

The electronic spectra of the thioxanthate complexes bear a strong resemblance to those of the xanthates and of those dithiocarbamates in which the low spin forms predominate.^{2,3} By analogy with the ferric dithiocarbamates, dithiophosphates,

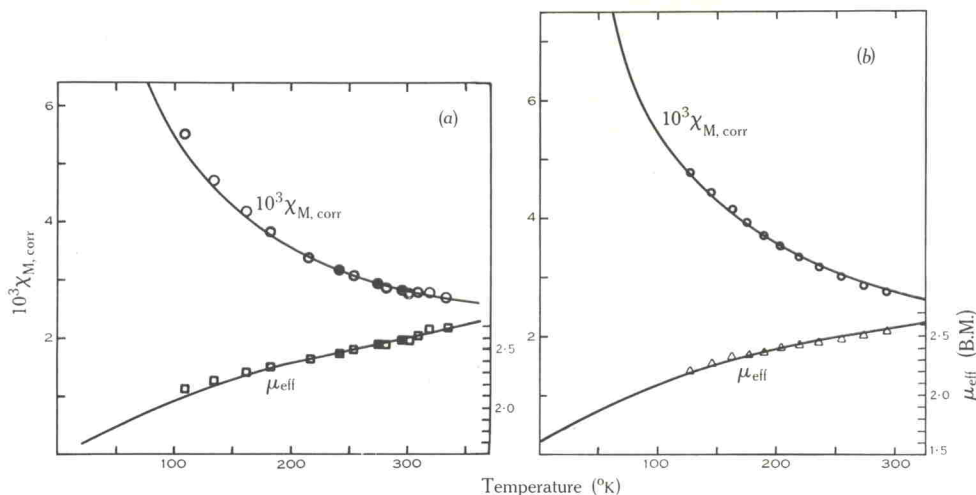


Fig. 3.—Variation of $10^3\chi_M$ and μ_{eff} with temperature. (a) $\text{Fe}(\text{S}_2\text{CSEt})_3$; (b) $\text{Fe}(\text{S}_2\text{CSBu})_3$. The full curves are calculated from equation (2).

and xanthates, assignments are suggested for the main features of the spectrum of the ferric ethyl thioxanthate (Table 3). This leads to values for the Racah parameters B and C of 640 and 2600 cm^{-1} , and hence to a value of 22300 cm^{-1} for the ligand field splitting $\Delta(^2T_2)$, and 17700 cm^{-1} for the electron-pairing energy π . These values

TABLE 3
COMPARISON OF ELECTRONIC SPECTRA
Wave numbers in cm^{-1} followed by $\log \epsilon$ in parentheses

$\text{Fe}(\text{S}_2\text{CSEt})_3$	Suggested Assignment	$\text{Fe}(\text{S}_2\text{COEt})_3$
35000sh (4.29)	charge transfer	35000sh (4.43)
31800 (4.45)	charge transfer	31500 (4.59)
27400 (4.41)	charge transfer	27400 (4.60)
22400sh (2.98)	$^2T_2 - ^2E_1$ (probably)	22100sh (2.82)
17600sh (2.10)	$^2T_2 - ^2T_1$	17800 (2.47)
8800 (1.04)	$^2T_2 - ^4T_1$	8600 (1.01)

are quite close to those obtained for ferric ethyl xanthate, some of the dithiocarbamates, and place the complex near the low spin end of the range. This is in good agreement with the magnetic and other results.

Nickel Complexes

Some nickel(II) complexes exhibit pressure (and temperature) dependent magnetic properties in solution,⁸ due to associative or conformational equilibria.

However, the thioxanthates appear to be planar and monomeric, a structure presumably shared by other nickel(II) dithiochelates.⁹⁻¹² A solution of the ethyl thioxanthate in dichloromethane was essentially diamagnetic and showed no appreciable pressure dependence. Solutions of this complex became partly paramagnetic within a couple of hours, and this as well as the decrease in optical absorption may be attributable to decomposition. On the other hand, in a solution containing pyridine, the complex immediately attained a paramagnetism which was pressure dependent (Table 1). The pressure dependence was found to be reversible. The magnetic and spectral results (Fig. 4) indicate that the nickel complexes readily form adducts with pyridine, even in dilute solution. These solutions were made up by weight and checked by metal analysis.

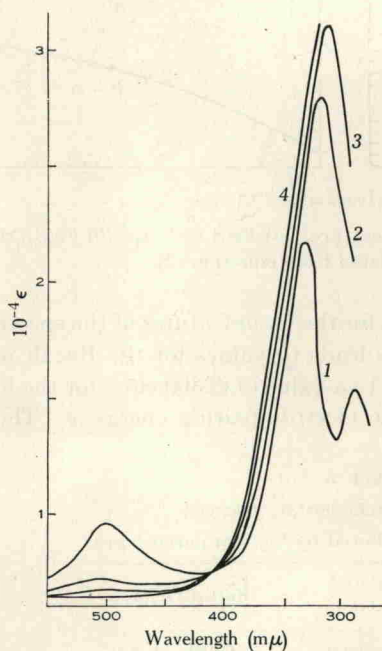


Fig. 4.—Absorption spectrum of $\text{Ni}(\text{S}_2\text{CSEt})_2$ in solvent containing pyridine and dichloromethane:
1, 0% pyridine;
2, 1.45% pyridine;
3, 4.63% pyridine;
4, 100% pyridine.

The appearance of an isobestic point around 400 $\text{m}\mu$ in the pyridine-concentration dependent spectrum of nickel ethyl thioxanthate (Fig. 4) suggests that the equilibrium occurs directly between planar (diamagnetic) nickel thioxanthate and its octahedral (paramagnetic) bispyridine adduct, rather than via a monopyridine intermediate. The same behaviour has been found¹¹ in bis(ethylxanthato)nickel(II), in contrast to bis(*O,O'*-dithiophosphato)nickel(II) which gave both a mono- and a bis-pyridine adduct.

Olive green pyridine adducts result from evaporation of dichloromethane from the above solutions containing pyridine. The adduct of the ethyl complex was microanalysed, and the results are indicative of the inherent poor stability of the