

of the corresponding ratio $T_{\max.}/T_{\min.}$. A computer was used to define this interdependence. If the experimental ratios do not conform, and in the majority of our cases they do not, then it is useless to try and fit the equation to the experimental results; on the other hand, if they do conform it is impossible simultaneously to determine g and E/ζ with any confidence. It is for this reason that we were compelled to consider a further elaboration of the calculations.

High-pressure susceptibility and measurements

Susceptibilities in chloroform solution were measured at pressures up to 3000 atm, and room temperatures, by a Gouy method (see Table 3). The sample tube was made of beryllium-copper (Berylco 25), internally electroplated with gold and rhodium. The tube used a Bridgman seal to confine the liquid, and a collar nut to hold the piston in place after it had been pushed into the tube by a small hydraulic press. Pressure inside the tube was calibrated in terms of the primary pressure on the ram of the press. The total weight of the tube was 109 g and its capacity approximately 3 ml.

TABLE 3. PRESSURE DEPENDENCE OF MAGNETIC PROPERTIES AT 24° C OF $\text{Fe}(\text{S}_2\text{C}\cdot\text{N}(\text{C}_4\text{H}_9)_2)_3$ IN CHLOROFORM SOLUTION (CONCN., 6.38% W/W) BETWEEN 1 AND 3000 ATM

pressure (atm)	density of solution (g cm ⁻³)	10 ⁶ χ_g (solution)	10 ⁶ χ_g (complex)	μ (B.m.)	equilibrium constant, K_2		
					$\mu^2 = 4$	$\mu^2 = 5$	$\mu^2 = 6$
1	1.479	0.217	10.60	4.24	0.83	0.76	0.70
1000	1.587	0.170	9.87	4.10	0.70	0.65	0.59
2000	1.659	0.126	9.18	3.96	0.61	0.56	0.50
3000	1.717	0.086	8.55	3.83	0.53	0.48	0.43

For susceptibility measurements the tube was calibrated in the standard way in terms of benzene and NiCl_2 solution. The tube constant was found to be independent of the position of the piston within the range required to compress the solutions to 3000 atm. The measurements and calibrations were made at fixed magnet currents giving fields of 2900, 4000 and 5000 G. Absolute values of susceptibilities have an error of about 4.5% while relative values are accurate to $\pm 3\%$. The usual diamagnetic corrections (418×10^{-6} c.g.s. e.m.u.) were applied in calculating the effective molecular moments.

The density of the *n*-butyl complex, required for the determination of the molar volume, was determined by flotation in sodium nitrate solutions: $d_4^{20} = 1.21$. Solution densities were derived from Bridgman's (1948) data for chloroform. The susceptibility of the latter was taken as $\chi_g = -0.490 \times 10^{-6}$ c.g.s. e.m.u. and was found to be unaffected by pressure.

Spectra

None of the solvents in which these compounds dissolve are suitable for low-temperature measurements. The low-temperature spectra were measured in an evacuated cell, in which a solid sample was clamped on to a copper block which in turn

was in contact with the refrigerant. For use in the visible region clear films of Perspex, containing the solute, could be made by allowing a chloroform solution of polymer plus solute to evaporate on a silica disk. Throughout the visible region the spectra, on cooling, became slightly better defined and also, interestingly, slightly less intense ($\sim 5\%$), but were not sufficiently different to merit reproduction here.

In the infra-red, much more concentrated samples were needed, and films were unsatisfactory. Pressed KCl disks were used, but at the high solute concentrations ($\sim 30\%$) required, these samples scattered badly and quantitative intensity measurements could not be made. The spectra are therefore simply records of per cent transmission on an arbitrarily expanded scale (cf. Bauman 1962), wherein the apparent absorption is believed to be essentially that of the solute alone. Pressed-disk spectra of the methyl, ethyl and *n*-butyl substituted complexes all showed temperature dependence, differing in detail but alike in their main features. Figure 8 reproduces a representative pair of these spectra. Different samples prepared from the same complex showed quantitative differences in peak intensities, but all the changes were qualitatively reproducible.

A Perkin-Elmer Spectracord spectrometer was used for these measurements.

The assistance of Miss Hanneke Waterman and Dr Ernest Kokot for obtaining in 1958 some of the preliminary χ_M-T data for the methyl, ethyl and *n*-butyl derivatives is gratefully acknowledged.

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