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Mixed-ligand Iron(III) Dithiocarbamates. Calculation of Ligand Field Parameters in Electron Spin Crossover d^5 Systems by Combination of Spectral and Magnetic Data

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New mixed-ligand iron(III) dithiocarbamate complexes of the general formula $Fe(R_2dtc)_2(R'_2dtc)$ *have been prepared and characterized. These complexes contain two different dithiocarbamate ligands with different ligand field strengths. Magnetic measurements show an electron spin crossover equilibrium that depends on the nature of the two dithiocarbamate ligands. Values of the ligand field parameters* Δ, *B and* β_{35} *are given and were calculated from a combination of the spectral and magnetic properties of the complexes. These values seem more reasonable than those previously reported, which were calculated on the basis of crystal field bands. Assignments for the charge transfer bands in the complexes have also been made.*

Introduction

In the last ten years, tris(dialkyldithiocarbamato)-iron(III) complexes have attracted much interest because of their often unusual electronic and structural properties [1–10]. Noteworthy properties of these complexes are the frequent occurrence of the doublet (S = 1/2; sextet (S = 5/2) spin equilibrium [1, 2, 5, 11, 12], the well-resolved isotropically shifted nmr spectra whose temperature dependencies reveal the spin equilibrium [3, 4] and their structures which are distorted toward a trigonal-prismatic geometry [13, 14].

Recently, some researchers [6, 15, 16] have prepared and studied, by the PMR technique, the dynamic stereochemistry of several interesting mixed-ligand iron complexes such as the bis(N,N-disubstituted dithiocarbamato)dithiolenes, $Fe(R_1R_2dtc)_2(S_2C_2R_2)$. Also, the formation of a number of mixed-ligand (dithiocarbamato)iron(III) complexes have been observed by nmr where equimolar amounts of two tris(dialkyldithiocarbamato)iron(III) complexes were present [17]. But, to our knowledge no single mixed-ligand dithiocarbamate iron complex has been isolated and studied.

The synthesis of the very interesting five-coordinate halogenobis(dialkydithiocarbamato)iron(III) complexes by Wickman and Trozzolo [18], and the isolation of a mixed-ligand dithiocarbamato–xanthato Cobalt(III) complex by Brinkhoff [19] prompted us to synthesize and study some new mixed-ligand dithiocarbamate iron(III) complexes.

Presented here are the results of our work on the synthesis, spectral study and magnetic properties of six new mixed-ligand dithiocarbamate iron(III) complexes of the general formula $Fe(R'_2dtc)\ (R_2dtc)_2$ where R_2 = Pyrr, R′ = Et or i-Pr; R'_2 = Pyrr, R = Et or i-Pr; R = Et, R′ = i-Pr; R = i-Pr, R′ = Et (Pyrr = pyrrolidyl, Et = ethyl, i-Pr = isopropyl, n-Pr = n-propyl). The characterization and study of these complexes were done by elemental analysis, molecular weight and magnetic susceptibility measurements, and by electronic and infrared spectroscopy. Similar mixed-ligand complexes with dithio- or diselenocarbamate, or xanthate ligands of the VA Group elements have already been prepared in this laboratory and the results will be published soon.

In this paper we are particularly interested in showing what behavioral differences appear as a consequence of the coexistence of the two dithiocarbamate ligands. The ligands have been selected to have different ligand field strengths and to involve amine groups of different stereochemical structures but of about the same electron releasing ability. In particular, the ligand $i\text{-}Pr_2dtc$ forms low-spin complexes with iron(III), the Et_2dtc forms complexes which lie at the crossover between high-spin and low-spin states and the Pyrrdtc forms high-spin complexes.

There exists some doubt about the assignment of the spectral bands and the values of the ligand field parameters found in the literature for the iron(III) dithiocarbamate complexes [2, 5]. The influence of the coexistence of the two ligands on the electronic, magnetic and stereochemical behavior of the complexes would seem to be important, because in the case of iron(III) the electronic and magnetic behavior depends greatly on the nature of the dithiocarbamate

TABLE I. Electronic Spectral Data.

Compound	Band I		Band II		Band III		Band IV		Band V		Band VI	
	$\tilde{\nu}$(kK)	$\epsilon_{mol} \times 10^{-4}$	$\tilde{\nu}$(kK)	$\epsilon_{mol} \times 10^{-4}$	$\tilde{\nu}$(kK)	$\epsilon_{mol} \times 10^{-4}$	$\tilde{\nu}$(kK)	$\epsilon_{mol} \times 10^{-3}$	$\tilde{\nu}$(kK)	$\epsilon_{mol} \times 10^{-3}$	$\tilde{\nu}$(kK)	ϵ_{mol}
(Pyrrdtc)Fe(Et$_2$dtc)$_2$	38.0	4.38	28.8	1.14	25.6	0.90	19.5	2.95	17.1	2.30	6.4	8.3
(Et$_2$dtc)Fe(Pyrrdtc)$_2$	38.2	4.73	28.4	1.13	25.5	0.91	19.7	3.34	16.9	3.01	6.4	9.1
(i-Pr$_2$dtc)Fe(Et$_2$dtc)$_2$	37.9	4.62	28.9	1.27	25.4	1.00	19.6	2.99	17.0	2.05	6.4	8.7
(Et$_2$dtc)Fe(i-Pr$_2$dtc)$_2$	37.3	4.10	28.6	1.33	25.2	1.00	19.5	2.34	16.2	1.04	6.95	7.5
(Pyrrdtc)Fe(i-Pr$_2$dtc)$_2$	37.3	3.63	28.6	1.16	25.1	0.87	19.7	2.07	16.3	0.97	7.25	7.0
(i-Pr$_2$dtc)Fe(Pyrrdtc)$_2$	38.3	5.53	28.0	1.21			19.7	4.08	16.8	3.93	6.32	8.5
Fe(Pyrrdtc)$_3$[a]	36.4		28.1				19.8		17.0		6.5	
Fe(Et$_2$dtp)$_3$[a]			27.8				20.1		16.6		10.8 7.5	
Fe(Et$_2$dtc)$_3$[b]	38.0	4.15	28.9	1.02	25.6	0.80	19.5	2.61	17.1	1.94	6.5	8.2
Fe(n-Pr$_2$dtc)$_3$[b]	37.5	3.32	29.0	1.05	26.0	0.85	19.4	3.2	16.7	2.5	6.5	4.35
	35.5	3.08									5.8	4.90
Fe(EtXant)$_3$[a]	36.0		27.2		22.1				17.8		8.6	
Fe(i-Pr$_2$dtc)$_3$[b]	36.9	3.90	28.5	1.35	25.4	1.03	19.9	2.10	15.8	0.6	7.4	7.1

