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# Studies of Nitro and Nitrito Complexes. III. Some Nitro Complexes of Nickel(II) and a Nitro–Nitrito Equilibrium

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The preparations are reported of a series of red complexes of formula $NiD_2(NO_2)_2$ (where D represents a C- or N-substituted ethylenediamine), the electronic and infrared spectra of which are consistent with the presence of nitro groups. The solid nitrito complexes Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ and Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ exist in a nitro–nitrito equilibrium in chloroform. The equilibrium for the latter compound has been studied over a temperature range, and the results have been used to calculate the approximate thermodynamic parameters $\Delta H = -2.3 \pm 0.6$ kcal/mole and $\Delta S = -7.2 \pm 1.3$ eu for the change $NiD_2(ONO)_2 \longrightarrow NiD_2(NO_2)_2$. The influence of steric factors on the linkage isomerism of the nitrite ion in complexes of this type is discussed.

## Introduction

We recently reported[1] the preparation of a series of stable, blue nitrito complexes of the general formula $NiD_2(NO_2)_2$ (where D = a C- or N-substituted ethylenediamine). It was suggested[1,2] that the nitrite ion adopted oxygen coordination in these compounds because of steric interaction with the bulky amine substituents. In order to test this and to continue our investigations into the factors influencing the manner of bonding of the nitrite ion we have prepared a further series of complexes of the above general formula, but using amines likely to have a smaller steric effect on the nitrite group. These compounds are red and have spectra consistent with their formulation as nitro complexes.

The solid nitrito complexes Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ and Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ exist in a nitro–nitrito equilibrium in chloroform, and we report here the results of studies on one of these systems.

## Experimental Section

**Preparation of Compounds.**—The compound $Ni(NH_3)_4(NO_2)_2$ was prepared by the method given by Palmer.[3] The preparations of Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ and Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ have been described previously.[1,4] The other complexes were prepared by the method used[4] for the complex with N,N-dimethylethylenediamine. Further details for individual complexes are given below.

**Ni(ethylenediamine)$_2$(NO$_2$)$_2$.**—Large red crystals formed from methanol solution. *Anal.* Calcd for $C_4H_{16}N_6NiO_4$: C, 17.73; H, 5.95; Ni, 21.67. Found: C, 17.95; H, 5.67; Ni, 21.64.

**Ni(1,2-diamino-2-methylpropane)$_2$(NO$_2$)$_2$.**—Large red crystals formed on recrystallization from nitromethane. *Anal.* Calcd for $C_8H_{24}N_6NiO_4$: C, 29.39; H, 7.40; N, 25.71; O, 19.57. Found: C, 29.31; H, 7.16; N, 25.66; O, 19.47.

**Ni(N-methylethylenediamine)$_2$(NO$_2$)$_2$.**—Pink, microcrystalline solid formed on recrystallization from 1-propanol. *Anal.* Calcd for $C_6H_{20}N_6NiO_4$: C, 24.09; H, 6.70; N, 28.11. Found: C, 23.95; H, 6.68; N, 28.41.

**Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$.**—Large red crystals formed on recrystallization from nitromethane. *Anal.* Calcd for $C_8H_{24}N_6NiO_4$: C, 29.39; H, 7.40; N, 25.71. Found: C, 29.54; H, 7.10; N, 25.99.

**Ni(*rac*-1,2-diphenylethylenediamine)$_2$(NO$_2$)$_2$.**—Red crystals formed on recrystallization from nitromethane. *Anal.* Calcd for $C_{28}H_{32}N_6NiO_4$: N, 14.61; Ni, 10.20; O, 11.12. Found: N, 14.20; Ni, 9.96; O, 11.04.

**Physical Measurements.**—The electronic spectra of solutions were recorded on a Perkin-Elmer Model 350 spectrometer. In the equilibrium studies the solution temperatures were varied by passing water from a thermostatically controlled water bath through the cell holder. The temperature was measured with a copper–constantan thermocouple in a sealed glass tube placed in the solution being studied; 5-cm cells were used.

