such mixtures is easy, since the thioxanthates are soluble in such solvents as CH_2Cl_2, $CHCl_3$, and CCl_4, whilst the hydroxides are insoluble in organic solvents, as are the thiolates, which are presumably polymeric.[13] 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 CS_2). This is in keeping with the observation[14] 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.[13]), and it appeared identical to the product of the addition of nickel chloride to the sodium thiolates (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.[2,3,9] 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.

[13] Jensen, K. A., *Z. anorg. Chem.*, 1944, **252**, 227.

[14] 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 $1\frac{1}{2}$ weeks at ambient temperature: C, $22\cdot8$; H, $3\cdot6$; Fe, $11\cdot6$. Calc. for $C_9H_{15}FeS_9$: C, $23\cdot1$; H, $3\cdot2$; Fe $11\cdot9\%$).

Tris(t-butylthioxanthato)iron(III), m.p. 98° (Found: C, $33\cdot9$; H, $6\cdot0$; Fe, $9\cdot9$. Calc. for $C_{15}H_{27}FeS_9$: C, $32\cdot7$; H, $4\cdot9$; Fe, $10\cdot1\%$).

Tris(di-s-butyldithiocarbamato)iron(III),[1] m.p. 130° (Found: C, $49\cdot3$; H, $8\cdot2$; Fe, $8\cdot6$. Calc. for $C_{27}H_{54}FeN_3S_6$: C, $48\cdot5$; H, $8\cdot1$; Fe, $8\cdot5\%$).

Bis(ethylthioxanthato)bispyridinenickel(II), dec. about 95° (Found: C, $42\cdot9$; H, $5\cdot4$; N, $6\cdot2$. Calc. for $C_{28}H_{20}N_2NiS_6$: C, $43\cdot9$; H, $5\cdot2$; N, $5\cdot7\%$).

Bis(N-cyclohexylsalicylaldimine)bispyridinenickel(II), dec. about 125° (Found: C, $69\cdot9$; H, $7\cdot1$; N, $8\cdot6$. Calc. for $C_{36}H_{42}N_4NiO_2$: C, $69\cdot6$; H, $6\cdot8$; N, $9\cdot0\%$).

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.[2,8] The moments were obtained from the corrected molar susceptibilities $\chi_{M,corr}$ using the relation $\mu_{eff} = 2\cdot828\sqrt{\chi_{M,corr}T}$. 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 $1\frac{1}{2}$ 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 mμ or 30000 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,