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Electronic Equilibrium between the $^6A_1$ and $^2T_2$ States in Iron(III) Dithio Chelates

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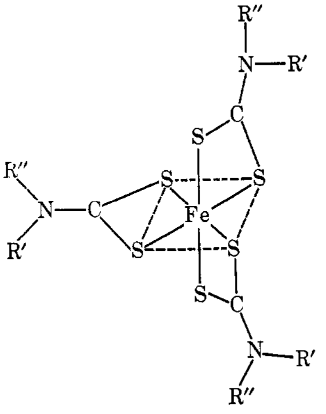
Further results are reported for ferric dithiocarbamate complexes $Fe(S_2CNR_2)_3$, which lie at the crossover between high-spin (sextet) and low-spin (doublet) states. Magnetic measurements made over a range of temperatures and pressures are used to estimate E, the separation of the zero-point energies of the $^2T_2$ and $^6A_1$ states, and ΔV, the difference between the volumes of the $^6A_1$ and $^2T_2$ states. The values of E extend over a large range, both positive and negative, for various complexes, while ΔV is generally 5–6 cm^3/mol; this corresponds to an increase of 0.1 Å of the Fe–S bond lengths in passing from the $^2T_2$ to the $^6A_1$ state. The compounds may be divided into four distinct classes on the basis of their solution magnetic moments (μ_{eff}); in order of decreasing μ_{eff} values (and hence decreasing population of the $^6A_1$ state), these are: (1) the pyrrolidyl complex where NR_2 = pyrrolidyl, μ_{eff} = 5.8 BM; (2) the N,N-di-*n*-alkyl complexes, μ_{eff} = 4.3 BM; (3) the N-alkyl, N-aryl complexes, μ_{eff} = 3.5 BM; (4) the N,N-di-*sec*-alkyl complexes, μ_{eff} = 2.5 BM. The RNR angle in the $Fe(S_2CNR_2)_3$ complexes is expected to increase from class 1 through to 4, with a corresponding change in the C–N bond order, which is expected to affect ligand field strength (Δ) and μ_{eff}. Comparisons of the electronic spectra of complexes falling into the various classes and the pressure dependence of the spectral positions and band intensities are used in the assignment of electronic transitions. From the tentative spectral assignments are estimated values of the ligand field strengths and the electronic pairing energies (π), and these are shown to obey the necessary inequality for the crossover situation: Δ(high spin) $< \pi <$ Δ(low spin). The results are extended to include other dithio chelates such as the xanthates $Fe(S_2COR)_3$, which are almost purely low spin, and the dithiophosphates $Fe(S_2P(OR)_2)_3$, which are high spin. Monoalkyldithiocarbamates $Fe(S_2CNHR)_3$ are found to be almost pure high spin.

Introduction

The magnetic moments of certain N-substituted ferric dithiocarbamates (I) vary between the limits of ~2 BM (low temperature, high pressure) and 5.9 BM (high temperature, low pressure). This anomalous behavior is known[1,2] to arise from a thermal equilibrium between the two possible ground states, $^2T_2$ and $^6A_1$, which are separated by an energy $\sim kT$. The low-spin $^2T_2$ usually lies lowest with the high-spin $^6A_1$ becoming increasingly populated as temperature rises according to a Boltzmann distribution.



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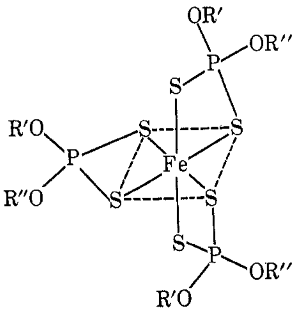

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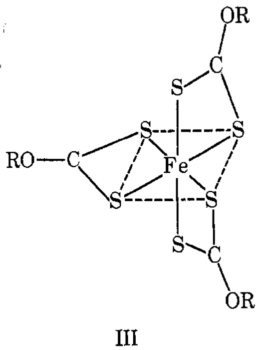

III

It has been shown[2] that a good representation of the magnetic behavior of ferric N,N-dialkyldithiocarbamates at atmospheric pressure may be given by

$$\mu_{eff}{}^2 = \frac{0.75g^2 + 8x^{-1}(1 + e^{-3x/2}) + 105Ce^{-(1+(E/\zeta))x}}{1 + 2e^{-3x/2} + 3Ce^{-(1+(E/\zeta))x}} \tag{1}$$

where the parameters are as previously described:[2] x is ζ/kT, ζ the one-electron spin–orbital coupling constant, g the spectroscopic splitting factor applicable to the $^2T_2$ state, E the separation of the zero-point energies of the $^2T_2$ and $^6A_1$ states, and $C = Q_a/Q_t$, the ratio of the molecular vibrational partition functions in $^6A_1$ and $^2T_2$. We report here experimental values which extend the earlier results to include a greater variety of dithiocarbamates as well as other types of dithio chelates such as dialkyldithiophosphates (II) and alkyl xanthates (III) and we develop further the previous model[2] in the light of our extended magnetic and spectral results.

A more refined treatment[3] has recently been developed, which takes into account interaction with $^4T_1$ and configurational mixing near the crossover point, and it was found that $\nu = 1.13\zeta$ and $\gamma = -1.29$, ζ being taken as 400 cm^{-1}. [ν and γ arise when the Hamiltonian terms $\lambda\mathbf{L}\cdot\mathbf{S} + \beta(\mathbf{L} + 2\mathbf{S})\cdot\mathbf{H}$ for $^{2S+1}P_J$ (p electrons) are replaced by $\nu\mathbf{L}\cdot\mathbf{S} + \beta(\gamma\mathbf{L} + 2\mathbf{S})\cdot\mathbf{H}$

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

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

[3] J. M. de Lisle and R. M. Golding, *ibid.*, **A296**, 457 (1967); R. M. Golding, "Applied Wave Mechanics," D. Van Nostrand Co., Inc., London, 1969.

for the corresponding $^{2S+1}T_{iJ}$ (d electrons)[4]]. We have similarly assumed ζ to be 370 cm^{-1}, but instead of calculating g, we have used it as a parameter in obtaining the optimal fit of the equation to the experimental data. The actual value of g can then be found to an accuracy that will depend on how sensitive the magnetism is to variations in g. Detailed calculations of the magnetic moments show that it makes no difference, within the accuracy warranted by the experimental results, which model is taken. In fact we had previously stipulated[2] that g should lie within 1.8–2.2. The $^4T_1$ state probably lies some 7000 cm^{-1} above the crossing states, a separation which is large compared to ζ, and the error introduced by ignoring it is small.

Further refinement of the theory would include distortions from the octahedral symmetry assumed in eq 1. Such distortions would not affect the spherical $^6A_1$ state, though the $^2T_2$ state (and the $^4T_1$ state) will be split and raised or lowered in energy to some extent. Detailed calculations show that the effect of the splitting of the $^2T_2$ state upon the magnetic properties is small and is adequately represented in eq 1 by allowing g to vary between 1.8 and 2.2. The raising or lowering of the $^2T_2$ state is necessarily incorporated in the parameter E.

The general physical properties of the various ferric dithio chelates are quite similar. They are black crystalline solids, soluble in organic solvents such as chloroform, dichloromethane, carbon disulfide, benzene, etc. The order of thermal stability is: N,N-dialkyl-DTC > N-alkyl,N-aryl-DTC > O,O′-dialkyl-DTP > (NH)N-alkyl-DTC ~ alkyl-X. The compounds on the left are quite stable, even when left open to the air, but compounds on the right side decompose rapidly at room temperature, and slowly even when kept frozen in sealed tubes. For the *n*-alkylxanthates, the stability decreases as the chain length increases; satisfactory measurements could be made on the methyl and ethyl complexes, but the *n*-propyl and *n*-butyl complexes were found to undergo fairly rapid decomposition.