The other physical measurements were carried out as described previously.[1] The complexes Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ and Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ were monomeric in chloroform (Table I).

## Results

**Electronic Spectra.**—Reflectance spectra were obtained over the range 30,000–4000 cm$^{-1}$, and the en-

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[1] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **3**, 1389 (1964).

[2] M. G. B. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc.*, 363 (1964).

[3] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, 1954, p 559.

[4] D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 5909 (1963).

Table I

Molecular Weight Data

| Compound[a] | Concn, *M* | $M_{obsd}$ | $M_{calcd}$ |
|---|---|---|---|
| Ni(N,N′-diethylethylenediamine)$_2$-(ONO)$_2$ | 0.04 | 435 | 383 |
| Ni(N,N-dimethylethylenediamine)$_2$-(ONO)$_2$ | 0.01 | 343 | 330 |

[a] Formulation refers to solid-state structure.

Table II

Electronic Spectra of the Complexes

| Compound | State | Band maxima, cm$^{-1}$ | Ref |
|---|---|---|---|
| Ni(NH$_3$)$_4$(NO$_2$)$_2$ | Solid | *a*, 20,350, 19,900, 12,000, ~11,200 | *c* |
| Ni(ethylenediamine)$_2$(NO$_2$)$_2$ | Solid | *a*, 19,650, 12,500, ~11,000 sh | *d* |
| Ni(N-methylethylenediamine)$_2$(NO$_2$)$_2$ | Solid | *a*, 20,120, 12,350, ~11,000 sh | *d* |
| Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ | Solid | *a*, 20,000, 12,350, ~11,300 sh | *d* |
| | CHCl$_3$ | *a*, 20,200 ($\epsilon_{molar}$ 15), *b* | *d* |
| Ni(1,2-diamino-2-methylpropane)$_2$(NO$_2$)$_2$ | Solid | 29,240, 19,230, 11,600 | *d* |
| Ni(*rac*-1,2-diphenylethylenediamine)$_2$(NO$_2$)$_2$ | Solid | *a*, 19,900, 12,500, 10,800 sh | *d* |
| Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ | Solid | 27,550, ~22,500 w, sh,[g] 17,000, 10,360 | *e* |
| | CHCl$_3$ | *a*, 20,400, ~17,000 sh, b | *d* |
| | C$_6$H$_6$ | *a*, ~20,000, 17,000, *b* | *d* |
| Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ | Solid | 27,250, 17,300 10,950, ~8740 sh | *f* |
| | CHCl$_3$ | *a*, 20,300, ~17,000 sh, 11,100 | *d* |

[a] Band obscured by strong ultraviolet absorption. [b] Region below 13,500 cm$^{-1}$ not studied. [c] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40,** 792 (1964). [d] This work. [e] Ref 1. [f] Ref 4. [g] Spin-forbidden transition.

ergies of the electronic bands are given in Table II, together with those found for Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$, Ni(N,N′-diethylethylenediamine)$_2$-(ONO)$_2$, and Ni(N,N-dimethylethylenediamine)$_2$-(ONO)$_2$ in solution. The vibrational bands of the organic ligands in the near-infrared region[4] have been omitted.

X-Ray studies have shown[5] that Ni(NH$_3$)$_4$(NO$_2$)$_2$ and Ni(ethylenediamine)$_2$(NO$_2$)$_2$ are nitro complexes. The close similarity of their solid-state electronic spectra to those of the complexes with N-methylethylenediamine, N-ethylethylenediamine, 1,2-diamino-2-methylpropane, and *rac*-1,2-diphenylethylenediamine strongly suggests that these other red complexes also contain N-bonded nitrite groups. For most of these compounds only the first two spin-allowed bands ($^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in O$_h$ symmetry, though the ligand fields are of lower symmetry than this) were observed (Table II), the other band ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in O$_h$) being hidden by strong absorption in the ultraviolet region. The bands for the nitro complexes are at appreciably higher energies than the corresponding ones for the solid nitrito complexes with N,N′-diethyl- and N,N-dimethylethylenediamine. This is in accord with the fact that the nitro group lies toward the "stronger" end of the spectrochemical series as compared with the nitrito group.

