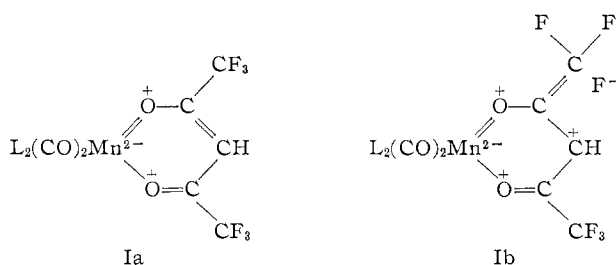


in the complex. Moreover, the signal occurs between τ 3.84 and 5.47, spanning a range of 1.63 ppm. In order to discuss this variation, it is convenient to treat the dicarbonyls and the tricarbonyls separately.

Among the complexes $\text{Mn}(\text{CO})_2\text{L}_2(\text{hfac})$ the resonance moves upfield in the order $\text{L} = \text{CO} \sim \text{P}(\text{OC}_6\text{H}_5)_3 < \text{P}(\text{OCH}_3)_3 < \text{P}(n\text{-C}_4\text{H}_9)_3 < \text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2 < \text{P}(\text{C}_6\text{H}_5)_2(\text{CH}_3) < \text{P}(\text{C}_6\text{H}_5)_3$. It thus appears that the better π -bonding ligands, *viz.*, CO and phosphites, give rise to signals at lower fields than the more basic and poorer π -bonding phosphines.²¹ Furthermore, triphenyl phosphite, which π bonds better than trimethyl phosphite in $\text{Mn}(\text{CO})_2\text{L}_2(\text{hfac})$, causes a larger downfield displacement of the proton resonance.

The positions of these signals suggest that the deshielding of the hexafluoroacetylacetonate hydrogen might result from a drift of π electrons from the ring toward the manganese. This drift would involve acceptance of π electrons from the ring oxygens by the metal²² and might be expected to increase with an increase in π -bonding capacity of the phosphite (or other neutral ligand). Two of the important contributing resonance structures are depicted in Ia, b.



(21) The relative π -bonding abilities of the phosphines and phosphites are reflected in the positions of the metal carbonyl stretching bands for these complexes, listed in Table II.

(22) That some ligands can function as π donors in metal carbonyl complexes has been already postulated.⁹

Of interest, of course, in this connection would be to examine the Mn-O stretching frequencies. However, the complexity of the infrared spectra of the derivatives has precluded an unambiguous assignment of absorption bands in this region.

Surprisingly, the chemical shifts of the ring proton in the phosphine complexes follow the order which is exactly the reverse of that expected from π -bonding abilities of PR_3 .²¹ Since displacement of the signal to higher fields increases with progressive substitution of alkyl moieties by the phenyl groups on the phosphorus, it is reasonable to postulate that long-range shielding of the proton in question by the aromatic rings²³ influences primarily the prevailing trend. In accordance with this, when the phenyl groups are placed farther away from the hexafluoroacetylacetonate ring, as is the case in $\text{Mn}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2(\text{hfac})$, the shielding effect no longer appears to be important.

The resonance of the chelate proton in $\text{Mn}(\text{CO})_2\text{L}(\text{hfac})$ moves to higher fields as L changes in the order $4\text{-CH}_3\text{C}_5\text{H}_4\text{N} < \text{C}_5\text{H}_5\text{N} < \text{As}(\text{C}_6\text{H}_5)_3 < \text{P}(\text{C}_6\text{H}_{11})_3$. The chemical shifts in the pyridine and arsine complexes are not unexpected; however, the position of the signal in the tricyclohexylphosphine complex comes as a surprise. This unusually large upfield shift is not understood at present, but it may result from distortion of the ring caused by steric requirements of the bulky phosphine.

Acknowledgment.—Financial support of this investigation by the National Science Foundation is gratefully acknowledged. We also wish to thank P. J. Pollock for assistance in obtaining the nmr spectra.

