TABLE 1. SPECTRA AND LIGAND FIELD PARAMETERS

| M | config. | B (free ion) (cm^{-1}) | $M(S_2CNMe_2)_3^a$ | | | | $M(H_2O)_6^{3+}$ | | | |
			$\nu_{max.}$ (10^3 cm^{-1})	Δ (cm^{-1})	B (complex) (cm^{-1})	β	$\nu_{max.}$ (10^3 cm^{-1})	Δ (cm^{-1})	B (complex) (cm^{-1})	β
Ti(d^1)	$t_2^1(^2T_2)$	—	—	$(18300)^c$	—	—	$(17\cdot4?)\ 20\cdot3(^2E)$	20300	—	—
V(d^2)	$t_2^2(^3T_1)$	860	$14\cdot0(^3T_2)$	$(15000)^c$	$(380)^c$	$(0\cdot44)^c$	$17\cdot8\ \ 25\cdot7(3T_1)$	19100	615	0·72
Cr(d^3)	$t_2^3(^4A_2)$	920	$15\cdot5(^4T_2),\ 20\cdot2(^4T_1)$	15500	440	0·48	$17\cdot4\ \ 24\cdot6$	17400	725	0·79
Mn(d^4)	$t_2^3e^1(^5E)$	965	$6\cdot0(^5T_2),\ 16\cdot0(^5T_2)$	b	—	—	$—\ \ 21\cdot0$	b	—	—
Fe(d^5)	$t_2^3e^2(^6A_1)$	1090	$6\cdot5(^4T_1?)$	$(12800)^c$	$(510)^c$	$(0\cdot47)^c$	$12\cdot6^d\ \ 18\cdot5^d$	14300	815	0·75
Co(d^6)	$t_2^6(^1A_1)$	1100	$15\cdot4(^1T_1),\ 20\cdot9(^1T_2)$	16100	395	0·36	$16\cdot6\ \ 24\cdot9$	17100	650	0·59

a Spectra measured in CHCl$_3$ solution. The ground-state assignments are based on magnetic measurements.

b No assignments because of Jahn–Teller splitting (Dingle 1962).

c Estimated; see text.

d 12·6 is $^4T_1 \leftarrow {^6A_1}$, 18·5 is $^4T_2 \leftarrow {^6A_1}$.

their spectra determined (White & Martin 1962, unpublished). The analysis of these spectra, and the calculations based thereon, are given in table 1, which also includes figures for the corresponding hexaaquo complexes.

The figures in this table locate dithiocarbamate in the nephelauxetic series and confirm Jørgensen's spectrochemical assignment: Δ is some 10 % less than that of water (relatively weak field) and β (dithiocarbamate) is $ca.\ 0\cdot61\beta$ (H_2O), implying a strong reduction in B. We can also estimate Δ and β for $[Fe(S_2CNMe_2)_3]$ in the $t_2^3 e^2$ configuration, using the corresponding values for $[Fe(H_2O)_6]^{3+}$ as a guide, and obtain $\Delta \sim 12\ 800\ cm^{-1}, \beta \sim 0\cdot47$. Taking B (free ion) $= 1090\ cm^{-1}$, we then have B (complex) $= 510\ cm^{-1}$. The mean pairing energy π is equal to $7\frac{1}{2}B + 5C \sim 27\frac{1}{2}B$ (making the usual assumption that $C \sim 4B$); whence finally $\pi \sim 14\,000\ cm^{-1}$.

The left-hand inequality in the set: $\Delta(^6A_1) < \pi < \Delta(^2T_2)$ thus appears to be satisfied; for $\Delta(^2T_2)$ we can only use Jørgensen's and Orgel's suggestions (Jørgensen 1962a, p. 128) that Δ increases by about 10 to 20 % for each electron transferred from between e and t_2 orbitals. This gives $\Delta(^2T_2) \sim 15\,400$–$17\,900\ cm^{-1}$, again meeting the requirements of the inequality. B and β for the $^2T_2$ state we cannot estimate. Both should be lower for this state than for $^6A_1$, since the metal-ligand distance, r, is less, and β increases with r, but very little is known about the rate of this decrease (Jørgensen 1962a, p. 145).

The origin of the decrease in B is, on the other hand, fairly well understood. It is attributed both to the variation of the effective charge in the partly filled shell and to the expansion of the d-orbitals which occurs when the ligand is especially polarizable or offers pathways of delocalization through π-bonding. The dithiocarbamate group probably acts in both these ways; the second of them is likely to be operative in the heteroaromatic ligand used by Stoufer *et al.*, and we envisage that their observations can be explained along these lines.

Finally, it is worth while noting how the variation in B affects the discussion of the crossover situation which we developed in terms of figure 2. Consider, in this figure, the $^6A_1$ and $^2T_2$ levels. The energy difference between them is made up of a term in Δ, that is in qr^{-5}, favouring $^2T_2$, and an r-independent term arising from interactions between the d-electrons, and favouring $^6A_1$. As r decreases, the first term eventually outweighs the second, and $^2T_2$ becomes the lower state. To generalize this picture to include variation of B, we may assume, as the simplest approximation, that B is determined solely by r (i.e. is independent of configuration), and decreases monotonically as r decreases. The crossover point will then be reached at a lower value of qr^{-5}. Hence, as expected, decrease in B has qualitatively the same effect as an increase in Δ.

Electronic spectrum

The uncertainties about the values of Δ and B for the $^2T_2$ state of these complexes preclude any serious attempt to assign the only d-shell absorption band observable in their solution spectra, ($\nu_{\max.} \sim 6500\ cm^{-1}$). The separation $^4T_1 \leftarrow {}^6A_1$ is calculable as $10B + 6C - \Delta \sim 34B - \Delta \sim 4500\ cm^{-1}$. The separation $^4T_1 \leftarrow {}^2T_2$ is $\Delta\ (^2T_2) - 5B - 4C \sim 4500$ to $7500\ cm^{-1}$ (using for B the $^6A_1$ value). Neither assignment of the $6500\ cm^{-1}$ absorption band can be securely eliminated by these approximate calculations. The pressed-disk spectra show a surprising amount of detail, but since both