The spectrum of Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ in chloroform in the visible region is similar to that of the solid compound. However, the solution spectra of the complexes with N,N-dimethyl- and N,N′-diethylethylenediamine in chloroform and some other solvents are quite different from those of the solids, having bands at ~20,000 cm$^{-1}$ as well as at ~17,000 cm$^{-1}$ (Table II and Figure 1).

The spectrum of the N,N′-diethylethylenediamine complex in chloroform was recorded over a temperature range in the region 30,000–14,000 cm$^{-1}$. The band at ~20,000 cm$^{-1}$ decreased in intensity with increase in temperature and a well-defined isosbestic point was observed at 17,650 cm$^{-1}$, indicating the presence of only two species (Figure 1).

Since the solid nitrito complex has a band at 17,000 cm$^{-1}$ and the closely-related nitro complex Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ has one at ~20,000 cm$^{-1}$ in both the solid state and in chloroform (see Figure 1), it seems likely that on dissolving Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in chloroform there is set up an equilibrium of the type

$$\text{Ni(diamine)}_2\text{(ONO)}_2 \rightleftharpoons \text{Ni(diamine)}_2\text{(NO}_2\text{)}_2$$

Although several other equilibria are theoretically possible, the one above, which involves species of a known type, fits the experimental observations well, and there is no evidence from the electronic spectrum, infrared spectrum, or molecular weight measurements for the presence of alternative species. This equilibrium will be discussed in detail in a later section.

The electronic spectra of Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in benzene, chlorobenzene, and nitromethane also revealed the presence of solution equilibria, systems with isosbestic points being observed.

**Infrared Spectra.**—The nitrite ion has three infrared-active vibrational modes: the antisymmetric N–O stretch ($\nu_{as}$), the symmetric N–O stretch ($\nu_s$), and the NO$_2$ deformation ($\delta$). The two stretching frequencies have previously been used to provide information concerning the mode of coordination of the nitrite group.[1,6–8]

The complexes listed in Table II have been studied over the range 2000–650 cm$^{-1}$. Identification of bands due to the nitrite group (Table III) was made by comparison with the spectra of suitable control compounds, usually the analogous halide or thiocyanate complexes. The red compounds have a very strong band at ~1300 cm$^{-1}$ but no nitrite bands in the region (1250–1100

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(5) M. A. Porai-Koshitz and L. M. Dikareva, *Kristallografiya*, **4,** 650 (1959); M. A. Porai-Koshitz and L. Kh. Munacheva, *Zh. Strukt. Khim.*, **5,** 642 (1964), and personal communication.

(6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds,' John Wiley and Sons, Inc., New York, N. Y., 1963, pp 151–155.

(7) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **4,** 721 (1965).

(8) In ref 1 and 7 we incorrectly assigned $\nu_{as}$ above $\nu_s$. The band assignment should be reversed (see A. Tramer, *Compt. Rend.*, **248,** 3546 (1959), and references therein), but the conclusions drawn from the infrared spectra are unaltered by this change in terminology.

