

nickel(II) complexes of the unsubstituted lactams suggest a donor order based on ring size of 5- < 6- ~ 7-membered. In contrast, in the chromium(III) complexes of the same lactams, no variation of donor strength with ring size is found. A monotonic decrease in donor strength with increasing ring size is indicated by the  $Dq$  values for the N-methyl lactam complexes of nickel(II). Here, however, steric factors may be of considerable importance in determining the order.

The phenol frequency shifts for the methyl lactams give a donor order of 5- < 6- ~ 7-membered ring. This is the same order given by the  $Dq$  values for the unsubstituted lactam complexes of nickel(II).

The  $\Delta H$  values for 1:1 complex formation between the methyl lactams and phenol, measured by ultraviolet spectrophotometry, give still a different order.<sup>9</sup> Finally, the  $pK_a$  values for the unsubstituted lactams indicate an order of basicity of 5- < 7- < 6-membered ring, which is similar to that shown by the  $Dq$  values for the nickel(II) complexes.<sup>12</sup>

Studies on the effect of ring size on the basicity of other cyclic carbonyl compounds such as saturated cyclic ketones<sup>13,14</sup> and lactones<sup>15</sup> indicated an increasing basicity with increasing ring size. The generally observed decreased basicity of the smaller (4- and 5-

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membered) ring compounds relative to the larger ones has been rationalized.<sup>12,15</sup> In general, it is found that the carbonyl stretching vibration occurs at higher frequencies for smaller ring compounds than for the larger ones. For example, the carbonyl bands for cyclobutanone, cyclopentanone, cyclohexanone, and cycloheptanone are at 1775, 1751, 1718, and 1706  $\text{cm}^{-1}$ , respectively.<sup>16</sup> The lactams show a similar decrease in the carbonyl stretching frequencies in going from the 4-membered to the 6-membered ring.<sup>15</sup> In the lactam case, the carbonyl stretching frequencies for BuL, VaL, and CaL are 1691, 1651, and 1560  $\text{cm}^{-1}$ , respectively.<sup>17</sup>

The  $Dq$  values for the nickel(II) complexes of the unsubstituted lactams correlate with the carbonyl stretching frequencies. However, the  $Dq$  values for the chromium(III) complexes do not, nor do the  $Dq$  values obtained for the methyl lactam complexes of nickel(II). From the data presented in this paper, it would appear that several varying factors are operative in determining the donor order of these lactams and a definitive statement regarding the effect of ring size cannot be made.

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## Octahedral Nickel(II) Complexes of Secondary and Tertiary N-Alkylethylenediamines<sup>1</sup>

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A series of tris complexes of nickel(II) perchlorate and several N-alkyl-substituted ethylenediamines has been isolated from nonaqueous solutions and characterized. The spectral and magnetic data indicate that the complexes possess octahedral structures. The first d-d transition ( ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ) of the complexes, in the solids and in their respective ligands as solvents, shifts systematically to lower energy values as the alkyl group on the ethylenediamine ligand becomes more complex. The resulting spectrochemical series is: en > N-methylen > N-ethylen > N-propylen > N,N'-dimethylen > N-methyl-N'-ethylen > N,N-dimethylen, where en = ethylenediamine. The smaller  $Dq$  values which result with increasing alkyl substitution demonstrate that steric interactions are of greater magnitude than the increased inductivity of the substituted ethylenediamines and of more importance in determining the coordination interaction with the Ni(II) ion.

### Introduction

Thermodynamic data on the relative base strengths of alkylamines are based mainly on measurements of acid-base equilibria in water and related hydroxylic solvents. However, Pearson and Vogelsong<sup>2,3</sup> and

Trotman-Dickenson<sup>4</sup> have shown that these equilibria are affected by solvation terms, ion-pair association, and entropy effects. The net result of these interactions in the series of alkylamines produces the following general sequence of basicity in water:  $R_2NH > RNH_2 > R_3N > NH_3$ .

Bjerrum<sup>5</sup> has tabulated the data of several investigators in such a manner as to emphasize the rather good

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958), and references contained therein.

(3) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1048 (1958), and references contained therein.

(4) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

(5) J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

correlation between the hydrogen ion affinity of particular ligands and their tendency toward complex formation with metal ions. Such a correlation would lead to the prediction that increasing alkyl substitution on nitrogen would produce better ligands than ammonia. However, many different investigators<sup>6</sup> have concluded that primary aliphatic amines coordinate less readily than ammonia, secondary amines coordinate less readily than do the primary, and tertiary amines are almost devoid of ability to coordinate to metal ions.

Basolo and Murmann<sup>7</sup> demonstrated that although alkyl substitution on one nitrogen of the ethylenediamine increased the base strength, the first, second, and total formation constants of the substituted ethylenediamines with Ni(II) and Cu(II) are all smaller than the corresponding constants for ethylenediamine.<sup>8</sup> Also Pearson, Boston, and Basolo<sup>9</sup> found that the rate of aquation of the *trans*-[Co(AA)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes increased with increasing length of the alkyl substituent on N-alkylethylenediamines except for the methyl derivative. The slower rate of hydrolysis for this one example was attributed to the inductive effect which more than compensated for the steric requirement of the methyl group.

