Contribution from the Department of Chemistry, Imperial College of Science and Technology, London S.W. 7, United Kingdom

Some New Amine Complexes of Nickel Nitrite and a Mixed Nitro-Nitritocomplex

D. M. L. Goodgame and M. A. Hitchman[1]

Received January 28, 1969

The preparation, electronic and infrared (2000-200 cm^{-1}) spectra of several new amine complexes of nickel nitrite are reported. The solid compounds $NiL_4(ONO)_2$ (L ≡ pyridine, 3-methylpyridine and 4-methylpyridine) are nitrito-complexes, but dissociate in benzene to give 2:1 complexes containing chelating anions. The complex Ni(o-phenylenediamine)$_2$(NO$_2$)$_2$ is a nitro-complex, while Ni(NNN'N'-tetraethylethylenediamine)(NO$_2$)$_2$ contains chelating nitrite groups. The manner of nitrite bonding in the solid complexes is apparently related to the steric requirements of the amines. With isoquinoline, nickel nitrite forms a mixed nitro-nitrito-complex of the type Ni(isoquinoline)$_4$(NO$_2$)$_2$. xNi(isoquinoline)$_4$(ONO)$_2$. Bands at 270-295 cm^{-1} for the nitrito-complexes are assigned as ν(Ni—O).

Introduction

Previous studies on amine and diamine complexes of nickel nitrite have suggested[2-5] that the method of nitrite coördination is greatly influenced by the steric nature of the amine ligands. Thus the chelating ligand 2,2'-bipyridine forms a nitro-complex[5] in which the phenyl groups probably lie essentially in the xy plane and so do not interact sterically with the nitrite groups. The compound $Ni(py)_4(ONO)_2$[6], however, in which significant steric interaction probably occurs between the phenyl groups and the anions, is a nitrito-complex,[2] and 2-methylpyridine, in which the methyl groups must cause considerable steric crowding around the nickel ion, forms only a 2:1 complex in which each nitrite group chelates.[3]

During extension of this work[7] to include other amines of differing steric influence, we isolated an isoquinoline complex which appears to contain both nitro- and nitrito-groups. We report here the properties of this compound, and those of some new complexes with related ligands, and also the low frequency infrared spectra of some nitrito-complexes.

Experimental Section

Analyses. C, H, N, and O were determined by the Microanalytical Laboratory, Imperial College. Nitrite was determined volumetrically using ceric sulphate.

Preparation of Compounds. Ni(3-methylpyridine)$_4$(ONO)$_2$. A methanolic solution of nickel nitrite was prepared matathetically from nickel nitrate hexahydrate and sodium nitrite. The resulting mixture was well cooled (acetone/solid CO_2) and then filtered. An excess of 3-methylpyridine was added and the mixture taken to dryness on the vacuum line. The crude product was recrystallised from acetone containing a little 3-methylpyridine and gave large, blue crystals in 50% yield. *Anal.* Calcd. for $C_{24}H_{28}N_6NiO_4$: C, 55.08; H, 5.39; N, 16.07; O, 12.23. Found: C, 55.21; H, 5.40; N, 16.08.

Ni(4-methylpyridine)$_4$(ONO)$_2$. This compound was prepared as for the 3-methylpyridine complex. However, it precipitated directly from the reaction mixture as a pale blue crystalline solid in 60% yield. *Anal.* Found: C, 55.52; H, 5.36; O, 12.39.

Ni(isoquinoline)$_4$(NO$_2$)$_2$. A brown, microcrystalline precipitate was obtained by the slow addition of a methanolic solution of nickel nitrite to a large excess of isoquinoline in a small amount of methanol. The complex could be recrystallised from acetone or nitromethane to give purple crystals in 70% yield. *Anal.* Calcd. for $C_{36}H_{28}N_6NiO_4$: C, 64.79; H, 4.23; N, 12.60; O, 9.59; NO_2^-, 13.79. Found: C, 64.18; H, 4.21; N, 12.70; O, 9.54; NO_2^-, 13.60.

Ni(NNN'N'-tetraethylethylenediamine)(NO$_2$)$_2$. This was obtained, in 70% yield, as bright green crystals by the method described previously[3] for its analog with NNN'N'-tetramethylethylenediamine. *Anal.* Calcd. for $C_{10}H_{24}N_4NiO_4$: C, 37.18; H, 7.49; N, 17.35. Found: C, 37.37; H, 7.26; N, 17.56.