[a] Ref. 5. [b] This work.

ligand. Thus, another main interest of this is the interpretation of the electronic spectra of the new complexes. More reasonable values for the ligand field parameters of the iron(III) dithiocarbamate complexes can be obtained from a combination of the spectral and magnetic data according to a treatment described in this paper.

Results and Discussion

It is well known [18] that iron(III) halides react easily with sodium dithiocarbamate salts, at appropriate relative amounts, to give halogenobis-(dialkyldithiocarbamate) complexes. These undergo further substitution of the halogen by a third dithiocarbamate group. This latter observation suggested the preparation of the mixed-ligand iron(III) dithiocarbamate complexes according to the following general reaction:

$$Fe(R_2dtc)_2X + M(R_2'dtc) \rightarrow Fe(R_2'dtc)(R_2dtc)_2 + MX$$

where M = Na, or $(R_2'NH_2)$, and X = Cl.

All are new compounds, and constitute the first isolated of a class of mixed-ligand dithiocarbamate complexes which contain two different dithiocarbamate ligands. The complexes are black or brown–black crystalline solids that are stable in the air. They undergo a gradual decomposition in $CHCl_3$. After several hours the solutions are decolorized and a brown precipitate appears. The analytical data, the molecular weights, and the spectral and magnetic data are presented in Tables I–IV. The complexes are soluble in chloroform, acetone, benzene, methylene chloride, and are insoluble in methanol, ethanol, petroleum ether, and water.

Electronic Spectral and Magnetic Data

The electronic spectral data of the mixed-ligand iron(III) dithiocarbamates and the corresponding iron(III) tris(dialkyldithiocarbamate) complexes are given in Table I. Also presented in Table I are the electronic spectral data for the high-spin iron(III) dithiophosphate complex, $Fe(Et_2dtp)_3$, the cross-over iron(III) di-n-propyldithiocarbamate complex, $Fe(n-Pr_2dtc)_3$, and the low-spin iron (III) ethylxanthate complex, $Fe(EtXant)_3$. The data for these known compounds are included, since they were used to help confirm the validity of the proposed method of calculation of the ligand field parameters from charge transfer bands.

The electronic spectra of the mixed-ligand and normal tris complexes may be conveniently divided into three regions; (i) 40.0–32.0 kK, (ii) 32.0–15.0 kK, and (iii) 15.0–5.0 kK. Region (i) contains the intraligand $\pi \rightarrow \pi^*$ transition of the dithiocarbamate groups and is found in the spectra of all dithiocarba-

TABLE II. Magnetic Data, the Contribution of the $^6A_1$ and $^2T_2$ States to the Frequencies of the CT Bands, and the Ligand Field Parameters.

Compound	μ_{eff}^{corr} (BM)	α	$\tilde{\nu}_2 - \tilde{\nu}_1$		D_q (cm^{-1})	B (cm^{-1})	β_{35}	z*
			Calc.	Exp.				
(Pyrrdtc)Fe(Et$_2$dtc)$_2$	4.51	0.39	11.76	11.7	1520	–	–	–
(Et$_2$dtc)Fe(Pyrrdtc)$_2$	4.97	0.25	11.52	11.5	1370	–	–	–
(i-Pr$_2$dtc)Fe(Et$_2$dtc)$_2$	4.22	0.47	11.90	11.9	1610	–	–	–
(Et$_2$dtc)Fe(i-Pr$_2$dtc)$_2$	3.24	0.76	12.39	12.4	1920	583	0.57	+0.75
(Pyrrdtc)Fe(i–Pr$_2$dtc)$_2$	3.05	0.81	12.48	12.3	1960	588	0.58	+0.77
(i-Pr$_2$dtc)Fe(Pyrrdtc)$_2$	5.41	0.12	11.30	11.2	1230	547	0.54	+0.64
Fe(Pyrrdtc)$_3$	5.83	0.00	11.10	11.1	1110 (1900)†	517 (750)†	0.51	+0.55
Fe(Et$_2$dtp)$_3$	5.61	0.06	11.20	11.2	1170 (735)†	560 (410)†	0.55	+0.68
Fe(Et$_2$dtc)$_3$	4.37	0.43	11.83	11.8	1570	–	–	–
Fe(η-Pr$_2$dtc)$_3$	4.14	0.49	11.93	12.3	1670	–	–	–
Fe(EtXant)$_3$	2.55	0.96	–	9.4	1800 (2240)†	447 (650)†	0.44	+0.36
Fe(i-Pr$_2$dtc)$_3$	2.41	1.00	12.80	12.8	2180	685	0.67	+1.13

†Ref. 5.