Results and Discussion

Solid-State Magnetic Measurements.—The magnetic measurements in the temperature range 90–400°K were fitted to theoretical curves obtained from eq 1. The results are shown graphically[5] in Figures 1 and 2, and the values of E, g, and C obtained assuming $\zeta = 370$ cm^{-1} are given in Table I. Those magnetic results not graphed are given in Table II. The fitting procedure is as previously described.[2] It has been pointed out that Q_a/Q_t, as defined in terms of ν_a and ν_t, depends on the temperature[2] was well as the pressure.[6] The temperature dependence can be approximated by $Q_a/Q_t = Q_0 e^{-Q_1/RT}$ over the temperature range of interest (80–400°K). Applying this relation to the approximate values of Q_a/Q_t obtained previously[2] over the range 80–400°K, we find that reasonable values of Q_0 and Q_1 would be ~5 and 30–40 cm^{-1}, respectively. Thus the temperature dependence of Q_a/Q_t has the effect of increasing E by a small amount of Q_1, of the order of 30 cm^{-1}, a negligible error.

As used in practice,[2] the fitting procedure will incorporate into C all of the weighting factors (such as distortion from octahedral geometry, lattice forces, higher order interaction of the $^2T_2$ state with the other states, etc.). The ratio of vibrational partition functions is only one of these, though undoubtedly the largest, so that the temperature dependence of the C used is not likely to be as great as that calculated using merely ν_a/ν_t. Hence the approximation that C is constant over the temperature range used, at atmospheric pressure, is a reasonable working approximation. By mathematical coincidence,[2] if both g and ζ were used as parameters, they would exercise a rather similar effect on the shape of eq 1. This may be seen by defining K as the ratio of the populations in the $^6A_1$ state and the lower (doubly degenerate) component of the $^2T_2$ state[2] and plotting log $K_1/3$ against $1/T$. The effect of varying ζ from 200 to 440 cm^{-1} for the compound $Fe(S_2CN(CH_3)_2)_3$ for $g = 2.00$ and that of varying g between 1.85 and 2.25 when $\zeta = 370$ cm^{-1} are illustrated in Figure 3. Fortunately only a limited range of g and ζ values may be reasonably used.[2,3] Nevertheless, in view of this fact, the actual derived values of E and Q_a/Q_t are only very approximate.

For the various compounds a range of values is obtained for log C, but most of them are close to 1.0, as might be expected. Golding[7] has also confirmed that the nmr results and the magnetic susceptibility can be explained by the same model providing the vibrational partition functions are included. The values of E obtained are reasonable and suggest that for the pyrrolidyl-, morpholyl-, and di-*n*-butyldithiocarbamates, the $^6A_1$ state lies the lowest, while it lies the highest for others. Typical energy level diagrams are given in Figure 4.

A recent single-crystal X-ray study has revealed that instead of being octahedral, the $Fe-S_6$ grouping of the ferric di-*n*-butyl complex is quite markedly distorted toward trigonal-prismatic symmetry,[8] while a smaller degree of distortion was observed in the $Co-S_6$ grouping of the cobalt(III) diethyl complex.[9] The effect of this trigonal distortion from octahedral symmetry has been investigated by Mössbauer spectroscopy and found to result in a splitting of 50–130 cm^{-1} in the $^2T_2$ state.[10] Thus, it appears that the electronic states of the molecules are not greatly changed by the distortion from pure octahedral symmetry. While theoretical

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(4) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London 1961.

(5) For the experimental magnetic data plotted in Figures 1 and 2, order Document No. NAPS-00564 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y., 10001. Remit \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

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

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

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

(9) S. Merlino, *Acta Cryst.*, **B24**, 1441 (1968).

(10) R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, **62**, 1713 (1966).

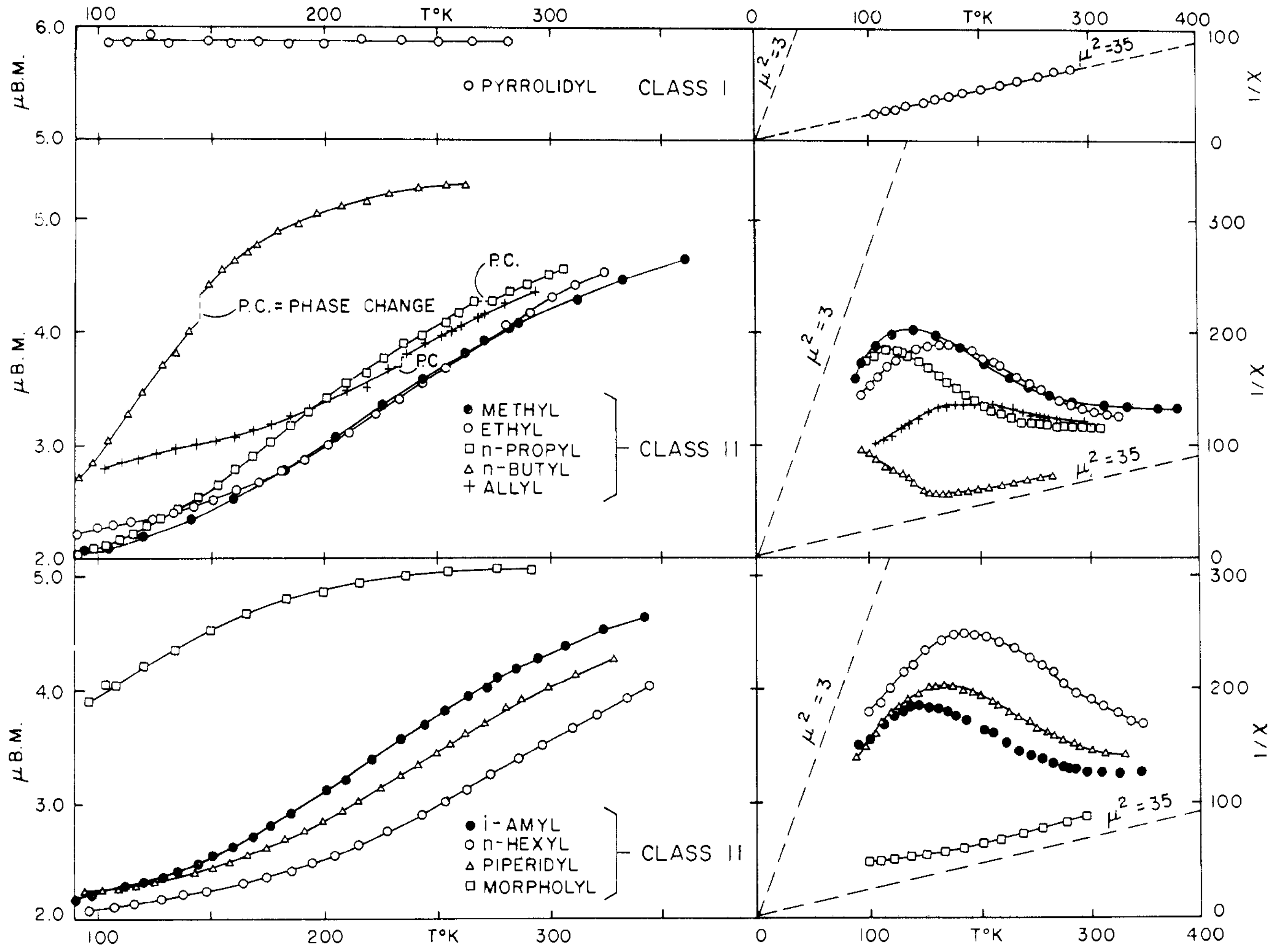

Figure 1.—Variation with temperature of magnetic moments of $Fe(S_2CNR_2)_3$ complexes, grouped under classes 1 and 2. The full curves are calculated from eq 1.

