kinetic inertness toward the substitution of phosphines by amines and the thermodynamic stability of the tris(phosphine) intermediates appear to be related. In fact, both are a consequence of the presence of CN^- groups in the molecule and are most likely attributable to the increased strength of the nickel–phosphorus bonds in the cyanide complexes.

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Studies of Some Nickel(II) Nitrite Complexes

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Complexes of the type $NiD_2(NO_2)_2$ were prepared where D represents any of the following chelating ligands: 2-(aminomethyl)pyridine, 2-(methylaminomethyl)pyridine, 2-(aminomethyl)-6-methylpyridine, and their saturated derivatives. Infrared and electronic spectra were used to determine the mode of bonding of the nitrite group in the complexes. Ni[2-(aminomethyl)piperidine]$_2(NO_2)_2$ was found to be a nitro complex whereas Ni[2-(methylaminomethyl)pyridine]$_2(ONO)_2$, Ni[2-(aminomethyl)-6-methylpyridine]$_2(ONO)_2$, and the corresponding piperidine complexes contained nitrito groups. It is suggested that Ni[2-(aminomethyl)pyridine]$_2(NO_2)_2$ may contain both nitro and nitrito groups. The nitrito complexes were stable in the solid state as well as in solution and did not show any isomerization.

Introduction

Earlier studies of nitrito complexes have been concerned with complexes of the type $[M(NH_3)_5ONO]^{n+}$, where M = Co(III), Cr(III), Rh(III), Ir(III), and Pt(IV), which with the exception of the Cr(III) compound rearrange to the corresponding nitro complexes.[2,3] Recently Goodgame[4] isolated some nitrito complexes of nickel(II) with disubstituted ethylenediamines and pyridine which in the solid state are quite stable with respect to isomerization to the nitro compounds. Further investigations seemed necessary to understand better the factors influencing the mode of bonding of the nitrite group.

Since nitrite complexes of nickel(II) with ethylenediamine and monosubstituted ethylenediamine gave nitro complexes[5] and the pyridine adduct formed a nitrito complex,[4] it was of interest to investigate 2-(aminomethyl)pyridine as a ligand. 2-(Aminomethyl)pyridine was considered since it is a chelating ligand which is structurally intermediate between ethylenediamine and 2,2′-bipyridine. The methyl derivatives, 2-(methylaminomethyl)pyridine and 2-(aminomethyl)-6-methylpyridine, were also used as bases, together with the corresponding saturated derivatives, 2-(aminomethyl)piperidine, 2-(methylaminomethyl)piperidine, and 2-(aminomethyl)-6-methylpiperidine.

Experimental Section

Materials.—2-(Aminomethyl)pyridine, 2-(methylaminomethyl)pyridine, and 2-(aminomethyl)-6-methylpyridine, from Aldrich Chemical Co., were used without further purification. Their saturated derivatives were obtained by reduction with sodium and alcohol[6] with a 40% yield. 2-(Aminomethyl)piperidine was obtained as a colorless oil (bp 51–52° (5 mm)) which turned yellow by exposure to the air. 2-(Methylaminomethyl)piperidine (bp 55–56° (8 mm)) and 2-(aminomethyl)-6-methylpiperidine (bp 59–60° (6 mm)) were also obtained as yellow oils.

Preparation of the Nickel(II) Nitrite Complexes.—The nickel(II) nitrite complexes were prepared in methanol by the addition of the stoichiometric amount of the chelating ligand to the nickel(II) nitrite solution.[7] The reacting mixture was left overnight.

Ni[2-(aminomethyl)piperidine]$_2$(NO$_2$)$_2$.—Red crystals were obtained in a blue solution. They were filtered, washed with cold ethanol and dry ether, and then dried under vacuum. The compound started to decompose at about 230° turning brown without melting. *Anal.* Calcd for $C_{12}H_{28}N_6NiO_4$: C, 38.01; H, 7.44; N, 22.16. Found: C, 37.59; H, 7.08; N, 21.76.