In an effort to resolve the conflicting situation regarding the relative Lewis basicities of primary, secondary, and tertiary amines compared with their transition metal complex stabilities, the ability of N-substituted ethylenediamines to coordinate with Ni(II) has been investigated. The instability of the secondary and tertiary amine complexes in aqueous solutions cannot be used as a quantitative measure of metal-amine interactions compared with ammonia or water because many other energy terms are operative. Therefore, nonaqueous solvents have been utilized in this laboratory for preparation of the complexes and for the spectral studies.

Very few tris-N-alkylethylenediamine complexes of Ni(II) have been reported previously. Keller and Edwards<sup>10</sup> isolated the N-methylethylenediamine complex, [Ni(N-methylen)<sub>3</sub>]Br<sub>2</sub>, and some tris-N-hydroxyalkylethylenediamine complexes of Ni(II) from ethanol, but no further work was undertaken to evaluate their stabilities compared to the ethylenediamine complex. Both N-methylethylenediamine and N-ethylethylenediamine were reported<sup>11</sup> to form tris Ni(II) complexes in solution, although no compounds were isolated.

This paper reports data pertinent to the magnitude of the Ni(II)-ligand interaction as a result of increasing inductive and steric effects. The spectrum of each of the complexes was determined in the solid state, in a solution of the respective amine as solvent, and in aqueous solutions. The spectral and magnetic data of

the tris(N-alkyl-substituted ethylenediamine) Ni(II) complexes provide an indication of the relative magnitude of the coordination tendency of secondary and tertiary ethylenediamines.

### Experimental

**Materials.**—Absolute ethyl alcohol was purified by refluxing with magnesium metal and iodine, followed by fractionation through a heated column, which was packed with helices. Nickel(II) perchlorate hexahydrate, Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, was obtained from G. F. Smith Chemical Co. and used without further treatment. 2,2-Dimethoxypropane was refluxed over barium oxide and then fractionated (b.p. 79°). Most of the N-alkyl-substituted ethylenediamines were distilled from sodium metal; in the case of the symmetrically substituted dialkylethylenediamines, barium oxide was employed. Anhydrous diethyl ether from Matheson Coleman and Bell was used without further purification. Practical grade nitromethane was purified by washing ten times with a 5% bicarbonate solution followed by drying 24 hr. over anhydrous calcium chloride. The solution was then decanted and fractionated. The fraction boiling at 101.0° was used for conductivity measurements.

**General Preparation of Complexes.**—Nickel(II) perchlorate was used to minimize anion coordination and enhance the possibility of forming tris-diamine complexes. A typical preparation involved 0.01 mole (3.66 g.) of nickel(II) perchlorate hexahydrate which was dehydrated with a 10% excess (6.1 ml.) of 2,2-dimethoxypropane<sup>12</sup> while stirring. The dehydration is endothermic, and when the resulting solution had warmed to room temperature, the reaction was considered to be complete; this usually required 20–30 min. The solution was diluted with 7–10 ml. of ethyl alcohol and filtered into an addition funnel which had been previously rinsed three times with the solvent. An excess amount of ligand was measured and transferred to the reaction flask with a syringe, thus eliminating contact with air and water vapor. The 4–8 ml. of the ligand used was diluted with 20 ml. of solvent and cooled to 0°. The solution of dehydrated metal ion was added dropwise to the ligand solution while stirring. Usually a precipitate formed before the addition was completed, but in the cases where this did not occur, slow addition of ether caused separation of the violet solid. The precipitate was isolated by filtration, washed three times with anhydrous ether, and dried in a moisture-free air stream for 15–20 min. The solid was dried under vacuum for 12 hr.; yields ranged from 80 to 90%.

**Preparation of Tris(N-methyl-N'-ethylethylenediamine)nickel(II) Perchlorate.**—Nickel(II) perchlorate hexahydrate (3.66 g.) was dehydrated with 6 ml. of 2,2-dimethoxypropane, and the resulting solution was added slowly to 8 ml. of freshly distilled N-methyl-N'-ethylethylenediamine while stirring at 0°. Anhydrous ethyl ether was added slowly to complete precipitation of the blue complex. The compound was isolated by filtration and dried. The reflectance spectrum indicated that the material contained both the bis and the tris complexes; thus the mixture was refluxed with 4 ml. of the ligand and 25 ml. of anhydrous ether for 4 hr. Subsequently, the reflectance spectrum showed no trace of the bis complex.

**Spectral Measurements.**—Spectra of finely ground solid samples were obtained with a Beckman DU spectrophotometer equipped with a standard Beckman reflectance attachment using U.S.P. MgCO<sub>3</sub> as a blank. The use of plastic cover plates permitted examination over the range from 1100 to 300 mμ. Readings were taken at 10-mμ intervals except in the regions of absorption maxima where readings were taken every 5 mμ.

