

TABLE III
 COMPARISON OF PRESSURE EFFECTS ON MAGNETIC EQUILIBRIA

Reaction ^c	No. of new bonds	Vol. contraction	No. of Ni atoms made (p)	Contraction per Ni atom made (p)	Pressure effect on magnetism
(1) Tetrahedral monomer (p) → planar monomer (d)	...	V_1	-1	$-V_1$	Appreciable but independent of the other equilibria Greater for (2) than (3)—see previous column
(2) Planar monomer (d) + 2py → monomer·(py) ₂	2	$2V_2$	1	$2V_2$	
(3) 2 planar monomer (d) → dimer (p)	3 ^a	$3V_2^b$	1	$1.5V_2$	
(4) Planar monomer (d) + dimer (p) → trimer (p)	3 ^a	$3V_2^b$	1	$3V_2$	Less than (2) or (3); process not analogous to (2) or (3)
(5) 2 tetrahedral monomer (p) → dimer (p)	3 ^a	$V_1 + 3V_2$	0	0	Negligible
(6) 2 dimer (p) → trimer (p) + planar monomer (d)	0	0	-1	0	Negligible

^a Depending on the structure of the associated complex only two new bonds might be formed. ^b If only two new bonds are formed the contraction will be $2V_2$ instead of $3V_2$. ^c (p) = paramagnetic, (d) = diamagnetic.

complexes. In accord with the high-pressure susceptibility results, the degree of association and the magnitude of the pressure effect seem to be a little less in dichloromethane than in chloroform; moreover the pressure effect falls off somewhat at higher pressures. Observation of the 383-m μ peak of bis(salicylaldehyde)-nickel(II) in pyridine shows that the effect of increased pressure is the same as that of decreased temperature or that of increased pyridine concentration;³³ *i.e.*, the concentration of the bis-pyridine adduct is increased.

In nickel(II) N,N'-di-2-naphthylaminotroponimineate the 820-m μ peak intensity increases with increasing pressure. This peak has been attributed to an absorption by the planar form of the complexes¹⁵ which is thus seen to be favored by pressure. (See Figure 5.)

Discussion

The effect of pressure on the various equilibria with which we are concerned can be compared qualitatively as shown in Table III. The rather sweeping assumption made in this comparison is that the formation of a metal ligand bond causes the same contraction in volume (V_2) no matter what the ligand and is only little affected by the solvent.

The last column in Table III gives the expected relative pressure effects on the magnetism of the solution. This will depend not only on the volume change associated with the equilibrium but also on the relation between the equilibrium constant and the magnetic moment of the equilibrium species. In eq 1 K is defined in terms of diamagnetic and paramagnetic nickel atoms and it is applicable to the equilibria 1, 2, and 3 in Table III. It is not applicable without redefinition to (4), (5), or (6), which involve equilibria between two paramagnetic forms. Equilibrium 5 involves a very large volume change and the equilibrium constant must be strongly affected by pressure, but this does not affect the magnetism of the solution except through some secondary effects.

Aminotroponimineates.—Both the magnetic and spectroscopic results indicate that the planar (dia-

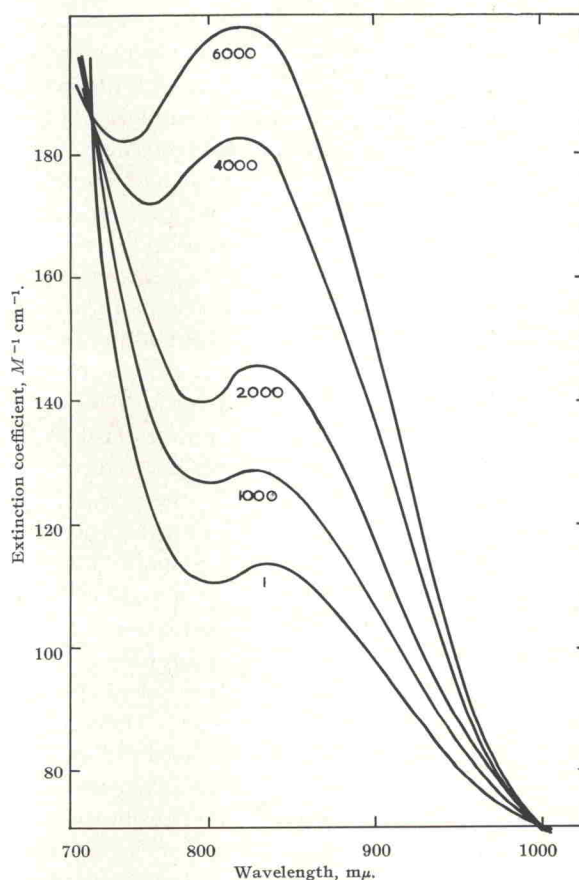


Figure 5.—Pressure dependence of spectrum of nickel(II) N,N'-di-2-naphthylaminotroponimineate in dichloromethane (1, 1000, 2000, 4000, and 6000 atm pressure).

magnetic) form of these complexes is favored by an increase in pressure. This is an indication that the partial molar volume of the planar form in solution is smaller than that of the tetrahedral form. The formation of the tetrahedral form from the planar complex involves the promotion of a d electron to a higher energy orbit. Such a promotion, involving spin uncoupling, has been shown to be accompanied by an increase in bond length in the case of Fe(III) dithiocarbamates¹ and it is reasonable to assume that the Ni-ligand distances are

(33) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 520 (1956).

similarly larger in the tetrahedral complex than in the planar. Solvation would also be expected to play a part in determining the partial molar volume of the complexes, and there is evidence from entropy data¹⁵ that the planar complex is more strongly solvated. Formation of the tetrahedral form will thus involve the release of some solvent which will contribute to the increase in volume, to an extent depending on the particular solvent. The equilibrium constants are smaller (*cf.* ref 15) and the ΔV values larger in CHCl_3 than in CH_2Cl_2 , indicating that the solvation of the planar form is greater in CHCl_3 .