TABLE III. Relevant I.r. Frequencies (cm^{-1}) of the Mixed-ligand Iron(III) Dithiocarbamates with their Assignments.

Compound	$\tilde{\nu}$(C···N) (cm^{-1})	$\tilde{\nu}$(C···S) (cm^{-1})
(Pyrrdtc)Fe(Et$_2$dtc)$_2$	1477 vs 1470 vs, sh	992 s 910 s 844 s
(Et$_2$dtc)Fe(Pyrrdtc)$_2$	1476 vs 1465 vs	996 s 943 s 908 s 843 m 828 m
(i-Pr$_2$dtc)Fe(Et$_2$dtc)$_2$	1480 vs	990 s 912 s 845 s
(Et$_2$dtc)Fe(i-Pr$_2$dtc)$_2$	1476 vs	1035 m 992 w 908 w 846 m
(Pyrrdtc)Fe(i-Pr$_2$dtc)$_2$	1474 vs	1035 m 944 w 845 w
(i-Pr$_2$dtc)Fe(Pyrrdtc)$_2$	1476 vs 1464 vs	997 w 943 m 909 w 827 w

mate complexes [20]. Region (ii) contains three or four bands which are attributed to metal-to-ligand and ligand-to-metal charge transfer transitions. Their high molar absorptivity ($\epsilon \sim 1000$–13000) is indicative of charge transfer bands [5, 21–23]. Region (ii) is of special concern in this investigation and will be discussed extensively.

In region (iii) (near infrared) the d → d electronic transition occur (crystal-field band). The low intensity of this band, as well as its width, is indicative of a spin forbidden transition as expected of Fe(III) in an octahedral environment. The band of this region is also fairly broad, because the $^6A_1 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_1$ transitions correspond to a change of configuration from $t_{2g}^3e_g^2$ to $t_{2g}^4e_g$ and from t_{2g}^5 to $t_{2g}^4e_g$ respectively. Its frequency increases from the high-spin to the low-spin complexes while its intensity does not vary significantly. The band is split and this behavior becomes more pronounced in those complexes whose magnetic moment is lower than that of the iron(III) diethyldithiocarbamate complex (μ_{eff} = 4.37 BM). This observation indicates that the near infrared band of the complexes consists of two overlapping bands: One is due to the high-spin state and the other to the low-spin state [2, 5].

Ewald *et al.* [5], on the basis of the crystal-field bands, have estimated the ligand field parameters. As they mentioned, their results do not seem reasonable, since it was not possible to obtain data unobscured by the charge transfer bands.

Four charge transfer bands are expected for an octahedral iron(III) complex [22, 24]. Jørgensen [25] has shown that, for complexes formally containing cations of d^q configuration, the position of the Laporte-allowed bands may be satisfactorily expressed by the following equations:

$$\pi \rightarrow t_{2g} \qquad \nu_1 = V_1 - q(E - A) + k_1D \qquad (1)$$

$$\pi \rightarrow e_g \qquad \nu_2 = V_1 - q(E - A) + k_2D + \Delta \qquad (2)$$

TABLE IV. Analytical Data and Some Physical Properties.

Compound	Color	M.P. (°C)	Analysis (%)								MW	
			C		H		N		Fe			
			Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$(Pyrrdtc)Fe(Et_2dtc)_2$	Black	228 d[a]	36.1	36.5	5.7	5.8	8.4	8.4	11.2	11.2	498.6	518
$(Et_2dtc)Fe(Pyrrdtc)_2$	Black	190 d	36.3	36.0	5.3	5.3	8.5	8.4	11.2	11.2	496.6	495
$(i\text{-}Pr_2dtc)Fe(Et_2dtc)_2$	Black	247 d	38.6	36.3	6.5	6.2	8.0	8.2	10.6	10.6	528.7	525
$(Et_2dtc)Fe(i\text{-}Pr_2dtc)_2$	Black	237 d	41.0	41.0	6.9	6.8	7.6	7.8	10.0	10.0	556.8	555
$(Pyrrdtc)Fe(i\text{-}Pr_2dtc)_2$	Brown	205 d	41.1	41.5	6.5	6.7	7.6	7.6	10.1	10.1	554.8	559
$(i\text{-}Pr_2dtc)Fe(Pyrrdtc)_2$	Brown–Black	265 d	38.9	37.8	5.8	5.1	8.0	7.7	10.6	10.6	524.7	537

[a] d = with decomposition.

$$t_{2g} \rightarrow \pi^* \qquad \nu_3 = V_2 + q'(E - A) + k_3D \qquad (3)$$

$$e_g \rightarrow \pi^* \qquad \nu_4 = V_2 + q'(E - A) + k_4D - \Delta \qquad (4)$$

A method combining the magnetic and electronic spectral data was applied for the calculation of the ligand field parameters for d^5 complexes as follows.

High-spin d^5 Complexes

For an octahedral high-spin (S = 5/2) d^5 complex, in the equations (1), (2), (3), and (4) $k_1 = k_2 = k_3 = k_4$, and the average contribution of the spin-pairing energy (ΔSPE) to the energy of the CT bands is equal to +8/3D. In reality the complexes are not octahedral, but for the present purpose it is a good approximation to treat them as such.

If equation (1) is substracted from (2), and (4) from (3), then for the case of the high-spin complexes:

$$(\nu_2 - \nu_1)_{(^6A_1)} = \Delta_{(^6A_1)} \qquad (5)$$

and

$$(\nu_3 - \nu_4)_{(^6A_1)} = \Delta_{(^6A_1)} \qquad (6)$$

Considering the fact that the first Laporte allowed CT band, at about 17.0 kK, of the iron(III) dithiocarbamate complexes is due to the charge transfer from the sulfur atom to the iron atom [26], ν_1 must be a $\pi \rightarrow t_{2g}$ band. This is in good agreement with the bibliographic data for other iron(III) complexes [23, 24, 27].

