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MAGNETICALLY ANOMALOUS THIO COMPLEXES OF IRON(III)  
AND NICKEL(II)

By A. H. EWALD\* and E. SINN\*†

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*Summary*

Thioxanthate complexes closely resemble the xanthates and the dithiocarbamates. Like the corresponding xanthates and dithiocarbamates, thioxanthates of iron(III), nickel(II), and copper(II) are black and those of cobalt(III) are dark green. In sufficiently dilute solutions, iron(III) and nickel(II) thioxanthates are more red than xanthates and dithiocarbamates which are brownish red. The pressure and temperature dependences of the magnetism show that the ferric thioxanthates exhibit a high-spin  $\rightleftharpoons$  low-spin electronic equilibrium, like the ferric dithiocarbamates and xanthates, though the low spin form predominates for the xanthates and thioxanthates.

Pyridine forms green paramagnetic adducts in the solid with the nickel(II) complexes which lose pyridine if left in the open, while in solution a concentration dependent equilibrium is set up between the planar thioxanthates and its bis-pyridine adduct.

In general the complexes are rather unstable at room temperature, but some kept fairly well if stored frozen in sealed tubes. The iron(III) thioxanthates  $\text{Fe}(\text{S}_2\text{C-S-R})_3$  are at least as stable as the corresponding xanthates. Analogously to the case of the xanthates, the stability of the thioxanthates decreases and the ability of the ligand to reduce the central metal atom increases with increasing chain length when R is an alkyl group. Some long-chain ligands are capable of reducing the central iron atom to form an iron(II) complex. Complexes with branched alkyl chains are more stable than the straight-chain analogues.

INTRODUCTION

High-spin  $\rightleftharpoons$  low-spin electronic equilibria (also called "cross-over") have been observed in a number of different complexes.<sup>1-6</sup> The best example of this so far reported are in iron(III) complexes.<sup>2,4</sup> In favourable cases, e.g. many dithiocarbamates, it is possible to obtain both a minimum and a maximum in the tem-

\* Division of Applied Chemistry, CSIRO, High Pressure Unit, Chemistry Department, University of Sydney, Sydney, N.S.W. 2006.

† Present address: Department of Inorganic Chemistry, University of New South Wales, Kensington, N.S.W. 2033.

<sup>1</sup> White, A. H., Kokot, E., Roper, R., Waterman, H., and Martin, R. L., *Aust. J. Chem.*, 1964, **17**, 294.

<sup>2</sup> Ewald, A. H., Martin, R. L., Ross, I. G., and White, A. H., *Proc. R. Soc. A*, 1964, **280**, 235.

<sup>3</sup> Ewald, A. H., Martin, R. L., Sinn, E., and White, A. H., unpublished data.

<sup>4</sup> Cambi, L., and Cagnasso, A., *Atti Accad. naz. Lincei Rc.*, 1931, **13**, 809; Cambi, L., and Szegö, L., *Ber. dt. chem. Ges.*, 1931, **64**, 259; 1933, **66**, 656; Cambi, L., Szegö, L., and Cagnasso, A., *Atti Accad. naz. Lincei Rc.*, 1932, **15**, 266, 329.

<sup>5</sup> Stoufer, R. C., Busch, D. H., and Hadley, W. B., *J. Am. chem. Soc.*, 1961, **83**, 3732.

<sup>6</sup> Sylva, R. N., and Goodwin, H. A., *Aust. J. Chem.*, 1964, **17**, 1366.

perature dependence of the susceptibility because the relative proportions of high and low spin species follow a Boltzmann distribution,<sup>2,7</sup> while the individual susceptibilities ( $\chi$ ) of the high and low spin forms each essentially follow a Curie-Weiss law. At low temperature ( $kT \ll E$ , where  $E$  is the difference in energy between high and low spin forms), the predominant effect on the susceptibility is the Curie-Weiss decrease of the low spin  $\chi$  with temperature, which outweighs the increase in  $\chi$  due to a small net conversion to high spin: at higher temperatures ( $kT \approx E$ ) the proportion of high and low spin species is very temperature dependent, and the increase in  $\chi$  is due to conversion of low to high spin species with increasing temperature outweighing the Curie-Weiss dependences for both the high and low spin forms. At still higher temperatures ( $kT \gg E$ ) the complex is mainly in the high spin form and the Curie-Weiss dependence for the latter predominates, so that  $\chi$  decreases again with temperature (Fig. 1).