Solution spectra of the complexes were obtained with a Cary Model 14 recording spectrophotometer using sets of matched 1, 5, and 10 cm. quartz cells. The ligand solutions were prepared by dehydrating a weighed amount of nickel(II) perchlorate hexahydrate in a volumetric flask using 2,2-dimethoxypropane and

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(8) F. Basolo and R. K. Murmann, *ibid.*, **74**, 5243 (1952).

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TABLE I  
 CHARACTERIZATION OF THE NICKEL(II)-N-ALKYLETHYLENEDIAMINE COMPLEXES

| Complex   | $\mu_{\text{eff}}$ , B.M. | Molar cond.<br>( $10^{-3} M$ in $\text{CH}_3\text{NO}_2$ ),<br>cm. <sup>2</sup> /ohm mole | Analyses <sup>a</sup> |       |        |       |        |       |
|---|---------------------------|---|-----------------------|-------|--------|-------|--------|-------|
|   |                           |   | C, %                  |       | H, %   |       | N, %   |       |
|   |                           |   | Calcd.                | Found | Calcd. | Found | Calcd. | Found |
| $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3](\text{ClO}_4)_2$                         | 3.21                      | 183   | 16.46                 | 16.20 | 5.52   | 5.47  | 19.19  | 19.04 |
| $[\text{Ni}(\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NH}_2)_3](\text{ClO}_4)_2$                       | 3.20                      | 181   | 22.52                 | 22.62 | 6.30   | 6.21  | 17.51  | 17.79 |
| $[\text{Ni}(\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_3](\text{ClO}_4)_2$            | 3.20                      | 189   | 27.61                 | 27.78 | 6.95   | 6.75  | 16.10  | 15.98 |
| $[\text{Ni}(\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_3](\text{ClO}_4)_2$ | 3.26                      | 182   | 31.94                 | 31.77 | 7.50   | 7.36  | 14.90  | 14.89 |
| $[\text{Ni}(\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NHCH}_2)_3](\text{ClO}_4)_2$                     | 3.28                      | 189   | 27.61                 | 27.30 | 6.95   | 6.82  | 16.10  | 15.84 |
| $[\text{Ni}(\text{C}_2\text{H}_5\text{NHCH}_2\text{CH}_2\text{NHCH}_2)_3](\text{ClO}_4)_2$            | 3.32                      | 198   | 31.94                 | 31.98 | 7.50   | 7.57  | 14.90  | 14.72 |
| $[\text{Ni}((\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3](\text{ClO}_4)_2$                    | 3.15                      | 186   | 27.61                 | 27.72 | 6.95   | 7.01  | 16.10  | 16.29 |
| $[\text{Ni}((\text{CH}_3)_2\text{CHNHCH}_2\text{CH}_2\text{NH}_2)_3](\text{ClO}_4)_2$                 | 3.10                      | 185   | 36.05                 | 36.89 | 8.47   | 8.18  | 16.82  | 16.59 |

<sup>a</sup> The microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

 TABLE II  
 SPECTRAL PROPERTIES OF THE SOLID COMPLEXES  $[\text{Ni}(\text{ligand})_3](\text{ClO}_4)_2$ 

| Ligand              | $\lambda_{\text{max.}}$ , <sup>a</sup> cm. <sup>-1</sup> | $Dq$ , cm. <sup>-1</sup> <sup>b</sup> | Racah $\beta$ | $\nu_3$ calcd.,<br>cm. <sup>-1</sup> |
|---------------------|--|---------------------------------------|---------------|--------------------------------------|
| en                  | $\nu_1$ 11,200   | 1120                                  | 0.826         | 17,890                               |
|                     | $\nu_2$ 12,700   |                                       |               |                                      |
|                     | $\nu_3$ 18,300   |                                       |               |                                      |
|                     | $\nu_4$ 29,000   |                                       |               |                                      |
| N-methylen          | 11,100   | 1110                                  | 0.831         | 17,754                               |
|                     | 12,600   |                                       |               |                                      |
|                     | 18,300   |                                       |               |                                      |
|                     | 28,700   |                                       |               |                                      |
| N-ethylen           | 10,800   | 1080                                  | 0.828         | 17,283                               |
|                     | 12,500   |                                       |               |                                      |
|                     | 17,800   |                                       |               |                                      |
|                     | 28,200   |                                       |               |                                      |
| N-propylen          | 10,700   | 1070                                  | 0.838         | 17,204                               |
|                     | 12,400   |                                       |               |                                      |
|                     | 17,600   |                                       |               |                                      |
|                     | 28,200   |                                       |               |                                      |
| N,N'-dimethylen     | 10,300   | 1030                                  | 0.822         | 16,600                               |
|                     | 12,300   |                                       |               |                                      |
|                     | 17,000   |                                       |               |                                      |
|                     | 27,300   |                                       |               |                                      |
| N-methyl-N'-ethylen | 10,100   | 1010                                  | 0.835         | 16,400                               |
|                     | 12,300   |                                       |               |                                      |
|                     | 16,700   |                                       |               |                                      |
|                     | 27,200   |                                       |               |                                      |
| N,N-dimethylen      | 10,000   | 1000                                  | 0.848         | 16,300                               |
|                     | 12,700   |                                       |               |                                      |
|                     | 17,000   |                                       |               |                                      |
|                     | 27,200   |                                       |               |                                      |