It is well known [27] that the dithiocarbamate ligands in the spectrochemical series are stronger than F^- but weaker than H_2O. Since the Δ value of the iron(III) pyrrolidyldithiocarbamate, a high-spin complex (μ_{eff} = 5.83 BM), is about 13500 cm^{-1} *i.e.* between $\Delta_{H_2O} = 14300\ cm^{-1}$ and $\Delta_{F^-} = 13000\ cm^{-1}$, the position of the $\pi \rightarrow e_g$ CT band can be roughly calculated. Thus, the $\pi \rightarrow e_g$ transition, ν_2, can be found in the region of about 30.0 kK. Actually, in the electronic spectra of the tri(pyrrolidyldithiocarbamato)iron(III) complex as well as in those of other iron(III) dithiocarbamates, there exists a band in this region; consequently, the absorption in the 28.0 kK region may be attributed to the second Laporte-allowed $\pi \rightarrow e_g$ CT band. The frequency of the absorption in the region of 17.0 kK decreases from the high- to low-spin complexes, while that of about 28.0 kK increases. This observation justifies the above band assignments because of the greater octahedral splitting in the low-spin complexes relative to the high-spin complexes. The energy of the $\pi \rightarrow \pi^*$ transition is about the same for the two types of complexes (Table I).

On the basis of the assignments for ν_1 and ν_2, the value of the ligand field parameter, Δ, can be calculated from the difference $\nu_2 - \nu_1$. The values obtained for the high-spin complexes are given in Table II.

From the calculated values of Δ from the CT bands and on the basis of the energy separation between ground and excited states ($^6A_1 \rightarrow {}^4T_1$) in the crystal field bands, which is 10B + 6C − Δ ≅ 34B − Δ for the high-spin complexes (if the usual assumption that C ≅ 4B is made), the Racah parameter, B, and the nephelauxetic ratio, β_{35}, can be calculated. The results are also shown in Table II.

Low-spin d^5 Complexes

In the low-spin d^5 complexes, as in the case of the tris(diisopropyldithiocarbamato)iron(III) (μ_{eff} = 2.41 BM), ΔSPE in equations (1) and (2) is equal to +2/3D and −4/3D respectively. Thus, it follows that

$$(\nu_2 - \nu_1)_{(^2T_2)} = \Delta_{(^2T_2)} - 2D \qquad (7)$$

Now, if the value of D is chosen to equal 4.5 kK, the average value of D calculated for the iron(III) complexes [23, 28], the values of Δ can be obtained for the low-spin complexes from $\nu_2 - \nu_1$. This value of D does not differ greatly from that of about 3.8 kK calculated from the spectral data of the high-spin iron(III) dithiocarbamates. Variation in the magnitude of D between 3.8 kK to 5.3 kK, from high-spin to low spin d^5 complexes, does not greatly influence the values obtained for the ligand field parameter Δ. Thus, a change in D from 4.5 kK to 5.3 kK results in larger values of Δ of about 10%. From the calculated values of Δ and the energy separation $^2T_2 \rightarrow {}^4T_1$ of the low-spin d^5 complexes, which is Δ − 5B − 4C ≅ Δ − 21B, B and β_{35} can be evaluated (Table II).

Electron Spin Crossover d^5 Complexes

For the iron(III) complexes whose magnetic susceptibilities show an equilibrium between high-spin and low-spin isomers, [S(= 5/2) ⇄ S (= 1/2)], it is not possible to determine Δ from equations (5) and (7). The difficulty is due to the unknown contribution of the spin pairing energy to the energy of the CT bands (k_1 and k_2 are unknown). For the spin crossover systems (Table II) Δ can be evaluated by a proper combination of the spectral and magnetic properties of the complexes. It is well established that the ratio, α which is the contribution of the magnetic moment of the low-spin isomer to the observed magnetic moment of the spin crossover system, is given by the relation

$$\alpha = \frac{\mu_{eff}^{H} - \mu_{eff}^{obs}}{\mu_{eff}^{H} - \mu_{eff}^{L}}$$

In this equation μ_{eff}^{H} is the magnetic moment of the high-spin isomer, μ_{eff}^{L} the magnetic moment of the low-spin isomer, and μ_{eff}^{obs} the measured magnetic moment of the spin crossover system [29]. If the contribution of the magnetic moments of the two isomers to the magnetic moment of the spin crossover system is multiplied by the corresponding differences of the energy between the two first Laporte-allowed CT bands ($\nu_2 - \nu_1$) of each isomer, the sum gives the energy difference ($\nu_2 - \nu_1$) for the spin crossover system (Table II), that is

$$(\nu_2 - \nu_1)_{(^6A_1 \rightleftarrows {}^2T_2)} = (1-\alpha)(\nu_2 - \nu_1)_{(^6A_1)} + \alpha(\nu_2 - \nu_1)_{(^2T_2)} \qquad (8)$$

In our calculations we consider as low-spin complex the tris(diisopropyldithiocarbamato)iron(III) (μ_{eff}^{L} = 2.41 BM) and as a high-spin complex the tri(pyrrolidyldithiocarbamato)iron(III) (μ_{eff}^{H} = 5.83 BM). The calculation assumes a value of 2.30 BM for the $^2T_2$ state and 5.83 BM for the $^6A_1$ state, which are very close to the values used in our treatment.

