and this contrasts dramatically with the pressure effect observed in the thioxanthate, for which the $^6A_1$ (high spin) population is appreciable.

TABLE 1

MAGNETIC MEASUREMENTS AT VARIOUS PRESSURES

| Pressure	$10^6\chi_{M,corr}$	μ_{eff}	10^2K_1	Pressure	$10^6\chi_{M,corr}$	μ_{eff}	K_2
	$Fe(S_2CSEt)_3$*†				$Ni(S_2CSEt)_2$‡		
	$(CH_2Cl_2;\ 24\cdot2\pm0\cdot2°)$				$(2\cdot55\%$ in $95\%\ CH_2Cl_2+2\cdot5\%\ C_5H_5N;$		
					$25\cdot0\pm0\cdot2°)$		
500 atm	2446	2·42 B.M.	2·95	1 atm	3956	3·08 B.M.	6·85
1000	2381	2·39	2·42	1000	3976	3·09	7·20
2000	2345	2·37	2·11	2000	4136	3·16	10·44
3000	2265	2·33	1·45	3000	4312	3·22	19·94

* $\Delta V = 5\cdot5$ ml/mole $= 9\cdot1$ Å^3/molecule. No measurement was made at 1 atm and the solution was put under pressure as rapidly as possible because decomposition is believed to be retarded by pressure. For this complex decomposition was assumed to be negligible under these conditions because the pressure effect was found to be reversible.

† $Fe(S_2CSBu^t)_3$ was also investigated at $24\cdot0\pm0\cdot3°$. Appreciable decomposition occurred, and quantitative results could not be obtained; however, a similar pressure dependence to the ethyl complex is indicated. The pressure effect was found to reverse qualitatively on decreasing the pressure.

‡ In pure CH_2Cl_2 this compound is essentially diamagnetic, but there is a very small increase in magnetism with pressure, which could be due to a very small degree of association of the complex molecules (cf.[8]).

For iron(III) cross-over complexes whose magnetic properties are close to those of pure low spin forms, the choice of the value of $\mu(^2T_2)$ in solution becomes very important in the evaluation of the pressure measurements by equation (3).

Fig. 2.—Pressure dependence of magnetic susceptibility. (a) $Fe(S_2CSEt)_3$ in CH_2Cl_2; (b) $Fe(S_2CNBu_2^s)_3$ in $CHCl_3$.
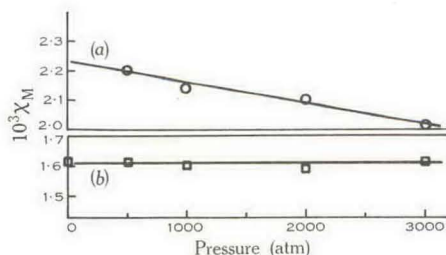
It is apparent from the results on ferric ethyl thioxanthate that $\sqrt{5}$ B.M. (as used in equation (2)) is a good choice, since it gives a value of about $5\cdot5$ ml/mole for ΔV, in good agreement with that found for other dithiochelates, and one would not expect ΔV to vary much from one dithiochelate to another.[2,3] The use of $\mu(^2T_2) = \sqrt{4}$ B.M. leads to $\Delta V \simeq 2\cdot5$ ml/mole, while $\mu(^2T_2) = \sqrt{6}$ B.M. cannot give meaningful results. A value close to $\sqrt{5}$ B.M. is thus probably the best choice for $\mu(^2T_2)$ for ferric dithiochelates in general at room temperature.

As mentioned above, the magnetic moments of low-spin $(^2T_2)$ iron(III) complexes depend on temperature. The temperature dependence of their magnetic

properties may be represented by a Curie–Weiss law $\chi_M \propto 1/(T+\theta)$. Thus for the complexes Fe dipy$_3$(ClO$_4$)$_2$,3H$_2$O and Fe phen$_3$(ClO$_4$)$_2$,3H$_2$O, which are considered to be low spin,[15] the values of the Weiss constant θ are 27° and 18° respectively. The temperature dependent measurements on the ferric ethyl and t-butyl thioxanthates (Table 2) can be fitted approximately to a Curie–Weiss law, if θ is about 85°.

TABLE 2

MAGNETIC MEASUREMENTS AT VARIOUS TEMPERATURES

(T in °K; μ_{eff} in B.M.)

T	$10^6\chi_{M,corr}$	μ_{eff}	T	$10^6\chi_{M,corr}$	μ_{eff}	T	$10^6\chi_{M,corr}$	μ_{eff}
Fe(S$_2$CSEt)$_3$			Fe(S$_2$CSBu^t)$_3$			Ni chsal py$_2$*		
diamag. corr. 243/mole			diamag. corr. 314/mole			diamag. corr. 438/mole		
109·1	5508	2·19	128·4	4796	2·23	114·7	10219	3·07
134·3	4721	2·25	145·5	4443	2·28	122·2	9688	3·09
161·8	4166	2·32	164·2	4163	2·35	127·2	9140	3·06
182·0	3790	2·35	176·2	3932	2·36	136·2	8614	3·08
216·9	3373	2·42	189·2	3714	2·38	147·9	7976	3·08
254·4	3061	2·50	204·2	3505	2·40	158·9	7454	3·09
282·3	2849	2·54	219·2	3307	2·42	169·5	6974	3·09
300·8	2758	2·57	235·9	3140	2·44	179·5	6461	3·06
309·7	2778	2·62	254·9	2984	2·46	189·5	6168	3·07
319·5	2777	2·66	273·2	2839	2·50	201·4	5782	3·06
333·1	2707	2·69	293·2	2727	2·54	213·2	5502	3·07
296·1	2814	2·58				227·2	5187	3·09
273·8	2927	2·53				241·4	4845	3·07
241·6	3130	2·46				254·9	4673	3·10
						267·9	4410	3·09
						281·1	4183	3·08
						293·2	4001	3·07

* Bis(N-cyclohexylsalicylaldimine)bispyridinenickel(II).

This is rather large and is in itself an indication that a Curie–Weiss law is not appropriate. Moreover, a better fit is obtained to equation (2), using the following values of the parameters for the ethyl complex (Fig. 3(a)):

$$Q_a/Q_t = 2, \; g = 1\cdot8, \; \zeta = 300 \text{ cm}^{-1}, \; E = 850 \text{ cm}^{-1}$$

Figure 3(b) shows the results for the t-butyl complex fitted to equation (2) using the same values for the parameters except that g was taken to be 1·85. It has already been pointed out[2] that such a set of parameters obtained by curve-fitting to equation (2) is not unique. One could, in fact, obtain a range of values by varying one of the parameters (within certain limitations[2]) and adjusting the others to get a reasonable fit to equation (2). The fact that a fit can be obtained merely shows that the temperature dependence of the magnetic properties is of a form appropriate to $^2T_2 - {}^6A_1$ cross-over and thus supports the deductions made from the pressure dependence.

[15] Figgis, B. N., *Trans. Faraday Soc.*, 1961, **57**, 204.