TABLE I

CROSSOVER PARAMETERS FOR THE FERRIC DISUBSTITUTED DITHIOCARBAMATES $Fe(S_2CNR_2)_3$

Substituent	E, cm^{-1}	g	Log C
Pyrrolidyl	. . .	2.00	. . .
Morpholyl	−192	2.10	+0.31
Di-*n*-butyl[a]	−19	2.10	+0.84
Di-*n*-butyl[b]	−28	2.10	+0.92
Di-*n*-propyl	194	1.95	+0.75
Diallyl	267	2.00	+0.84
Diisoamyl	347	2.10	+0.94
Dimethyl	392	2.05	+1.06
Dihexyl	594	1.95	+1.08
Piperidyl	501	2.10	+1.08
n-Propylphenyl	194	2.00	+0.88
Ethylphenyl	336	2.10	+1.13
Dibenzyl	403	2.00	+0.96
Isoamylphenyl	581	2.10	+0.81
Methylphenyl	1490	2.15	+2.18
Diisobutyl	890	1.95	+1.23
Diisopropyl	1411	1.90	+1.97
Dicyclohexyl	>2000	2.25	. . .

[a] Low-temperature form. [b] High-temperature form.

calculations[10] have shown that the Mössbauer effect spectra are very sensitive to such splittings, analogous calculations indicate that the magnetic properties are rather insensitive to splittings of this magnitude, even in purely low-spin iron(III).[11] As a result of the splitting of the $^2T_2$ state (and similar splittings of other $^{2S+1}T_i$ states) we would expect double bands for some of the electronic spectral transitions. However, since the splittings are so small, compared to the broadness of the observed spectral bands, no resolution of these doublets could be expected. The electronic spectra of the dithiocarbamate molecules, like the magnetic properties, may now be interpreted on the basis of pseudooctahedral symmetry.

The Lattice Effect.—It is to be expected that solid-state forces will affect the relative populations of $^6A_1$ and $^2T_2$ in the solid state. Crystal lattice forces are likely to act through two mechanisms. (a) The crystalline state imposes distortion from octahedral geometry, which are related, but in only an (*a priori*) unpredictable way, to the intrinsic distortion of the individual unbound molecule. (b) The strength of the ligand field in a molecule may be affected to some extent by atoms belonging to neighboring molecules in the lattice. Thus lattice forces can have an effect on the terms in eq 1. E is very sensitive to variations in the ligands, so it will be just as sensitive to changes in

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(11) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198, 204 (1961).

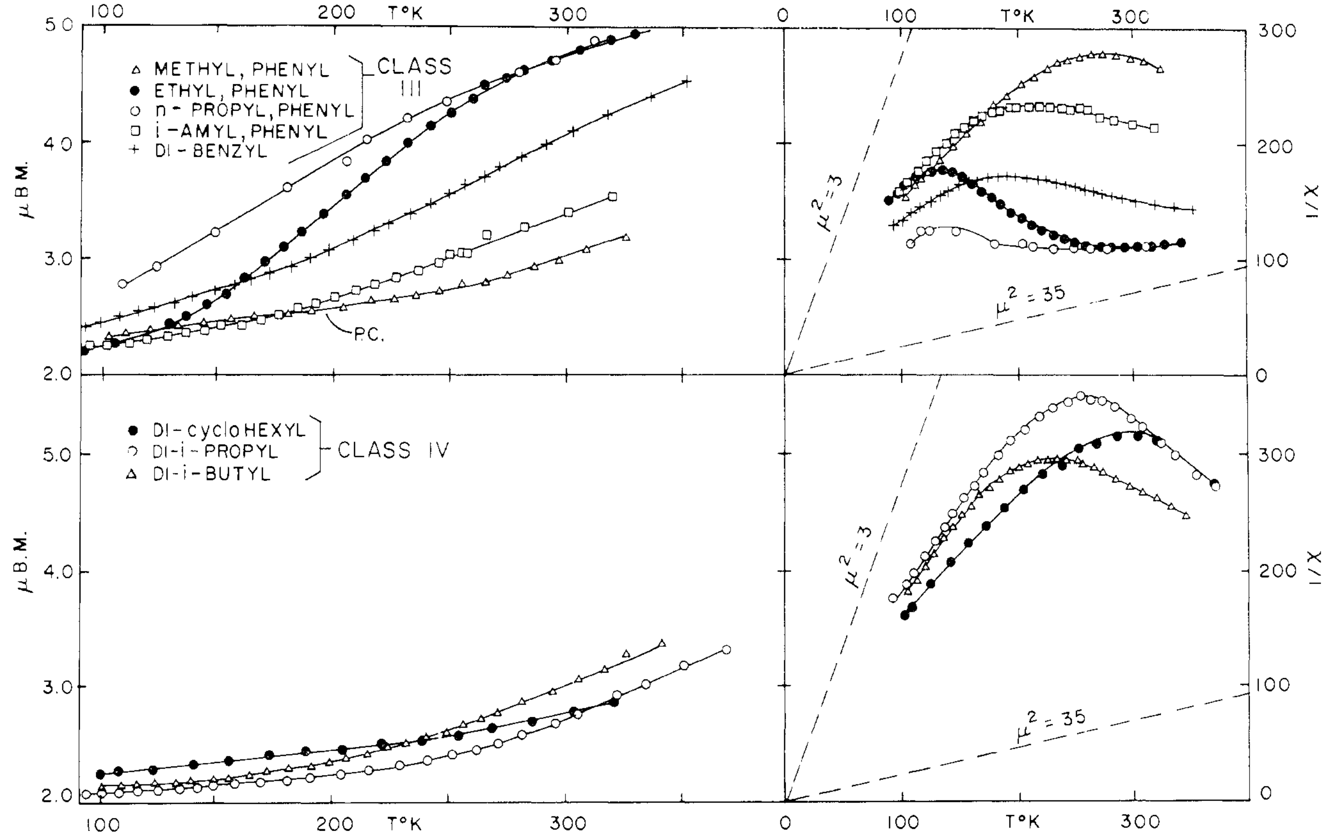


Figure 2.—Variation with temperature of magnetic moments of $Fe(S_2CNR_2)_3$ complexes, grouped under classes 3 and 4. The full curves are calculated from eq 1.

the crystal forces. The ratio of the vibrational stretching frequencies ν_a/ν_t, and therefore Q_a/Q_t, must also be very sensitive to lattice energies. It is unlikely that the dependence of g and ζ on the lattice energies will be appreciable.

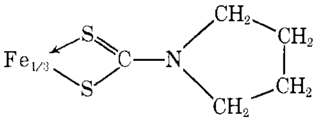
In a crystal of a particular complex the effects (a) and (b) mentioned above are not likely to change very much with temperature, and should therefore not bestow any appreciable temperature dependence on E or Q_a/Q_t. However, some substances can exist in two (or more) solid modifications. In such a case there are fairly sharp transition temperatures (at constant pressures) between two phases, and in a ferric dithiocarbamate, the transition should be accompanied by a change in E and Q_a/Q_t and hence in the magnetic properties. In fact, for some of the complexes, there are reproducible discontinuities in the $1/\chi$ *vs.* T curves, the $^2T_2$–$^6A_1$ equilibrium persisting above and below the discontinuity temperature (Figures 1 and 2).