Ni(o-phenylenediamine)$_2$(NO$_2$)$_2$. Addition of a saturated solution of *o*-phenylenediamine in an equivolume mixture of acetone and methanol to a methanolic solution of nickel nitrite gave a red, microcrystalline precipitate in 40% yield. *Anal.* Calcd. for $C_{12}H_{16}N_6NiO_4$: C, 39.26; H, 4.39; N, 22.91. Found: C, 39.00; H, 4.38; N, 23.20.

---

(1) Present address: Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, England.
(2) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 3, 1389 (1964).
(3) D. M. L. Goodgame and M. A. Hitchman *ibid.*, *4*, 721 (1965).
(4) D. M. L. Goodgame and M. A. Hitchman *ibid.*, *5*, 1303 (1966).
(5) L. El-Sayed and R. O. Ragsdale *ibid.* 6, 1640 (1967).
(6) We shall use the following ligand abbreviations: py = pyridine; 3-mepy = 3-methylpyridine; 4-mepy = 4-methylpyridine; i-quin = isoquinoline; *o*-phen = orthophenylenediomine, teteen = NNN'N'-tetraethylethylenediamine.
(7) M. A. Hitchman, Ph. D. Thesis, University of London, 1966.

Table I. The Infrared Frequencies of the Nitrite Groups and Metal-Anion Stretches in the Complexes.

Compound	state	ν(N—O), cm^{-1}	$\delta(NO_2)$, cm^{-1}	νNi—O, cm^{-1}
$Ni(py)_4(ONO)_2$	solid [a]	1393 s, 1114 vs	825 m	292 s
	C_6H_6	1300 m, 1190 vs	860 w br, 840 w	
$Ni(3\text{-}mepy)_4(ONO)_2$	solid	1389 s, 1126 vs	[b]	287 s
	C_6H_6	1300 m, 1195 vs	860 w br	
$Ni(4\text{-}mepy)_4(ONO)_2$	solid	1401 s, 1144 vs, 1119 vs	[b]	288 sh, 276 s
	C_6H_6	[b] 1190 vs	860 w br	
$Ni(i\text{-}quin)_4(NO_2)_2$	solid	1397 s, 1314 ms, 1124 vs	[b]	289 sh [c], 255 s br [c]
$Ni(teteen)(NO_2)_2$	solid	[b] 1199 vs	[b]	[b]
	C_6H_6	[b] 1200 vs	[b]	

[a] Measured as nujol and hexachlorobutadiene mulls. [b] Band obscured by amine absorption. [c] these bands are probably due to both $\nu_{Ni\text{-}O}$ and ν_{Ni-N} see text

Physical Measurements. Infrared spectra in the range 400-200 cm^{-1} were obtained with a Grubb-Parsons D.M. 4 Spectrometer. The other measurements were carried out as described previously.[3]

Results and Discussion

Infrared Spectra. The infrared frequencies of the nitrite groups in the complexes are listed in Table I and, as in previous work[2-4,8] the shifts of the two ν(N—O) bands from their free ion positions can be used to infer the manner of nitrite coordination.

The values of ν(N—O) for solid $Ni(3\text{-}mepy)_4(ONO)_2$ and its 4-mepy analog are very similar to those[2] of $Ni(py)_4(ONO)_2$ and suggest that in these compounds the anions are present as nitrito-groups. However, benzene solutions of these complexes show bands characteristic of chelating nitrite groups, as does $Ni(teteen)(NO_2)_2$ in both the solid state and in benzene.

The 4:1 compound of nickel nitrite with isoquinoline has a more complicated set of nitrite bands. There are two strong nitrite peaks at frequencies close to those of the nitritogroups in $NiL_4(ONO)_2$ [L ≡ py, 3-mepy and 4-mepy]. However, in addition to these, the isoquinoline complex also shows a medium-strong band at 1314 cm^{-1} suggesting the presence of nitro-groups. The spectrum of the compound in the region 1000-1700 cm^{-1} is shown in Figure 1, together with that of the corresponding bromide for comparison.

