

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:

$$\Delta V = -2.303 d(\log K_1)/dP \quad (4)$$

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.

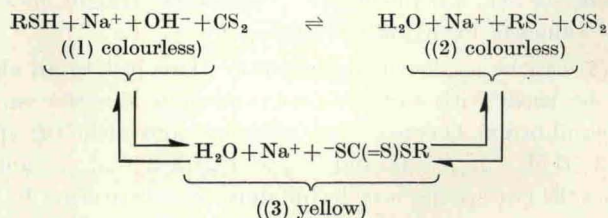
Base adducts with planar nickel complexes are quite common, and the xanthates<sup>11,12</sup> and the thioxanthates form bis-pyridine adducts which partially dissociate in solution and set up equilibria that should be very sensitive to temperature, pressure, and concentration.

## 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.