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

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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 $Fe(S_2C–S–R)_3$ 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.[1–6] The best example of this so far reported are in iron(III) complexes.[2,4] In favourable cases, e.g. many dithiocarbamates, it is possible to obtain both a minimum and a maximum in the tem-

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[1] White, A. H., Kokot, E., Roper, R., Waterman, H., and Martin, R. L., *Aust. J. Chem.*, 1964, **17**, 294.

[2] Ewald, A. H., Martin, R. L., Ross, I. G., and White, A. H., *Proc. R. Soc.* A, 1964, **280**, 235.

[3] Ewald, A. H., Martin, R. L., Sinn, E., and White, A. H., unpublished data.

[4] 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.

[5] Stoufer, R. C., Busch, D. H., and Hadley, W. B., *J. Am. chem. Soc.*, 1961, **83**, 3732.

[6] 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,[2,7] while the individual susceptibilities (χ) 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 χ with temperature, which outweighs the increase in χ due to a small net conversion to high spin: at higher temperatures ($kT \simeq E$) the proportion of high and low spin species is very temperature dependent, and the *increase* in χ 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 χ decreases again with temperature (Fig. 1).
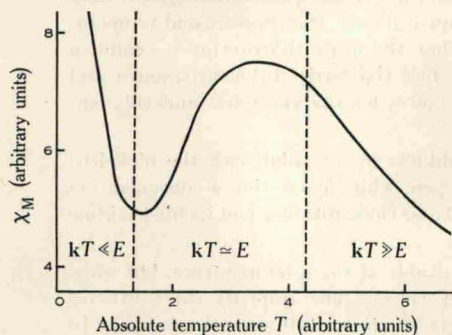

Fig. 1.—Temperature dependence (schematic) of magnetic susceptibility for a compound exhibiting a $^2T_1 - {}^6A_1$ equilibrium.

In simple paramagnetic substances, the susceptibility and the moment (μ_{eff}) are independent of pressure.[2] 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 χ and μ_{eff} decrease with increasing pressure.[2,3]

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[2]

$$\mu^2_{eff} = \frac{\frac{3}{4}g^2 + 105C \exp\{-(1+E/\zeta)x\}\exp(-P\Delta V/\mathbf{R}T) + 8x^{-1}\{1-\exp(-\frac{3}{2}x)\}}{1 + 2\exp(-\frac{3}{2}x) + 3C \exp\{-(1+E/\zeta)x\}\exp(-P\Delta V/\mathbf{R}T)} \quad (1)$$

where x is $\zeta/\mathbf{k}T$, ζ 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 ΔV the difference in molar volume of the complex in the two states. The factor g should be in the range $1\cdot 8 - 2\cdot 0$, ζ between 300 and 400 cm^{-1}, while E can vary over any range, depending on the compound.

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

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