TABLE II: MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS

Nickel(II) N-Substituted Salicylaldimines.[g] The First Line for Each Complex Gives Values $10^{-6}X_M$; the Second Line Gives μ in BM

N substituent (solvent)	Pressure, atm: 1	500	1000	2000	3000	500 (after 3000 atm)	$-\Delta V$, cc/mole[h]
Methyl[a]	1717	1318	1079	1413	1468	474	~10
(4.1% $CHCl_3$)	2.12	1.88	1.73	1.94	1.98	1.24	
Methyl[b]	291		371	1204	1604		~8
(1.0% CH_2Cl_2)	1.06		1.09	1.82	2.07		
Ethyl	229	437	699	1053	1380	551	10
(4.6% $CHCl_3$)	1.01	1.24	1.47	1.74	1.95	1.34	
Ethyl	−97	−1	51	341	304	96	10
(3.2% CH_2Cl_2)	0.57	0.67	0.77	1.14	1.10	0.50	
n-Propyl	414	544	700	894	1153	627	7.5
(5.5% $CHCl_3$)	1.24	1.36	1.49	1.64	1.82	1.43	
Isopropyl	2073	2333	2533	2702	2891	2399	4.5
(3.0% $CHCl_3$)	2.34	2.48	2.58	2.66	2.75	2.52	
n-Butyl	504	573	712	846	1036	529	6
(4.7% $CHCl_3$)	1.33	1.39	1.51	1.61	1.75	1.44	
n-Pentyl	571	640	726	999	1148	615	6
(4.7% $CHCl_3$)	1.41	1.47	1.54	1.74	1.84	1.45	
n-Pentyl	428	553	619	673	703	568	3
(5.2% CH_2Cl_2)	1.29	1.40	1.46	1.47	1.52	1.41	
n-Hexyl	404	522	551	625	727	554	3.5
(6.9% CH_2Cl_2)	1.29	1.39	1.42	1.48	1.56	1.42	
n-Hexyl[c]	626	696	734	976	(Froze)	652	~7
(4.9% CCl_4)	1.48	1.54	1.56	1.74	...	1.50	
n-Heptyl[d]	874	1053	1132	1265	1404	1025	3.5
(8.7% CH_2Cl_2)	1.69	1.81	1.86	1.95	1.0	1.79	
n-Octyl	−195	16	78	458	785	59	10
(4.8% $CHCl_3$)	0.59	0.92	1.00	1.38	1.64	0.98	
n-Octyl	−225	−135	−79	−96	Seal		~5
(7.3% CS_2)	0.53	0.70	0.79	0.77	collapsed		
n-Dodecyl	196	592	637	990	1284	592	8
(10.8% $CHCl_3$)	1.23	1.57	1.61	1.85	2.03	1.57	
n-Dodecyl	−196	−125	−99	−57	36	−194	
(7.5% CS_2)	0.76	0.86	0.89	0.96	1.07	0.77	
Phenyl	3583	3645	3623	3675	3702	3562	2
(8.3% $CHCl_3$)	3.01	3.04	3.03	3.05	3.07	3.00	
H	1353	1437	2152	2156	2425		
(0.8% py)	2.46	2.27	2.26	1.85	1.80		
3,4-Diiminotolyl			160	445	964		~15
(1.3% py)			0.94	1.25	1.48		

Nickel N,N′-Disubstituted Aminotroponeimineates

N,N′ substituents (solvent)	Pressure, atm: 1	500	1000	2000	3000	500	$-\Delta V$, cc/mole
Methyl	Essentially diamagnetic						
(3.7% $CHCl_2$, 4.1% CH_2Cl_2)							
Ethyl[e]	3757	3556	3482	3184	3055	3570	7.5
(2.8% $CHCl_3$)	3.14	3.06	3.03	2.91	2.85	3.07	
n-Propyl[e]	4101	4041	4042	3898	3898	4047	8
(2.6% $CHCl_3$)	3.26	3.24	3.23	3.18	3.16	3.24	
β-Naphthyl	889	659	523	307	95	766	8.5
(3.8% $CHCl_3$)	1.78	1.63	1.53	1.35	1.15	1.70	
β-Naphthyl[f]	1033	528	482	17	−48	535	5
(3.9% CH_2Cl_2)	1.89	1.54	1.51	1.08	1.01	1.55	
p-Anisidyl	1094	802	700	388	231	784	7.5
(4.9% $CHCl_3$)	1.89	1.70	1.63	1.36	1.24	1.69	
p-Anisidyl[f]	1239	715	687	655	416	729	
(4.1% CH_2Cl_2)	1.97	1.63	1.61	1.58	1.40	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 CCl_4 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 $CHCl_3$ solution of the *n*-hexyl complex of unknown concentration showed a pressure dependence similar to that of the CCl_4 solution. [d] A $CHCl_3$ 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 A^3/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.)