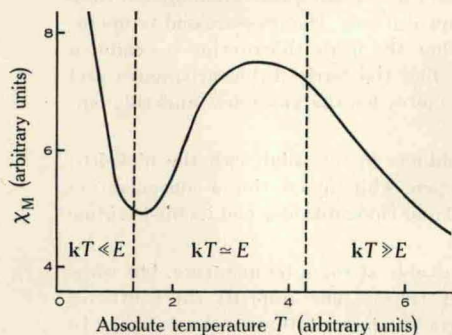


Fig. 1.—Temperature dependence (schematic) of magnetic susceptibility for a compound exhibiting a  ${}^2T_1 - {}^6A_1$  equilibrium.

In simple paramagnetic substances, the susceptibility and the moment ( $\mu_{\text{eff}}$ ) are independent of pressure.<sup>2</sup> For complexes which exhibit an electronic equilibrium in solution without any change in structure, pressure shifts the equilibrium in favour of the low spin species, which have the smaller volume, so that  $\chi$  and  $\mu_{\text{eff}}$  decrease with increasing pressure.<sup>2,3</sup>

The dependence of an electronic equilibrium in an octahedral  $d^6$  configuration on temperature ( $T$ ) and pressure ( $P$ ) may be expressed quantitatively by the equation<sup>2</sup>

$$\mu_{\text{eff}}^2 = \frac{\frac{3}{4}g^2 + 105C \exp\{-(1+E/\zeta)x\} \exp(-P\Delta V/RT) + 8x^{-1}\{1 - \exp(-\frac{3}{2}x)\}}{1 + 2 \exp(-\frac{3}{2}x) + 3C \exp\{-(1+E/\zeta)x\} \exp(-P\Delta V/RT)} \quad (1)$$

where  $x$  is  $\zeta/kT$ ,  $\zeta$  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  ${}^2T_2$  state,  $C (= Q_a/Q_t)$  the ratio of the molecular vibrational partition functions in  ${}^6A_1$  and  ${}^2T_2$ , and  $\Delta V$  the difference in molar volume of the complex in the two states. The factor  $g$  should be in the range 1.8–2.0,  $\zeta$  between 300 and 400  $\text{cm}^{-1}$ , while  $E$  can vary over any range, depending on the compound.

At atmospheric pressure  $\exp(-P\Delta V/RT)$  is sufficiently close to unity to be neglected, but it becomes quite important at higher pressures. Thus, for the iron(III)

<sup>7</sup> Van Vleck, J. H., "The Theory of Electronic and Magnetic Susceptibilities." p. 182. (Oxford University Press 1932, repr. 1965.)

dithiochelates in general, where  $\Delta V$  is about  $5-6 \text{ cm}^3 \text{ mole}^{-3}$ , a pressure of 3000 atm has the effect of lowering the zero point energy of the  ${}^2T_2$  state with respect to that of the  ${}^6A_1$  by about  $150 \text{ cm}^{-1}$ . For atmospheric pressure work, equation (1) may thus be approximated as the temperature dependent equation:<sup>2</sup>

$$\mu_{\text{eff}}^2 = \frac{\frac{3}{4}g^2 + 105C \exp\{-(1+E/\zeta)x\} + 8x^{-1}\{1 - \exp(-\frac{3}{2}x)\}}{1 + 2 \exp(-\frac{3}{2}x) + 3C \exp\{-(1+E/\zeta)x\}} \quad (2)$$

$C$ , and hence  $Q_a/Q_t$ , is assumed to be constant. Rough calculations<sup>2,3</sup> show that  $Q_a/Q_t$  has a temperature dependence which has the effect of adding about  $30-40 \text{ cm}^{-1}$  to the value of  $E$ . Since vibrational amplitudes must be affected by pressure,  $Q_a/Q_t$  should have a pressure dependence as well. Moreover,  $C$  will incorporate other (though less significant) deviations<sup>3</sup> from the idealized octahedral model, in addition to the vibrational effects, so that good estimates of  $C$  cannot be made *a priori*, but neither its temperature nor its pressure dependence is likely to be significant.