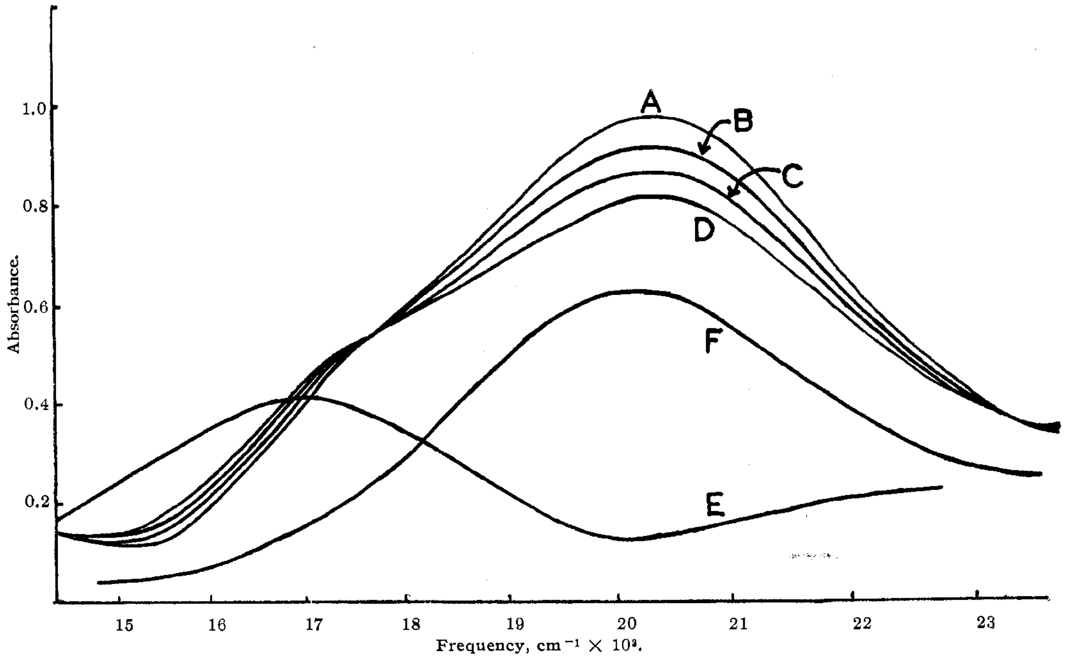

Figure 1.—Visible spectra of: A–D, Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in chloroform, 0.015 *M* at various temperatures [A, 280°K; B, 292°K; C, 305°K; D, 317°K]; E, Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$, solid, by reflectance; F, Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ in chloroform, 0.00815 *M*.

cm$^{-1}$) where $\nu_{as}$ is observed[1,8] for the related, blue nitrito complexes. Accordingly, we assign the band at ~1300 cm$^{-1}$ to $\nu_{as}$, the frequency range agreeing well with $\nu_{as}$ for other nitro complexes of nickel(II), *e.g.*, $K_2BaNi(NO_2)_6$ (Table III).

The $\nu_s$ band at 1344 cm$^{-1}$ for $K_2BaNi(NO_2)_6$ is much weaker and sharper than $\nu_{as}$. The $\nu_s$ bands for the compounds Ni(diamine)$_2$(NO$_2$)$_2$ behave similarly, and, in many cases, the presence of amine bands prevented an unambiguous identification of $\nu_s$. For $Ni(NH_3)_4(NO_2)_2$, a band at 1360 cm$^{-1}$, which we tentatively assign as $\nu_s$, is quite strong compared with the $\nu_s$ bands for the other compounds. However, it is probable that part of the intensity arises from the first overtone of the M–NH$_3$ rock at 680 cm$^{-1}$.

TABLE III

NITRITE FREQUENCIES (CM$^{-1}$) FOR THE COMPLEXES

| Compound | State | $\nu_s$ | $\nu_{as}$ | $\delta$ |
|---|---|---|---|---|
| $Ni(NH_3)_4(NO_2)_2$ | Mull | 1360 s[a] | 1300 vs | 814 w |
| Ni(ethylenediamine)$_2$(NO$_2$)$_2$ | Mull | 1333 m, sp | 1299 vs | 807 m |
| Ni(N-methylethylenediamine)$_2$(NO$_2$)$_2$ | Mull | 1353 sh, w[b] | 1335 vs | 813 m |
| Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ | Mull | 1333 w, sp[b] | 1303 vs | 837 m |
|  | CHCl$_3$ | *b* | 1320 vs | *b* |
| Ni(1,2-diamino-2-methylpropane)$_2$(NO$_2$)$_2$ | Mull | *b* | ~1325 vs, br | 832 w, 818 m |
| Ni(*rac*-1,2-diphenylethylenediamine)$_2$(NO$_2$)$_2$ | Mull | ~1320 sh | ~1300 s, br | 814 mw |
| Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ | Mull[c] | 1337 s | 1205 s | 812 m |
|  | CHCl$_3$ | *b* | 1316 s | *b* |
| Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ | Mull[c] | 1387 s | 1130 s | 817 m |
|  | CHCl$_3$ | 1389 w | 1314 s, 1130 m | *b* |
| $K_2BaNi(NO_2)_6$ | Mull | 1344 sp, w | 1307 vs | 837 w, 812 m |