Ni[2-(aminomethyl)pyridine]$_2$(NO$_2$)$_2$.—Reddish violet crystals were formed in the methanol solution. They were washed and dried as described above. *Anal.* Calcd for $C_{12}H_{16}N_6NiO_4$: C, 39.27; H, 4.39; N, 22.90. Found: C, 38.93; H, 4.43; N, 22.52.

Ni[2-(methylaminomethyl)pyridine]$_2$(ONO)$_2$.—Blue-violet crystals were obtained after evaporation of the methanol solution to dryness and recrystallization of the crude product from absolute ethanol. *Anal.* Calcd for $C_{14}H_{20}N_6NiO_4$: C, 42.56; H, 5.10; N, 21.27. Found: C, 42.74; H, 5.36; N, 20.89.

Ni[2-(methylaminomethyl)piperidine]$_2$(ONO)$_2$.—Blue crystals were obtained after recrystallization from absolute ethanol. *Anal.* Calcd for $C_{14}H_{32}N_6NiO_4$: C, 41.29; H, 7.92; N, 20.64. Found: C, 41.23; H, 7.66; N, 21.24.

Ni[2-(aminomethyl)-6-methylpyridine]$_2$(ONO)$_2$.—Blue crystals were obtained on recrystallization of the crude product from absolute ethanol. *Anal.* Calcd for $C_{14}H_{20}N_6NiO_4$: C, 42.56; H, 5.10; N, 21.27. Found: C, 42.10; H, 5.31; N, 20.55.

Ni[2-(aminomethyl)-6-methylpiperidine]$_2$(ONO)$_2$.—Blue-gray crystals were recrystallized from absolute ethanol. *Anal.*

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[1] Abstracted from the Ph.D. thesis of L. El-Sayed.

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TABLE I

INFRARED FREQUENCIES OF THE NO_2^- GROUPS (CM^{-1})

Compound	ν_{as}	ν_s	ν_b
$NaNO_2$[b,c]	1328 ± 2	1261 ± 2	828
Ni[2-(aminomethyl)pyridine]$_2$(NO_2)$_2$	1338 s, 1368 s	1318 sh, 1251 m	813, 819[a]
Ni[2-(methylaminomethyl)pyridine]$_2$(ONO)$_2$	1375 s	1180 s	817, 822[a]
Ni[2-(aminomethyl)-6-methylpyridine]$_2$(ONO)$_2$	1351 b	1212 s	859
Ni[2-(aminomethyl)piperidine]$_2$(NO_2)$_2$	1334 s	1315 s	810
Ni[2-(methylaminomethyl)piperidine]$_2$(ONO)$_2$	1372 b	1208 s	828, 832[a]
Ni[2-(aminomethyl)-6-methylpiperidine]$_2$(ONO)$_2$	1341 b	1206 s	813, 827[a]

[a] Assignment was uncertain owing to the presence of a ligand band in this region. [b] J. Chatt, L. A. Duncauson, B M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959). [c] R. E. Weston and T. F. Brodasky, *J. Chem. Phys.*, **27**, 683 (1957).

Calcd for $C_{14}H_{32}N_6NiO_4$: C, 41.29; H, 7.92; N, 20.64. Found: C, 41.22; H, 7.64; N, 20.06.

Preparation of the Nickel(II) Chloride and Nickel(II) Isothiocyanate Complexes.—Methods similar to those described in the literature[7] were used in the preparation of the complexes. Violet to blue crystals were obtained from the ethanol solutions.

Physical Measurements.—The infrared spectral data were obtained on a Beckman IR-4 spectrophotometer equipped with sodium chloride optics. The position of the bands was determined more precisely on an expanded scale (0.1 μ/in.). Calibration was made using a polystyrene film. Nujol and hexachlorobutadiene mulls were used in the 800–850- and 1200–1500-cm^{-1} regions, respectively. The far-infrared spectra were obtained on the same Beckman IR-4 spectrophotometer by interchanging to the potassium bromide optics. Calibration was made using $K_2Ca[Ni(NO_2)_6]$ which showed a wagging mode,[8] $\rho_w(NO_2)$, at 462 cm^{-1}. The potassium bromide technique was used in the far-infrared region.