For measurements at constant temperature and various pressures, it is convenient to define an equilibrium constant  $K$  by the relation:

$$K = \frac{\mu_{\text{obs}}^2 - \mu_{\text{low}}^2}{\mu_{\text{high}}^2 - \mu_{\text{obs}}^2} \quad (3)$$

The magnetic moment,  $\mu_{\text{low}}$ , of the pure low spin form (obtained when  $E \rightarrow \infty$  in equation (1)) is about  $\sqrt{5}$  B.M. at room temperature. The corresponding high spin moment,  $\mu_{\text{high}}$ , is equal to  $\sqrt{35}$  B.M. ( $E \rightarrow -\infty$  in equation (1)), and the volume difference between the equilibrium species is given by the equation:

$$\Delta V = -2.303 \text{ d}(\log K_1)/\text{d}P \quad (4)$$

where  $K_1$  is given by

$$K_1 = (\mu_{\text{obs}}^2 - 5)/(35 - \mu_{\text{obs}}^2)$$

In practice this may be evaluated using the slopes of the straight lines drawn through the experimental values of  $\log K$  plotted against  $P$ .

Equation (3) can be applied more generally than just to an electronic equilibrium. It may be used, with suitable modification to describe an associative or conformational equilibrium between high- and low-spin nickel(II) species.<sup>8</sup> In this case  $\mu_{\text{high}} = 3.3$  B.M.,  $\mu_{\text{low}} = 0$  and  $K_2 = \mu_{\text{obs}}^2/(3.3^2 - \mu_{\text{obs}}^2)$ , and the volume difference between the two species may be obtained by substituting  $K_2$  in equation (4).

For some complexes there is only a small proportion of the high spin form present at room temperature, and instability of the complexes preclude experiments at higher temperatures. This applies to some dithiocarbamates,<sup>3</sup> and especially to xanthates<sup>3</sup> and thioxanthates. In such cases it is difficult to get a unique fit of the magnetic properties to a temperature dependent equation (such as equation (2)) because the dependence of  $\mu_{\text{eff}}$  on temperature due to the electronic equilibrium is not very large, and the temperature dependence of the moment of the low spin state due to spin-orbit coupling may be of nearly the same order. The pressure dependence, likewise, will not be very great so that the accuracy of quantitative

<sup>8</sup> Ewald, A. H., and Sinn, E., *Inorg. Chem.*, 1967, 6, 40.

results is limited, especially since the pressure measurements are made in solution, where unstable complexes can decompose quite readily. For such cases, investigation of the pressure dependence is more rewarding than that of temperature dependence, because  $\chi$  and  $\mu_{\text{eff}}$  for the low spin forms are completely independent of pressure within experimental error.<sup>2,3</sup> This can be seen in the plot of  $\chi$  against pressure for the low-spin iron(III) di-*s*-butyldithiocarbamate<sup>3</sup> (Fig. 2).

The magnetic properties of ferric xanthates and dithiocarbamates have been correlated with their infrared spectra.<sup>9</sup> The C-O bond order of the xanthates  $\text{Fe}(\text{S}_2\text{C-OR})_3$  is essentially one,<sup>9</sup> while the C-N bond order is about 1.3 for the dialkyl dithiocarbamates  $\text{Fe}(\text{S}_2\text{C-NR}_2)_3$ <sup>10</sup> and even higher for monoalkyl dithiocarbamates  $\text{Fe}(\text{S}_2\text{C-N(H)R})_3$ .<sup>9</sup> These complexes are nearly low spin, intermediate, and nearly high spin respectively.<sup>3</sup> This correlation between magnetism and bond order is far from proven, but in the particular case of the thioxanthates, one would expect both a magnetic moment near to low spin, and a C-S bond order of one, by analogy with the xanthates.

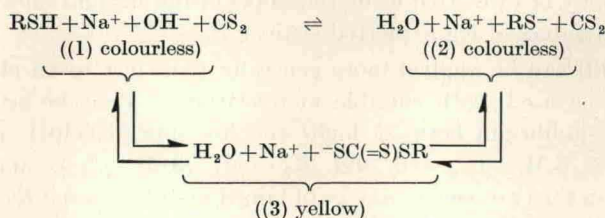
Base adducts with planar nickel complexes are quite common, and the xanthates<sup>11,12</sup> and the thioxanthates form bis-pyridine adducts which partially dissociate in solution and set up equilibria that should be very sensitive to temperature, pressure, and concentration.