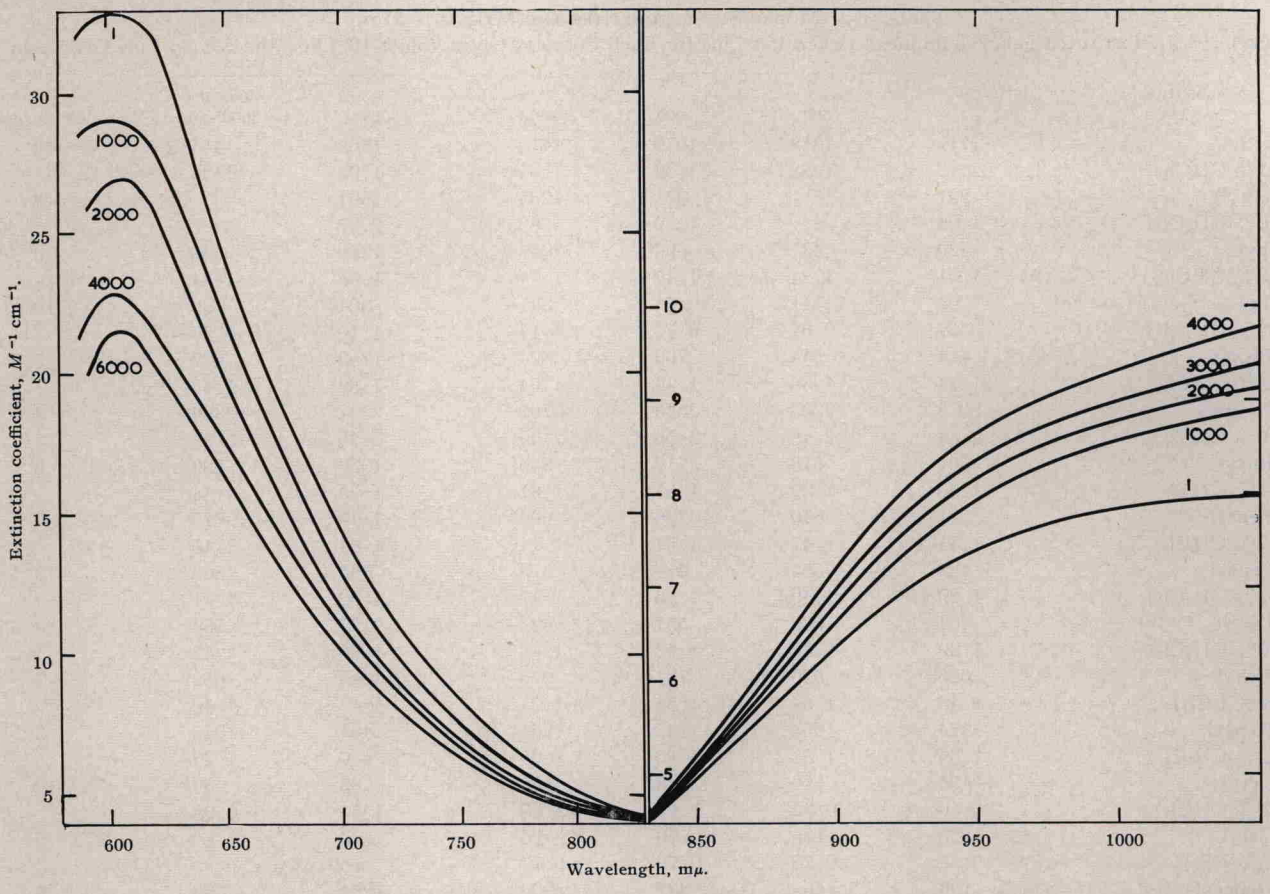

Figure 3.—Pressure dependence of spectrum of bis(N-phenylsalicylaldimine)nickel(II) in dichloromethane (1, 1000, 2000, 4000, and 6000 atm pressure).

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 mμ, attributed to the associated species[9] 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-mμ peak, attributed to the monomeric species.[9]

The broad peak between 1000 and 1200 mμ 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-methylsalicylaldimine[8]

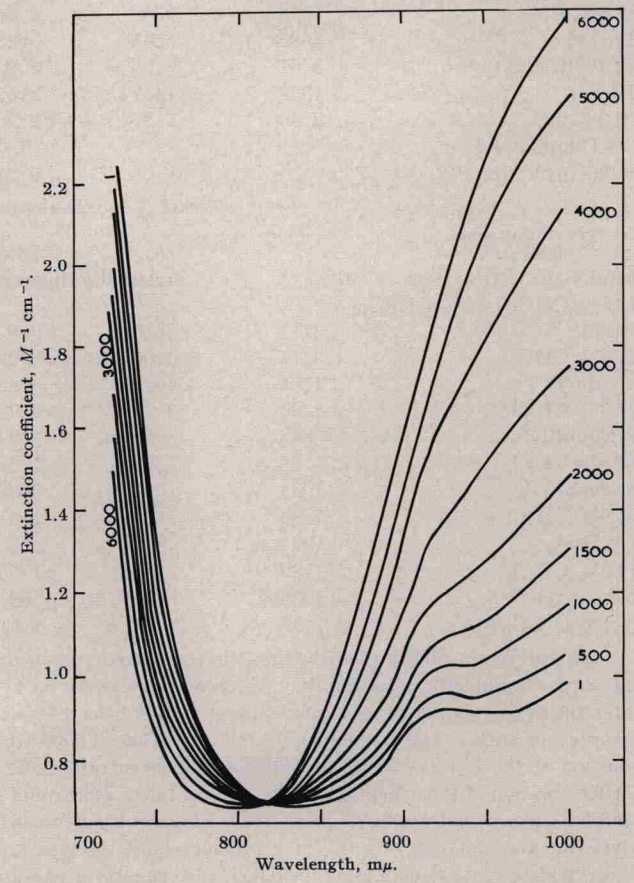

Figure 4.—Pressure dependence of spectrum of bis(N-*n*-pentylsalicylaldimine)nickel(II) in chloroform (1, 500, 1000, 1500, 2000, 3000, 4000, 5000, and 6000 atm pressure).