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Pressure in Coordination Chemistry. I. Nickel(II) Salicylaldimines and Aminotroponeiminateates

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The anomalous magnetic and spectroscopic behavior of a number of N-substituted Ni(II) salicylaldimine and aminotroponeimine complexes in solution has been examined over a range of pressures. The susceptibility of the aminotroponeimineates is found to decrease with pressure, indicating that the planar, diamagnetic form of the complex has a smaller volume in solution than the tetrahedral form. The susceptibility of the salicylaldimine complexes, on the other hand, is found to increase with pressure indicating that the associated complexes are formed with a decrease in volume. For *n*-alkyl but not *sec*-alkyl salicylaldimines the contribution of a planar-tetrahedral equilibrium to the pressure dependence is negligible.

Introduction

In recent years many coordination compounds have been shown to deviate, in the solid state and in solu-

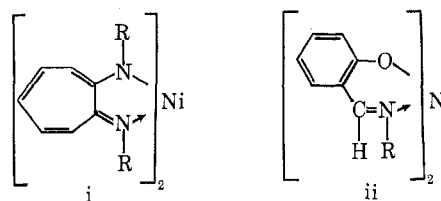
tion, from the Curie and Curie-Weiss laws for magnetic susceptibility. The mechanisms giving rise to these deviations may be divided into four main types.

One type occurs when the electron-pairing energy of a complex lies between the ligand field strengths of possible high-spin and low-spin forms and results in a high-spin \rightleftharpoons low-spin equilibrium which has been observed in a number of different systems.¹⁻⁴ A second type arises from the antiferromagnetic interaction between the unpaired electrons of two or more metal atoms in a complex.^{5,6} The last two mechanisms depend on the changes in ligand field energy when the conformation about the central atom changes, either by association of monomeric complex molecules or by reorientation of the ligands in a planar \rightleftharpoons tetrahedral conformational equilibrium. In the present paper we shall be concerned mainly with the effect of pressure on these last two mechanisms. Similar studies will be reported on the crossover and antiferromagnetic equilibria.^{2,7}

In several series of complexes⁸⁻¹¹ deviations from normal diamagnetic or paramagnetic behavior have been found to be the result of the coordination of the metal atom of one complex with donor atoms of other molecules in such a way that the metal atom achieves pseudo-octahedral coordination. Such association occurs, for example, in solutions of *N*-alkyl-substituted salicylaldehyde^{8,9} and β -diketone complexes of Ni(II). In some related compounds, such as the *N*-*sec*-alkylsalicylaldehydes,¹²⁻¹⁴ a tetrahedral (paramagnetic) \rightleftharpoons planar (diamagnetic) conformational equilibrium plays a major part in addition to the associative equilibrium. Where these two equilibria coexist, their pressure dependence and temperature dependence are opposite; a rise in temperature favors the planar, monomeric species compared with the associated species and also favors the tetrahedral species over the planar. (This is not necessarily true in all cases; *e.g.*, in the *t*-butyl complex the planar form is the higher energy form.¹²⁻¹⁴) Increasing pressure has, broadly speaking, the same effect as decreasing temperature. As a result their relative contributions can sometimes be sorted out, particularly with the assistance of other results, such as nmr contact shifts.

It cannot be predicted *a priori* whether the associative or the conformational equilibrium will be more important under various conditions of temperature and pressure, since the effect of pressure depends entirely on the relative volumes of the species which coexist in solution. However the contributions of the

two equilibria can be separated by analogy arguments if one examines related systems for which it is known that only one of the equilibria plays a part.



Some Ni(II) aminotroponimineates (i) form solutions with anomalous magnetic properties which have been shown¹⁵ to result entirely from planar \rightleftharpoons tetrahedral equilibria. Pressure measurements on such solutions have shown (Figure 1) a decrease in susceptibility with increasing pressure; this indicates that the equilibrium is shifted toward the planar, diamagnetic form. Solutions of nickel(II) *N*-*n*-alkylsalicylaldehyde (ii), on the other hand, show paramagnetism at atmospheric pressure which increases with increasing pressure. If the initial paramagnetism is due in part to the presence of some tetrahedral molecules, their concentration, by analogy with the aminotroponimineates, will be reduced by an increase in pressure. Thus the *n*-alkyl salicylaldehydes form a group in which only the associative equilibrium has any significant effect on the magnetic properties. Because of the important bearing of the measurements on the aminotroponimineates on the interpretation of the studies made on salicylaldehydes, the results for the two groups are presented together.