## EXPERIMENTAL

### Syntheses

Thioxanthic acids  $\text{HSC(=S)SR}$ , like the analogous xanthic acids  $\text{HSC(=S)OR}$ , cannot themselves be isolated but form complexes of the type  $\text{M}(\text{S}_2\text{CSR})_n$  for a limited number of alkyl substituents R.

When the parent thiol and carbon disulphide were added to concentrated aqueous sodium hydroxide at 0° the sodium thioxanthate,  $\text{Na}(\text{S}_2\text{C-S-R})$ , was formed immediately as a bright yellow crystalline mass. In aqueous solution, the sodium thioxanthates exist in an equilibrium mixture:



The equilibrium lies strongly towards (3). The equilibrium (1)  $\rightleftharpoons$  (2) occurs readily in the absence of  $\text{CS}_2$  to form the colourless thiolate. In the presence of  $\text{CS}_2$  even the solid (white) sodium thiolates immediately form the yellow thioxanthates (equilibrium (2)  $\rightleftharpoons$  (3)). This is probably an indication that  $\text{RSCS}_2\text{H}$  is a stronger acid than  $\text{HSR}$ . When the yellow solutions of the sodium thioxanthates are heated,  $\text{CS}_2$  and some thiol are evolved. Thus the thioxanthates are not very stable in solution, and the addition of sodium thioxanthates to aqueous metal salts will obviously yield mixtures of metal thioxanthates, thiolates, and hydroxides. Separation of

<sup>9</sup> Brown, D. J., Ph.D. Thesis, Syracuse University, N.Y., 1963.

<sup>10</sup> Chatt, J., Duncanson, L. A., and Venanzi, L. M., *Nature*, 1956, **177**, 1042.

<sup>11</sup> Carlin, R. L., Dubnoff, J. S., and Huntress, W. T., *Proc. chem. Soc.*, 1964, 228.

<sup>12</sup> Willis, J. B., and Mellor, D. P., *J. Am. chem. Soc.*, 1947, **69**, 1237.

such mixtures is easy, since the thioxanthates are soluble in such solvents as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ , whilst the hydroxides are insoluble in organic solvents, as are the thiolates, which are presumably polymeric.<sup>13</sup> It was found desirable to prepare the compounds in a nitrogen tent whose outlet led into a fume cupboard.

The ferric thioxanthates were obtained by adding cold concentrated aqueous ferric chloride to the sodium derivative, filtering, extracting into a minimum of dichloromethane, and evaporating under vacuum. Attempts to isolate the ferric complexes from the dichloromethane solution by precipitation with ethanol and filtration generally resulted in decomposition. Use of the solvents less volatile than dichloromethane was found to be unsatisfactory; in carbon disulphide considerable decomposition occurred and in chloroform the yield was quite low. A brown solid was also precipitated in the reaction, but did *not* dissolve in dichloromethane, chloroform, carbon disulphide, or ethanol. It contained a negligible amount of carbon and was probably hydrated ferric oxide (possibly containing a little thiol-Fe complex), and it closely resembled the product of the addition of ferric chloride to the sodium thiolates (i.e. the above synthesis, leaving out the  $\text{CS}_2$ ). This is in keeping with the observation<sup>14</sup> that the analogous ferric alkoxide complexes cannot be prepared from aqueous solution, and when isolated, are decomposed by water.

Nickel(II) thioxanthates were obtained by adding cold concentrated aqueous nickel chloride to the sodium derivative, extracting into dichloromethane and evaporating under vacuum. An insoluble black solid was co-precipitated with the thioxanthates. It was probably largely a nickel thiol complex (cf.<sup>13</sup>), and it appeared identical to the product of the addition of nickel chloride to the sodium thiolates ( $\text{NaSR}$ ) (i.e. the above synthesis, omitting the addition of carbon disulphide).

Copper(II) and cobalt(III) t-butyl thioxanthates were formed in solution in order to establish their existence but no attempts were made to characterize them.

The complexes are very dark and appear black in any appreciable concentration (except the cobalt(III) complexes which are very dark green), as a result of the very intense charge-transfer bands associated with dithiochelates.<sup>2,3,9</sup> In very dilute solution, iron(III) and nickel(II) xanthates and dithiocarbamates are brownish red in colour while the thioxanthates are a brighter red.