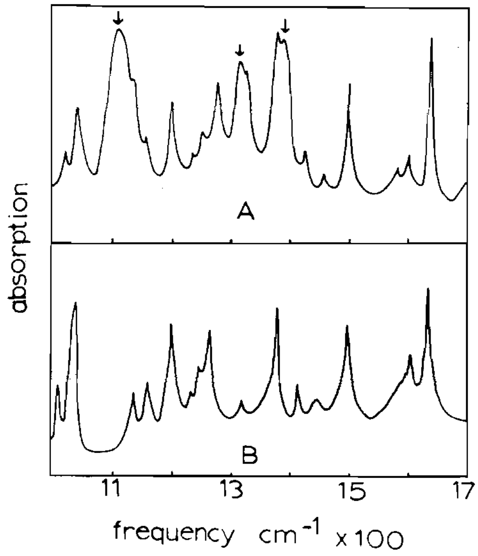

Figure 1. The infrared spectra of: A $Ni(isoquinoline)_4(NO_2)_2$; B $Ni(isoquinoline)_4Br_2$. The nitrite bands are indicated by arrows.

Although $Ni(o\text{-}phen)_2(NO_2)_2$ exhibited a strong band at ~1280 cm^{-1} which could be due to nitro-groups, the nitrite frequencies could not be identified unambiguously because the amine bands altered significantly on going from one control compound to another.

In addition to the perturbed fundamental vibrations of the anions, metal nitrite complexes exhibit bands in the region 700-200 cm^{-1} assignable to metal-ligand vibrations. The nitro-complexes $K_2CaNi(NO_2)_6$ and $K_2BaNi(NO_2)_6$ have bands in the ranges 430-460 (m), 280-295 (s) and 250-260 (w) cm^{-1} and these have been assigned as ρ_w, ν(Ni—N) and ρ_r respectively.[10]

Although no nitrito-complexes had previously been studied in this region, it had been suggested[9,11] that the wagging vibration ρ_w should occur at significantly lower energy in a nitrito-complex than in a similar nitro-complex.

The three nitrito-complexes $NiL_4(ONO)_2$[L = py, 3-mepy and 4-mepy] each show a strong band or pair of bands in the range 270-295 cm^{-1} and we assign these as ν(Ni—O). These frequencies are therefore, quite close to the values of ν(Ni—N) found for $Ni(NO_2)_6^{4-}$, and are also similar to ν(M—O) in comparable nitrate and sulphate complexes (*e.g.* ν(Co—O) = 271 s 316 sh in $Co(NO_3)_2$[12]). No bands assignable to ρ_w and ρ_r were observed in the three nitrito-complexes, and these probably occur below 200 cm^{-1}. The compound $Ni(i\text{-}quin)_4(NO_2)_2$ shows a strong, broad band with distinguishable maxima at 280 cm^{-1} and 252 cm^{-1}. It seems likely that this is a superposition of bands due to ν(Ni—O) from the nitrito-groups and ν(Ni—N) and ρ_r from the nitro-groups.

The frequency ρ_w due to the nitro-groups was not observed, but this is not surprising as it is probably fairly weak, and isoquinoline has a strong band at 470 cm^{-1}.

---

(8) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley and Sons, Inc., New York, N. Y. 1963 pp. 151-155. Note, however, that the values of ν_{as} and ν_s for uncoordinated NO_2^- are incorrectly reversed in this reference; see A. Tramer, *Compt. Rend. 248,* 3546 (1959) and references therein.

(9) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc., 80,* 4817 (1958).

(10) See reference 8, page 153 for a description of these modes.

(11) G. Blyholder and A. Kittila, *J. Phys., Chem., 67,* 2147 (1963).

(12) J. R. Ferraro and A. Walker, *J. Chem. Phys., 42,* 1273, (1965).

