

${}^2T_2$  and  ${}^4T_1$  are split by spin-orbit coupling such complexity does not necessarily indicate a superposition of transitions. Additionally some of this detail is probably due to vibrational overtones. The observation that these spectra are transformed by lowering the temperature offers no more than qualitative support to our model.

The position of the band would be expected to shift slightly with changes in the alkyl groups. There is indeed a slight upward trend with increasing ligand field strength (*n*-butyl:  $6400\text{ cm}^{-1}$ , isobutyl:  $6700\text{ cm}^{-1}$ , isopropyl (magnetically similar to isobutyl):  $7400\text{ cm}^{-1}$ ) but the data we have at present are not extensive. Spectra in this region are best measured in  $\text{CCl}_4$  solution, and many of the complexes are insufficiently soluble in this solvent.

#### *Other physical measurements*

Finally, we note that the coexistence of two molecular states of significantly different dimensions, in thermal equilibrium, may confer unusual properties on the solid in respect of thermal expansion, heat capacity, and phase equilibria. We envisage obtaining further information about the nature of the binding from the proton resonances in the n.m.r. spectrum, and from the Mössbauer spectrum of the iron atom in these unusual complexes.

### EXPERIMENTAL

#### *Materials*

The methods of preparation, purification and analysis of the iron (III) *N,N*-dialkyl-dithiocarbamates studied here are reported in detail elsewhere (White *et al.* 1964).

#### *Magnetic measurements*

The temperature dependence of the magnetic susceptibility of the polycrystalline compounds was determined by the Gouy method. The molar susceptibility  $\chi_M$  (corrected for the underlying diamagnetism of all atoms) and the effective magnetic moment,  $\mu$ , calculated from the expression,  $\mu = 2.84 (\chi_M T)^{\frac{1}{2}}$  are listed in table 2. No correction for temperature independent paramagnetism has been applied.

Several samples were studied at two different field strengths, *ca.* 4000 and 8000 G, the mean of the two susceptibilities being taken. No evidence was obtained for dependence of susceptibility upon the strength of the magnetic field.

Equation (1) for  $\mu^2$  contains three disposable parameters ( $g$ ,  $E$ ,  $\zeta$ ) and might be expected to be able to accommodate fairly well any susceptibility curve of the right general shape. In fact the right-hand side of equation (1) proves to be a rather limited kind of function for this purpose. The development of maxima and minima depends on two parameters only, namely  $E/\zeta$  and  $g$ . It happens that they exercise rather similar effects on the shape of the function, an increase in  $g$  causing much the same deformations as a decrease in  $E/\zeta$ . This may be seen in figure 5, wherein the broken curves can be tolerably well superimposed upon the full curves by appropriate scale changes (that is, by a different choice of the third parameter,  $\zeta$ ). A given value of say the ratio  $\chi_{\text{max}}^{-1}/\chi_{\text{min}}^{-1}$  (the subscripts referring to the maxima and minima of the  $\chi_M^{-1}(T)$  curve) therefore determines within close limits the theoretical value

TABLE 2. EXPERIMENTAL MOLAR SUSCEPTIBILITIES ( $\chi_M$ , C.G.S., E.M.U.) AND MAGNETIC MOMENTS (B.M.) AT VARIOUS TEMPERATURES ( $^{\circ}$ K)

temp.	$10^6\chi_M$	$\mu$	temp.	$10^6\chi_M$	$\mu$
tris (dimethyldithiocarbamato) iron (III)*					
87.7	6200	2.09	242.7	6590	3.59
95.0	5670	2.08	262.1	6900	3.82
104.7	5270	2.11	282.3	7170	4.04
120.0	4980	2.20	285.2	7240	4.08
140.6	4880	2.35	312.1	7310	4.29
159.5	5000	2.54	332.7	7420	4.46
181.5	5290	2.78	360.1	7440	4.65
204.2	5740	3.07	378.7	7390	4.75
225.3	6210	3.36	405.7	7280	4.88
tris (di- <i>n</i> -butyldithiocarbamato) iron (III)†					
91.0	10140	2.73	165.6	16700	4.72
97.8	10430	2.87	170.0	16700	4.79
104.9	11180	3.07	179.2	16580	4.90
112.5	11860	3.28	187.5	16310	4.97
119.6	12550	3.48	197.0	16010	5.05
128.8	13210	3.71	206.8	15620	5.11
134.0	13610	3.84	218.0	15140	5.16
140.4	14300	4.02	228.4	14820	5.23
148.3	16350	4.42	241.3	14360	5.29
153.7	16550	4.53	253.2	13770	5.30
159.6	16700	4.64	263.8	13310	5.32
tris (di- <i>isobutyldithiocarbamato</i> ) iron (III)†					
102.2	5500	2.13	215.1	3420	2.44
110.0	5250	2.16	223.9	3410	2.48
117.2	4960	2.17	231.7	3410	2.52
125.1	4690	2.18	240.1	3420	2.57
133.2	4420	2.18	248.0	3420	2.62
140.8	4240	2.19	255.9	3470	2.68
149.0	4070	2.21	263.1	3510	2.73
156.9	3940	2.23	270.3	3560	2.79
165.4	3790	2.25	281.2	3650	2.88
173.9	3700	2.28	294.2	3720	2.97
182.2	3620	2.31	305.4	3790	3.06
190.7	3530	2.33	317.2	3880	3.15
198.1	3500	2.37	329.2	3970	3.25
206.4	3470	2.40	341.8	4090	3.36
tris (pyrrolidylthiocarbamato) iron (III)‡					
104.9	40810	5.88	183.7	23090	5.85
113.2	38030	5.87	200.3	21190	5.85
123.2	35420	5.93	216.8	19890	5.90
132.9	32000	5.86	234.4	18400	5.90
148.0	29060	5.89	251.4	17110	5.89
159.0	26820	5.86	265.6	16200	5.89
171.2	25010	5.88	281.7	15220	5.88

\* Diamagnetic correction,  $\Delta = -205 \times 10^{-6}$ ; mol. wt. = 416.† Diamagnetic correction,  $\Delta = -418 \times 10^{-6}$ ; mol. wt. = 669.‡ Diamagnetic correction,  $\Delta = -258 \times 10^{-6}$ ; mol. wt. = 495.