The phase changes have also been found to occur when the pressure on the solid ferric complexes is increased at constant temperature (Table III). In general, the densities, melting points, and X-ray diffraction patterns, etc., indicate that the cobalt(III) dithiocarbamates are isomorphous with the iron(III) complexes.[12] These cobalt complexes were tested for similar phase changes. None was found. The determining factor in the phase changes appears to be the presence of the $^2T_2$–$^6A_1$ equilibrium and the volume change it involves. In a few cases, this volume change on increase in pressure or on change in temperature is sufficient to cause a phase change in the iron complex. Cambi[13] has also observed that two different crystalline forms of the same iron(III) complex, obtained by varying the means of preparation, can have different magnetic moments.

The lattice forces do not vary in a simple manner depending on the substituents R, so no subdivision of the complexes on the basis of substituents is readily made from the solid-state μ_{eff} values. However, the effect of lattice forces can be "washed out" by dissolving the complexes in organic solvents, and then quite a different picture emerges.

Solution Magnetic Measurements.—We give the solution magnetic measurements at room temperature and pressure in Table IV. It seems reasonable to classify the complexes into four groups on a phenomenological basis.

(1) $\mu_{eff} = 5.8 \pm 0.1$ **BM.**—This groups includes the pyrrolidyl complex



where the CNC angle may be different from the normal trigonal angle owing to strain in the five-membered ring, and the dialkyldithiophosphate complexes.

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(12) A. H. White, unpublished work.

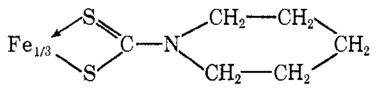
(13) L. Cambi and L. Malatesta, *Ber.*, **70**, 2067 (1937).

TABLE II

EXPERIMENTAL MOLAR SUSCEPTIBILITIES (χ_M, CGS EMU) AND MAGNETIC MOMENTS (BM) AT VARIOUS TEMPERATURES (°K) FOR THE COMPOUNDS NOT IN FIGURES 1 AND 2

Temp	$10^6\chi_M$	μ_{eff}	Temp	$10^6\chi_M$	μ_{eff}	Temp	$10^6\chi_M$	μ_{eff}
Tris(O-methylxanthato)iron(III)								
91	6,072	2.11	173	3,659	2.26	258	2,692	2.37
101	5,591	2.13	189	3,376	2.27	273	2,620	2.40
125	4,658	2.17	208	3,149	2.28	293	2,546	2.45
143	4,209	2.20	241	2,827	2.34			
Tris(O-ethylxanthato)iron(III)								
108.3	5,478	2.19	242.8	3,112	2.47	323.8	3,241	2.91
141.2	4,528	2.27	270.2	3,045	2.58	344.8	3,387	3.07
173.9	3,814	2.31	296.6	3,095	2.72	364.6	3,567	3.24
207.4	3,342	2.36	305.9	3,140	2.78			
Tris(O-isopropylxanthato)iron(III)								
97	5,737	2.12	186	3,487	2.29	311	2,674	2.59
118	5,082	2.20	201	3,364	2.34			
137	4,484	2.23	244	2,905	2.39			
153	4,136	2.26	272	2,774	2.47			
Tris(O-*sec*-butylxanthato)iron(III)								
93	6,480	2.20	196	3,511	2.36	293	2,170	2.53
125	5,028	2.26	224	3,251	2.42			
144	4,509	2.29	250	2,296	2.43			
173	3,912	2.33	275	2,733	2.46			
Tris(O,O′-dimethyldithiophosphato)iron(III)								
100.8	39,590	5.67	186.6	22,250	5.79	239.0	14,460	5.85
141.8	28,860	5.74	229.2	18,570	5.86			
150.0	27,420	5.76	268.0	15,780	5.84			
Tris(O,O′-diethyldithiophosphato)iron(III)								
103.8	37,590	5.61	169.8	23,120	5.63	289.4	13,810	5.68
111.2	35,110	5.61	211.9	18,750	5.66			
139.8	28,070	5.63	245.3	16,800	5.66			
Tris(O,O′-di-*n*-propyldithiophosphato)iron(III)								
96.4	41,380	5.67	159.9	25,400	5.72	257.9	16,170	5.80
105.4	37,970	5.68	191.8	21,560	5.76	297.8	14,000	5.80
132.0	30,580	5.71	224.8	18,470	5.79			
Tris(O,O′-diisopropyldithiophosphato)iron(III)								
116.8	35,780	5.81	188.0	22,360	5.82	257.2	16,380	5.83
152.2	27,450	5.81	222.8	19,000	5.84	303.1	13,900	5.83
Tris(N,N′-diphenyldithiocarbamato)iron(III)								
294.0	2,695	2.52						

(2) μ_{eff} = **4.3 ± 0.2 BM.**—This group includes complexes where the nitrogen substituents R and R′ are *n*-alkyl groups or a nonstrained ring such as piperidyl



(3) μ_{eff} = **3.5 ± 0.2 BM.**—This group includes N-alkyl,N-aryl complexes. Some steric repulsion is likely between the substituents.

(4) μ_{eff} = **2.5 ± 0.2 BM.**—This group includes N,N-di-*sec*-alkyl complexes, where considerable steric repulsion is likely between the substituents, and alkylxanthate complexes.

The RNR angle in the disubstituted dithiocarbamates is likely to increase from group 1 through to 4, with a corresponding change in the C–N bond order.

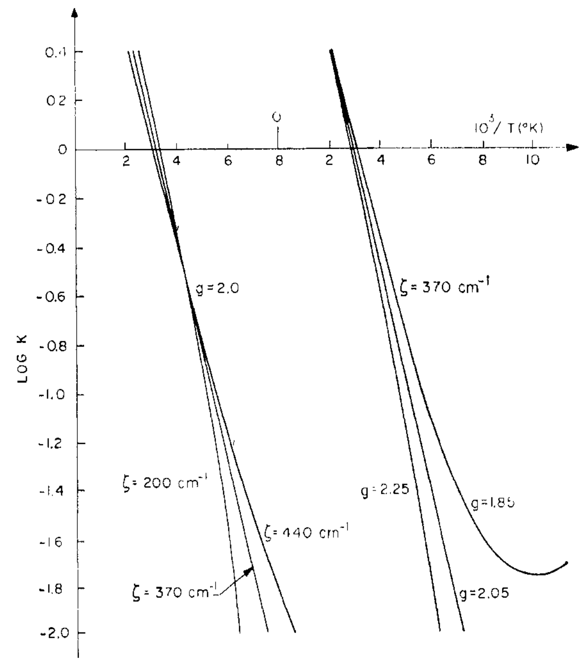


Figure 3.—Effect of variations in ζ and *g* on the plot of log *K* against inverse temperature, where *K* (see ref 1) is the ratio of the populations in the $^6A_1$ state and the lower (doubly degenerate Γ_7) component of the $^2T_2$ state.

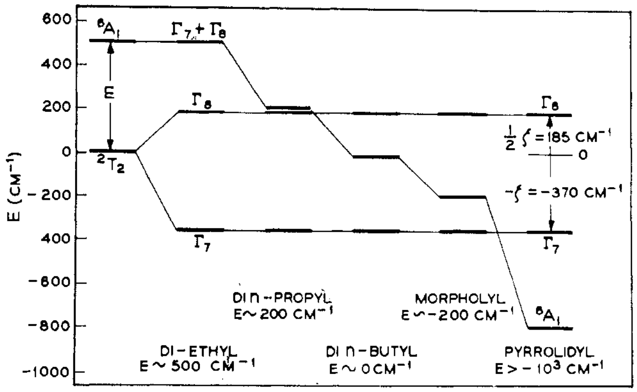


Figure 4.—Relative energy level diagrams in a range of Fe(S_2CNR_2)$_3$ complexes.