<sup>a</sup> The values represent the energy for the transitions:  $\nu_1$ ,  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ;  $\nu_2$ ,  ${}^3A_{2g} \rightarrow {}^1E_g$ ;  $\nu_3$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ; and  $\nu_4$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ , respectively. <sup>b</sup> The error limits of  $Dq$  are  $\pm 5$  cm.<sup>-1</sup>.

then adding the particular ligand to the volumetric mark to form the complex and act as solvent. In the cases of the symmetrical dialkylethylenediamines small amounts of dimethylformamide were required to maintain solution. The solution spectra were examined over the wave length range from 1300 to 330  $m\mu$ . A sharp dip in the absorption band at 1050  $m\mu$  was observed in the ligand spectra and was found to be caused by the presence of acetone and methyl alcohol in the sample cell which originated from the 2,2-dimethoxypropane used for dehydration of the nickel salt. Since the positions and intensities of the absorption bands of the complexes showed no changes due to the presence or absence of 2,2-dimethoxypropane or any of its reaction products, it was employed regularly as the dehydrating agent.

Aqueous solutions were prepared from weighed amounts of analyzed complexes in distilled water. The solubility of these complexes in water decreased with increasing molecular weight for the monosubstituted ethylenediamines.

**Magnetic Measurements.**—Magnetic moments were determined by the Gouy method at room temperature using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the standard. The molar susceptibility in each case was corrected for the diamagnetism of the ligands.<sup>13</sup>

**Conductivity Measurements.**—Conductivity determinations were performed at 24.6° using an Industrial Instruments, Inc., Model RC-16B conductivity bridge. The measurements were obtained in approximately  $10^{-3} M$  solutions of nitromethane. The colors of the resulting solutions were the same as the colors of the original solids for all compounds except  $[\text{Ni}(\text{N-methyl-N'-ethylen})_3](\text{ClO}_4)_2$ , which changed to a green color in nitromethane.

**Calculations.**—Assignment of the electronic transitions and calculation of the ligand field parameters were based on the procedure which has been reported.<sup>14</sup>

## Results

The magnetic moments and analyses for the solid compounds are listed in Table I, which also includes conductivity data for solutions. The magnetic data

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TABLE III  
 DATA DERIVED FROM SOLUTION SPECTRA USING THE RESPECTIVE LIGANDS AS SOLVENTS

| Ligand         | $\epsilon_{\nu_1}/\epsilon_{\nu_2}^a$ | $\epsilon_{\max}^b$ | $\lambda_{\max}, \text{cm.}^{-1c}$ | $Dq, \text{cm.}^{-1d}$ | $\nu_2/\nu_1$ | Racah $\beta$ | $\nu_2$ calcd.,<br>$\text{cm.}^{-1}$ | $\nu_2$ obsd. - $\nu_2$ calcd.,<br>$\text{cm.}^{-1}$ |
|----------------|---------------------------------------|---------------------|------------------------------------|------------------------|---------------|---------------|--------------------------------------|--|
| en             | 1.42                                  | 7.0                 | 11,360<br>12,500                   | 1136                   | 1.62          | 0.823         | 18,053                               | 297  |
| N-methylen     | 1.59                                  | 6.7                 | 18,350                             | 1094                   | 1.64          | 0.832         | 17,515                               | 435  |
|                |                                       | 9.5                 | 29,070                             |                        |               |               |                                      |  |
|                |                                       | 7.9                 | 10,940                             |                        |               |               |                                      |  |
| N-ethylen      | 1.60                                  | 7.1                 | 17,950                             | 1076                   | 1.66          | 0.837         | 17,282                               | 578  |
|                |                                       | 11.3                | 28,490                             |                        |               |               |                                      |  |
|                |                                       | 8.3                 | 10,760                             |                        |               |               |                                      |  |
| N-propylen     | 1.72                                  | 6.5                 | 17,860                             | 1066                   | 1.67          | 0.843         | 17,164                               | 626  |
|                |                                       | 10.4                | 28,260                             |                        |               |               |                                      |  |
|                |                                       | 8.5                 | 10,660                             |                        |               |               |                                      |  |
| N,N-dimethylen | 1.94                                  | 6.7                 | 17,790                             | 1000                   | 1.69          | 0.848         | 16,255                               | 605  |
|                |                                       | 11.5                | 28,170                             |                        |               |               |                                      |  |
|                |                                       | 8.0                 | 10,000                             |                        |               |               |                                      |  |
|                |                                       | 6.7                 | 16,860                             |                        |               |               |                                      |  |
|                |                                       | 13.0                | 27,170                             |                        |               |               |                                      |  |
|                |                                       |                     |                                    |                        |               |               |                                      |  |