Pyridine Adducts.—Solutions of many planar Ni(II) complexes can become paramagnetic by forming adducts with strongly coordinating solvents such as pyridine. Probably all four-coordinated salicylaldehydes combine with pyridine to some extent; most form stable bispyridine adducts^{16,17} but some, such as the parent bis(salicylaldehyde)nickel(II),¹⁷ bis(*o*-phenylenediiminosalicylaldehyde)nickel(II), and bis(3,4-diminotoluenealdehyde)nickel(II), are not fully paramagnetic even in pyridine solution. This results from an equilibrium between the planar complexes and their octahedral pyridine adducts. The effects of temperature and pressure on this equilibrium are qualitatively the same as those on the associative equilibrium discussed above.

Experimental Section

A Gouy method was used for the magnetic measurements (*cf.* ref 1). A beryllium-copper (Berylco 25) sample tube, with a moving piston carrying a Bridgman seal, was used to contain the compressed samples in solution or suspension. Water,¹⁸ benzene,¹⁸ nickel chloride solution,¹⁸ and cesium tetrachlorocobaltate solution¹⁹ were used for the magnetic calibrations. Pressures inside the tube were calibrated as in ref 1 by observing the known phase transitions of carbon tetrachloride, benzene, and bromo-

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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 Poultier-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 isosbestic point. The isosbestic 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(salicylaldimine)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 salicylaldimine 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
n-Propyl	1.425	161
Isopropyl	1.350	205
n-Butyl	1.350	142
Isobutyl	1.235	154-155
n-Pentyl	1.250	148
n-Hexyl	1.220	122
n-Heptyl	1.20 \pm 0.01	109
n-Octyl	1.170	105
n-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
o-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

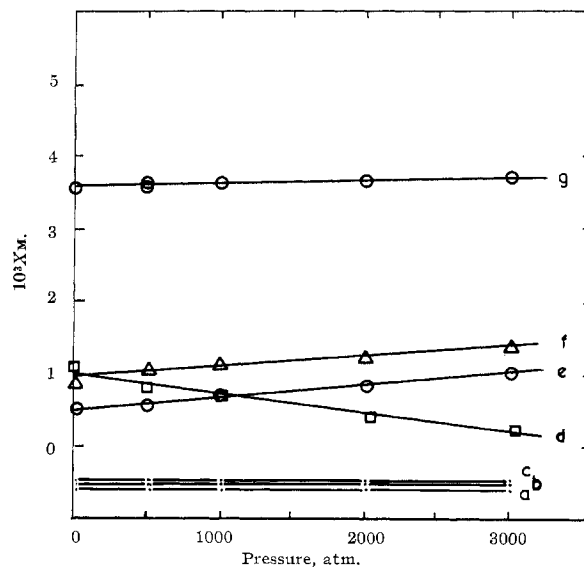


Figure 1.—Pressure dependence of molar susceptibility: (a) ethylene glycol; (b) dichloromethane; (c) chloroform; (d) nickel(II) N,N'-di-*p*-anisidylaminotroponimineate; (e) bis(N-*n*-propylsalicylaldimine)nickel(II); (f) bis(N-*n*-heptylsalicylaldimine)nickel(II); (g) bis(N-phenylsalicylaldimine)nickel(II).

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

(26) P. W. Bridgman, "Physics of High Pressure," G. Bell and Sons, London, 1949 [chloroform, dichloromethane: *Proc. Am. Acad. Arts Sci.*, **74**, 411 (1942); carbon tetrachloride: *ibid.*, **66**, 212 (1931); carbon disulfide: *ibid.*, **49**, 1 (1913); **74**, 415 (1942)].