The electronic spectra were recorded using a Cary Model 14 recording spectrophotometer. The Nujol mull spectra were obtained using the technique described by Kleinberg, *et al.*[9]

Chemical Analyses.—C, H, and N analyses were performed by Alfred Bernhardt Mikroanalytischen Laboratorium, Mülheim (Ruhr), Germany.

Results and Discussion

Infrared Spectra.—The nitrite group (C_{2v} symmetry) has three fundamental vibrational modes which are all active in the infrared region and upon coordination the band positions are shifted as compared to the free nitrite frequencies. The shifts exhibited by the asymmetric and symmetric stretching frequencies are used to indicate the mode of bonding of the nitrite group, whether it coordinates through the nitrogen atom (nitro complex) or through the oxygen atom (nitrito complex).[4] The first assignments for the NO_2 and ONO ligands were made by observing changes in the infrared spectrum of nitritopentaamminecobalt(III) chloride as it isomerizes to nitropentaamminecobalt(III) chloride.[10] In this work the infrared bands for the nitrite groups were identified by comparison of the nitrite complexes with the nickel chloride and nickel isothiocyanate analogs. The infrared frequencies for the nitrite bands are listed in Table I. The infrared spectrum of a nitrito complex, Ni[2-(aminomethyl)-6-methylpyridine]$_2$(ONO)$_2$, is shown in Figure 1.

In the case of nitro complexes, both $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ are shifted to higher frequencies as compared to the free nitrite ion.[2,3,8,10,11] In the nitrito complexes, $\nu_{as}(NO_2)$ lies at higher and $\nu_s(NO_2)$ at lower values than the free-ion frequencies.[10,12,13] With Ni[2-(aminomethyl)piperidine]$_2$(NO_2)$_2$ both $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ lie at higher frequencies, a result which suggests the presence of nitro rather than nitrito groups. In fact, this compound is red like the other known nitro compounds of nickel such as $Ni(NH_3)_4(NO_2)_2$[14] and Ni(monosubstituted ethylenediamine)$_2$(NO_2)$_2$.[5]

In the bis[2-(aminomethyl)pyridine]nickel(II) nitrite complex, two sets of bands were obtained for $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$. The two values of the $\nu_{as}(NO_2)$ are higher than in the free ion. For the $\nu_s(NO_2)$ one band lies at a lower and the other at a higher frequency. This implies the presence of both nitro and nitrito groups in the complex. This compound is neither red like the typical nitro complexes of nickel,[5,14] nor blue like the nitrito complexes;[4] it is red-violet. The other nickel complexes listed in Table I are blue and the values of $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ are in accord with the presence of nitrito groups, ν_{as} being shifted to higher frequencies than in the case of $NaNO_2$, whereas ν_s is shifted to lower values. The $\nu_s(NO_2)$ lies as low as 1180 cm^{-1} for the 2-(methylaminomethyl)pyridine complex and as high as 1212 cm^{-1} for the 2-(aminomethyl)-6-methylpyridine compound, but always remains at lower values than the $\nu_s(NO_2)$ of the free NO_2^-.

All of the nickel nitrite complexes isolated in this work have only one band for the bending mode, $\nu_b(NO_2)$. The *cis*-dinitro compounds[11] have two bands belonging to that mode, because the in-phase as well as the out-of-phase vibrations are infrared active. Consequently, it is assumed that the NO_2^- groups in the nickel complexes are in the *trans* positions.