[a] See text for discussion of this assignment. [b] Band obscured or assignment uncertain due to the presence of ligand or solvent bands. [c] From ref 1 (but see footnote 8).

The infrared spectrum of a chloroform solution of Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ contains bands at 1389 and 1130 cm$^{-1}$ corresponding to the $\nu_s$ and $\nu_{as}$ bands of the solid (Table III), but it also has a strong band at 1314 cm$^{-1}$ assignable as $\nu_{as}$ for a nitro isomer. Thus the infrared spectrum also indicates the presence of a nitro–nitrito equilibrium in solution. Chloroform solutions of Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ also show a strong band (at 1316 cm$^{-1}$) indicative of a nitro form, but, in this case, the region where $\nu_{as}$ for the nitrito isomer would be expected was obscured by solvent absorption. Moreover, the $\nu_{as}$ band for the nitrito component was not observed, probably due to its proximity (in the solid compound it is at 1337 cm$^{-1}$) to the strong 1316 cm$^{-1}$ band of the nitro isomer.

**Nitro–Nitrito Equilibrium in Chloroform.**—It was stated above that the electronic spectra of chloroform solutions of Ni(N,N-dimethylethylenediamine)$_2$(ONO)$_2$ and Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ indicated the presence of equilibria of the type

$$\text{Ni(diamine)}_2\text{(ONO)}_2 \rightleftharpoons \text{Ni(diamine)}_2\text{(NO}_2\text{)}_2 \qquad (1)$$

The visible spectrum of the N,N′-diethylethylenediamine complex in this solvent has been studied between 276 and 325°K (Figure 1). In contrast to the results for this system the visible spectrum of Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ in chloroform showed no evidence for a nitro–nitrito equilibrium. Moreover, the intensity of the band at 20,000 cm$^{-1}$ did not change significantly between 293 and 323°K, suggesting that

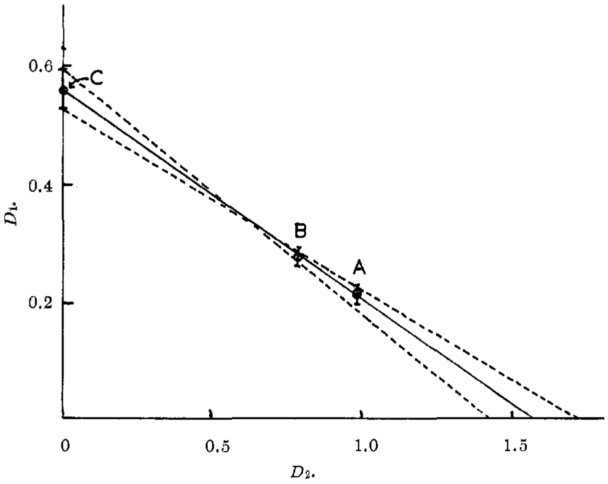

Figure 2.—Plot of $D_1$ against $D_2$ for 0.015 *M* solutions of Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in chloroform (see text for definition of $D_1$ and $D_2$). The dotted lines represent the estimated error limits.

the variation of the extinction coefficient with temperature was small.