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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

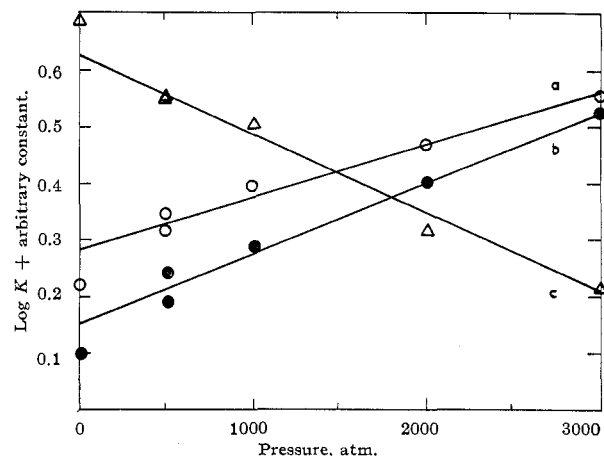


Figure 2.—Pressure dependence of $\log K$: (a) bis(*N*-isopropylsalicylaldimine)nickel(II) in chloroform; (b) bis(*N*-*n*-propylsalicylaldimine)nickel(II) in chloroform; (c) nickel(II) *N,N'*-di-*p*-anisidylaminotroponimineate in chloroform.

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 aminotroponimineate 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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TABLE II: MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS
 Nickel(II) N-Substituted Salicylaldimines.^a The First Line for Each Complex Gives Values $10^{-9}X_M$; the Second Line Gives μ in BM

N substituent (solvent)	Pressure, atm						$-\Delta V$, cc/mole ^b
	1	500	1000	2000	3000	500 (after 3000 atm)	
Methyl ^a (4.1% CHCl ₃)	1717 2.12	1318 1.88	1079 1.73	1413 1.94	1468 1.98	474 1.24	~10
Methyl ^b (1.0% CH ₂ Cl ₂)	291 1.06		371 1.09	1204 1.82	1604 2.07		~8
Ethyl (4.6% CHCl ₃)	229 1.01	437 1.24	699 1.47	1053 1.74	1380 1.95	551 1.34	10
Ethyl (3.2% CH ₂ Cl ₂)	-97 0.57	-1 0.67	51 0.77	341 1.14	304 1.10	96 0.50	10
<i>n</i> -Propyl (5.5% CHCl ₃)	414 1.24	544 1.36	700 1.49	894 1.64	1153 1.82	627 1.43	7.5
Isopropyl (3.0% CHCl ₃)	2073 2.34	2333 2.48	2533 2.58	2702 2.66	2891 2.75	2399 2.52	4.5
<i>n</i> -Butyl (4.7% CHCl ₃)	504 1.33	573 1.39	712 1.51	846 1.61	1036 1.75	529 1.44	6
<i>n</i> -Pentyl (4.7% CHCl ₃)	571 1.41	640 1.47	726 1.54	999 1.74	1148 1.84	615 1.45	6
<i>n</i> -Pentyl (5.2% CH ₂ Cl ₂)	428 1.29	553 1.40	619 1.46	673 1.47	703 1.52	568 1.41	3
<i>n</i> -Hexyl (6.9% CH ₂ Cl ₂)	404 1.29	522 1.39	551 1.42	625 1.48	727 1.56	554 1.42	3.5
<i>n</i> -Hexyl ^c (4.9% CCl ₄)	626 1.48	696 1.54	734 1.56	976 1.74	(Froze) ...	652 1.50	~7
<i>n</i> -Heptyl ^d (8.7% CH ₂ Cl ₂)	874 1.69	1053 1.81	1132 1.86	1265 1.95	1404 1.0	1025 1.79	3.5
<i>n</i> -Octyl (4.8% CHCl ₃)	-195 0.59	16 0.92	78 1.00	458 1.38	785 1.64	59 0.98	10
<i>n</i> -Octyl (7.3% CS ₂)	-225 0.53	-135 0.70	-79 0.79	-96 0.77	Seal collapsed		~5
<i>n</i> -Dodecyl (10.8% CHCl ₃)	196 1.23	592 1.57	637 1.61	990 1.85	1284 2.03	592 1.57	8
<i>n</i> -Dodecyl (7.5% CS ₂)	-196 0.76	-125 0.86	-99 0.89	-57 0.96	36 1.07	-194 0.77	
Phenyl (8.3% CHCl ₃)	3583 3.01	3645 3.04	3623 3.03	3675 3.05	3702 3.07	3562 3.00	2
H (0.8% py)	1353 2.46	1437 2.27	2152 2.26	2156 1.85	2425 1.80		
3,4-Diiminotolyl (1.3% py)			160 0.94	445 1.25	964 1.48		~15

