

TABLE II: MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS  
 Nickel(II) N-Substituted Salicylaldimines.<sup>a</sup> The First Line for Each Complex Gives Values  $10^{-6}X_M$ ; the Second Line Gives  $\mu$  in BM

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

## Nickel N,N'-Disubstituted Aminotroponeimineates

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

<sup>a</sup> Drop in susceptibility over the first three measurements is due to precipitation of complex from the supersaturated solution. Thus  $\Delta V$  can be found only approximately. <sup>b</sup> Solubility too low for accurate results. <sup>c</sup> The CCl<sub>4</sub> 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<sub>3</sub> solution of the *n*-hexyl complex of unknown concentration showed a pressure dependence similar to that of the CCl<sub>4</sub> solution. <sup>d</sup> A CHCl<sub>3</sub> solution of the *n*-heptyl complex gave a linear increase of susceptibility with pressure. <sup>e</sup> The moment is quite close to pure high spin for these complexes at all pressures. Thus accuracy must be greatly reduced. <sup>f</sup> Pressure dependence nonlinear. The  $\Delta V$  value given for the last entry is the high-pressure limit. <sup>g</sup> 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. <sup>h</sup> 1 cc/mole = 1.66 Å<sup>3</sup>/molecule. The densities of the solid complexes (Table I) may be used to relate the  $\Delta V$  values to the molar volumes of the compounds. (Such a comparison involves the assumption that volumes are additive in solution.)

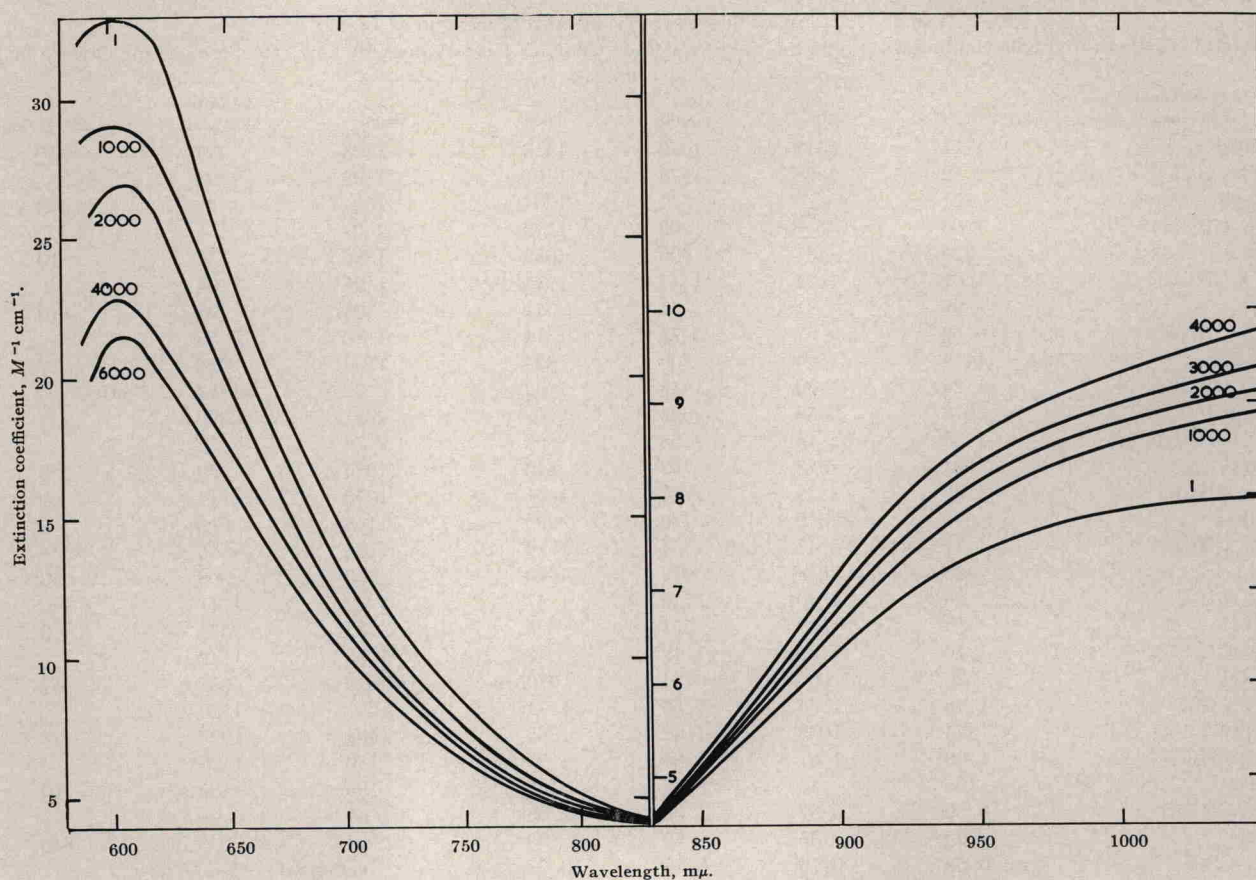


Figure 3.—Pressure dependence of spectrum of bis(*N*-phenylsalicylaldimine)nickel(II) in dichloromethane (1, 1000, 2000, 4000, and 6000 atm pressure).

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 species<sup>9</sup> 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.<sup>9</sup>

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<sup>9</sup> and the *N*-methylsalicylaldimine<sup>8</sup>

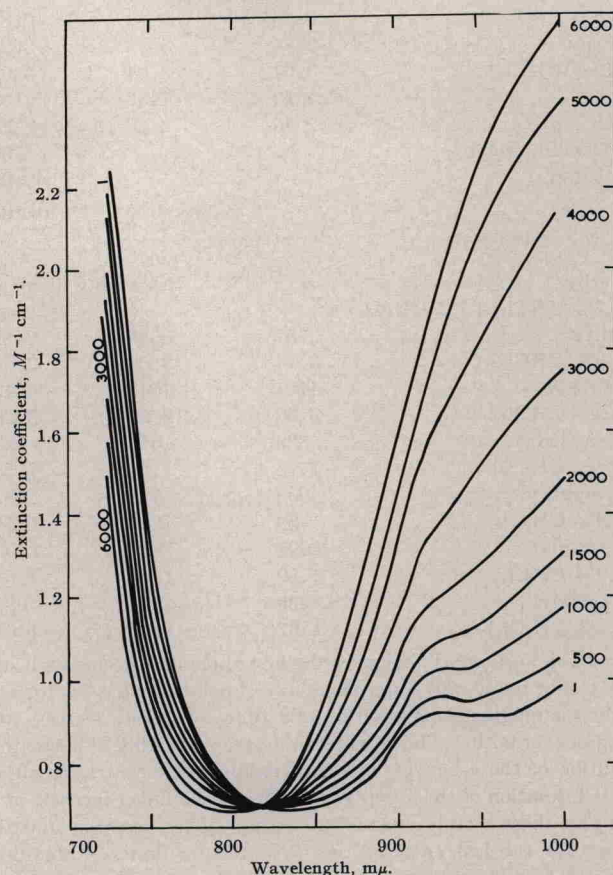


Figure 4.—Pressure dependence of spectrum of bis(*N-n*-pentylsalicylaldimine)nickel(II) in chloroform (1, 500, 1000, 1500, 2000, 3000, 4000, 5000, and 6000 atm pressure).