The thioxanthates form a little more readily than the xanthates, even up to such long chains as n-octyl, and the ferric complexes seem to be a little more stable than the corresponding xanthates. However, they all decompose quite rapidly at room temperature, especially when the substituent R is n-propyl or longer.

The more unstable thioxanthates, like other unstable dithiochelates, are strong reducing agents and sometimes ignite spontaneously if left in air. Ferric complexes can undergo auto-reduction by the ligands to some ferrous complex; the ferric n-propyl and n-butyl complexes, after being kept for a short time at room temperatures, were both found to be essentially diamagnetic. The n-octyl complex, on heating in air, yielded first metallic iron, then ferric oxide. Branched-chain alkyl complexes such as t-butyl are more stable than the corresponding n-alkyls. Iron(III) and nickel(II) phenyl thioxanthates and phenyl xanthates do not form by the method described. This indicates that thiophenols and phenol are stronger acids than the hypothetical thioxanthic and xanthic acids.

The ethyl and t-butyl complexes were found to keep quite well when deep-frozen in airtight containers. After 12 months of such storage, a sample of the ethyl compound still had a good iron analysis, but its melting point was lower, and there was a very small residue insoluble in dichloromethane, indicating partial decomposition.

The thioxanthates, like the xanthates, are black solids and very soluble in organic solvents such as the chlorinated hydrocarbons, carbon disulphide, and aromatic solvents.

<sup>13</sup> Jensen, K. A., *Z. anorg. Chem.*, 1944, **252**, 227.

<sup>14</sup> Adams, R. W., Bishop, E., Martin, R. L., and Winter, G., *Aust. J. Chem.*, 1966, **19**, 2076; Adams, R. W., Martin, R. L., and Winter, G., *Aust. J. Chem.*, 1966, **19**, 363.

*Analyses*

Tris(ethylthioxanthato)iron(III), m.p. 90° (Found, after 1½ weeks at ambient temperature: C, 22.8; H, 3.6; Fe, 11.6. Calc. for C<sub>9</sub>H<sub>15</sub>FeS<sub>3</sub>: C, 23.1; H, 3.2; Fe 11.9%).

Tris(*t*-butylthioxanthato)iron(III), m.p. 98° (Found: C, 33.9; H, 6.0; Fe, 9.9. Calc. for C<sub>15</sub>H<sub>27</sub>FeS<sub>3</sub>: C, 32.7; H, 4.9; Fe, 10.1%).

Tris(*di-s*-butyldithiocarbamato)iron(III),<sup>1</sup> m.p. 130° (Found: C, 49.3; H, 8.2; Fe, 8.6. Calc. for C<sub>27</sub>H<sub>54</sub>FeN<sub>3</sub>S<sub>6</sub>: C, 48.5; H, 8.1; Fe, 8.5%).

Bis(ethylthioxanthato)bispyridinenickel(II), dec. about 95° (Found: C, 42.9; H, 5.4; N, 6.2. Calc. for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>NiS<sub>2</sub>: C, 43.9; H, 5.2; N, 5.7%).

Bis(*N*-cyclohexylsalicylaldimine)bispyridinenickel(II), dec. about 125° (Found: C, 69.9; H, 7.1; N, 8.6. Calc. for C<sub>36</sub>H<sub>42</sub>N<sub>4</sub>NiO<sub>2</sub>: C, 69.6; H, 6.8; N, 9.0%).

The samples were kept sealed and deep-frozen between synthesis and measurement.

Spectra were measured on a Perkin-Elmer Spectracord 4000A, and a Perkin-Elmer infrared spectrophotometer 221 with a sodium chloride prism/grating. The n.m.r. spectra were run on a Varian A60 spectrometer. The magnetic measurements were made by the Gouy method, as previously described.<sup>2,8</sup> The moments were obtained from the corrected molar susceptibilities  $\chi_{M,corr}$  using the relation  $\mu_{eff} = 2.828 \sqrt{\chi_{M,corr} T}$ . The temperature dependent magnetic measurements on the ferric ethyl thioxanthates were made first at increasing and then decreasing temperatures, to ensure that the results were reversible.