Far-Infrared Spectra.—The far-infrared spectra of the nickel nitrite complexes were compared with those of the corresponding nickel halide analogs to check for the presence of bands which could be attributable to the wagging mode ρ_w. The presence of this band is another evidence for the nitro complexes.[13,15,16] Ni[2-

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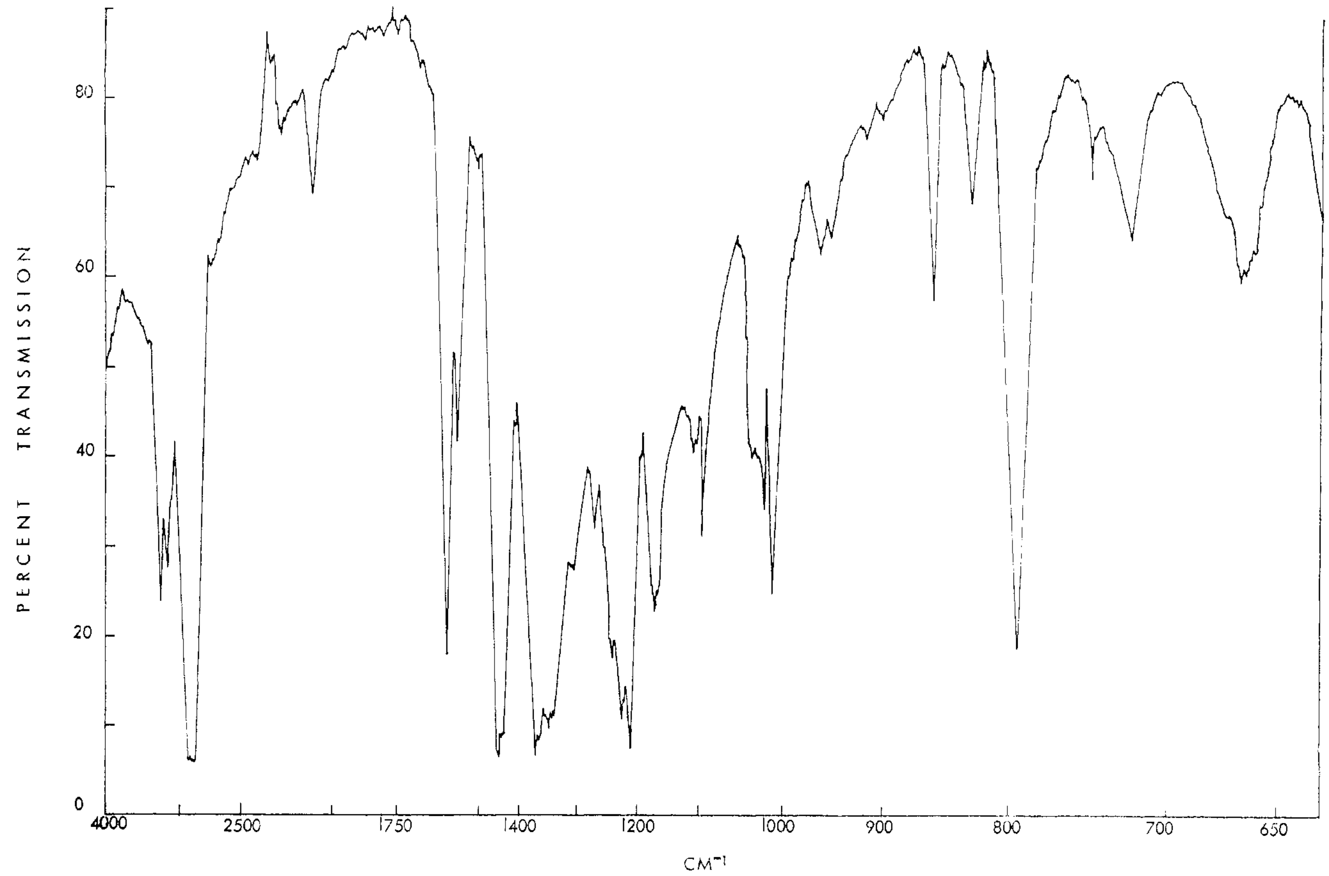

Figure 1.—Infrared spectrum of the nitro complex Ni[2-(aminomethyl)-6-methylpyridine]$_2$(ONO)$_2$ in Nujol mull.

