

Inhibition of Reactivity in Square Planar Complexes of Ni(II) with 2,6-Disubstituted Pyridines. A Novel Effect in Steric Hindrance

W. L. DARBY and L. M. VALLARINO*

Department of Chemistry, Auburn University, Auburn, Ala. 36830, U.S.A.

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The reaction of Ni(II) halides or thiocyanate with doubly hindered substituted (2,6-dimethyl-, 2,3,6-trimethyl-, 2,4,6-trimethyl-) pyridines, when carried out under controlled conditions to prevent hydrolysis, yields a series of crystalline complexes of the general formula $[NiX_2L_2]$ ($X = Cl, Br, I, NCS$), having a trans-planar geometry. These complexes are unique among the many known Ni(II)-pyridine derivatives in that they are inert to exchange with other potential ligands, including water, and are not attacked even by strong mineral acids. The reasons for this inertness are discussed in terms of the electronic and steric properties of the complexes.

Introduction

The relative importance of electronic and steric effects in coordination chemistry has been the object of extensive investigation, especially for those transition metal ions, such as Ni(II), Co(II), and Cu(II), which can exhibit a variety of coordination numbers and geometries. Among the ligands, pyridine and its substituted derivatives have proven to be remarkably interesting and versatile, for they offer a fairly wide range of electronic and steric requirements while maintaining constant the fundamental nature of the ligating atom. The nickel(II) complexes of substituted pyridines, for example, have been reported to exist as square-planar, tetrahedral, trigonal bipyramidal, or octahedral species [1–6], depending on the particular substituted pyridine, or on the anion, or both.

The information available in the literature generally suggests that steric hindrance acts as a limiting factor in regard to the number of substituted pyridines that can coordinate to each metal ion. For example, four – but not more than four – ‘unhindered’ pyridines (e.g., pyridines with no substituents adjacent to the N-donor atom) were found to coordinate to Ni(II) salts, yielding 4:1 complexes of the

general type NiX_2L_4 ($X =$ mononegative ligand) [1, 3]. In contrast, ‘mono-hindered’ ligands (e.g., those with one substituent adjacent to the N-donor atom) were found to form almost exclusively 2:1 complexes [2, 3] of formula NiX_2L_2 , a few 3:1 complexes, NiL_3X_2 , being exceptionally obtained with $X = NCS$. As for the ‘doubly-hindered’ ligands (e.g. 2,6-dimethylpyridine), the scarce available data [2, 7–9] seemed to indicate considerable difficulties in the preparation of Ni(II) complexes; furthermore, even when crystalline products were formed, they often appeared to be mixtures and could not be satisfactorily characterized.

The synthetic difficulties encountered for complexes of doubly-hindered pyridines were originally believed to result from their high steric hindrance. Recently, however, the question has been reopened by a report on the preparation of a series of 2:1 complexes of the bulky tertiary amine quinuclidine with a series of transition metal ions [10], including Ni(II). That work suggested that the occurrence of hydrolysis, rather than steric hindrance, might be primarily responsible for the difficulty in forming Ni(II) complexes of the doubly-hindered pyridines. With this in mind, we set out to investigate the reaction of several doubly-hindered pyridine ligands (2,6-dimethylpyridine, 2,3,6-trimethylpyridine, 2,4,6-trimethylpyridine) with Ni(II) salts, under conditions carefully controlled to prevent hydrolysis. We thus succeeded in obtaining a complete series of the desired complexes, whose unusual properties we report in this paper.

Experimental

Starting Materials

The pyridine derivatives (Aldrich Chemical Co.) were dehydrated over KOH pellets, distilled under reduced pressure, and stored over Linde 4A molecular sieves. The purity of each sample was checked by gas chromatography under conditions that would ensure separation of the isomers; also, the infrared

*Author to whom correspondence should be addressed.

spectra agreed with those previously reported [11]. Analytical grade, anhydrous nickel(II) chloride, bromide, and thiocyanate were further dried in an oven at 120 °C and stored over phosphorus(V) oxide. Ni(II) iodide hexahydrate was stored at 0 °C in a sealed container. All solvents were reagent or spectroscopic grade, and anhydrous.