<sup>a</sup> Octahedral complexes of Ni(II) with other bidentate ligands give typical ratios of 1.4 to 1.8 [C. K. Jørgensen, *Acta Chem. Scand.*, 10, 887 (1956)]. <sup>b</sup>  $\epsilon$  is given in l. mole<sup>-1</sup> cm.<sup>-1</sup> from the equation  $\log I/I_0 = \epsilon cl$ . <sup>c</sup> The energies of the respective peaks are reported as in Table II. <sup>d</sup> The error limits of  $Dq$  are  $\pm 4$  cm.<sup>-1</sup>.

demonstrate that the nickel ions in these compounds have two unpaired electrons and that the moment has an orbital contribution of typical magnitude. Conductivity measurements indicate that all of these compounds are bi-univalent electrolytes in nitromethane; this agrees with the proposed formulation of the compounds, *i.e.*,  $[\text{Ni}(\text{ligand})_3](\text{ClO}_4)_2$ . The reflectance spectra (Table II) are characteristic of  $d^8$  octahedral systems and are interpreted accordingly. The elemental analyses, coupled with the magnetic susceptibility, conductivity, and spectral data, substantiate that all of the compounds are pseudo-octahedral complexes of the N-substituted ethylenediamines.

The band maxima of the absorption spectra in Tables II, III, and IV are listed in order of increasing energy. The energies represent the electronic transitions from the  ${}^3A_{2g}$  ground state to the successively higher excited states  ${}^3T_{2g}$ ,  ${}^1E_g$ ,  ${}^3T_{1g}(F)$ , and  ${}^3T_{1g}(P)$ .

For all complexes both reflectance spectra and solution spectra were obtained in order to detect any gross changes in electronic or geometrical structures which might occur on dissolution. No significant differences were observed between the spectra of the solid and the corresponding ligand solution except for the typically lower resolution obtained from reflectance spectra. A small amount of dimethylformamide (DMF) must be added to the solutions of the N,N'-dialkylethylenediamine complexes to maintain solution, and, as a result, the lowest energy band of these two complexes is split into two peaks which are separated by approximately 350 cm.<sup>-1</sup>. The splitting of  $\nu_1$  suggests that the complexes distort from octahedral geometry in the DMF solutions. Therefore, the spectral data for these complexes are not included in Table III.

The spectra of aqueous solutions of the complexes of N,N'-dimethylen,<sup>15</sup> N,N-dimethylen, and N-methyl-N'-ethylen showed signs of extensive hydrolysis. A flocculent precipitate formed in the cells within 10 min., and the band maxima moved toward lower energy. Since the reaction with water limits the significance of the spectral data for the above complexes, these three were not included in Table IV.

### Discussion

The N-monoalkyl-substituted amines become slightly more basic with increasing length of the alkyl chain.<sup>16</sup> However, the spectra of the nickel complexes of these same ligands show a systematic decrease in  $Dq$  values as the alkyl group becomes more complex. This effect is illustrated in Figure 1. The same trend is demonstrated in the  $Dq$  values of the N,N'-dialkylethylenediamines (Table II).

While it is true that the ethyl group is more electron-releasing than the methyl group,<sup>17</sup> this effect is often offset by its larger steric requirements. Thus, in the case of simple amines, trimethylamine is a stronger base toward trimethylborane than ethyldimethylamine<sup>18</sup> or triethylamine.<sup>19</sup> Here steric requirements outweigh inductive effects. Since both N,N'-dimethylethylenediamine and N-methyl-N'-ethylethyl-

(15) The following abbreviations will be used throughout this paper and in subsequent papers in this series for the ligands: en, ethylenediamine; N-methylen, N-methylethylenediamine; N-ethylen, N-ethylethylenediamine; N-propylen, N-n-propylethylenediamine; N,N'-dimethylen, N,N'-dimethylethylenediamine; N,N-dimethylen, N,N-dimethylethylenediamine; N-methyl-N'-ethylen, N-methyl-N'-ethylethylenediamine; and N,N-diethylen, N,N-diethylethylenediamine.

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(17) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 71.

(18) H. D. Kaesz and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6213 (1960).

(19) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947).

TABLE IV  
 DATA DERIVED FROM AQUEOUS SOLUTION SPECTRA OF THE COMPLEXES

| Ligand     | $\epsilon_{\nu_1}/\epsilon_{\nu_3}$ | $\epsilon_{\max}$ | $\lambda_{\max}, \text{cm.}^{-1}$ | $\nu_3/\nu_1$ | Racah $\beta$ |
|------------|-------------------------------------|-------------------|-----------------------------------|---------------|---------------|
| en         | 1.29                                | 7.08              | 11,230                            | 1.63          | 0.834         |
|            |                                     |                   | 12,600                            |               |               |
|            |                                     |                   | 18,320                            |               |               |
|            |                                     |                   | 28,990                            |               |               |
| N-methylen | 1.50                                | 7.80              | 10,870                            | 1.64          | 0.835         |
|            |                                     |                   | 12,350                            |               |               |
|            |                                     |                   | 17,860                            |               |               |
|            |                                     |                   | 28,410                            |               |               |
| N-ethylen  | 1.82                                | 7.16              | 10,730                            | 1.62          | 0.822         |
|            |                                     |                   | 12,790                            |               |               |
|            |                                     |                   | 17,390                            |               |               |
|            |                                     |                   | 28,010                            |               |               |
| N-propylen | 1.73                                | 7.4               | 10,570                            | 1.64          | 0.836         |
|            |                                     |                   | 12,850                            |               |               |
|            |                                     |                   | 17,320                            |               |               |
|            |                                     |                   | 27,930                            |               |               |

enediamine are stronger bases than ethylenediamine, the smaller  $Dq$  values for these two ligands indicate that the steric effect is of greater magnitude than the increased inductivity of the substituted ethylenediamine ligands and of more importance in determining

