

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 μ_{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 μ_{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,¹² 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 workers¹² 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.¹³

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 cm^{-1} for the ethyl and 600-570 cm^{-1} for the *t*-butyl complexes,¹⁶⁻¹⁸ 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 cm^{-1} in the thioxanthates is significant in view of the assignment of this band to the C-N linkage¹⁹ 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

¹⁶ Sheppard, N., *Trans. Faraday Soc.*, 1950, **46**, 429.

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

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

¹⁹ 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.

ACKNOWLEDGMENTS

We are indebted to Mr E. S. Merritt for his assistance with the construction and maintenance of apparatus, and to Mr R. Beck who ran many of the atmospheric pressure spectra for us. One of us (E.S.) acknowledges financial assistance received under the University of Sydney Research Grant (R6/66/26).