TABLE III

PHASE TRANSITION POINTS IN A NUMBER OF COMPLEXES

(a) Tris(N,N-di-*n*-butyldithiocarbamato)iron(III)

Transition points $\begin{cases}\text{1150 atm, } -67°\\ \text{1310 atm, } 0°\end{cases}$

$\Delta V \approx 88\ \text{cm}^3\ \text{mol}^{-1}$ $\quad \dfrac{\Delta V}{V_0} \approx 0.16$

$\Delta H \approx 1.4\ \text{kcal mol}^{-1}$

(b) Tris(N-methyl,N-phenyldithiocarbamato)iron(III)

Transition points $\begin{cases}\text{None, } -68°\\ \text{520 atm, } 0°\\ \text{650 atm, } 20°\end{cases}$

$\Delta V \approx 48\ \text{cm}^3\ \text{mol}^{-1}$ $\quad \dfrac{\Delta V}{V_0} \approx 0.10$

$\Delta H \approx 2\ \text{kcal mol}^{-1}$

(c) Tris(N,N-di-*n*-propyldithiocarbamato)iron(III)

Transition points $\begin{cases}\text{1 atm, } 0°\\ \text{(magnetic data)}\\ \text{100 atm, } 20°\end{cases}$

$\Delta V \approx 16\ \text{cm}^3\ \text{mol}^{-1}$ $\quad \dfrac{\Delta V}{V_0} \approx 0.04$

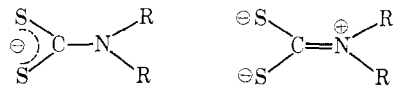
$\Delta H \approx 3\ \text{kcal mol}^{-1}$

TABLE IV

MAGNETIC MOMENT DATA IN SOLID AND SOLUTION PHASES AT 23° FOR THE COMPLEXES $Fe(S_2CNR_2)_3$ (B = BENZENE, C = CHLOROFORM SOLUTION)

Substituents	μ_{eff}(solid), BM	μ_{eff}(soln), BM
Group 1. μ_{eff}(soln) = 5.8 ± 0.1 BM		
NR_2 = $-N(CH_2)_4$ (pyrrolidyl)	5.83	5.82 (B)
Group 2. μ_{eff}(soln) = 4.3 ± 0.2 BM		
R = methyl	4.17	4.20 (C)
ethyl	4.24	4.41 (B, C)
n-propyl	4.48	4.42 (B)
n-butyl	5.32	4.34 (B)
isoamyl	4.30	4.57 (B)
n-hexyl	3.52	4.42 (B)
allyl	4.40	4.34 (B)
NR_2 = piperidyl	4.01	4.16 (C)
morpholyl	5.12	
Group 3. μ_{eff}(soln) = 3.45 ± 0.15 BM		
R_1R_2 = methyl, phenyl	2.99	3.33 (C)
ethyl, phenyl	4.70	3.63 (C)
n-propyl, phenyl	4.68	3.55 (B)
isoamyl, phenyl	3.36	3.43 (B)
dibenzyl	4.02	3.60 (B)
Group 4. μ_{eff}(soln) = 2.45 ± 0.15 BM		
R = isopropyl	2.62	2.34 (B)
cyclohexyl	2.75	2.62 (C)
isobutyl	3.02	2.88 (B, C)

This would lead to increased electron density on the S atoms and an increased ligand field strength



We cannot cite infrared evidence to support this, since the spectra are too complex for resolution in the region 1200–1600 cm^{-1}, and detailed X-ray evidence is not yet available. However, a study[14] of the ^{59}Co nmr spectra of the cobalt(III) dithiocarbamates provides strong evidence that the ligand field strength does, in fact, increase from class 1 to 4.

A further general classification that can be made is that the ligand field strengths generated are in the order: alkylxanthate > dialkyldithiocarbamate > dialkyldithiophosphate. The ^{59}Co nmr and spectroscopic studies have confirmed this.[14]

Solution Magnetic Measurements under Pressure.—The $^2T_2$–$^6A_1$ equilibrium is pressure dependent, and the $^2T_2$ state having the smaller volume is favored by increasing pressure. The difference in volume, ΔV, between the two states is given by the relation[2]

$$\Delta V = -RT\left(\frac{\partial \ln K}{\partial P}\right)_T \qquad (2)$$

where K is the population ratio of molecules in the $^6A_1$ and $^2T_2$ states. In calculating K, the moment for the $^2T_2$ state was taken as $\sqrt{5}$ BM. (Values of $\sqrt{4}$ and $\sqrt{6}$ were also tested and found, in most cases, to cause only slight variations in ΔV.)

The same principle has been applied to the pressure dependence of the magnetic equilibria in salicylaldimine and aminotroponiminate complexes of nickel(II),[15] where the paramagnetic pseudooctahedral form of the former and diamagnetic planar form of the latter were found to be favored by increasing pressure.

The results of the magnetic measurements under pressure are given in Table V, together with the calculated values of ΔV, and the densities of the ferric complexes and their cobalt(III) analogs. The densities may be used to obtain the molar volumes and hence calculate ΔV as a contraction per unit volume of the complex. Uncertainties are introduced into the calculation by the fact that solution volumes may not be exactly additive.

In general, the value of ΔV is of the order of 5–6 cm^3/mol and can be attributed to the contraction in the FeS_6 core for 1 mol of the complex passing from the $^6A_1$ state to the $^2T_2$ state. This represents a change in the Fe–S bond length of about 0.1 Å. This change in bond length may well be accompanied by a change in molecular geometry, but until the complete crystal structures of a range of ferric dithiocarbamates with both $^6A_1$ and $^2T_2$ ground states have been determined, it cannot be decided whether and to what extent the degree of distortion depends on the spin state of the central iron atom. This X-ray work has been undertaken.[12]

For most dithiocarbamates, a plot of log K against pressure fits fairly well to a straight line, but considerable nonlinearity was obtained for the N-alkyl,N-aryl complexes, though this nonlinearity was not completely reproducible. Possibly this is due to larger experimental scatter of the results for these complexes.

It is interesting that the pyrrolidyl complex, which exhibits pure high-spin magnetic and spectral behavior over a temperature range, can be forced into an appreciable $^2T_2$ population in solution by the application of pressure. This is not too surprising in view of the relaxation of lattice forces in solution and the pressure dependence of E and Q_a/Q_t. The solution spectrum of this complex similarly exhibits a pressure dependence.

Electronic Spectra.—The spectra of the ferric dithio chelates show definite trends as the populations in the $^6A_1$ and $^2T_2$ states are varied, either by modification of the ligands (Figure 5) or by variation of the pressure (Figure 6) and temperature. This allows reasonable assignments to be made for a number of the bands. These are given in Table VI, together with the ligand field parameters estimated from them.[4] The pyrrolidyl and dicyclohexyl dithiocarbamates may be taken as fairly representative high- and low-spin complexes, respectively; the weak bands (in parentheses) of the dicyclohexyl complex may be due to residual $^6A_1$ population. The peak positions given for the dialkyldithiophosphate and alkylxanthate complexes are in substantial agreement with those previously recorded by Jørgensen.[16]

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(14) R. L. Martin and A. H. White, unpublished results; A. H. White, Ph.D. Thesis, University of Melbourne, 1966.

(15) A. H. Ewald and E. Sinn, *Inorg. Chem.*, **6**, 40 (1967).