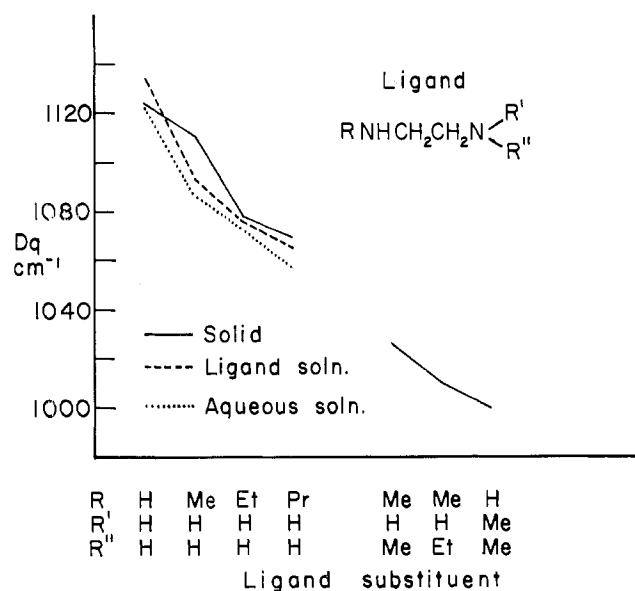


Figure 1.— $Dq$  vs. N-alkyl substituent on the ligand in  $[\text{Ni}(\text{ligand})_3](\text{ClO}_4)_2$ .

the degree of interaction with the Ni(II) ion. Also, it is interesting that we were unable to prepare the tris complex of N,N'-diethylethylenediamine. Instead, the compound which was isolated repeatedly corresponded to  $[\text{Ni}(\text{N,N}'\text{-diethylen})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , even when the dimethoxypropane dehydration procedure was followed. Previous attempts<sup>11,20</sup> to prepare the tris complex of N,N'-diethylen also were unsuccessful. The  $Dq$  values, which reflect the net result of steric and inductive factors, produce the following spectrochemical series: en > N-methylen > N-ethylen > N-propylen > N,N'-dimethylen > N-methyl-N'-ethylen > N,N-dimethylen.

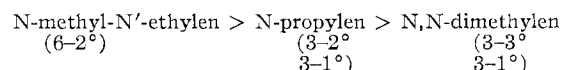
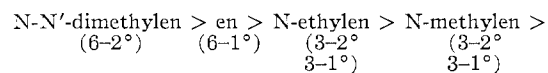
The spin-forbidden transition ( ${}^3A_{2g} \rightarrow {}^1E_g$ ) in the spectra of these compounds always appears as a

(20) D. L. Leussing, *Inorg. Chem.*, **2**, 79 (1963).

shoulder on the high energy side of  $\nu_1$ , as one would predict<sup>21</sup> for the intermediate range ( $Dq = 1000\text{--}1130 \text{ cm.}^{-1}$ ) of field strengths exhibited by these ligands.

The ratio of  $\nu_3/\nu_1$  gradually increases as  $Dq$  decreases; this is related to the interaction between the  ${}^3T_{1g}(\text{F})$  and  ${}^3T_{1g}(\text{P})$  term states. Reference to an Orgel diagram for an octahedral  $d^8$  ion shows that if no interaction occurred between these two term states,<sup>22</sup> the energy of the  ${}^3T_{1g}(\text{F})$  would be linear with respect to  $Dq$  and the  $\nu_3/\nu_1$  ratio would be 1.80. However, as the  $Dq$  value increases, the degree of interaction increases and the  ${}^3T_{1g}(\text{F})$  is depressed below the calculated value, and, thus, the ratio of  $\nu_3/\nu_1$  is less than 1.80. All of the compounds reported here have  $\nu_3/\nu_1$  ratios below 1.80, but the ratios approach this theoretical limit with decreasing field strengths of the ligands.

The ratio of the energy of the  ${}^3P\text{--}{}^3F$  term splitting in the complex compared with the free ion value gives the Racah parameter,  $\beta$ . One can correlate qualitatively the extent to which the d-electrons of the metal are delocalized on the ligand orbitals with this ratio. The  $\beta$  values of the complexes (Table II) produce the following nephelauxetic series<sup>23</sup>



The nephelauxetic effect seems to be less sensitive to steric interaction than the  $Dq$  values. One can explain the nephelauxetic series as being dependent primarily on inductive and polarization factors.<sup>24</sup> The greatest nephelauxetic effect is produced by N,N'-dimethylethylenediamine because the tris complex of this ligand presents six easily distortable secondary amino groups around the Ni(II) ion. The enhanced polarization and inductive factors of the secondary nitrogen atoms

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(22) C. J. Ballhausen, *Kgl. Danske. Videnskab. Selskab, Mat.-fys. Medd.*, **29**, No. 4 (1954).