General Procedures

Microanalyses (C, H, and N) were performed by Atlantic Microlab, Atlanta, Georgia. Nickel was determined by titration with EDTA; halides and thiocyanate by the Volhard method. The analytical data are reported in Table I. *Magnetic susceptibility measurements* were made by the Gouy method on powdered solids at room temperature. All Ni(II) compounds described in this paper were found to be diamagnetic. *Decomposition temperatures* were determined on a Fischer melting-block apparatus; the crystalline compounds decomposed without melting, in the range 180–220 °C. *Ultraviolet-visible-near-infrared absorption spectra* were recorded with a Cary Model 17 spectrophotometer; solid samples were examined by diffuse reflectance, in the range 300–1800 nm. Absorption maxima and relative intensities are given in Table II. *Infrared absorption spectra* (4000–180 cm^{-1}) were recorded with a Perkin Elmer Model 580 Spectrophotometer. The samples were examined as mulls in Nujol and hexachlorobutadiene, between cesium iodide or polyethylene plates; relevant frequencies are listed in Tables III, IV, and V.

Preparation of the Complexes

The $[\text{Ni}(\text{NCS})_2\text{L}_2]$ complexes

A solution of Ni(II) thiocyanate in ethanol containing 5% of triethylorthoformate was heated to boiling for a few minutes. The hot solution was then added dropwise and with stirring to a large excess of the pure liquid ligand, heated to 70–80 °C. (In a representative experiment, 2 ml of a nearly saturated Ni(NCS)₂ solution were added to 5 ml of pure ligand). As the boiling-hot green Ni(II) solution was added to the hot colorless ligand, a beautiful rosy-red color developed, which persisted for several minutes before precipitation of dark rosy-red crystals began. The mixture was heated and stirred for 5 min, allowed to cool to room temperature, and filtered. The rosy-red product (long, needle-like prisms) was washed on the filter with hot ethanol and dried *in vacuo*.

The $[\text{NiI}_2\text{L}_2]$ complexes

Crystalline NiI₂·6H₂O was washed several times with dichloromethane and then once with a small volume of ice-cold ethanol, to remove any iodine formed by air-oxidation. The clean, bright-green crys-

tals of NiI₂·6H₂O were dissolved in a small volume of ethanol containing 5% of triethylorthoformate, and warmed for a few minutes under a dry-nitrogen atmosphere. The resulting ethanol solution (light yellow-green in color) was then added to an excess of the hot, stirred liquid ligand as described for the isothiocyanato complexes. A fleeting dark green color was observed in the solution and dark green crystals (elongated prisms) precipitated almost immediately. The product was isolated as described for the isothiocyanate complexes.

The $[\text{NiBr}_2\text{L}_2]$ complexes

These complexes were prepared similarly to the isothiocyanate complexes, but greater care was required to avoid the presence of moisture. Also, the products were obtained in a purer form if the NiBr₂-ethanol solution was dehydrated by storage over molecular sieves (Linde 4A) rather than by reaction with reagents such as triethylorthoformate of 2,2'-dimethoxypropane. If traces of water were present in the reaction mixture, the bright-blue crystalline $[\text{NiBr}_2\text{L}_2]$ complexes were contaminated by yellow-green amorphous solids, whose infrared spectra revealed the presence of hydroxo-groups and protonated ligands.

The $[\text{NiCl}_2\text{L}_2]$ complexes

The chloro-complexes could not be obtained by the same general procedure described for their NCS, I, and Br analogs, since the addition of an ethanol solution of NiCl₂ to the ligands produced yellow amorphous precipitates containing the ligands in protonated form. (These could be identified by their characteristic infrared spectra). Prolonged refluxing of finely powdered NiCl₂ with a large excess of the ligand produced the desired $[\text{NiCl}_2\text{L}_2]$ species (as small blue crystals) for the 2,6-triMepy and 2,4,6-triMepy ligands, but not for 2,3,6-triMepy. The products thus obtained had the expected infrared and electronic spectra, but their analyses showed the presence of some unreacted NiCl₂. Small quantities of very pure complexes were obtained as follows.