Since

$$(\nu_2 - \nu_1)_{(^6A_1 \rightleftarrows {}^2T_2)} = \Delta_{(^6A_1 \rightleftarrows {}^2T_2)} - KD, \qquad (9)$$

by combining equations (5), (7), (8), and (9) equation (10) is obtained.

$$\Delta_{(^6A_1 \rightleftarrows {}^2T_2)} - KD = (1-\alpha)\Delta_{(^6A_1)} + \alpha\Delta_{(^2T_2)} - 2\,\alpha D \qquad (10)$$

But, by taking into account that in mixed-ligand octahedral complexes the cubic field magnitude is the weighted average of the cubic ligand fields associated with each of the complete set of ligands separately [30], and subtracting the relationship

$$\Delta_{(^6A_1 \rightleftarrows {}^2T_2)} = (1-\alpha)\Delta_{(^6A_1)} + \alpha\Delta_{(^2T_2)}$$

from equation (10), results in

$$K = 2\alpha$$

Consequently, for the calculation of Δ for the spin crossover systems, the following equation is used:

$$(\nu_2 - \nu_1)_{(^6A_1 \rightleftarrows {}^2T_2)} = \Delta_{(^6A_1 \rightleftarrows {}^2T_2)} - 2\alpha D \qquad (11)$$

The results obtained are given in Table II and are in good agreement with the values obtained on the basis of the average-environment rule.

In order to judge the validity of our approach to the assignements of the CT bands and the correctness of the Δ values obtained, the optical electronegativity, X_{opt}, of sulfur for both high-spin and low-spin complexes was calculated. Values for X_{opt} for Fe^{3+} of 2.5 for the high-spin and 2.1 for the low-spin complexes were used [31]. The calculation was done by using the L → M CT bands [32]. The result obtained is 2.8 and is in good agreement with those previously reported of 2.6 to 2.7 for sulfur in dithiocarbamate complexes [26].

The results for Δ, according to the proposed method, are smaller than those calculated on the basis of the crystal-field bands [5] (Table II), but they are in good agreement with those obtained for other dithiocarbamate complexes [19, 33]. In addition, the calculated Δ values for the low-spin iron(III) dithiocarbamates are in good agreement with those for other low-spin iron(III) complexes which were calculated from the crystal-field bands, sufficiently free of CT bands, of their spectra [34, 35].

Furthermore, Δ values for the complexes Fe(Et_2dtp)$_3$ and Fe(Et_2dtc)$_3$ are in good agreement with the values calculated on the basis of the equation [25]

$$\Delta = f_{\mathrm{ligand}} \times g_{\mathrm{ion}} \qquad (12)$$

where $g_{Fe^{3+}} = 14.0$ and $f_{\mathrm{ligand}} = 0.83$ for Et_2dtp and 0.90 for Et_2dtc [29]. The results for Δ based on this equation are 11600 cm^{-1} and 12600 cm^{-1} for Fe(Et_2dtp)$_3$ and Fe(Et_2dtc)$_3$ respectively, and indicate that the Δ values for the dithiocarbamate complexes calculated according to the method proposed here are reasonable.

The Δ values for the complexes lead to the following spectrochemical series:

$$\begin{array}{ccccc} \text{Pyrrdtc} < & Et_2\text{dtp} < & F^- < & H_2O < & Et_2\text{dtc} < \\ 11100 & 11700 & 13000 & 14300 & 15700 \end{array}$$

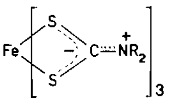
$$\begin{array}{ccc} n\text{-}Pr_2\text{dtc} < & \text{EtXant} < & i\text{-}Pr_2\text{dtc} \\ 16700 & 18000 & 21800 \end{array}$$

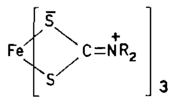
Here, the ligands F^-, Et_2dtc, Et_2dtp, and EtXant have the same position as they have in the series suggested by Jørgensen [27]. The only exception is the position of H_2O which is after EtXant in the series of Jørgensen. In our opinion, the position of water in the Jørgensen series, in the case of iron(III) complexes, is not the proper one. According to the magnetic moment of the $Fe(H_2O)_6^{3+}$ complex (μ_{eff} = 5;9 BM), water should be near F^- and certainly before EtXant and Et_2dtc.

The mean pairing energy ($\pi = 7\ 1/2\ B + 5C \cong 27\ 1/2\ B$) was also determined from the B values and it was found to be about 14000 cm^{-1} for high-spin and about 19000 cm^{-1} for low-spin complexes. These values are lower than those estimated by Griffith *et al.* [36], but they are in agreement with the suggestion of Ewald *et al.* [2] that the pairing energy might be as large as the ligand field parameter Δ. The values satisfy the requirements of the inequality $\Delta(^6A_1) < \pi < \Delta(^2T_2)$ which is valid for the spin crossover complexes. In the case of the tris(di-n-propyldithiocarbamato)iron(III) complex, whose room temperature magnetic moment indicates about a 50% contribution of each of the low- and high-spin states, the value of Δ will be equal to that of the mean pairing energy, π, at the crossover point. This is about 16500 cm^{-1}.

The nephelauxetic parameter, β_{35}, for the low- and high-spin complexes is readily obtained from the relation $\beta_{35} = B/B_0$, where B_0 = 1015 cm^{-1} for iron(III). In the case of the spin crossover complexes, B and β_{35} can not be calculated. The reason is that the contribution of the energy of the d → d transitions of the low- and high-spin isomers to the energy of the d → d transition of the spin crossover systems is unknown. In any case, the values of B of the spin crossover systems should lie between 520 and 650 cm^{-1} and those of β_{35} between 0.51 and 0.67.