(23) Listed in parentheses are the number and the types of nitrogen atoms present in the tris complexes; 1°, primary amine; 2°, secondary amine; 3°, tertiary amine.

(24) R. S. Drago, D. W. Meek, R. Longhi, and M. D. Joesten, *Inorg. Chem.*, **2**, 1056 (1963).

more than offset the steric interaction with respect to delocalization of the d-electrons of the metal on the ligand atoms. The reverse behavior is exemplified by N,N-dimethylethylenediamine. Although the tertiary nitrogen atom in this ligand potentially has larger distortability and inductive effects, it is apparent that steric considerations override whatever contribution these tertiary nitrogens may offer and cause this ligand to occupy the last position in the nephelauxetic series. The remaining ligands seem to follow a logical order, with the possible exception that N-ethylen might have been expected to occupy a relative position between N-methylen and N-propylen. It is conceivable that N-ethylen might exert a greater nephelauxetic effect than N-methylen or N-propylen due to a combination of more favorable inductive and steric requirements<sup>26</sup> of the ethyl group. However, the small variation in the value of  $\beta$  for the three ligands approaches the experimental error and limits the importance that should be attached to the relative position of N-ethylen as determined by these data.

The energy differences between the observed and calculated  $\nu_3$  are relatively small, providing evidence that any distortions from an octahedral structure must be small. For all the complexes the calculated energy value is less than that actually observed. This indicates that there is slightly less interaction between the two  ${}^3T_{1g}$  terms than would be expected for a purely octahedral case, and may arise from a trigonal distortion present in these compounds. This is particularly important in the N,N-dimethylen complex, where the difference between the values of the observed and calculated  $\nu_3$  is almost twice that for the other ligands. Whatever distortion may be present, however, is apparently weak in nature, for none of the spectral bands showed any asymmetry, as would be expected for either a trigonal or a tetragonal distortion.

The position of the first spin-allowed band for each of the ligand solutions is almost identical with the corresponding band in the reflectance spectra (Figure 1). Thus the same spectrochemical series results from the spectra of the ligand solutions as for the solid state. This indicates that the ligand field conditions are essentially equivalent in the two environments.

A ligand solution of the unsymmetrical N,N-diethylethylenediamine complex exhibited a  $\lambda_{max}$  at  $\sim 10,300 \text{ cm}^{-1}$ . Since the steric requirement for the tris-N,N-diethylen complex would be greater than for the tris-N,N-dimethylen compound, one would expect the  $Dq$  value to be less than  $1000 \text{ cm}^{-1}$ . The  $1030 \text{ cm}^{-1}$  value suggests that  $[\text{Ni}(\text{N,N-diethylen})_3]^{2+}$  is not present in the solution. A possible species is the six-coordinate  $[\text{Ni}(\text{N,N-diethylen})_4]^{2+}$ ; such a complex would have four primary amino and two tertiary amino groups coordinated to the Ni(II) and would be expected to exhibit the higher  $Dq$  value of  $1030 \text{ cm}^{-1}$ . However, the spectrum of the analogous tetrakis complex of N-isopropylethylenediamine exhibits small splittings

in the first and second bands, typical of tetragonal Ni(II) complexes with a triplet ground state. The spectrum, which is consistent with a  $D_{4h}$  symmetry complex, differs significantly from that of the Ni(II) complex which is present in the solution of N,N-diethylethylenediamine. Attempts to isolate any compound other than the square-planar  $[\text{Ni}(\text{N,N-diethylen})_2](\text{ClO}_4)_2$  from the N,N-diethylen solutions were unsuccessful.

The ratio of the molar extinction coefficients for the second and third spin-allowed bands<sup>26</sup> has been used as evidence for the presence of octahedral nickel(II). For the above series, this ratio and the values of the extinction coefficients determined from ligand solutions are within the range expected for chelated octahedral compounds. There is a gradual increase in the  $\epsilon_{max}$  values of the complexes as the size of the N-alkyl substituent on the ligand increases. The  $\epsilon_{max}$  values reflect small distortions from  $O_h$  site symmetry since the electronic transitions become more probable as the distortion progresses from an octahedral to a trigonal structure.

The values of the Racah parameter,  $\beta$ , determined from the ligand solution spectra, produce the following nephelauxetic series: en > N-methylen > N-ethylen > N-propylen > N,N-dimethylen. The definition of this series is more distinct than that determined from the reflectance spectra. Also, the position of N-ethylen is clearly between N-methylen and N-propylen in this series, whereas its position was not so definitive from the spectra of the solids.

The difference between the observed and the calculated value of  $\nu_3$  in the ligand solution spectra increases with increasing size of the N-alkyl group. This effect is larger in the solution spectra than in the spectra of the solids and may be related to the compressed crystalline field<sup>27</sup> of the solid complexes compared to the solution environment. Sterically hindered systems should relax more in solution than would be possible in the crystal and produce a larger difference, in agreement with the data.