One ml of a saturated solution of NiCl₂ in ethanol (dehydrated by prolonged storage over Linde 4A molecular sieves) and 2 ml of nitromethane were added to 4 ml of the hot stirred solution of the ligand. A yellow amorphous precipitate formed immediately, while the supernatant solution remained colorless. The mixture was boiled with stirring, until the ethanol and nitromethane had almost completely evaporated and the solution had turned a dark blue color. At this point the hot mixture was transferred to a heated test tube, stoppered tightly, and centrifuged. The hot clear blue solution was transferred to another heated test tube, stoppered, and allowed to cool undisturbed. (The blue solution was quite hygroscopic, and its handling was carried out in a moisture-

TABLE I. Colors and Analytical Data for [NiX₂L₂] Complexes Containing 2,6-Disubstituted Pyridines.

Complex	Color	C%		H%		N%	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
[NiCl ₂ (2,6-diMepy) ₂]	dark blue	48.9	48.7	5.3	5.3	8.14	8.14
[NiCl ₂ (2,4,6-triMepy) ₂]	dark purple	51.7	51.6	5.96	6.00	7.5	7.6
		Ni%		X%			
		Calcd.	Found	Calcd.	Found		
[NiBr ₂ (2,6-diMepy) ₂]	bright blue	13.57	13.2	36.95	36.7		
[NiBr ₂ (2,3,6-triMepy) ₂]	bright blue	12.75	12.9	34.73	34.5		
[NiBr ₂ (2,4,6-triMepy) ₂]	bright blue	12.75	12.7	34.73	34.6		
[NiI ₂ (2,6-diMepy) ₂]	olive green	11.15	11.2	48.21	47.9		
[NiI ₂ (2,3,6-triMepy) ₂]	olive green	10.59	10.7	45.77	45.9		
[NiI ₂ (2,4,6-triMepy) ₂]	olive green	10.59	10.7	45.77	45.3		
[Ni(NCS) ₂ (2,6-diMepy) ₂]	rose	15.10	15.0	29.88	29.9		
[Ni(NCS) ₂ (2,3,6-triMepy) ₂]	rose	14.08	14.1	27.87	27.8		
[Ni(NCS) ₂ (2,4,6-triMepy) ₂]	rose	14.08	14.1	27.87	27.8		

TABLE II. Electronic Absorption Spectra^a of *trans*-Square-Planar Complexes of Ni(II) Halides and Thiocyanate with 2,6-Disubstituted Pyridines (values for the *trans*-square-planar complexes of 2,5-dimethylpyridine are included for comparison).

Complex	Absorption Bands ^b		
	ν_1^c	ν_2^d	ν_3^e
[NiCl ₂ (2,6-diMepy) ₂]	1,250(0.2)	588(1.0)	320(1.1)
[NiCl ₂ (2,4,6-triMepy) ₂]	1,200(0.2)	588(1.0)	324(1.2)
[NiCl ₂ (2,3,6-triMepy) ₂] ^f		600(1.0)	335(1.1)
[NiCl ₂ (2,5-diMepy) ₂]	1,100(0.2)	550(1.0)	
[NiBr ₂ (2,6-diMepy) ₂]	1,200(0.3)	615(1.0)	375(1.1)
[NiBr ₂ (2,4,6-triMepy) ₂]	1,200(0.2)	615(1.0)	350(1.4)
[NiBr ₂ (2,3,6-triMepy) ₂]	1,100(0.2)	630(1.0)	360(1.4)
[NiBr ₂ (2,5-diMepy) ₂]	1,100(0.2)	585(1.0)	340(1.4)
[NiI ₂ (2,6-diMep ^y) ₂]	1,100(0.1)	650(1.0)	450–380(1.6)
[NiI ₂ (2,4,6-triMepy) ₂]	1,100(8.2)	650(1.0)	400(1.6)
[NiI ₂ (2,3,6-triMepy) ₂]	1,100(0.3)	663(1.0)	400(1.2)
[NiI ₂ (2,4-diMepy) ₂]	1,000(0.3)	620(1.0)	390(1.4)
[NiI ₂ (2,5-diMepy) ₂]	1,000(0.2)	620(1.0)	390(1.2)
[NiI ₂ (2-Mepy) ₂]	1,029(0.2)	630(1.0)	410(1.2)
[Ni(NCS) ₂ (2,6-diMepy) ₂]	1,200(0.1)	525(1.0)	360(1.2)
[Ni(NCS) ₂ (2,4,6-triMepy) ₂]	1,220(0.1)	525(1.0)	360(1.1)
[Ni(NCS) ₂ (2,3,6-triMepy) ₂]	1,100(0.1)	530(1.0)	365(1.1)
[Ni(NCS) ₂ (2,5-diMepy) ₂]		505(1.0)	337(1.4)
[Ni(NCS) ₂ (2-Mepy) ₂]		505(1.0)	340(1.2)

