

benzene at various temperatures. Values listed by Selwood¹⁸ were used to correct for the diamagnetism of the ligands and metal atoms. All the measurements were made at room temperature (about 20°), which did not vary by more than 1° during any one run. The density of a substance at various pressures is a function of its compressibility, which decreases with increasing pressure; thus, to determine the gram susceptibility of a solution, its compressibility must be known (see below). The solutions were assumed to obey the Wiedemann mixture law. Density measurements on solid complexes were made at 20° by suspending their crystals in solutions of equal density. Sodium thiosulfate solutions were used for densities below 1.45 g/cc and potassium iodide solutions for higher densities. Soap was added to the solutions to ensure wetting of the crystals. The densities of the suspending solutions were measured with a set of hydrometers calibrated to 0.0005 g/cc. Except where otherwise stated the figures quoted are considered accurate and reproducible to ± 0.005 g/cc.

High-pressure spectral measurements were made in a bomb having Poulter-type sapphire windows, on an adapted Unicam SP500 spectrophotometer. The sample was contained in a small stainless steel cell with silica windows.²⁰ Various corrections to the optical density were allowed for by making measurements relative to a neighboring isobestic point. The isobestic point was found by making measurements at 1 atm at various temperatures and concentrations on a Perkin-Elmer Spectracord 4000A, and the optical density found for it was used to correct the relative absorbances to absolute optical densities.

Salicylaldimines.—Bis(salicylaldehyde)nickel(II) dihydrate was prepared²¹ and refluxed with the parent primary amine neat or in a suitable organic solvent.^{9,17,21,22} Most salicylaldimines can be recrystallized from chloroform, chloroform-ether, or ethanol, but some require toluene or dimethylformamide.

Bis(salicylaldehyde)nickel(II).—In the hope of obtaining a complex containing a formimide group, bis(salicylaldehyde)nickel(II) dihydrate was heated in formamide. In fact, formamide was hydrolyzed under the conditions of the reaction and boiling the aldehyde complex in formamide yielded the parent salicylaldehyde complex in high purity. As the temperature rose, the aldehyde complex dissolved to form a deep green solution (containing, perhaps, some formamide complex) which turned deep red as the boiling point of formamide was approached. The red product separated as fine needles on cooling. This was recrystallized from dimethylformamide and then from toluene. This synthesis has advantages over the conventional method,²¹ both in convenience and in the purity of the product, as it goes through a solution phase which may be filtered to remove impurities and yields a product that is pure even before recrystallization.

Aminotroponimineates.—The ligands for these complexes and some N,N'-dimethyl complex were prepared by members of the Du Pont group in accordance with their own published methods^{23,24} and were kindly sent to us by Dr. Eaton. The complexes were prepared by allowing the ligands to react with methanolic nickel acetate or ammoniacal aqueous nickel chloride.^{24,25}

Microanalyses.—Some of the complexes were analyzed by the Australian Microanalytical Service and their composition confirmed within analytical limits, but well-known compounds, considered to be quite pure and stable, were not analyzed.

Solvents.—All solvents were used as supplied (BDH Analar grade), without further purification or drying, except that they were deoxygenated with a stream of dry nitrogen.

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TABLE I

N substituent	Density, g/cc	Mp, °C
Methyl	1.598	197
Ethyl	1.460	175
<i>n</i> -Propyl	1.425	161
Isopropyl	1.350	205
<i>n</i> -Butyl	1.350	142
Isobutyl	1.235	154-155
<i>n</i> -Pentyl	1.250	148
<i>n</i> -Hexyl	1.220	122
<i>n</i> -Heptyl	1.20 \pm 0.01	109
<i>n</i> -Octyl	1.170	105
<i>n</i> -Dodecyl	1.055 \pm 0.01	93
H ^a	1.085	325
H ^b		324
Phenyl	1.340	\sim 240 dec
Ethylenediimine	1.325	337
<i>o</i> -Phenylenediimine	1.525	\sim 340
3,4-Diiminotolyl	1.530	\sim 330 dec
Nickel(II) salicylaldehyde dihydrate	1.340	\sim 300° dec