Nickel N,N'-Disubstituted Aminotroponimineates

N,N' substituents (solvent)	Pressure, atm						$-\Delta V$, cc/mole
	1	500	1000	2000	3000	500	
Methyl (3.7% CHCl ₃ , 4.1% CH ₂ Cl ₂)	Essentially diamagnetic						
Ethyl ^e (2.8% CHCl ₃)	3757 3.14	3556 3.06	3482 3.03	3184 2.91	3055 2.85	3570 3.07	7.5
<i>n</i> -Propyl ^e (2.6% CHCl ₃)	4101 3.26	4041 3.24	4042 3.23	3898 3.18	3898 3.16	4047 3.24	8
β -Naphthyl (3.8% CHCl ₃)	889 1.78	659 1.63	523 1.53	307 1.35	95 1.15	766 1.70	8.5
β -Naphthyl ^f (3.9% CH ₂ Cl ₂)	1033 1.89	528 1.54	482 1.51	17 1.08	-48 1.01	535 1.55	5
<i>p</i> -Anisidyl (4.9% CHCl ₃)	1094 1.89	802 1.70	700 1.63	388 1.36	231 1.24	784 1.69	7.5
<i>p</i> -Anisidyl ^f (4.1% CH ₂ Cl ₂)	1239 1.97	715 1.63	687 1.61	655 1.58	416 1.40	729 1.64	~4

^a Drop in susceptibility over the first three measurements is due to precipitation of complex from the supersaturated solution. Thus ΔV can be found only approximately. ^b Solubility too low for accurate results. ^c The CCl₄ solution was at first stable at 2000 atm, but later the magnetism showed a rapid time-dependent decrease at 2000 atm, indicating freezing of the solution or crystallization of the complex, or both. The magnetism decreased further at 3000 atm. The process quickly reversed on decreasing the pressure. A CHCl₃ solution of the *n*-hexyl complex of unknown concentration showed a pressure dependence similar to that of the CCl₄ solution. ^d A CHCl₃ solution of the *n*-heptyl complex gave a linear increase of susceptibility with pressure. ^e The moment is quite close to pure high spin for these complexes at all pressures. Thus accuracy must be greatly reduced. ^f Pressure dependence nonlinear. The ΔV value given for the last entry is the high-pressure limit. ^g Measurements on bis(salicylaldehyde-*o*-phenylenediimine)nickel(II) and bis(salicylaldehydeethylenediimine)nickel(II) also suggest a pressure-dependent increase of susceptibility, but this cannot be said with certainty since the solubilities are too low. The latter complex appears to form a pyridine adduct. ^h 1 cc/mole = 1.66 A³/molecule. The densities of the solid complexes (Table I) may be used to relate the ΔV values to the molar volumes of the compounds. (Such a comparison involves the assumption that volumes are additive in solution.)