For a solution of given concentration, *C*, the equilibrium constant, *K*, for (1) may be obtained from: $K = (D - D_{ONO})/(D_{NO_2} - D)$, where $D$ is the measured optical density at any suitable wavelength, and $D_{ONO}$ and $D_{NO_2}$ are the optical densities at this wavelength which would be found for separate solutions, each of concentration *C*, of the pure nitrito and nitro isomers, respectively. Unfortunately, neither $D_{ONO}$ nor $D_{NO_2}$ can be determined directly here, but, because of the unusual nature of the equilibrium, we have attempted to estimate them using the following method in order to obtain approximate thermodynamic parameters for the system.

It appears from the spectral results obtained for Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in chloroform (Table II, Figure 1) that the position of the band for the nitrito component in solution differs little from that of the solid, though the band of the latter is broader as is usually the case for reflectance spectra. (In the related nitrito complex with N,N-diethylethylenediamine, which shows no tendency to change to a nitro form in methylene chloride, the band positions in the solid state and in this solvent differ by only 150 cm$^{-1}$.[9]) The isosbestic point at 17,650 cm$^{-1}$ lies quite close in energy to the band maximum (17,000 cm$^{-1}$) of the solid compound and must lie on the curve for the nitrito form as the concentration of the nitro isomer vanishes to zero. Therefore a lower limit may be obtained for, and an estimate made of, the molar extinction coefficient of the 17,000 cm$^{-1}$ band of the nitrito isomer in solution; these values are 7.1 and 7.5 ± 0.5, respectively.

Graphical Gaussian analysis was then carried out on the spectra obtained at 280 and 324°K, which are approximately the limits of study. The band contours obtained agreed well with those of related compounds (Ni(N-ethylethylenediamine)$_2$(NO$_2$)$_2$ in chloroform for the nitro component and Ni(N,N-diethylethylenediamine)$_2$(ONO)$_2$ in methylene chloride for the nitrito component[9]). From this analysis, the optical density at 17,000 cm$^{-1}$ due to the nitrito component ($D_1$) and that at 20,400 cm$^{-1}$ due to the nitro isomer ($D_2$) were estimated at each of the above temperatures. These values are points A and B in Figure 2, a plot of $D_1$ against $D_2$. Point C on this plot (where $D_1 = 0.56 \pm 0.035$ and $D_2 = 0$) was obtained from the value (7.5 ± 0.5) of the molar extinction coefficient of the 17,000 cm$^{-1}$ band as estimated from the position of the isosbestic point (see above). If the equilibrium involves only two species, points A, B, and C should lie on a straight line, which, within experimental error, appears to be the case. Extrapolation of this line to $D_1 = 0$ then permitted an estimate of $D_{NO_2}$ at 20,400 cm$^{-1}$ as 1.57 ± 0.15 (corresponding to a molar extinction coefficient $\epsilon_{NO_2}$ of 21 ± 2).

The equilibrium constant for (1) was calculated from the equation $K = (D - D_{ONO})/(D_{NO_2} - D)$, where the values of $D$, $D_{ONO}$, and $D_{NO_2}$ here all refer to data at 20,400 cm$^{-1}$ (where the greatest change in optical density with temperature occurs). Three separate 0.015 *M* solutions were studied and the values of $D$ are listed in Table IV. These were plotted against temperatures to average out experimental errors, and $D$ values at seven different temperatures were read off from the plot (Table V). The value of $D_{NO_2}$ was taken to be 1.57 ± 0.15 (see above). The value of $D_{ONO}$ at 20,400 cm$^{-1}$ is small compared with that of $D_{NO_2}$ and was estimated to be 0.07 ± 0.05.[10] At each of the temperatures listed

Table IV

Experimental Optical Density Values at 20,400 Cm$^{-1}$ for 0.015 *M* Solutions of Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in Chloroform at Various Temperatures

| Temp, °K | Solution no. | Optical density | Temp, °K | Solution no. | Optical density |
|---|---|---|---|---|---|
| 278 | 1 | 1.005 | 305 | 2 | 0.860 |
| 278 | 2 | 1.000 | 307 | 3 | 0.855 |
| 280 | 2 | 0.975 | 311 | 3 | 0.835 |
| 281 | 1 | 0.975 | 312 | 2 | 0.835 |
| 289 | 2 | 0.955 | 317 | 2 | 0.805 |
| 292 | 2 | 0.915 | 322 | 3 | 0.785 |
| | | | 324 | 2 | 0.780 |