^aDiffuse reflectance spectra of the finely powdered, undiluted complexes at room temperature. ^bRelative intensities are given in parentheses. ^cMidpoint of weak, very broad band (half-width, 400–500 nm). ^dMidpoint of slightly symmetric band (half-width, ~200 nm). ^eOnly the top portion of the high-energy side of the band could be recorded using a CARY Model 17 diffuse reflectance attachment. ^fSolution in 2,3,6-trimethylpyridine.

TABLE III. Metal-Ligand Vibrations (cm^{-1})^a of *trans*-[NiX₂L₂] Complexes Containing 2,6-Disubstituted Pyridines.

L	X = NCS ^a	X = Cl	X = Br	X = I
<i>Nickel-Anionic Ligand Stretching Vibrations</i>				
2,6-diMepy	400	382	260	227
2,3,6-diMepy	405	(b)	260	225
2,4,6-triMepy	425	405	275	230
<i>Nickel-Aromatic Nitrogen Stretching Vibrations</i>				
2,6-diMepy	355	340	340	340
2,3,6-triMepy	350	(b)	340	340
2,4,6-triMepy	345	330	330	330

^aThe crystalline complexes were examined as thick Nujol mulls between cesium iodide and/or polyethylene plates, using a dry-nitrogen purge. ^bThis complex could not be obtained in a pure crystalline form.

free atmosphere). After several hours, a small crop of beautiful dark blue crystals (prisms for the 2,6-diMepy complex, thick needles for the 2,4,6-triMepy complex) separated on the walls of the test tube, while the supernatant solution became colorless. The crystals were filtered, washed first with ethanol and then with hexane, and dried *in vacuo*. Attempts to obtain the electronic absorption spectra of the hot blue solutions gave poor results, because the solutions became cloudy during scanning.

A somewhat different behavior was observed for 2,3,6-trimethylpyridine. With this ligand, the blue solution obtained by the procedure outlined above did not have any tendency to crystallize and its electronic spectrum, which showed only the presence of the square planar [NiCl₂L₂] species, remained unchanged for as long as a week. No crystalline complex of the type [NiCl₂(2,3,6-triMepy)₂] could be isolated by this procedure or any modification of it.

Solubility of the complexes

All complexes were insoluble in organic solvents and in water; they did not react with solutions of strong bases, ammonium hydroxide, ethylenediamine, or EDTA; they were not attacked by strong acids in the cold. However, the complexes decomposed upon prolonged warming in an aqueous solution of hydrochloric or nitric acids, or upon standing in pyridine or dimethylformamide.

Copper(II) complexes

The complexes [CuX₂L₂] (X = Cl, Br; L = 2,6-diMepy, 2,3,6-, and 2,4,6-triMepy) were prepared similarly to the Ni(II)-NCS complexes, and were characterized as described for the Ni(II) analogs.

TABLE IV. Typical Isothiocyanate Vibrations (cm^{-1}) of *trans*-[Ni(NCS)₂L₂] Complexes Containing 2,6-Disubstituted Pyridines.