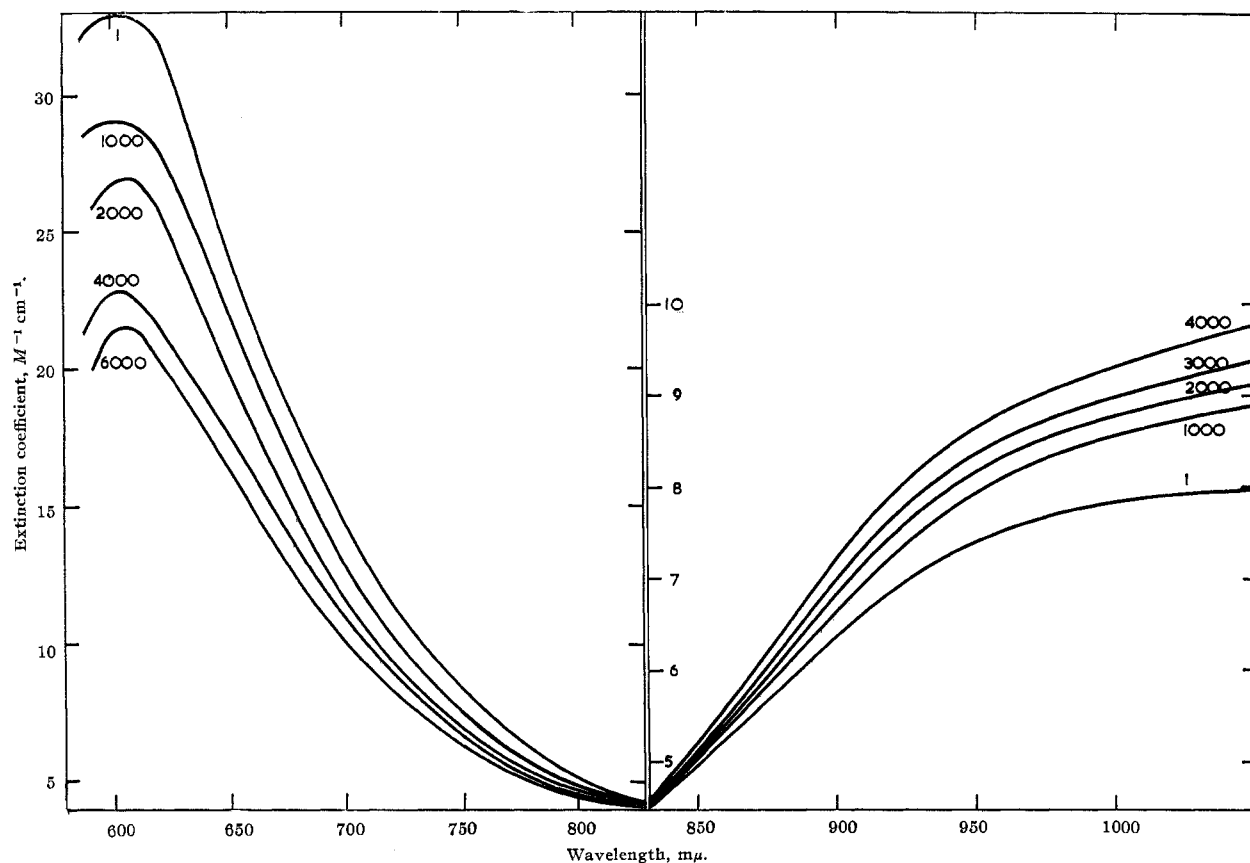


Figure 3.—Pressure dependence of spectrum of bis(*N*-phenylsalicylaldimine)nickel(II) in dichloromethane (1, 1000, 2000, 4000, and 6000 atm pressure).

this case no estimate could be made of the volume change, because paraffin wax was found to become hard and crystalline under pressure, and thus a poor pressure-transmitting medium.

***N-n*-Dodecyl.**—A viscous suspension of the *n*-dodecyl complex (32.0%) in water showed a small but measurable increase in susceptibility with pressure. This corresponds to a volume change of less than 1 cc/mole.

It is concluded that the ability of the salicylaldimines to associate is much smaller in the solid than in solution. Further, permanent polymerization is not readily induced; the effect of pressure is reversed when the pressure is reversed.

Spectra.—Complexes exhibiting associative or conformational equilibria do not obey Beer's law. The pressure dependences of the spectra of some of these complexes are shown in Figures 3 and 4. These entirely confirm the high-pressure susceptibility measurements.