(16) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

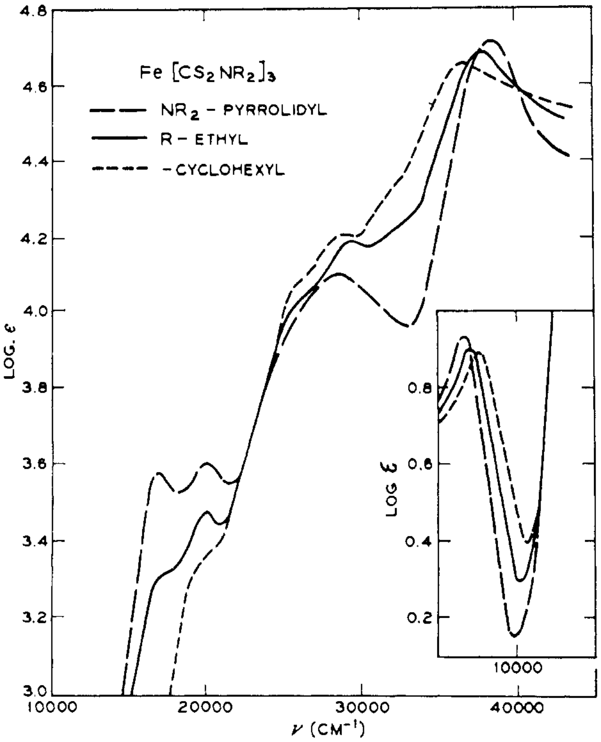


Figure 5.—Electronic spectra in chloroform solution for $Fe(S_2CNR_2)_3$ complexes, where NR_2 = pyrrolidyl (— — —), N,N-diethyl (——), and N,N-dicyclohexyl (– – –).

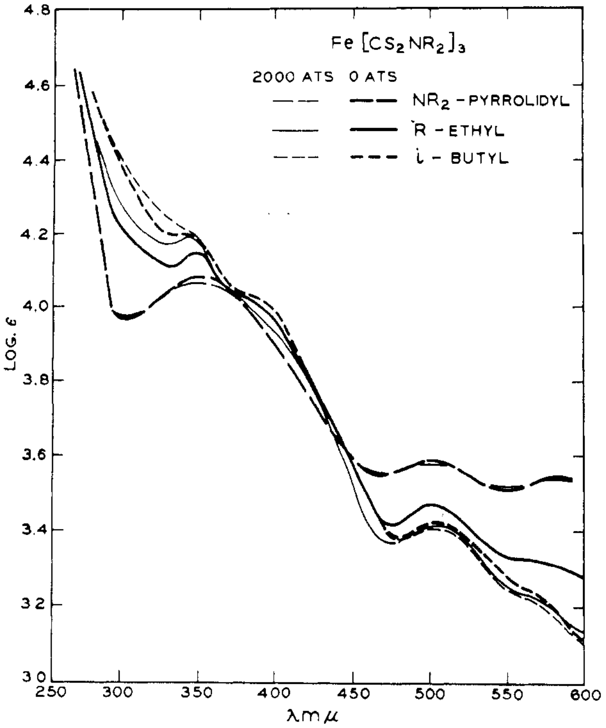


Figure 6.—Electronic spectra, in chloroform solution, for $Fe(S_2CNR_2)_3$ complexes, at atmospheric pressure (heavy lines) and at 2000 atmospheres (light lines).

The visible and ultraviolet spectra of the ferric dithio chelates are characterized by intense bands attributed to internal ligand transitions ($\epsilon \sim 40{,}000$) and metal–ligand and ligand–metal charge-transfer bands ($\epsilon \sim 1000$–$10{,}000$). These intensities change markedly with changes in populations of the two states. A near-infrared band ($\epsilon \sim 8$), whose intensity and band width identify it as an electronic transition, increases in frequency as the strength of the ligand field increases (pyrrolidyl, 6500 cm^{-1}; dimethyl, 7000 cm^{-1}; diisopropyl, 7500 cm^{-1}), and, while the intensity does not vary significantly, the band width and band symmetry depend on the alkyl substituents and hence probably on the ligand field strength. This can be attributed to the presence of two overlapping bands of which the higher frequency one is characteristic of the low-spin form and the other of the high-spin form, so that one band increases when the other decreases. The bands correspond to the energy expected for the transitions $^6A_1 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_1$. These transitions are normally observed in the range 10,000–14,000 cm^{-1} but are necessarily much lower near the crossover[2] and, in view of the proximity of $^2T_2$ and $^6A_1$, must be almost superimposed in some of the dithio chelates.

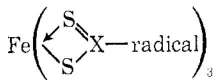
In the dialkyldithiophosphates there is an additional band with similar extinction coefficient, suggesting the assignment $^6A_1 \rightarrow {}^4T_2$. This band is not observed in the pyrrolidyldithiocarbamate, presumably being obscured by charge-transfer bands.

The 19,200-cm^{-1} absorption in ferric dicyclohexyldithiocarbamate is of similar intensity to the d–d transitions in Co(III) and Cr(III) dithio chelates and might correspond to the transition $^2T_2 \rightarrow {}^2T_1$, although the ferric absorption is only a shoulder, and comparison is inadequate. However, as there is no sign of such a transition below this frequency, this may have to be regarded as a minimum energy. If so, the ligand field parameters (Table VI) are far higher than estimated previously,[2] when it was necessary to estimate B and Δ for $^6A_1$ from $Fe(H_2O)_6{}^{3+}$, but a definite trend is still observed, which parallels the observed magnetic properties. It is seen that the condition for "crossover" $\Delta(^6A_1) < \pi < \Delta(^2T_2)$ still holds for those complexes whose magnetic properties require it, but the ligand field parameters, particularly B, seem less reasonable than those estimated previously.[2] Distortion from octahedral symmetry might be partially responsible for this. As it was not possible to obtain data unobscured by the charge-transfer bands, we see no means of resolving this problem at present.

Infrared Spectra.—The region of most likely occurrence of the $Fe-S_6$ stretching mode[2] is 300–400 cm^{-1}, and the spectra for this range are displayed in Figure 7. The high-spin pyrrolidyl complex (class 1) has a single band at 320 cm^{-1}, little changed by cooling to liquid air temperature. The essentially low-spin diisopropyl, diphenyl, and dicyclohexyl complexes (class 4) possess two well-defined bands of equal intensity (at 320 and 365 cm^{-1} for the diisopropyl complex). These are also insensitive to cooling and may well be indicative of Jahn–Teller distortion in $^2T_2$. The spectra, and their temperature dependences, do not indicate simple superpositions of the $^6A_1$ and $^2T_2$ spectra, weighted according to population, which might have been expected if the po-