## RESULTS AND DISCUSSION

*Stability*

Only the ethyl and *t*-butyl thioxanthates were studied in detail as they are much more stable than the others. The ferric ethyl complex gave fairly good analyses even after 1½ weeks at ambient temperatures. Longer-chain *n*-alkyl complexes gave poor analyses under these conditions, and even when stored frozen in airtight containers were largely decomposed after several weeks. Thus physical measurements cannot easily be made on these complexes under readily accessible conditions. The decomposition of longer-chain *n*-alkyl complexes is accompanied by a measurable decrease of the magnetic moment with time, and the compounds become diamagnetic (probably iron(II)) after a few days. For a sample of the ethyl complex, the moment was constant within experimental error over a period of 24 hr.

In solution stability is quite poor, except for the ferric ethyl complex. Decomposition can be followed magnetically, as well as spectrally by the decrease of the peaks near 320  $\mu$ m or 30000  $\text{cm}^{-1}$  (see below), and of several i.r. peaks, and by the accompanying increase in other i.r. peaks attributable to decomposition products, though the latter were not identified. Thus after 1 hr decomposition was of the order of 10% for the ferric *t*-butyl and nickel ethyl complexes and 30% for nickel *t*-butyl, but was negligible for the ferric ethyl complex.

*Iron(III) Complexes*

The magnetic results at various pressures are given in Table 1. Figure 2 compares the magnetic susceptibility over the pressure range 0–3000 atm, of tris(ethylthioxanthato)iron(III) with that of tris(*N,N*-*di-s*-butyldithiocarbamato)iron(III). The susceptibility of the latter low spin complex is independent of pressure,

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

TABLE I  
MAGNETIC MEASUREMENTS AT VARIOUS PRESSURES

Pressure	$10^6\chi_{M,corr}$	$\mu_{eff}$	$10^2K_1$	Pressure	$10^6\chi_{M,corr}$	$\mu_{eff}$	$K_2$
Fe(S <sub>2</sub> CSEt) <sub>3</sub> *† (CH <sub>2</sub> Cl <sub>2</sub> ; 24.2 ± 0.2°)				Ni(S <sub>2</sub> CSEt) <sub>2</sub> ‡ (2.55% in 95% CH <sub>2</sub> Cl <sub>2</sub> + 2.5% C <sub>5</sub> H <sub>5</sub> N; 25.0 ± 0.2°)			
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

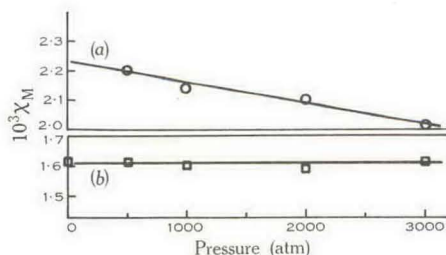
\*  $\Delta V = 5.5$  ml/mole =  $9.1 \text{ \AA}^3$ /molecule. No measurement was made at 1 atm and the solution was put under pressure as rapidly as possible because decomposition is believed to be retarded by pressure. For this complex decomposition was assumed to be negligible under these conditions because the pressure effect was found to be reversible.

† Fe(S<sub>2</sub>CSBu)<sub>3</sub> was also investigated at  $24.0 \pm 0.3^\circ$ . 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<sub>2</sub>Cl<sub>2</sub> 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.<sup>8</sup>).

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<sub>2</sub>CSEt)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>;  
(b) Fe(S<sub>2</sub>CNBu)<sub>3</sub> in CHCl<sub>3</sub>.



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 5.5 ml/mole for  $\Delta V$ , in good agreement with that found for other dithiochelates, and one would not expect  $\Delta V$  to vary much from one dithiochelate to another.<sup>2,3</sup> The use of  $\mu(^2T_2) = \sqrt{4}$  B.M. leads to  $\Delta V \simeq 2.5$  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  $\text{Fe dipy}_3(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Fe phen}_3(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ , which are considered to be low spin,<sup>15</sup> the values of the Weiss constant  $\theta$  are 27° and 18° respectively. The temperature dependent measurements on the ferric ethyl and t-butyl thioan-thates (Table 2) can be fitted approximately to a Curie-Weiss law, if  $\theta$  is about 85°.