The nephelauxetic effect has been correlated with the covalency of ligand-metal σ bonds. In the case of the iron(III) dithiocarbamates, the β_{35} values show that the M–S bonds of the low-spin complexes are more covalent than those of the high-spin complexes. Of the two structures, (I) and (II), structure (I) is expected to produce stronger ligand fields.


I


II

In structure (II) the increased electron density on the sulfur atoms reduces the covalency of the M–S bonds. As a result, the metal–sulfur bonds are lengthened and the high-spin state is favored. This is in agreement with the observations of Eley *et al.* [7], but contrary to the suggestions of Ewald and his collaborators [5].

The fact that structure (I) favors the formation of low-spin complexes is supported on the basis of a determination of the effective positive charge of the cation. The effective positive charge, z*, is usually calculated from B values according to the equation of Jørgensen [37]:

$$B(cm^{-1}) = 384 + 58q + 124(z^* + 1) - 540/(z^* + 1)$$

Because of the interaction of partially filled d orbitals of the metal with empty π orbitals of the ligand (π-back donation), it is in structure (I) that the metal atom would be expected to have the greater effective positive charge. This has been observed for the complexes presented here; thus, an effective positive charge of +1.13 for the low-spin and +0.55 for the high-spin complexes has been calculated. This comparison is permissible because the amine groups of the dithiocarbamate ligands used are of about the same electron releasing ability.

Both β_{35} and z* values calculated in the present work confirm the results of Eley *et al.* [7], and support the hypothesis of Cervone *et al.* [26], that the degree of covalency is possibly higher in the low-spin iron(III) dithiocarbamate complexes than in the high-spin complexes.

In the spectra of the high-spin complexes there is a band in the 20.0 kK which appears at about 25.0 kK for the low-spin complexes. Both bands may be assigned to a $t_{2g} \rightarrow \pi^*$ CT transition. This assignment is supported by the observed blue shift. In the spectra of the spin crossover systems both bands appear and it is evidence for a doublet–sextet spin-state equilibrium.

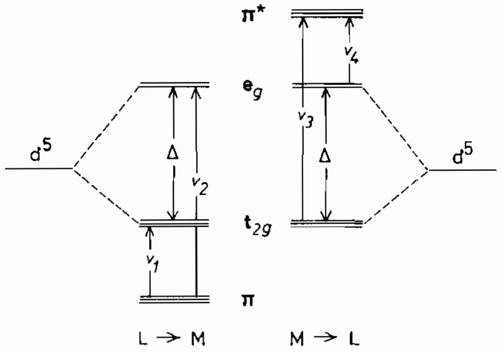


Figure 1. Possible CT transitions for an O_h d^5 configuration.

In the case of the high-spin complexes, the sum of the energies of the $\pi \rightarrow t_{2g}$ and $t_{2g} \rightarrow \pi^*$ transitions gives the energy of the $\pi \rightarrow \pi^*$ transition. In the low-spin complexes, however, the sum is greater than the energy of the $\pi \rightarrow \pi^*$ transition because of the contribution made by the SPE (Fig. 1).

The band which is due to the $e_g \rightarrow \pi^*$ transition should not exist in the spectra of low-spin complexes because of the lack of electrons in the e_g orbitals. In the high-spin complexes, this same transition is expected to occur in the region of about 8 kK in accord with the above assignments.

Our assignments for the charge transfer bands do not agree with those made by Lintvedt *et al.* [34], for the CT bands of the spectra of the iron(III) acetylacetonates. If the assignments proposed by these authors are accepted for the complexes studied here, then the calculated values of the X_{opt} for sulfur are considerably different from those referred to in the literature [26].

The above assignments of the CT bands may also be confirmed on the basis of the equations (1), (2), (3), and (4), if V_1 and V_2 are constant for all complexes and if the magnitude of the $\pi \rightarrow \pi^*$ separation of the appropriate ligand orbital holds within ±2 kK. Thus, if the values $V_1 = 29.3$, $V_2 = 19.6$, and $D = 4.5$ kK are used, the positions of the CT bands are in fact well reproduced by using the values 2.7 and 4.0 kK for $E - A$ for the low- and high-spin complexes respectively. These values have already been used by other authors in iron(III) octahedral complexes [23, 38]. The results obtained are $\nu_1 = 16.1$ kK and $\nu_2 = 28.9$ kK for the low-spin $Fe(i\text{-}Pr_2dtc)_3$ complex, and $\nu_1 = 17.3$ kK and $\nu_2 = 28.4$ kK for the high-spin $Fe(Pyrrdtc)_3$ complex. Now, if the assumption is made that, in the case of the high-spin complexes, the sum $(\pi \rightarrow t_{2g}) + \Delta + (e_g \rightarrow \pi^*)$ gives the energy of the $\pi \rightarrow \pi^*$ transition, the frequencies of the ν_3 and ν_4 are calculated to be equal to 19.1 kK and 8.0 kK respectively, which agree well with the experimental data.

Infrared Spectra

Table III contains the frequencies (cm^{-1}) of the most relevant infrared bands with their assignments.

The characteristic band in the region 1480 cm^{-1} is attributed to the stretching vibration of the C···N bond. Although there are two different dithiocarbamate ligands in the mixed-ligand complexes, only one band is observed in the 1480 cm^{-1} region. The position of the maximum is nearly the same as that for the corresponding tris(dialkyldithiocarbamate) complex with the major ligand component. The maximum for the minor ligand component in the mixed-ligand complex appears as a shoulder. Thus, the band at 1480 cm^{-1} for the mixed-ligand complexes is a composite resulting from the overlap of the bands of the two different dithiocarbamate ligands.