For bis(*N*-phenylsalicylaldimine)nickel(II), the very broad peak between 1000 and 1200 $m\mu$, attributed to the associated species⁹ of this complex, is seen to increase in intensity with pressure (Figure 3). Thus pressure enhances association. This is confirmed by the decrease in the intensity of the 610- $m\mu$ peak, attributed to the monomeric species.⁹

The broad peak between 1000 and 1200 $m\mu$ in bis(*N-n*-pentylsalicylaldimine)nickel(II) similarly increases with pressure (Figure 4). We attribute this peak to the associated species, in analogy with the similar assignments for the *N*-aryl-⁹ and the *N*-methylsalicylaldimine⁸

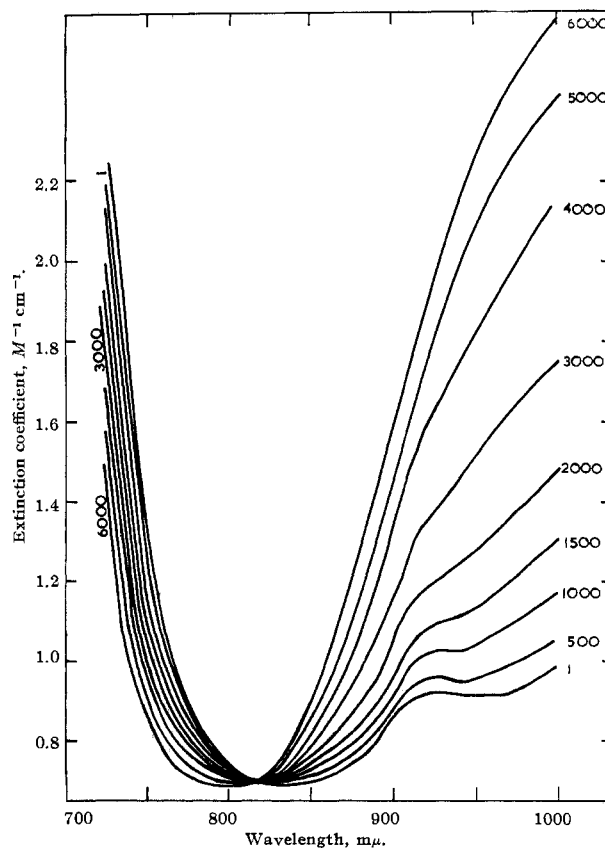


Figure 4.—Pressure dependence of spectrum of bis(*N-n*-pentylsalicylaldimine)nickel(II) in chloroform (1, 500, 1000, 1500, 2000, 3000, 4000, 5000, and 6000 atm pressure).

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 of the other equilibria
(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(salicylaldimine)-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-naphthylaminotroponimine-ate 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-

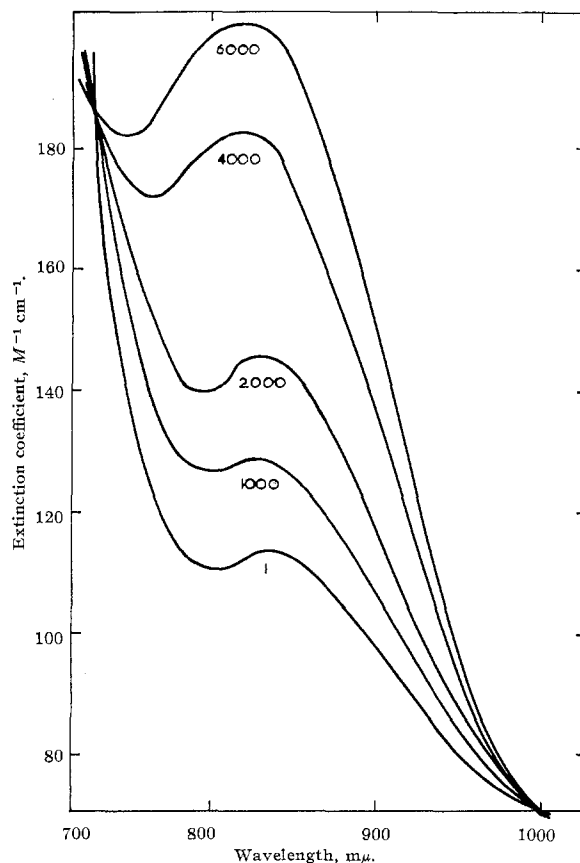


Figure 5.—Pressure dependence of spectrum of nickel(II) N,N'-di-2-naphthylaminotroponimine-ate in dichloromethane (1, 1000, 2000, 4000, and 6000 atm pressure).