(aminomethyl)piperidine]$_2$(NO$_2$)$_2$ has an absorption band at 637 cm^{-1} which can be attributed to ρ_w. The 2-(aminomethyl)pyridine complex has ligand bands in this region so that no assignment could be made for a wagging mode. No bands assignable to ρ_w were found for the blue complexes which have been formulated as pure nitrito complexes in Table I.

Electronic Spectra.—The electronic absorption spectra of the nickel nitrite complexes and their analogous nickel isothiocyanate compounds were studied in the visible and infrared regions. Mull and solution spectra were made; the energies of the maxima are shown in Table II. Dichloromethane was used as solvent wherever possible to minimize the interactions between the solvent and the solute, but it was necessary to use methanol for four complexes as shown in Table II.

Since the nitro group is a strong-field ligand and the nitrito group a weak-field ligand, it is possible to differentiate between nitro and nitrito complexes by means of their electronic spectra.[17] Hare and Ballhausen[18] showed that the polarized crystal spectrum of Ni(NH$_3$)$_4$(NO$_2$)$_2$ is unlike that of Ni(NH$_3$)$_4$(NCS)$_2$ owing to the different positions of the isothiocyanate and the nitro groups in the spectrochemical series. The nitro groups were shown[14] to coordinate through the nitrogen atom and to be *trans* in Ni(NH$_3$)$_4$(NO$_2$)$_2$. As shown in Table II, the energies of the bands in the nickel nitrite complexes are all very close to those observed for their isothiocyanate analogs, with the exception of Ni[2-(aminomethyl)piperidine]$_2$(NO$_2$)$_2$. The absorption maxima of this complex are shifted to higher energies and correspond closely with those of Ni(NH$_3$)$_4$(NO$_2$)$_2$ thus indicating coordination through the nitrogen atom. The presence of nitro groups in this complex was also supported by the infrared spectral data and the presence of a wagging mode in the far-infrared region. In methanol, however, the band maxima lie at lower energies than in the mull spectra. The 2-(aminomethyl)piperidine complex is practically insoluble, but if shaken in methanol, the red crystals give a light blue solution. There are two possibilities: displacement of the nitro groups by solvent molecules or isomerization to the nitrito complex. For the other nickel nitrite complexes the electronic spectra provide evidence for their formulation as nitrito complexes.

The nickel nitrite complex with 2-(aminomethyl)piperidine was characterized as a nitro compound. When the size of the ligand was increased by a methyl group on the piperidine ring (2-(aminomethyl)-6-methylpiperidine) or a methyl-substituted nitrogen (2-(methylaminomethyl)piperidine), nitrito complexes were formed. Since the nitrito group (structure I) requires less space in the coordination sphere of nickel(II) ion than the nitro group (structure II), only the nitrito complex will be formed with the more bulky ligands. This conclusion is in accordance with the

[17] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London, 1962, p 109.

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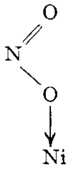
TABLE II