Table II. The Electronic Spectra of the Complexes

Compound	State	Absorption max., cm^{-1}	(E_{molar} for solns)
$\mathrm{Ni(py)_4(ONO)_2}$	Solid ^{a}	10,400, 13,000 sh ^{b}	16,900
	$\mathrm{C_6H_6}$	10,000 (4) ^{c}	16,400 (15)
$\mathrm{Ni(3\text{-}mepy)_4(ONO)_2}$	Solid	10,600, 13,000 sh ^{b}	17,400, 22,000 sh ^{b}
	$\mathrm{C_6H_6}$	9,700 (7) ^{c}	16,300 (15)
$\mathrm{Ni(4\text{-}mepy)_4(ONO)_2}$	Solid	10,500, 13,000 sh ^{b}	17,150, 23,300 sh ^{b}
	$\mathrm{C_6H_6}$	9,500 (6) ^{c}	16,100 (18)
$\mathrm{Ni(i\text{-}quin)_4(NO_2)_2}$	Solid	11,000	17,400 21,280
Ni(*o*-phen)$_2$(NO$_2$)$_2$	Solid	11,000 sh, 12,500	19,600 sh, 21,200
$\mathrm{Ni(teteen)(NO_2)_2}$	Solid	9,300 ^{a}	15,600 25,600 sh
	$\mathrm{C_6H_6}$	9,200 (6) ^{a}	15,600 (16), 25,300 sh (30)

^{a} Diffuse reflectance spectrum. ^{b} Very weak band assigned as a spin-forbidden transition. ^{c} Band assymetric to lower energy.

Electronic Spectra. The band maxima in the electronic spectra of the complexes are listed in Table II. The spectra of the solid complexes $\mathrm{NiL_4(ONO)_2}$ (L = py, 3–mepy and 4–mepy), resemble those of other, similar nitrito-complexes[2] and are quite consistent with the position of the nitrito-group just below pyridine in the spectrochemical series. These blue compounds produce emerald green solutions in benzene, with each of the observed electronic transitions shifting to lower energy by 500-1000 cm^{-1}, (Figure 2 shows the solid state and solution spectra of $\mathrm{Ni(4\text{–}mepy)_4(ONO)_2}$.

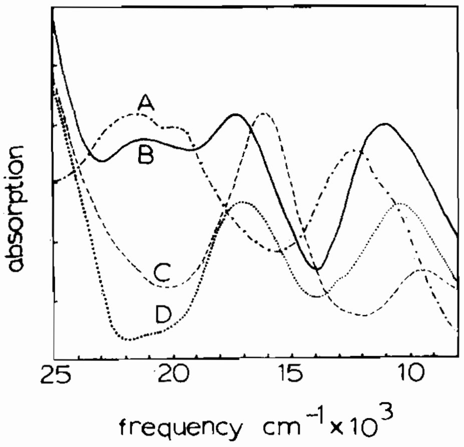

Figure 2. The electronic spectra (arbitrary absorbance units) of: A Ni(*o*-phenylenediamine)$_2$(NO$_2$)$_2$ by reflectance; B Ni(isoquinoline)$_4$(NO$_2$)$_2$ by reflectance; C A solution of Ni(4-methylpyridine)$_4$(ONO)$_2$ in benzene; D Ni(4-methylyridine)$_4$(ONO)$_2$ by reflectance.

This energy shift is consistent with a dissociation of the type $\mathrm{NiL_4(ONO)_2 \rightarrow NiL_2(NO_2)_2 + 2L}$ on dissolving the compounds in benzene. The six coordination of the nickel ion in solution is maintained by chelation of the nitrite groups. It is known that the compounds $\mathrm{NiL_4I_2}$ (L = py and 3–mepy) also dissociate in solution to form the pseudotetrahedral species $\mathrm{NiL_2I_2}$.[13] The electronic spectrum of $\mathrm{Ni(teteen)(NO_2)_2}$ is also consistent with a distorted octahedral environment for the nickel ion with chelation of each nitrite group. The electronic transitions in the red complex Ni(*o*–phen)$_2$(NO$_2$)$_2$ are at considerably higher energy (Figure 2) than those of the complexes containing oxygen bonded nitrite groups. This suggests that Ni(*o*–phen)$_2$(NO$_2$)$_2$ contains nitrogen bonded anions, as the nitro-group lies at the strong end of the spectrochemical series (*o*–phen is known to produce a ligand field very similar to pyridine, having a value of 10Dq = 10.650 cm^{-1} in Ni(*o*–phen)$_3^{2+}$).[14,15]