^a Prepared by boiling bis(salicylaldehyde)nickel(II) dihydrate in formamide. ^b Prepared by the method of Tyson and Adams.²¹

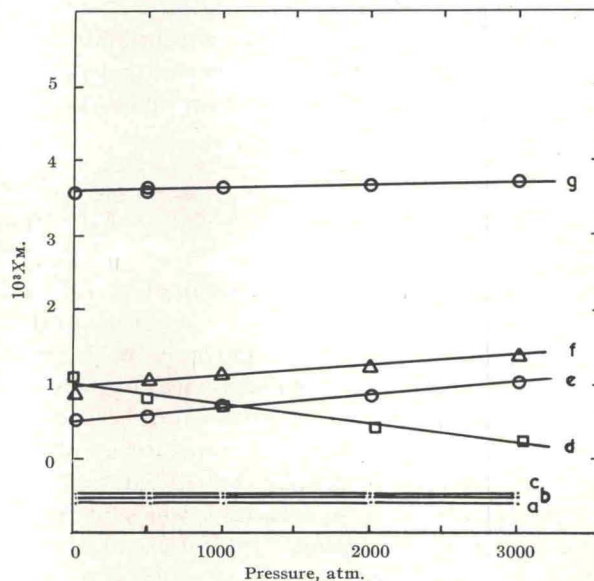


Figure 1.—Pressure dependence of molar susceptibility: (a) ethylene glycol; (b) dichloromethane; (c) chloroform; (d) nickel(II) N,N'-di-*p*-anisidylaminotroponimineate; (e) bis(N-*n*-propylsalicylaldehyde)nickel(II); (f) bis(N-*n*-heptylsalicylaldehyde)nickel(II); (g) bis(N-phenylsalicylaldehyde)nickel(II).

Results

The susceptibility of solvents of known compressibility was determined at various pressures to establish its independence of pressure (see Figure 1; CHCl₃, CH₂Cl₂, (CH₂OH)₂). Their densities at various pressures were obtained from Bridgman's compressibility data,²⁶ and the thermal expansion coefficients²⁷ were used to correct to the temperature of the sample tube

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at the time of compression of the liquid. The densities of the solutions were measured at one temperature and atmospheric pressure and their compressibilities and thermal expansion coefficients were assumed to be the same as those of the solvents used. Errors caused by this assumption are negligible for dilute solutions, since the compressibility of a complex in solution should not be very different from that of the organic solvent containing it.

Use of Solvents of Unknown Compressibility.—In the absence of chemical interactions, the susceptibilities of solvents should be independent of pressure and it should thus be possible to determine their compressibilities from the measurements of their volume susceptibilities. Pyridine and dimethylformamide (DMF) were assumed to satisfy these conditions and their compressibilities were estimated using the relation

$$d_p = (BF_p + K_0)/X_g = d_{1 \text{ atm}}/(1 - (\Delta V/V_0))$$

where $\Delta V/V_0$ is the change in relative volume, F_p the force exerted by the magnet, X_g the gram susceptibility, $d_{1 \text{ atm}}$ the density at atmospheric pressure, B a calibration constant, and K_0 the volume susceptibility of air. Relative densities found for the samples actually used in the susceptibility measurements are shown below.

	Pressure, atm				
	1	500	1000	2000	3000
Dimethylformamide	1	1.036 [1.031]	1.058 [1.054]	1.097 [1.092]	1.111 ...
Pyridine	1	1.025	1.032	1.058	1.080

The compressibility of dimethylformamide has recently been measured²⁸ up to 1900 atm, and these values, extrapolated to 2000 atm, are shown in brackets. In the context of the susceptibility measurements the differences are not significant. (Recent direct measurements in our laboratory at room temperature confirmed Brummer's values for distilled and dried (molecular sieves) DMF and gave the following values for distilled and dried (NaOH) pyridine: 1.025 (500 atm), 1.047 (1000 atm), 1.084 (2000 atm), 1.109 (3000 atm).)