Ligand	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}-\text{S})$	$\delta(\text{Ni}-\text{NCS})$
2,6-diMepy	2055	858	472
2,3,6-diMepy	2055	855	475
2,4,6-triMepy	2056	862 ^a	475

^aOverlaid by ligand absorption.

The derivatives of 2,6-diMepy and 2,4,6-triMepy have been previously reported [12-14].

Results and Discussion

General Properties of the Complexes

The reaction of Ni(II) halides and thiocyanate with doubly-hindered substituted pyridines, carried out as described in the Experimental, yielded a series of complexes of the general formula [NiX₂L₂]. All complexes were well-crystallized solids (Table I), which decomposed without melting in the range 180-220 °C; they were diamagnetic and had electronic spectra (Table II) clearly diagnostic of a four-coordinate planar environment. The infrared spectra of the complexes (Tables III and IV) showed the Ni-X and Ni-N (aromatic) stretching vibrations, and also the (C≡N) stretching vibrations of the [Ni(NCS)₂L₂] species, as single sharp absorptions, indicating a *trans*-arrangement of the two pairs of identical ligands. The values of the (C-S) stretching absorptions (860 cm^{-1}) further identified the NCS-groups as typical N-bonded isothiocyanato ligands.

The *trans*-[NiX₂L₂] complexes thus constitute an isostructural series, in which the steric requirements of the substituted pyridines remain essentially constant, while the basicity increases gradually from 2,6-diMepy to 2,3,6-triMepy and 2,4,6-triMepy. The size and polarizability of the coordinated anions also vary gradually from NCS to Cl, Br, and I; hence the spectral properties of the complexes may be expected to exhibit and indeed do exhibit, some meaningful trends which will be discussed below.

Undoubtedly the most remarkable feature of this series of complexes is their lack of solubility and chemical reactivity. The crystalline complexes are insoluble in most organic solvents, hot as well as cold, and are unattacked by water and by aqueous solutions of strong chelating ligands such as ethylenediamine or ethylenediaminetetraacetic acid. In fact, even solutions of strong acids, e.g. hydrochloric and nitric, have no effect on the crystalline complexes except after prolonged heating. This behaviour is

especially striking if compared to that of other NiX_2L_2 complexes of unhindered or mono-hindered pyridines, which are soluble in dichloromethane, chloroform, nitromethane and other organic solvents, and are instantly decomposed by water and acids.

Electronic Spectra

Significant trends are observed in the electronic spectra, which typically show two major absorptions – a single strong symmetrical band in the visible and a strong, sometimes split band in the ultraviolet region. (Incidentally, the ‘visible tail’ of this ultraviolet band is responsible for the olive-green color of the iodo-complexes, which would otherwise appear blue like their bromo-analogs). An extremely weak, broad band also appears in the near infrared. Even without a detailed assignment of these absorptions, which might be somewhat doubtful in the absence of data from single crystal polarized spectra, the energy of the ‘visible band’ offers a good indication of the average ligand field acting on the Ni(II) ion. For the complexes of each ligand L, the energy of the visible band decreases in the sequence $\text{NCS} > \text{Cl} > \text{Br} > \text{I}$, as expected from the order of these ligands in the spectrochemical series. In turn, for the complexes of each anion X, a small but consistent energy shift occurs as a function of the ligand L. Specifically, the energy decreases, however slightly, in the order: 2,5-diMepy $>$ 2,6-diMepy = 2,4,6-triMepy $>$ 2,3,6-triMepy.