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

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 aminotroponeimineates 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) aminotroponeimineates 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) aminotroponeimineates. 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 aminotroponeimineates, 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.

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5T_2 - 1A_1 Equilibria in Some Iron(II)-Bis(1,10-phenanthroline) Complexes¹

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Magnetic susceptibilities of the compounds $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (I) and $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ (II) have been measured as a function of temperature between 440 and 77°K. The magnetic moments, which are ~ 5.20 BM at 440°K for both I and II, exhibit a pronounced decrease at a critical temperature T_c of 174°K for I and of 232°K for II and approach 0.65 BM for I and 0.84 BM for II at 77.4°K. The results agree qualitatively with predictions made on the basis of the Van Vleck equation for a 1A_1 ground state slightly separated from a higher lying 5T_2 state. Mössbauer effect investigations show at 293°K large quadrupole splittings ΔE_Q of 2.67 mm/sec for I and 2.52 mm/sec for II, as expected for a 5T_2 state and, at 77°K, small values of 0.34 mm/sec for I and 0.18 mm/sec for II, indicating a 1A_1 state. Correspondingly, the isomer shifts δ are about 1.00 mm/sec at 293°K and 0.36 mm/sec at 77°K for both I and II. It is concluded that the two compounds exist above T_c in a 5T_2 state and below T_c in a 1A_1 state. This inference is supported by the temperature dependence of the electronic and vibrational infrared spectra. The values of the spectral parameters $\Delta = 11,900 \text{ cm}^{-1}$ and $B \sim 640 \text{ cm}^{-1}$ for the 5T_2 state as well as $\Delta \sim 16,300 \text{ cm}^{-1}$ and $B \sim 580 \text{ cm}^{-1}$ for the 1A_1 state of both I and II were estimated from the d-d transitions. The thermal equilibrium between the 5T_2 and 1A_1 ground states is associated with significant changes in the molecular dimensions.

Introduction

Depending upon the strength of the ligand field, octahedral transition metal complexes with configurations d^4 , d^5 , d^6 , and d^7 exist in two different electronic ground states, referred to as high-spin and low-spin configurations.³ According to ligand field theory, the transition between these states should occur discontinuously at a certain value of the field strength Δ , often called the mean spin-pairing energy π . This situation may be illustrated best by the crossing over of ground-state terms in the Tanabe-Sugano diagrams.⁴

If, at a field strength Δ close to π , the separation of the two states of different multiplicity attains values within the thermally accessible range, equilibria between these states are expected to occur. Although considerable effort has been spent in seeking new compounds displaying this sort of behavior, few examples have been established definitely. These include compounds of the configurations d^5 and d^7 in octahedral symmetry and compounds of the configurations d^5 and d^8 in lower symmetry.⁵

The series of iron(II)-bis(1,10-phenanthroline) complexes $[\text{Fe}(\text{phen})_2\text{X}_2]$ seems to be a particularly suitable place to look for spin-state equilibria within compounds of configuration d^6 . This series includes both high-spin and low-spin compounds, the multiplicity of the ground state being dependent on the position of the ligand X in the spectrochemical series. If X = Cl, Br, I, N₃, OCN, HCOO, CH₃COO, high-spin compounds are formed.^{6,7} At room temperature, they show magnetic moments of 5.0–5.3 BM, *i.e.*, slightly higher moment values than predicted from the spin-only formula.⁸ If X = CN, CNO, NO₂, diamagnetic low-spin compounds are obtained.^{9–11}

For $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$, Baker and Bobonich¹² reported the observation of an unusual change of the magnetic moment with temperature. In this paper, we are presenting results which clearly demonstrate that the observed magnetic behavior is caused by the presence of spin-state equilibria between 5T_2 and 1A_1 ground states.¹³ This investigation has

(1) This paper has been presented at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, 1966.

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(3) This statement holds exactly for perfect octahedral symmetry only, though it is valid for most six-coordinated, quasi-octahedral complexes as well. Additional high-spin and low-spin configurations may occur on application of lower symmetries (*viz.*, d^8 nickel(II)-bis(salicylaldimine) complexes and others).

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