The spectrochemical series, the ratios of  $\nu_3/\nu_1$ , the nephelauxetic series, and the colors of the complexes are identical in both the solid state and in solution. These factors, coupled with the solution  $\epsilon_{max}$  values, show that the same octahedral complex must be present both in the solid state and in the ligand solutions. These results are in contrast to those obtained from aqueous solutions of the complexes, which are discussed below.

The absorption bands of all the compounds shift to lower energy values in aqueous solutions. More extensive hydrolysis occurred when  $[\text{Ni}(\text{N,N'-dimethylen})_3](\text{ClO}_4)_2$ ,  $[\text{Ni}(\text{N-methyl-N'-ethylen})_3](\text{ClO}_4)_2$ , and  $[\text{Ni}(\text{N,N-dimethylen})_3](\text{ClO}_4)_2$  were dissolved in water.

Changes in the values of the  $\nu_3/\nu_1$  ratio,  $\epsilon_{\nu_3}/\epsilon_{\nu_1}$ ,  $\beta$ , and the energies of the bands in water compared to the spectra in ligand solution and in the solid are most

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dramatic for the  $[\text{Ni}(\text{N-ethylen})_3](\text{ClO}_4)_2$  complex. For example, the Racah parameters,  $\beta$ , derived from aqueous solution spectra produce a nephelauxetic series where N-ethylen displays the largest nephelauxetic effect and the remaining ligands are essentially equivalent. These data, coupled with the  $Dq$  value, indicate that the inductive character of N-ethylen is more pronounced in water than that of the other ligands, or that species other than the tris complex are present in the aqueous solution. An obvious possibility is *trans*- $[\text{Ni}(\text{N-ethylen})_2(\text{H}_2\text{O})_2]^{2+}$ . In fact, the aqueous spectrum of an authentic sample of this

compound is identical with that observed by dissolving  $[\text{Ni}(\text{N-ethylen})_3](\text{ClO}_4)_2$  in water.

It is apparent that the general shift of the absorption bands in aqueous solution, the visible hydrolysis reactions, and the unexpected changes in  $\epsilon_{\text{max}}$  demonstrate the complexity of aqueous solutions of amine coordination compounds and the subsequent care that must be exercised in interpreting data quantitatively in such solutions.

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## Structural Interconversions of Octahedral, Planar, and Tetrahedral Nickel(II) Complexes

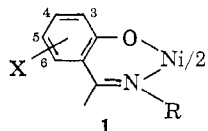
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A series of bis(N-R-salicylaldimine)nickel(II) complexes has been prepared in which the R group contains a site capable of coordination. Complexes with  $\text{R} = \text{CH}_3\text{CHCH}_2\text{OCH}_3$  but differing in the extent and position of chelate ring substitution have been thoroughly studied. For these complexes it has been shown from measurement of ligand field spectra and proton contact shifts that in the temperature range  $-40$  to  $50^\circ$  in chloroform solution discrete octahedral, planar, and tetrahedral stereoisomers are present in equilibrium. At low temperatures the octahedral form predominates; at higher temperatures the equilibrium is displaced toward the planar and tetrahedral forms. For two complexes the temperature dependence of the distribution of stereoisomers has been estimated from spectral data. The spectra of the octahedral complexes were found to be quite similar to those of associated paramagnetic bis(salicylaldimine)nickel(II), suggesting quasi-octahedral coordination in the latter. The spin density distributions in the coordinated ligand systems were shown to be similar in sign in the octahedral and tetrahedral stereoisomers.

### Introduction

Recent and extensive investigations of variously substituted bis(salicylaldimine)nickel(II) complexes (1) have clearly revealed that the particular structure or



structures exhibited in the crystalline, molten, and solution phases is a sensitive function of the nitrogen substituent R and, to a lesser extent, of the ring substituent X. When  $\text{R} = n$ -alkyl the complexes are diamagnetic in solution at and above room temperature and have a planar structure.<sup>2,3</sup> When  $\text{R} = sec$ -alkyl or *t*-Bu a square-planar  $\rightleftharpoons$  tetrahedral equilibrium exists in solution which has been thoroughly studied,<sup>4-9</sup>

especially by nuclear magnetic resonance.<sup>4,7,9</sup> A similar equilibrium apparently exists in the molten *n*-alkyl complexes.<sup>10</sup> A more complicated behavior exists in solutions of the methyl,<sup>3</sup> *n*-alkyl,<sup>11</sup> and *sec*-alkyl<sup>6,12</sup> complexes below room temperature due to the formation of detectable amounts of paramagnetic associated species. When  $\text{R} = \text{aryl}$  associated species are frequently stable in solution below and considerably above room temperature<sup>13,14</sup>; above  $\sim 100^\circ$  associated, planar, and tetrahedral species exist in equilibrium with the latter favored at the higher temperatures.<sup>14</sup>

All nickel(II) salicylaldimine complexes which have been studied in any detail contain as R substituents only simple alkyl and aryl groups, so that in their monomeric forms only planar or tetrahedral structures are

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