In both solvents the difference in volume between the species decreases with increasing pressure, as shown by the decreasing slope of plots of $\log K$ against P , and this is considered to result from the decreasing effect of solvation at higher pressures. The lack of any tendency of aminotroponimineates to assume octahedral configuration (either by coordination with pyridine or by association) has been pointed out,¹⁵ and our measurements show that this persists even at high pressure.

Ni Salicylaldimines.—For these complexes both the magnetic and optical measurements at high pressure indicate that the monomer \rightleftharpoons associated equilibrium is shifted toward the side of the associated complex. A planar \rightleftharpoons tetrahedral equilibrium can exist side by side with the association equilibrium, but solution susceptibilities indicate that the concentration of the tetrahedral form is small in *n*-alkylsalicylaldimines. Our measurements on Ni(II) aminotroponimineates have shown that increase in pressure tends to decrease the concentration of such tetrahedral species still further. The pressure effect observed for Ni(II) *n*-alkylsalicylaldimines indicates an increase in the paramagnetic form, and we conclude that tetrahedral complexes can play only a minor role in these compounds.

The formation of a Ni(II) dimeric salicylaldimine complex involves the formation of two or three (depending on what one assumes the structure to be)^{8,9,29} new metal–ligand bonds and this would be expected to cause an appreciable decrease in volume. The promotion of an electron to form an octahedral bond will also make a positive contribution to the volume as in the case of the Ni(II) aminotroponimineates. The observed pressure effect will be the result of the sum of these contributions and it appears, from the large volume decrease which it indicates, that the bond formation is the predominant factor. As for the aminotroponimineates, solvation also plays a part, and chloroform solvates more strongly than dichloromethane. Moreover, the dimer is apparently more strongly solvated than the two constituent monomers. Such strong solvation of the dimer is not surprising in view of the structures proposed for it.^{8,9,29}

In pyridine solutions of Ni(II) salicylaldimine complexes strong association with the solvent leads to an equilibrium of the diamagnetic, planar complex with a paramagnetic, octahedral dipyridine adduct (see (2) in Table III). The formation of the adduct involves the formation of two metal–ligand bonds per Ni atom, and the pressure dependence of the equilibrium, as measured

by the magnetic susceptibility, should be appreciably greater than that for a monomer–dimer association in a noncoordinating solvent.

Association in noncoordinating solvents probably involves only dimers, but higher oligomers cannot be ruled out with certainty. The association of two monomeric molecules to form a dimer makes two Ni atoms paramagnetic, while association of a dimer with another monomer to form a trimer only makes one Ni atom paramagnetic. Both processes should involve the formation of the same number of new bonds and hence the same pressure dependence for the reaction. The formation of trimer thus gives a larger volume contraction per Ni atom made paramagnetic and hence a smaller pressure dependence as indicated by change in susceptibility.

The only case where trimerization could be very important is for very high dimer concentrations, where the moment is near the high-spin moment (μ_∞). Thus, as trimerization becomes increasingly prominent, it becomes less easy to detect, since it is represented by a change in the already small deviation from μ_∞ . The small volume change observed for the phenyl salicylaldimine complex may be due to trimerization, but it is possibly a result of the greater errors that arise when moments vary in the small range near μ_∞ .

The small pressure dependence of X_M for isopropylsalicylaldiminenickel(II) is due to the coexistence of two equilibria with opposing pressure dependences: associative and tetrahedral \rightleftharpoons planar^{12–14} ((2) and (3) in Table III). For such complexes, the contribution of the conformational equilibrium would become smaller and smaller as increasing pressure converts the tetrahedral molecules to monomeric planar or directly to associated forms. This last conversion is of course not observable magnetically, although it must result in a large volume contraction. ((5) in Table III.)

Existence of Planar Triplet Molecules.—Theoretical calculations indicate that planar triplet Ni(II) species might exist^{34,35} in complexes with a planar ligand field which is so weak that solvent interaction might decrease the singlet–triplet separation (Δ) sufficiently to make the triplet state thermally accessible. The situation would then be similar to the first type of equilibrium mentioned in the Introduction for which it has been shown^{1,2,7} that pressure favors the singlet form. The pressure dependence of the magnetic properties of the Ni(II) salicylaldimines are in the opposite direction to that expected for such a singlet \rightleftharpoons triplet equilibrium, when it is assumed that Δ is not highly pressure dependent. If solvent distortion is enhanced by pressure, Δ would decrease with rising pressure, but this could hardly be enough to lead to the reversal of the pressure dependence expected for constant Δ . We conclude that the planar singlet–planar triplet equilibrium is not present to any appreciable extent.

(34) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

(35) C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).