The stretching vibration of the C···S bonds occur in the 800 - 1000 cm^{-1} region of the spectra for the mixed-ligand complexes, and the positions of the absorption maxima are the same as those found for the corresponding tris(dialkyldithiocarbamate) complexes. This region, 800–1000 cm^{-1}, was used by several authors [39] to distinguish between the two bonding possibilities in the complexes formed by dithiocarbamate ligands. The coexistence of both monodentate and bidentate groups in dithio complexes results in the appearance of additional bands not found for complexes having only bidentate ligands. In the case of the mixed-ligand iron(III) complexes, the presence of two bands between 800 and 1000 cm^{-1} does not imply the coexistence of mono- and bidentate coordination. This notion is supported by the fact that none of the bands are split either in the mixed-ligand or in the tris(dialkyldithiocarbamato)-iron(III) complexes. Thus, the appearance of additional bands between 800 and 1000 cm^{-1} indicates the coexistence of nonequivalent dithiocarbamate ligands in accordance with the suggestions of Bhat *et al.* [40].

Experimental

Physical Measurements

Electronic absorption spectra were obtained using a Zeiss PMQ II spectrophotometer with freshly prepared $CHCl_3$ solutions at about 30 °C.

Magnetic susceptibility measurements in solution were done by the Evans method using chloroform solutions 2% v/v in TMS. Susceptibilities were calculated from TMS signal separation and the following diamagnetic corrections (cgsu/mol × 10^{-6}) obtained from Pascal's constants were applied to the measured susceptibilities: $(Pyrrdtc)Fe(Et_2dtc)_2$, −270; $(Et_2dtc)Fe(Pyrrdtc)_2$, −264; $(i\text{-}Pr_2dtc)Fe(Et_2dtc)_2$, −299.7; $(Et_2dtc)Fe(i\text{-}Pr_2dtc)_2$, −323.4; $(Pyrrdtc)Fe(i\text{-}Pr_2dtc)_2$, −317.4; $(i\text{-}Pr_2dtc)Fe(Pyrrdtc)_2$, −287.7.

Infrared spectra were recorded with a Perkin–Elmer 257 spectrophotometer using either KBr discs or chloroform solutions. No significant differences between solid-state and solution spectra were noted.

Molecular weights were determined using a Perkin–Elmer molecular weight apparatus Model 115 at a concentration range 3×10^{-3} to 6×10^{-4} *m* in CHCl$_3$ solution.

Preparation of the complexes

The tris(dialkyldithiocarbamato)iron(III) complexes were prepared by published methods [1]. The chlorobis(dialkyldithiocarbamato)iron(III) complexes were prepared by reacting the tris complex, Fe(R$_2$-dtc)$_3$, with excess of ferric halide according to the method of Wickman and Trozzolo [18]. The sodium dialkyldithiocarbamates used were prepared by standard methods, and were used without dehydration.

The mixed-ligand complexes were prepared as follows:

Pyrrolidyldithiocarbamatobis(diethyldithiocarbamato)iron(III), (Pyrrdtc)Fe(Et$_2$dtc)$_2$

To a solution of chlorobis(diethyldithiocarbamato)iron(III) (10.0 mmol) in 60 ml CHCl$_3$, a solution of Na(Pyrrdtc)·2H$_2$O (10.0 mmol) in 100 ml acetone was added dropwise at room temperature with constant stirring. Then, the mixture was stirred at room temperature for 30 min. The reaction mixture was filtered. The filtrate was evaporated to about 30 ml and 150 ml of ethanol was added to yield the mixed-ligand complex as a black crystalline precipitate. The precipitate was isolated by filtration and dried under vacuum. Purification of the complex was carried out by dissolving the crude product in 80 ml of benzene without heating, filtering the solution, and diluting the filtrate with 150 ml of petroleum ether.

Diethyldithiocarbamatodi(Pyrrolidyldithiocarbamato)iron(III), (Et$_2$dtc)Fe(Pyrrdtc)$_2$

A method similar to that described above was followed. 10.0 mmol of chlorodi(Pyrrolidyldithiocarbamato)iron(III) dissolved in 80 ml CHCl$_3$ and 10.0 mmol of Na(Et$_2$dtc)·3H$_2$O dissolved in 50 ml of acetone were employed. Purification of the complex was carried out by dissolving the crude product in 50 ml of benzene and reprecipitating it with 100 ml of petroleum ether.

Diisopropyldithiocarbamatobis(diethyldithiocarbamato)iron(III), (i-Pr$_2$dtc)Fe(Et$_2$dtc)$_2$

10.0 mmol of chlorobis(diethyldithiocarbamato)-iron(III) dissolved in 80 ml of CHCl$_3$ was treated with 10.0 mmol of (i-Pr$_2$dtc) (i-Pr$_2$NH$_2$) dissolved in 20 ml of CHCl$_3$ according to the method described above. The reaction mixture was treated with 80 ml of ethanol and the complex precipitated out as black crystals. The crude product was purified by dissolving it in 50 ml of CHCl$_3$ and reprecipitating it with ethanol.

Diethyldithiocarbamatobis(diisopropyldithiocarbamato)iron(III), (Et$_2$dtc)Fe(i-Pr$_2$dtc)$_2$

A procedure similar to that described above was followed. 10.0 mmol of chlorobis(diisopropyldithiocarbamato)iron(III) dissolved in 70 ml of CHCl$_3$ and 10.0 mmol of Na(Et$_2$dtc)·3H$_2$O dissolved in 25 ml of methanol were employed. Purification of the complex was achieved by dissolving it in 40 ml of CHCl$_3$ and reprecipitating it with 130 ml of petroleum ether.