TABLE 2  
MAGNETIC MEASUREMENTS AT VARIOUS TEMPERATURES  
( $T$  in °K;  $\mu_{\text{eff}}$  in B.M.)

$T$	$10^6 \chi_{M,\text{corr}}$	$\mu_{\text{eff}}$	$T$	$10^6 \chi_{M,\text{corr}}$	$\mu_{\text{eff}}$	$T$	$10^6 \chi_{M,\text{corr}}$	$\mu_{\text{eff}}$
Fe(S <sub>2</sub> CSEt) <sub>3</sub>			Fe(S <sub>2</sub> CSBu <sup>t</sup> ) <sub>3</sub>			Ni chsal py <sub>2</sub> *		
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)):

$$Q_a/Q_t = 2, g = 1.8, \zeta = 300 \text{ cm}^{-1}, E = 850 \text{ cm}^{-1}$$

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<sup>2</sup> 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<sup>2</sup>) 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.

<sup>15</sup> Figgis, B. N., *Trans. Faraday Soc.*, 1961, 57, 204.



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.<sup>2,3</sup> By analogy with the ferric dithiocarbamates, dithiophosphates,

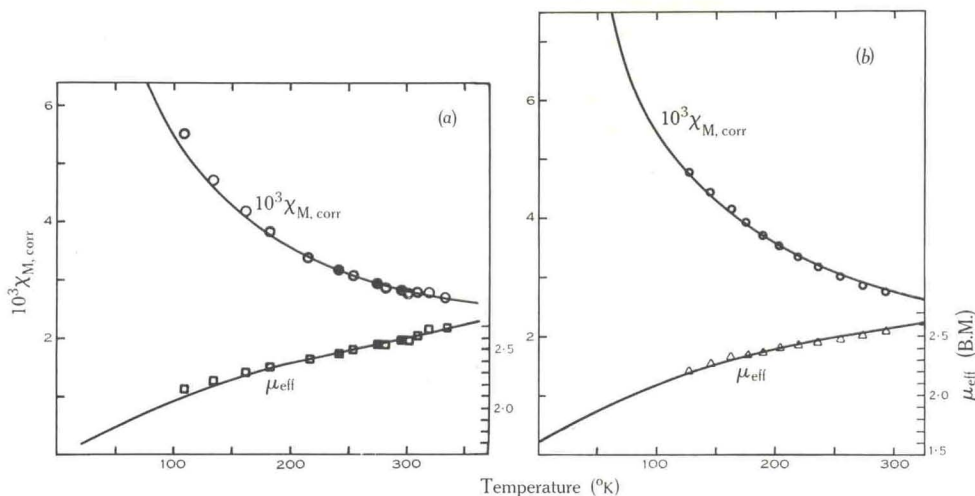


Fig. 3.—Variation of  $10^3\chi_M$  and  $\mu_{\text{eff}}$  with temperature. (a)  $\text{Fe}(\text{S}_2\text{CSEt})_3$ ; (b)  $\text{Fe}(\text{S}_2\text{CSBu})_3$ . The full curves are calculated from equation (2).

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  $\text{cm}^{-1}$ , and hence to a value of 22300  $\text{cm}^{-1}$  for the ligand field splitting  $\Delta(^2T_2)$ , and 17700  $\text{cm}^{-1}$  for the electron-pairing energy  $\pi$ . These values

TABLE 3  
COMPARISON OF ELECTRONIC SPECTRA  
Wave numbers in  $\text{cm}^{-1}$  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,<sup>8</sup> due to associative or conformational equilibria.

However, the thioxanthates appear to be planar and monomeric, a structure presumably shared by other nickel(II) dithiochelates.<sup>9-12</sup> 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.

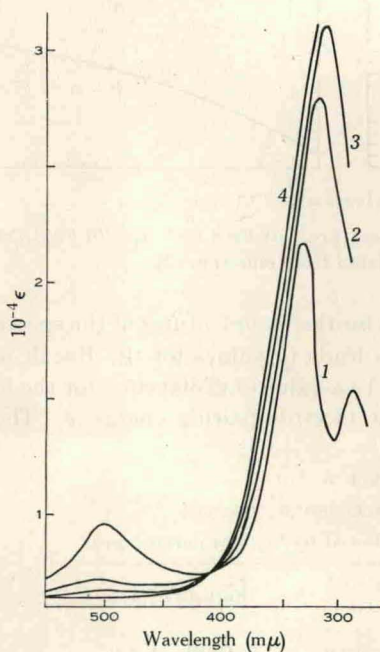


Fig. 4.—Absorption spectrum of  $\text{Ni}(\text{S}_2\text{CSEt})_2$  in solvent containing pyridine and dichloromethane: 1, 0% pyridine; 2, 1.45% pyridine; 3, 4.63% pyridine; 4, 100% pyridine.