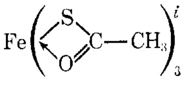
TABLE V

MAGNETIC SUSCEPTIBILITIES OF A NUMBER OF IRON(III) DITHIO CHELATES AS A FUNCTION OF PRESSURE



X-radical (solvent)	Magnetic moments (μ_{eff}, BM) at various pressures (P, atm)						ΔV,[a] cm^3 mol^{-1}	Density of solid, g cm^{-3}	
	1	500	1000	2000	3000	500		Fe	Co
CN-dimethyl (3.5% $CHCl_3$)	4.15	4.06	3.98	3.75	3.56		6.3 ± 0.4	1.515	1.525
CN-diethyl (2.2% $CHCl_3$)	4.41	4.36	4.27	4.07	3.85		5.4 ± 0.4	1.230	1.230
CN-di-*n*-propyl									
(7.6% $CHCl_3$)	4.04	3.98	3.89	3.72	3.52		5.2 ± 0.4	1.220	1.220
CN-diisopropyl									
(5.0% $CHCl_3$)	2.53	2.58	2.55	2.51	2.46	2.54	3	1.213	
CN-di-*n*-butyl									
(4.6% $CHCl_3$)	4.18	4.12	4.03	3.87	3.70		5.0 ± 0.2	1.142	1.15
(5.4% CH_2Cl_2)	4.25	4.21	4.13	3.97	3.83	4.23	5.0 ± 0.8		
CN-diisobutyl									
(7.6% $CHCl_3$)	3.31	3.24	3.17	3.04	2.92		5.2 ± 0.3		
CN-di-*sec*-butyl									
(5.4% $CHCl_3$)	2.20	2.17	2.19	2.19	2.20	2.22			1.215
CN-di-*n*-amyl									
(6.7% $CHCl_3$)	3.92	3.87	3.75	3.62	3.46	3.81	4.5 ± 0.4	1.135	1.120
(10% CH_2Cl_2)	4.03	3.96	3.87	3.75	3.57	3.98	4.7 ± 0.6		
(7.9% C_6H_5Cl)	4.13	4.10	4.02	3.89	3.73	4.11	4.4 ± 0.6		
CN-di-*n*-hexyl									
(5.2% $CHCl_3$)	4.20	4.15	4.08	3.96	3.78	4.14	4.5 ± 0.6	1.12	
(4.8% CH_2Cl_2)	4.45	4.39	4.35	4.22	4.10	4.43	4.3 ± 0.5		
CN-di-*n*-heptyl									
(3.4% $CHCl_3$)	5.23	5.12	5.01	4.91	4.72	5.15	5.5 ± 0.6	1.090	
(4.6% CH_2Cl_2)	5.59	5.48	5.48	5.31	5.23	5.58	5.9 ± 0.6		
CN-di-*n*-dodecyl									
(2.8% $CHCl_3$)	4.25	4.12	3.99	3.83	3.54	3.88	~4.5		
$CN(CH_2CH_2OH)_2$									
(6.8% DMF)	5.84		5.65	5.45	5.34		~6		
C(N-ethyl,N-butyl)									
(4.8% $CHCl_3$)	4.60	4.49	4.41	4.26	4.11	4.47	4.5 ± 1.0	1.170	
(4.6% CH_2Cl_2)	4.79	4.67	4.61	4.54	4.42	4.77			
CN-dicyclohexyl									
(6.5% $CHCl_3$)	2.55		2.58	2.59	2.57	2.60	...	1.14	
CN-dibenzyl									
(3.5% $CHCl_3$)	3.66	3.73	3.68	3.60	3.48	3.72	3.5 ± 1.0	1.305	1.340
C(N-methyl,N-phenyl)[b,c]									
(1.6% CH_2Cl_3)	3.52	3.46	3.22	3.12	3.05		~5	1.480	1.480
C(N-ethyl,N-phenyl)[c]									
(4.5% $CHCl_3$)	3.71	3.62	3.57	3.40	3.25		~5	1.370	1.375
C(N-*n*-propyl,N-phenyl)[c]									
(3.8% $CHCl_3$)	3.73	3.65	3.57	3.42	3.33		~6		
C(N-isoamyl,N-phenyl)[c,d]									
(3.2% $CHCl_3$)	3.10	2.97	2.79	2.76	2.66		~6		
(7.9% CH_2Cl_2)	3.41	3.23	3.13	3.01	2.94	3.21	~6		
C(N-ethyl,N-*m*-toluidyl)[c]									
(6.3% $CHCl_3$)	3.88	3.79	3.67	3.56	3.46	3.81	4.1 ± 0.5	1.360	
(6.6% CH_2Cl_2)	4.07	3.90	3.86	3.74	3.67	3.97	4.0 ± 0.6		
C(N-ethyl,N-*o*-anisidyl)[c]									
(4.7% $CHCl_3$)	3.71	3.64	3.65	3.48	3.45	3.72	4.0 ± 0.8	1.330	
(5.2% CH_2Cl_2)	3.64	3.66	3.62	3.56	3.39	3.70	4.0 ± 1.0		
C(N-ethyl,N-2,4-dimethylphenyl)[c]									
(3.7% $CHCl_3$)	5.22	4.43	4.29	4.19	4.06	4.64	5	1.170	
(3.7% CH_2Cl_2)	4.87	4.49	4.33	4.32	4.15	4.45	4.4 ± 0.6		
C-morpholyl									
(6.7% $CHCl_3$)	3.83	3.76	3.65	3.47	3.29		6.2 ± 0.3	1.565	
C-piperidyl									
(3.7% $CHCl_3$)	4.09	4.03	3.98	3.77	3.62		4.6 ± 0.5	1.352	
C-pyrrolidyl[e]									
(4.0% $CHCl_3$)	5.90		5.83	5.78	5.73	5.88	5	1.535	
P(O-ethyl)$_2$									
(3.8% $CHCl_3$)	5.61	5.77	5.71	5.60	5.48	5.67	...		
(3.5% CH_2Cl_2)	5.76	5.85	5.58	5.71	5.67	5.58	...		

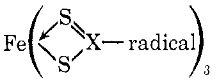
TABLE V (*Continued*)

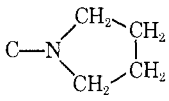
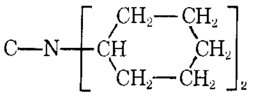
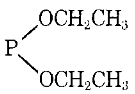
X-radical (solvent)	Magnetic moments (μ_{eff}, BM) atvarious pressures (*P*, atm) 1	500	1000	2000	3000	500	ΔV,[a] cm^3 mol^{-1}	Density of solid, g cm^{-3} Fe	Co
P(O-isopropyl)$_2$									
(4.4% $CHCl_3$)	5.72	5.70	5.71	5.68	5.67	5.67	...	1.340	
(5.7% CH_2Cl_2)	5.76	5.84	5.79	5.81	5.82	5.78	...		
P(O-*sec*-butyl)$_2$									
(5.4% $CHCl_3$)	5.75		5.62	5.55	5.55	5.39	...		
CO-methyl[f]									
(4.9% $CHCl_3$)	2.41	2.40	2.36	2.34	2.33		5.6 ± 0.9		
CO-ethyl									
(8.3% $CHCl_3$)	2.55	2.54	2.52	2.49	2.46	*g*	2.3		
CO-isopropyl[h]									
(5.3% $CHCl_3$)	2.68	2.66	2.65	2.62	2.63		1.6		
CO-*sec*-butyl[h]									
(5.6% $CHCl_3$)	2.36	2.36	2.36	2.36	2.33		3		
CO-allyl[h]									
(4.6% $CHCl_3$)		2.53	2.50	2.48	2.46		3		
 [i]									
(3.4% CH_2Cl_2)	1.76		1.87	2.00	1.93	1.85	...		
(4.0% $CHCl_3$)	1.84		1.96	1.86	1.94	1.85	...		

[a] Assuming 1 cm^3/mol = 1.66 Å^3/molecule. [b] Solubility too low for accurate measurement. [c] For N-alkyl,N-phenyldithiocarbamates, log *K vs P* is usually nonlinear, so that ΔV can only be estimated approximately. [d] A small amount of the complex came out of the solution under pressure. [e] Too close to pure high spin to estimate ΔV accurately. [f] The pressure effect was confirmed by a second run on this compound. [g] Returned to 1 atm, and μ was found to be 2.56 BM. [h] μ increases with time owing to decomposition in solution. This counteracts the *P* effect and makes accurate estimation of ΔV impossible. The decomposition appears to be somewhat retarded at higher pressures. [i] The complex is unstable and decomposes fairly rapidly. No pressure effect.