Pure carbon tetrachloride freezes at about 1000 atm at room temperature, but solutions in carbon tetrachloride were compressed to beyond 2000 atm without freezing. The required density values for this range were obtained by extrapolation of Bridgman's data²⁶ for carbon tetrachloride at 90 and 50°.

Equilibrium Constant.—The difference in molar volume between two species of different magnetic properties in equilibrium is given by $\Delta V = -2.303RT d(\log K)/dP$, where the equilibrium constant K is given by

$$K = \frac{\mu_{\text{obsd}}^2 - \mu_{\text{low}}^2}{\mu_{\text{high}}^2 - \mu_{\text{obsd}}^2} \quad (1)$$

Plots of $\log K$ against pressure (see Figure 2) are mostly curved at low pressure but more linear at high pressure. The accuracy of the data does however not justify using limiting slopes at 1 atm, and the slopes of straight lines drawn through the high-pressure

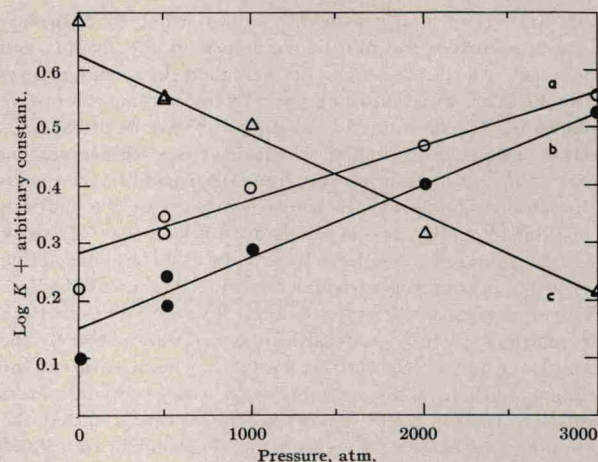


Figure 2.—Pressure dependence of $\log K$: (a) bis(*N*-isopropylsalicylaldimine)nickel(II) in chloroform; (b) bis(*N*-*n*-propylsalicylaldimine)nickel(II) in chloroform; (c) nickel(II) *N,N'*-di-*p*-anisidylaminotroponeimineate in chloroform.

points were used to obtain the values of ΔV given in Table II.

For an associative equilibrium, K applies to the concentrations of central atoms in high- or low-spin states. Thus the ΔV value estimated from K expresses the change in volume on association per mole of unassociated complex. The μ_{eff} values for pure high-spin species were obtained from literature values; for salicylaldimines, 3.30 BM was chosen for the solution moment in analogy to similar solid moments of paramagnetic salicylaldimines,^{9,12,13,29-31} and 3.20 BM was assumed for bispyridine adducts of salicylaldimine complexes.^{18,19,32} For aminotroponeimineate complexes, μ_{eff} was taken as 3.30 BM for the paramagnetic form.¹⁵ Planar low-spin nickel(II) is diamagnetic and the moment was taken as 0.

In Table II we present the magnetic susceptibilities and magnetic moment found at various pressures. The second value at 500 atm shown for each compound was measured after compression to 3000 atm and serves to indicate to what extent decomposition or precipitation, if any, occurred during the measurements. The concentration in per cent by weight and the solvent are given in parentheses.

Effect of Pressure on Solid Salicylaldimines. *N*-Methyl.—The methyl complex was compressed to 45,000 atm and returned to normal pressure, in the hope of forming the buff-colored polymer.²⁹ However, the complex remained green and diamagnetic, and presumably unchanged.

***N*-*n*-Octyl.**—A solid solution of the *n*-octyl complex in paraffin wax was formed by chilling a liquid (100°) solution. There was some increase in susceptibility of the solid with increasing pressure. Presumably some microcrystallites of the complex had formed, and some dimerization had occurred under pressure. In

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