ABSORPTION MAXIMA OF $NiD_2(NO_2)_2$ AND $NiD_2(NCS)_2$

Compound	State	Absorption max, cm^{-1} (ϵ, l. $mole^{-1}$ cm^{-1})
Ni[2-(aminomethyl)pyridine]$_2$(NO_2)$_2$	Mull	*a*, 18,180, 10,000
Ni[2-(aminomethyl)pyridine]$_2$(NO_2)$_2$	In CH_3OH	*a*, 17,860 (13), 11,000 (12)
Ni[2-(aminomethyl)pyridine]$_2$(NCS)$_2$	Mull	*a*, 17,960, 10,960
Ni[2-(methylaminomethyl)pyridine]$_2$(ONO)$_2$	Mull	*a*, 17,860, 10,200
Ni[2-(methylaminomethyl)pyridine]$_2$(ONO)$_2$	In CH_3OH	~24,390 sh, 17,860 (20), 11,000 (12)
Ni[2-(methylaminomethyl)pyridine]$_2$(NCS)$_2$	Mull	*a*, 17,540, 10,700
Ni[2-(aminomethyl)-6-methylpyridine]$_2$(ONO)$_2$	Mull	*a*, 17,240, 10,200
Ni[2-(aminomethyl)-6-methylpyridine]$_2$(ONO)$_2$	In CH_3OH	*a*, 16,900 (20), 10,200 (15)
Ni[2-(aminomethyl)-6-methylpyridine]$_2$(NCS)$_2$	Mull	*a*, 17,600, ~15,040 sh, 10,750, 10,140
Ni[2-(aminomethyl)piperidine]$_2$(NO_2)$_2$	Mull	*a*, 20,200, 12,345, ~11,360 sh
Ni[2-(aminomethyl)piperidine]$_2$(NO_2)$_2$	In CH_3OH	*a*, 17,730 (13), 10,870 (9)
Ni[2-(aminomethyl)piperidine]$_2$(NCS)$_2$	Mull	28,170, 17,540, 10,750
Ni[2-(methylaminomethyl)piperidine]$_2$(ONO)$_2$	Mull	27,930, 22,120, 17,480, 10,810
Ni[2-(methylaminomethyl)piperidine]$_2$(ONO)$_2$	In CH_2Cl_2	*a*, ~20,830 sh, 18,050 (12), 10,990 (18)
Ni[2-(methylaminomethyl)piperidine]$_2$(NCS)$_2$	Mull	27,780, 17,700, 10,500
Ni[2-(aminomethyl)-6-methylpiperidine]$_2$(ONO)$_2$	Mull	~22,420 sh, 16,900, 10,200
Ni[2-(aminomethyl)-6-methylpiperidine]$_2$(ONO)$_2$	In CH_2Cl_2	*a*, 17,180 (11), 10,590 (10)
Ni[2-(aminomethyl)-6-methylpiperidine]$_2$(NCS)$_2$	Mull	28,170, 17,100, 9430
$Ni(NH_3)_4(NO_2)_2$[b]	Solid	20,350, 19,900, ~12,750 sh, 12,000, 11,200
$Ni(NH_3)_4(NCS)_2$[b]	Solid	28,000, 27,900, 17,500, 17,350, ~13,000 sh, 10,750

[a] Obscured by strong ultraviolet absorption. [b] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

work of Goodgame[4] concerning the formation of nitrito complexes with bulky disubstituted ethylenediamines as ligands.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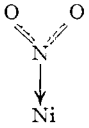
II

With the 2-(aminomethyl)pyridine complex the infrared spectrum supports the presence of both nitro and nitrito linkages, but the electronic spectrum only gives evidence for the nitrito group. One possibility is that the extra peaks in the infrared spectrum could arise from solid-state effects. Before commenting further, it is of interest to consider the 2,2′-bipyridine–nickel complex in which the chelating ligands are coplanar with the nickel ion and a red nitro complex was obtained. This is in contrast to $Ni(py)_4(ONO)_2$ where the pyridine rings form an angle of ~45° with the Ni–N_4 plane[4] so that coordination of the nitrite group occurs through the oxygen. In the ligand 2-(aminomethyl)pyridine, which is structurally intermediate between ethylenediamine and 2,2′-bipyridine, the planar pyridine ring must form an appreciable angle with the Ni–N_4 plane in order to provide enough steric effect to cause the approach of the nitrito group rather than the nitro group. Whether or not both isomers are formed with 2-(aminomethyl)pyridine must be left open to question. With the introduction of a methyl on the pyridine ring or on the amine nitrogen, sufficient steric repulsion is gained between the ligand and nitrite group so that only nitrito complexes are formed.

The nickel nitrito complexes discussed in this paper do not show any isomerization in solution. This is in contrast to Ni(N,N′-dimethylethylenediamine)$_2$(ONO)$_2$ and Ni(N,N′-diethylethylenediamine)$_2$(ONO)$_2$ which exist in a nitro–nitrito equilibrium in chloroform.[5] The increase of steric effects (although a difference in basicity of the ligands could also be an important factor) in the chelating ligands considered in this work makes the nitrito form much more favored than the nitro isomer so that solution equilibria are not observed.

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