Pyrrolidyldithiocarbamatobis(diisopropyldithiocarbamato)iron(III), (Pyrrdtc)Fe(i-Pr$_2$dtc)$_2$

10.0 mmol of chlorobis(diisopropyldithiocarbamato)iron(III) in 40 ml of CHCl$_3$ was treated with 10.0 mmol of Na(Pyrrdtc)·2H$_2$O in 25 ml of methanol according to the procedure already described. Recrystallization was carried out from a mixture of CHCl$_3$ and petroleum ether.

Diisopropyldithiocarbamatodi(Pyrrolidyldithiocarbamato)iron(III), (i-Pr$_2$dtc)Fe(Pyrrdtc)$_2$

To a solution of chlorobis(diisopropyldithiocarbamato)iron(III) (10.0 mmol) in 100 ml of CHCl$_3$' 2.79 g (10.0 mmol) of (i-Pr$_2$dtc)(i-Pr$_2$NH$_2$) was added in small portions with constant stirring. The mixture was stirred for an additional 30 min and 150 ml of ethanol was added. No precipitate formed. The mixture was then concentrated to about 50 ml and it was left in a refrigerator for several hours where upon black crystals separated out. Recrystallization was carried out from a mixture of chloroform and ethanol.

References

1 A. H. White, R. Roper, E. Kokot, H. Waterman and R. L. Martin, *Aust. J. Chem., 17,* 294 (1964).

2 A. H. Ewald, R. L. Martin, I. G. Ross and A. H. White, *Proc. Roy. Soc., Ser. A, 280,* 235 (1964).

3 R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin and A. H. White, *J. Chem. Phys., 45,* 2688 (1966).

4 R. M. Golding, W. C. Tennant, J. P. M. Bailey and A. Hudson, *J. Chem. Phys., 48,* 764 (1968).

5 A. H. Ewald, R. L. Martin, E. Sinn and A. H. White, *Inorg. Chem., 8,* 1837 (1969).

6 L. H. Pignolet, R. A. Lewis and R. H. Holm, *J. Am. Chem. Soc., 93,* 360 (1971).

7 R. R. Eley, R. R. Myers and N. V. Duffy, *Inorg. Chem., 11,* 1128 (1972).

8 B. L. Edgar, D. J. Duffy, M. C. Palazzotto and L. H. Pignolet, *J. Am. Chem. Soc., 95,* 1125 (1973).

9 M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr. and L. H. Pignolet, *J. Am. Chem. Soc., 95,* 4537 (1973).

10 M. J. Tricker, *J. Inorg. Nucl. Chem., 36,* 1543 (1974).

11 A. H. Ewald and E. Sinn, *Aust. J. Chem., 21,* 927 (1968).

12 R. L. Martin and A. H. White, *Transition Metal Chem., 4,* 113 (1968).

13 B. F. Hoskins and B. P. Kelly, *Chem. Commun.,* 1517 (1968).

14 B. F. Hoskins and B. P. Kelly, *Chem. Commun.,* 45 (1970).

15 L. H. Pignolet, R. A. Lewis and R. H. Holm, *Inorg. Chem., 11,* 99 (1972).

16 L. H. Pignolet, G. S. Patterson, J. F. Weiher and R. H. Holm, *Inorg. Chem., 13,* 1263 (1974).

17 D. J. Duffy and L. H. Pignolet, *Inorg. Chem., 13,* 2045 (1974).

18 H. H. Wickman and A. M. Trozzolo, *Inorg. Chem., 7,* 63 (1968).

19 H. C. Brinkhoff, *Inorg. Nucl. Chem. Lett., 7,* 413 (1971).

20 H. P. Koch, *J. Chem. Soc.,* 401 (1949).

21 D. W. Barnum, *J. Inorg. Nucl. Lett., 21,* 221 (1961).

22 C. K. Jϕrgensen, *Acta Chem. Scand., 16,* 2406 (1962).

23 A. Syamal, *Can. J. Chem., 47,* 1693 (1969).

24 H. F. Steger, *J. Inorg. Nucl. Chem., 37,* 39 (1975).

25 C. K. Jϕrgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon N.B., Oxford (1962).

26 E. Cervone, F. Camassei, M. L. Luciani and C. Furlani, *J. Inorg. Nucl. Chem., 31,* 1101 (1969).

27 C. K. Jϕrgensen, *J. Inorg. Nucl. Chem., 24,* 1571 (1962).

28 C. K. Jϕrgensen, "Progress in Inorganic Chemistry", Vol. 4, p. 112, Interscience, N.Y. (1962).

29 J. E. Huheey, "Inorganic Chemistry, Principles of Structure and Reactivity", Harper, London (1975).

30 B. N. Figgis, "Introduction to Ligand Fields", Interscience, N.Y. (1966).

31 C. K. Jϕrgensen, "Orbitals in Atoms and Molecules", Academic Press, London (1962).

32 W. Byers, B. Fa-Chun Chou, A. B. P. Lever and R. V. Parish, *J. Am. Chem. Soc., 91,* 1329 (1969).

33 E. R. Price and J. R. Wasson, *J. Inorg. Nucl. Chem., 36,* 67 (1974).

34 R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem., 9,* 491 (1970).

35 G. A. Renovitch and W. A. Baker, Jr., *J. Am. Chem. Soc., 90,* 3585 (1968).

36 J. S. Griffith and L. E. Orgel, *Quart. Rev. Chem. Soc., 11,* 381 (1957).

37 C. K. Jϕrgensen, *Helv. Chim. Acta,* 131 (1967).

38 G. St. Nikolov, *Inorg. Chim. Acta, 4,* 610 (1970).

39 F. Bonati and R. Ugo, *J. Organometal. Chem., 10,* 257 (1967).

40 A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark and S. H. Strauss, *Inorg. Chem., 13,* 886 (1974).