to shift progressively to lower frequencies as the coordination number of the metal increases from four to six, although the trend may be confused by the effects of steric interaction, double bonding, and differences in d subshell populations.[27] In the present instance, the increase in length of the Fe–Cl bond from 2.19 A in the $[FeCl_4]^-$ anion to 2.27 A in the complex species $[FeCl(S_2CN(C_2H_5)_2)_2]$ parallels the marked lowering of frequency.

The Fe–S stretching mode at 353 $cm^{-1}$ lies in the range 300–400 $cm^{-1}$ which we have observed for a wide variety of disubstituted dithiocarbamates of the first-row transition metals in their tervalent oxidation state.[4] It will be noticed that the comparisons are made with $Co(dtc)_3$ rather than $Fe(dtc)_3$, since the Fe–S stretching vibrations in the latter complex are greatly broadened by the coexistence of $^2T_2$ and $^6A_1$ states in equilibrium and also perhaps because of Jahn–Teller instability in the former level. The C–N frequency is considerably raised to 1500 $cm^{-1}$, which suggests extensive $\pi$ conjugation in this ligand,[28] a fact confirmed by the planarity of the ligand and the shortened C–N bond length of 1.31 A (C–N single bond distance 1.472 A).[13] The occurrence of the $\nu$(Fe–Br) stretching mode at 225 $cm^{-1}$ is expected, and the ratio $\nu$(Fe–Br):$\nu$(Fe–Cl) = 0.73 is the usual value observed for compounds of the first-row transition metals.[27] The corresponding $\nu$(Fe–I) vibration is expected[29,30] at $\sim 0.65\nu$(Fe–Cl), *i.e.*, at about 200 $cm^{-1}$ or slightly lower which is outside the range of the instrument used in these studies.

An interesting feature of these studies was our failure to prepare analogous compounds of the type $[M^{III}X(S_2CNR_2)_2]$ with $M^{III}$ = Cr and Co, using the same synthetic procedure as for $M^{III}$ = Fe. It would appear that the tris(diethyldithiocarbamato) chelates of $Cr^{III}$ ($t_{2g}^3$) and $Co^{III}$ ($t_{2g}^6$) are kinetically inert, and that the lability of the $Fe(dtc)_3$ system is a reflection of the presence of the equilibrium between low-spin ($t_{2g}^5$) and high-spin ($t_{2g}^3e_g^2$) states.[4] Taube has suggested that a similar unexpected lability of $[Co(H_2O)_6]^{3+}$ may likewise arise from the presence of a low-lying paramagnetic excited (and labile) state of the hexaaquo complex.[31,32]

In conclusion, we note that Wickman and Trozzolo[33] have recently published the Mössbauer spectra of several complexes which they believed to be of the type $[Fe(S_2CN(CH_3)_2)_3]$ and $[Fe(S_2CN(i\text{-}C_3H_7)_2)_3]$. A feature of the spectra (which consist of two sharply defined peaks at 300°K) is the large quadrupole splittings of 2.68 mm/sec = 3.14 Mc/sec ($^{57}$Co:Pd source) which are much larger than those normally observed for low-spin iron(III) octahedral compounds. A subsequent erratum by these workers[34] explains that the complexes studied were not of the type $[Fe(dtc)_3]$, but, in fact, were the monochlorobis(dithiocarbamato)iron(III) derivatives discussed here. Certainly, their observed quadrupole splittings are quite consistent with the very large electric field gradient at the iron nucleus expected for the $C_{2v}$ point symmetry. More recent studies by several groups working independently have shown that the Mössbauer spectra of complexes of the type $[Fe(dtc)_3]$ are characterized at room temperature by quadrupole splittings in the range $\Delta E_Q$ = 0.2–0.7 mm/sec and isomer shifts of $\delta$ = 0.1–0.3 mm/sec (relative to a $^{57}$Co:Cu source).[35-37] Very recently, Wickman, *et al.*,[38] have confirmed that the magnetic susceptibility of the diethyl complex follows the Curie law with a paramagnetic Curie temperature of 3.6°K with $\mu_{eff}$ = 3.98 BM. An interesting feature which emerges from their measurements is that a ferromagnetic transition occurs at $T_c = 2.51 \pm 0.05$°K. The quadrupole doublet Mössbauer spectrum changes little between 300 and 3°K, but below 3°K broadening occurs and at 2.4°K the spectrum is completely washed out indicating that the ferromagnetic transition has occurred. The sharp six-line spectrum expected for an ordered magnetic spectrum is observed at 1.6°K.[39]

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(39) NOTE ADDED IN PROOF.—Recent epr and Mössbauer measurements in the helium temperature range by Dr. H. H. Wickman have shown that the zero-field splittings in the spin quartet leave the $|+^3/_2\rangle$ doublet lying lowest and that mixing of the $|\pm^1/_2\rangle$ levels into the ground state is small. The lower doublet $|\pm^3/_2\rangle$ is effectively nonresonant ($g_{||} = 6$; $g_\perp = 0$) and therefore does not contribute to the epr measurements at room temperature discussed above. A detailed account of these low-temperature studies will appear elsewhere.