TABLE VI

ELECTRONIC SPECTRA AND SOME TENTATIVE ASSIGNMENTS FOR



X-radical	λ, cm^{-1}	log ε	Tentative assignment	Ligand field parameters
	6,500	0.93	$^4A_1 \rightarrow {}^4T_1$	$B \approx 750$ cm^{-1}
	17,000	3.56		
	19,800	3.57		$\Delta(^6A_1) \approx 19{,}000$ cm^{-1}
	28,100	4.07		$\pi(^6A_1) \approx 20{,}600$ cm^{-1}
Pyrrolidyl-DTC	36,400	4.71		
	7,500	0.88	$^2T_2 \rightarrow {}^4T_1$	$B \approx 835$ cm^{-1}
	[16,300]	[2.76]		$\Delta(^2T_2) \approx 25{,}000$ cm^{-1}
	19,200 sh	3.33	$^2T_2 \rightarrow {}^2T_1$, ^2A	$\pi(^2T_2) \approx 22{,}900$ cm^{-1}
	[25,000 vw, sh]	[3.99]		
	28,200 sh	4.16		
Dicyclohexyl-DTC	31,700 sh	4.31		
	36,600	4.66		
	[40,000 vw, sh]	[4.59]		
C—OCH_2CH_3	8,600		$^2T_2 \rightarrow {}^4T_1$	$B \approx 650$ cm^{-1}
Ethyl-X	17,800		$^2T_2 \rightarrow {}^2T_1$	$\Delta \approx 22{,}400$ cm^{-1}
	22,100		$^2T_2 \rightarrow {}^2E_1$ (?)	
	27,200			
	36,000			
	7,500 sh (?)		$^6A_1 \rightarrow {}^4T_1$	$B \approx 410$ cm^{-1}
	10,800 sh (?)		$^6A_1 \rightarrow {}^4T_2$	$\Delta \approx 7350$ cm^{-1}
	16,600			
	20,100		Charge transfer	
Diethyl-DTP	27,800			

tential energy barrier between the crossing states were appreciable. Calculations of the Wall–Glockler[17] type, on vibrational doubling, indicate that splittings of the order of 1–100 cm^{-1} might be expected for a potential energy barrier of 1000–2000 cm^{-1}. Most likely, the zero-point energies of the two states are roughly equal, and the potential energy barrier is small, leading to an averaged vibrational spectrum, which is probably further complicated by Jahn–Teller distortion.

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(17) F. T. Wall and G. Glockler, *J. Chem. Phys.*, **5**, 314 (1937).

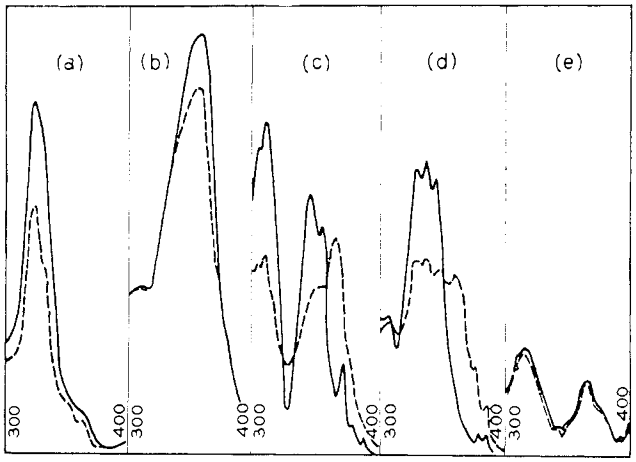

Figure 7.—Infrared spectra at low (——) and at room temperatures (– – –), for $Fe(S_2CNR_2)_3$ complexes with substituents NR_2 = (a) pyrrolidyl, (b) N,N-di-*n*-butyl, (c) N,N-di-*n*-propyl, (d) N,N-diethyl, and (e) N,N-diisopropyl.

Although unequivocal conclusions cannot be drawn from the infrared results at this stage, the temperature dependence of the magnetism is clearly in good accord with, and well explained by, the model and correlates well with the interpretation of the electronic spectra.

Experimental Section

The xanthate and dithiophosphate complexes were prepared by one of the methods described[1] for the dithiocarbamates: the sodium salt of the ligand was treated with a ferric salt in concentrated aqueous solution, and the resulting complex recrystallized from an organic solvent such as chloroform.

The magnetic measurements at various temperatures and pressures and density measurements on solid complexes were carried out as described previously.[2,15] The densities of solutions of complexes were measured at one temperature and atmospheric pressure, and their compressibilities and thermal expansion coefficients were assumed to be the same as that of the solvents used. No appreciable errors are introduced by this assumption.[15] The compressibility of chlorobenzene was obtained from ref 18, and references for the other solvents have been given elsewhere.[15]

Phase changes in solid complexes under pressure were investigated by compressing the samples in polythene tubes inserted into a steel cylinder. Reproducible discontinuities in the plot of volume against pressure were taken to be phase changes.

Infrared spectra were obtained at low and at room temperatures by mounting the samples in KBr disks on a copper block capable of being chilled with liquid air.

Acknowledgment.—We are indebted to Mr. E. S. Merritt for his assistance with the construction and maintenance of apparatus, to Dr. S. D. Hamann for access to a variable-pressure spectrophotometer, to Dr. J. M. James for access to a Unicam SP700 spectrophotometer, and to Dr. W. Zimmermann for the microanalytical figures.

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(18) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **77**, 129 (1349).

Contribution from the Chemistry Department,
McGill University, Montreal, Canada

Infrared Spectra of Divalent Metal Dithioacetylacetonates[1]

By OLAVI SIIMANN and JAMES FRESCO

Received April 7, 1969

The infrared spectra of iron(II), cobalt(II), nickel(II), palladium(II), and platinum(II) complexes of dithioacetylacetone have been recorded from 4000 to 300 cm^{-1}. Vibrational assignments were obtained by normal-coordinate analyses. Except for metal–sulfur vibrations, the spectra have been slightly affected by the nature of the coordinated metal. Metal–ligand bonding in dithioacetylacetonates and similar complexes was discussed on the basis of their molecular spectra.

Introduction

Although infrared spectra of several metal chelates of dithioacetylacetone have been reported,[2,3] normal-coordinate analyses have not previously been performed on these complexes. Where band assignments have been made, ordinary inspection methods were used. These assignments should be considered tentative since group frequencies are unreliable in the low-frequency region and the possibility of intramolecular vibrational coupling was ignored.

Normal-coordinate analyses[4-6] have been carried out for a number of acetylacetonates whose molecular structures are similar to the dithioacetylacetone metal chelates. These calculations were performed for a 1:1 metal–ligand model in which the methyl groups were considered as point masses. More recently, they were extended[7] by considering the total symmetry of the complex, either as 1:2 or 1:3 metal–ligand structures. Reasonably good agreement with the simple 1:1 model exists for band assignments in the region of intermediate frequency and for metal–oxygen vibrations in the low-frequency region. However, calculated force constants were found to be approximately 20% greater for the 1:1 chelate model in the lower frequency region.

As part of our investigation of the spectra of chelates of sulfur analogs of β-diketones, the infrared spectra of iron(II), cobalt(II), nickel(II), palladium(II), and

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(1) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968.

(2) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966).

(3) A. Ouchi, M. Hyodo, and Y. Takahashi, *Bull. Chem. Soc. Japan*, **40**, 2819 (1967).

(4) K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

(5) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).

(6) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

(7) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 1037 (1967).