The decrease in ligand field energy from 2,5-diMepy ($\text{pK}_A = 6.55$) to 2,6-diMepy ($\text{pK}_A = 6.72$) may logically be attributed to the increased steric hindrance of the doubly-hindered pyridine. Steric hindrance, however, cannot account for the energy lowering from 2,6-diMepy and 2,4,6-triMepy ($\text{pK}_A = 7.63$) to 2,3,6-triMepy ($\text{pK}_A = 7.40$). Nor can basicity be considered a determining factor, since the complexes of 2,6-diMepy and 2,4,6-triMepy have virtually identical spectra despite the considerable difference in their pK_A values [15]. The observed energy trend also holds for the chloro-series, in which the 2,3,6-triMepy-complex was examined in solution, and hence cannot result only from a less effective crystal packing due to lack of symmetry in the 2,3,6-ligand. Rather, the observed spectral effect may be ascribed to the electronic situation of the pyridine ring, which in the symmetric 2,6- and 2,4,6-derivatives may be expected to be slightly more favorable to metal–ligand bonding than in the asymmetric 2,3,6-derivative. In fact, both the molecular orbital calculations for a number of methyl-substituted pyridines [16], and the experimental values [17] of the ^{14}N nuclear quadrupole resonance of the pure ligands, agree that the total electron density at the N atom is slightly greater for *ortho*-, *para*-, or *ortho-para* ($-\text{CH}_3$) substituted derivatives, than for those with $-\text{CH}_3$ substituents in *meta*-positions.

Infrared Spectra

The vibrational spectra of the $[\text{NiX}_2\text{L}_2]$ complexes offer some further insight into their structure. First of all, it is noteworthy that the various complexes of each ligand exhibit an identical spectral pattern, except for the anion-related absorptions. This strict similarity further extends from the $[\text{NiX}_2\text{L}_2]$ complexes to their Cu(II) and Pd(II) analogs; specifically, the spectral patterns of the $[\text{NiX}_2(2,6\text{-lutidine})_2]$ species ($\text{X} = \text{Cl}, \text{Br}$) are almost superimposable on those of the corresponding Cu(II) complexes, for which a single crystal X-ray study has recently shown a *trans*-planar configuration with D_{2h} symmetry [12]. Thus the patterns of the vibrational spectra of the substituted pyridine ligands, which are known to be quite sensitive to geometrical changes in the coordination sphere, may be taken as an additional diagnostic feature for the structure of the $[\text{NiX}_2\text{Cl}_2]$ complexes.

The constancy of the ligand absorptions allows the Ni–anion and Ni–N (aromatic) stretching vibrations – and their Cu(II) counterparts – to be identified with confidence, especially since these vibrations usually appear as rather strong, well-resolved bands. The reliability of the observed values is important in view of the uncertainty that still exists in regard to metal–ligand vibrational frequencies and their relationship to the coordination number and stereochemistry of the metal. For example, in a series of some twenty complexes of the same general formula $\{\text{Cu}(\text{halide})_2(\text{amine})_2\}$, the copper–halogen stretching vibrations were reported to range randomly from 336 to 206 cm^{-1} [18], thus raising reasonable doubt on either the assignment of the frequencies, or the assumed structure of the complexes, or possibly both. Similarly, the copper–halogen and copper–nitrogen vibrations of some twenty-five CuX_2L_2 complexes of methyl-substituted pyridines were collectively assigned on the basis of D_{2h} symmetry, without consideration of the fact that some of the complexes investigated have a *trans*-planar four-coordinate configuration [14], others are halogen-bridged five-coordinate dimers [19], and still others are halogen-bridged six-coordinate polymers [20]. In the case of our $[\text{NiX}_2\text{L}_2]$ complexes, the values of the Ni–anion and Ni–N (aromatic) stretching frequencies (Tables III and IV) may appear to be abnormally high as they exceed (in some cases by as much as 100 cm^{-1}) the values commonly observed for the many known tetrahedral and octahedral 1:2 Ni(II)–pyridine complexes [21]. However, the Ni–Cl and Ni–Br frequencies observed for our compounds compare rather well with those reported for the few other available *trans*-planar complexes of Ni(II): for example, in several *trans*- $[\text{NiCl}_2(\text{PMe}_3)_2]$ complexes the $\nu(\text{Ni}-\text{Cl})$ vibration appears at 408–403 cm^{-1} [22]. It may be concluded that the ‘more covalent’ character of the metal–ligand bonds in

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