The electronic spectrum of the purple complex $\mathrm{Ni(i\text{–}quin)_4(NO_2)_2}$ (Figure 2) is quite unlike that of any of the other nickel nitrite complexes but is rather similar to the spectrum of Ni(NN'dimethylethylenediamine)$_2$(NO$_2$)$_2$ in chloroform in which it is thought that a nitro-nitrito equilibrium occurs.[4] The reflectance spectrum of $\mathrm{Ni(i\text{–}quin)_4(NO_2)_2}$ seems to be a superposition of the spectra of two isomeric forms of this compound, one a nitrito-complex and the other a nitro-complex. The broad absorption at 11,000 cm^{1-} probably contains the first spin-allowed transitions which occur at ~10,000 cm^{-1} and ~12,000 cm^{-1} in similar nitrito- and nitro-complexes respectively, while the greater separation of the second spin - allowed transitions of the two isomers allows these to be resolved as the peaks at 17,400 and 21,280 cm^{-1}. The electronic spectrum thus suggests that the formula of the complex is better written $\mathrm{Ni(i\text{–}quin)_4(NO_2)_2 \,.\, xNi(i\text{–}quin)_4(ONO)_2}$. This is in accord with the infrared results. It is unlikely that the species $\mathrm{Ni(i\text{–}quin)_4(NO_2)(ONO)}$ is present in any quantity, as this would presumably have an electronic spectrum intermediate between those of a nitro-complex and a nitrito-complex and not the superposition of spectra actually observed. The facts that the single crystals of $\mathrm{Ni(i\text{–}quin)_4(NO_2)_2 \,.\, xNi(i\text{–}quin)_4(ONO)_2}$ all look identical under the polarizing microscope, and that the infrared and electronic spectra did not alter on recrystallization, suggest that the two linkage isomers are present in the same crystal lattice, rather than as a physical mixture. The compound thus resembles in this respect $\mathrm{Ni[(C_6H_{11})(C_6H_5)_2P]_2Br_2}$ in which both planar and tetrahedral isomers occur in the same lattice.[16]

Discussion

It was previously suggested[4] that the anions in nickel nitrite complexes bond via nitrogen when the other

---

[13] R. H. Holm, G. W. Everett, and W. Horrocks, *J. Am. Chem. Soc.*, *88*, 1071 (1966).

[14] D. R. Marks, D. J. Phillips, and J. P. Redfern, *J. Chem. Soc.* (*A*), 1464 (1967).

[15] J. A. Kakazai and G. A. Melson, *Inorg. Chim. Acta*, *2*, 186 (1968).

[16] B. T. Kilbourn and H. M. Powell, *Proc. Chem. Soc.*, 207 (1963).

ligands offer little or no steric hindrance and via oxygen when significant steric interaction is present. In agreement with this, Ni(o–phen)$_2$(NO$_2$)$_2$, in which the benzene rings are probably essentially in the xy plane, is a nitro-complex but the compounds NiL$_4$(ONO)$_2$ [L = py, 3–mepy and 4–mepy] in which the heterocyclic rings are probably at a significant angle to the NiN$_4$ plane, are nitrito-complexes. It is therefore rather surprising that the 4:1 isoquinoline compound should exist in a nitro-form, even as a component in a mixed nitro-nitrito complex, as isoquinoline is expected to produce a similar, or even greater anion-amine steric interference than pyridine. The orientations of the relatively large isoquinoline ligands, however, are likely to be strongly influenced by intermolecular crystal packing energies, and presumably in the particular lattice adopted some of the molecules have amine configurations producing small enough steric interference to allow nitro-coordination of the anions. An x-ray examination of the crystals of the isoquinoline complex would certainly be interesting. It may be noted in this context that in Ni(4–mepy)$_4$(ONO)$_2$ ν(Ni–O) and the lower frequency band ν(N–O) are both split, suggesting that the metal-anion bonding may vary in the molecules comprising the lattice of this compound. Also, El-Sayed and Ragsdale observed nitrite infrared bands assignable to both nitro- and nitrito groups in solid Ni[2–(aminomethyl)pyridine]$_2$(NO$_2$)$_2$. However, the electronic spectrum of this compound suggested that only nitrito groups are present, so that no firm conclusions can yet be drawn about the nature of the metal-nitrite bonding in this complex.

Acknowledgement. One of us (M.A.H.) thanks the S.R.C. for a maintenance grant.