Table V

Values of Log *K* for the Nitro ⇄ Nitrito Equilibrium of Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ in Chloroform (0.015 *M*)

| | | Log $K^a$ | | |
|---|---|---|---|---|
| $D$ | Temp, °K | I$^b$ | II$^b$ | III$^b$ |
| 1.005 | 276 | 0.219 | 0.139 | 0.329 |
| 0.985 | 280 | 0.194 | 0.118 | 0.2985 |
| 0.935 | 290 | 0.134 | 0.0665 | 0.2255 |
| 0.890 | 300 | 0.081 | 0.020 | 0.162 |
| 0.840 | 310 | 0.023 | −0.031 | 0.094 |
| 0.795 | 320 | −0.029 | −0.077 | 0.033 |
| 0.775 | 324 | −0.052 | −0.0975 | 0.007 |

[a] Calculated from $K = (D - D_{ONO})/(D_{NO_2} - D)$. [b] For I, $D_{ONO} = 0.07$, $D_{NO_2} = 1.57$; II, $D_{ONO} = 0.02$, $D_{NO_2} = 1.72$; III, $D_{ONO} = 0.12$, $D_{NO_2} = 1.42$.

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(9) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 616 (1963).

in Table V three values of log $K$ were calculated. One value used the mean values of $D_{\mathrm{ONO}}$ and $D_{\mathrm{NO_2}}$ quoted above, while for the others, values of $D_{\mathrm{ONO}} = 0.02$, $D_{\mathrm{NO_2}} = 1.72$ and $D_{\mathrm{ONO}} = 0.12$, $D_{\mathrm{NO_2}} = 1.42$ were employed (the last two pairs of $D_{\mathrm{ONO}}$ and $D_{\mathrm{NO_2}}$ values give the extreme values of log $K$ which appear to correlate the data). ~~Three values for the parameters $\Delta H$ and $\Delta S$ for~~ the change

$$\mathrm{Ni(N,N'\text{-}diethylethylenediamine)_2(ONO)_2} \longrightarrow \mathrm{Ni(N,N'\text{-}diethylethylenediamine)_2(NO_2)_2}$$

were then calculated graphically by plotting each set of values of log $K$ against $1/T$. If the relatively small errors in measuring $D$ are also allowed for, the following values were obtained: $\Delta H = -2.3 \pm 0.6$ kcal/mole and $\Delta S = -7.2 \pm 1.3$ eu.

## Discussion

The present and previous[1,2,7] results together suggest that the primary factor deciding the mode of bonding of the nitrite ion in the compounds $\mathrm{NiL_4(NO_2)_2}$ ($L$ = a monodentate amine or $L_2$ = a chelating diamine) is steric. Comparing the behavior with N-substituted ethylenediamines, N,N,N′,N′-tetramethylethylenediamine (tetmen) forms $\mathrm{Ni(tetmen)(NO_2)_2}$, in which the anions are chelating through the oxygen atoms,[7,11] whereas with di-N-substituted ethylenediamines nitrito complexes, $\mathrm{Ni(diamine)_2(ONO)_2}$, result.[1] With ethylenediamine and mono-N-substituted ethylenediamines the nitrite ion adopts what is normally considered to be its more usual manner of bonding, namely, as a nitro group.