The appearance of an isosbestic 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 found<sup>11</sup> 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

complexes. The pyridine adducts lose pyridine unless kept in an excess of pyridine or kept frozen in sealed tubes. When the olive green adducts are dissolved in organic solvents an equilibrium is set up between the planar complex and its pyridine adduct, and the solution is greenish black when concentrated and reddish black when dilute; the adduct formation is also reversed by washing with water, which slowly dissolves out the pyridine. The magnetic moments of the adducts are about 3.5 B.M. For the *t*-butyl adduct the  $\mu_{\text{eff}}$  was found to be 3.55 B.M. at 213.3°K but its temperature dependence was found to be improbably high compared with that of the bipyridine adduct of bis(*N*-cyclohexylsalicylaldimine)nickel(II), which was found (see Table 2) to obey the Curie law between 114 and 293°K with  $\mu_{\text{eff}}$  3.08 B.M. The temperature dependence of the thioxanthate adduct may thus be due to partial oxidation or decomposition. It seems likely now that the pyridine adduct of the analogous nickel ethyl xanthate was actually isolated by Willis and Mellor,<sup>12</sup> but had partially decomposed by the time it was analysed (the decomposition being quite probably catalysed by the presence of pyridine); as a result these workers<sup>12</sup> thought that they had been unable to isolate this adduct.

The fact that complex formation with thioxanthates appears to be more successful with iron(III) than with nickel(II) is unusual for a sulphur ligand. The very affinity of nickel for sulphur may be a cause of the instability of the nickel thioxanthates; possibly the complexes rearrange to form the polymeric mercaptan complexes.<sup>13</sup>

If the complexes contain a C-S-C linkage then the single bond C-S-C stretching vibrations are expected as weak bands in the region 660-630  $\text{cm}^{-1}$  for the ethyl and 600-570  $\text{cm}^{-1}$  for the *t*-butyl complexes,<sup>16-18</sup> and such bands are indeed observed in the iron and the nickel complexes. However, skeletal bands can also occur in this region, so that assignments cannot be made with certainty. Thus the observed bands must be regarded as merely circumstantial evidence for the C-S-C linkage. The absence of any absorptions in the region 1480-1542  $\text{cm}^{-1}$  in the thioxanthates is significant in view of the assignment of this band to the C-N linkage<sup>19</sup> in the dithiocarbamates  $\text{M}(\text{S}_2\text{C-N-R}_2)_n$ .

The n.m.r. spectrum of bis(ethylthioxanthato)nickel(II) has the methyl triplet at -77, -84, and -91 c/s, and the methylene quartet at -182, -189, -196, and -203 c/s; the spectrum shows no appreciable shift between 40° and -56°. This is what would be expected for a simple planar diamagnetic nickel(II) complex. N.m.r. studies on the ferric xanthates and thioxanthates, as would be expected, show great similarities between the two groups; these results will be published together with the Mössbauer studies which are also being made.

The results of the pressure and temperature studies show that the properties of iron(III) and nickel(II) xanthates are not greatly changed by the substitution of

<sup>16</sup> Sheppard, N., *Trans. Faraday Soc.*, 1950, **46**, 429.

<sup>17</sup> Rao, C. N. R., "Chemical Applications of Infrared Spectroscopy." (Academic Press: New York 1963.)

<sup>18</sup> Bellamy, L. J., "The Infra-red Spectra of Complex Molecules." (Methuen: London 1958.)

<sup>19</sup> Chatt, J., Duncanson, L. A., and Venanzi, L. M., *Suom. Kem.*, 1956, **298**, 75.

sulphur for oxygen. It seems likely that other analogues, such as selenoxanthates  $M(S_2C-Se-R)_n$ , could be similarly made and would have properties similar to those of the xanthates and thioxanthates.

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