The importance of steric effects is clearly illustrated in the complexes of stoichiometry $\mathrm{Ni(diamine)_2(NO_2)_2}$ formed by the *meso* and the *rac* forms of 1,2-diphenylethylenediamine. With the *meso* form of the ligand the anions are bonded through oxygen,[1] but with the *rac* form they are present as nitro groups. The only difference between these two diamines is in the position of the benzene rings; in the complexed *rac* form these are in equatorial positions, but in the *meso* analogs they are axially directed[12] and offer much more steric repulsion toward anions on the $z$ axis. This repulsion causes many nickel complexes with the *meso* base to be diamagnetic and probably only four-coordinate, whereas their counterparts with the *rac* form are paramagnetic and six-coordinate,[13] and it is probably this repulsion which causes the change in mode of coordination of the anion in the nickel nitrite complexes.

This dependence upon steric factors raises the possibility of preparing stable, solid nitro and nitrito isomers of stoichiometry $\mathrm{Ni(diamine)_2(NO_2)_2}$, somewhat analogous to the existence of the paramagnetic and the diamagnetic forms of Ni(*meso*-1,2-diphenylethylenediamine)$_2$($\mathrm{CCl_3CO_2}$)$_2$,[13] but such pairs of isomers were not obtained in the solid state. Although both $\mathrm{Ni(N,N'\text{-}diethylethylenediamine)_2(ONO)_2}$ and $\mathrm{Ni(N,N\text{-}dimethylethylenediamine)_2(ONO)_2}$ displayed nitro ⇌ nitrito equilibria in chloroform, these solutions gave only the nitrito complexes again on precipitation ~~with ether or evaporation~~ of the solvent. A red solid, probably mainly a nitro isomer, was obtained by freezing a chloroform solution of $\mathrm{Ni(N,N'\text{-}diethylethylenediamine)_2(ONO)_2}$, treating the solid mass with cold petroleum ether, and filtering rapidly. However, this reverted to the normal nitrito form within a few seconds. Also, although the reaction $1,6\text{-}[\mathrm{Co(NH_3)_2(py)_2(ONO)_2}]^+ \rightarrow 1,6\text{-}[\mathrm{Co(NH_3)_2(py)_2(NO_2)_2}]^+$ is thought[14] to involve a mixed nitro–nitrito intermediate, such species were not detected in the equilibrium studied here.

The solution nitro ⇌ nitrito equilibrium mentioned above is of interest in relation to previous studies[15] on the kinetics of the formation of nitrito complexes of $\mathrm{Co^{III}}$ and of their rearrangement to the more stable nitro analogs. For the $\mathrm{Co^{III}}$ compounds the nitro ⇌ nitrito equilibria lie well toward the nitro isomer. The formation of the nitrito complexes and the relative slowness of their rearrangement to their nitro isomers are attributed to the inertness of the $\mathrm{Co^{III}\text{–}O}$ bond.

With the labile nickel(II) complexes studied here, the establishment of the equilibrium in solution, where the influence of lattice forces has been removed, shows that the factors deciding the mode of coordination of the nitrite ion may be finely balanced.

The enthalpy term for the equilibrium $\mathrm{Ni(N,N'\text{-}diethylethylenediamine)_2(ONO)_2} \rightleftharpoons \mathrm{Ni(N,N'\text{-}diethylethylenediamine)_2(NO_2)_2}$ favors the nitro isomer, as expected. However, the entropy term favors the nitrito form, in agreement with less steric interaction, and greater freedom of movement, when the anions bond through oxygen rather than nitrogen.[16] It appears that with N,N′-diethylethylenediamine and N,N-dimethylethylenediamine the increase in metal–anion bond energy on going from a nitrito to a nitro complex is approximately equal to the energy lost by the increased steric interaction expected for an N-bonded nitrite ion compared with one coordinated through oxygen. Changes in the steric requirements of the diamine may make either the nitro or the nitrito form much more favored, as appears to be the case for N-ethyl- and N,N-diethylethylenediamine, respectively, where solution equilibria were not observed.

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(10) Values in the range 0.05–0.09 were found by assuming curve shapes similar to those of related complexes $\mathrm{Ni(diamine)_2X_2}$, where X is an oxyanion.

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(16) This ignores solvent effects, though these are likely to be relatively small in chloroform.