Synthesis and Properties of 3-, 4-, and 5-Nitro-2-pyridinecarbaldehyde 2-pyridylhydrazones and Characterization of Their Metal Complexes

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Three hydrazones, 3-, 4-, and 5-nitro-2-pyridinecarbaldehyde 2-pyridylhydrazones, were synthesized. Their properties and reactivities with metal ions and the extraction and characteristics of the resultant complexes have been investigated and compared with one another. As a result, useful information on the molecular design of highly sensitive hydrazone reagents has been obtained.

Recently, we studied the effect of various substituents introduced to the pyridine ring in the hydrazine moiety of 2-pyridinecarbaldehyde 2-pyridylhydrazone (PAPH) for the purpose of improving its sensitivity as a spectrophotometric reagent for metal ions, and found that the introduction of an electron-withdrawing nitro group to the 5-position of the pyridine ring is very effective for this purpose, and reported[1] that 2-pyridinecarbaldehyde 5-nitro-2-pyridylhydrazone (PA-5-NPH) reacts with various metal ions to form complexes with large molar absorptivities, especially with copper(II) and nickel(II) to from complexes having molar absorptivities of the order of 10^5. In this work, in order to estimate the effect of a nitro group introduced to the aldehyde moiety of PAPH and obtain information on the molecular design of highly sensitive hydrazone reagents, three new hydrazones, in which a nitro group was introduced to the 3-, 4-, or 5-position of the pyridine ring in the aldehyde moiety of PAPH (3-NPAPH, 4-NPAPH, and 5-NPAPH, respectively, or HL), were synthesized, and their chromogenic properties and reactivities with metal ions and the extractability of their metal complexes have been investigated in detail.

Experimental

Synthesis of Hydrazones. 3-, 4-, and 5-NPAPH were synthesized according to Scheme 1 as follows.

Synthesis of 3-NPAPH (5). 3-Nitro-2-pyridinecarbaldehyde (3): 2-Methyl-3-nitropyridine (**2**, 7.91 g, 57.3 mmol), which was prepared from 2-chloro-3-nitropyridine (**1**) according to the procedure of Dunn and Thimm,[2] was dissolved in 1,4-dioxane (40 cm³) and water (4 cm³). To this solution was added 40 cm³ of a 1,4-dioxane solution of selenium dioxide (7.51 g, 68.3 mmol) at 50°C, and the mixture was refluxed for 3.5 h. Furthermore selenium dioxide (3.5 g, 31.8 mmol) was added. After refluxing for additional 9 h, the mixture was cooled, filtered and evaporated. Water was removed as the benzene azeotrope, and the residue was extracted with chloroform, dried over anhydrous sodium sulfate, and evaporated to give a dark brown oil (11.0 g). This crude oil was used in the next step without purification. ¹H NMR (CDCl₃) $\delta=10.24$ (s, 1, CHO), 9.00 (d, 1, H₆), 8.32 (d, 1, H₄), 7.76 (dd, 1, H₅).

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3-NPAPH (5): Crude 3-nitro-2-pyridinecarbaldehyde (**3**, 1.23 g, 8.1 mmol) in ethanol (100 cm³) was added to a hot ethanol solution (100 cm³) of 2-pyridylhydrazine (**4**, 1.0 g, 6.6 mmol), and the mixture was refluxed for 2 h and then cooled. The solution was evaporated until red-brown solids were precipitated. This precipitate was collected by filtration, washed with hot ethanol, and purified in a column of silica gel by elution of 2 % v/v methanol in chloroform to afford pure crystals (0.63 g). Mp 185—186°C, IR (KBr) $\nu_{C=N}$ 1600 cm⁻¹, ν_{NO_2} 1340 cm⁻¹. Anal. Calcd for $C_{11}H_9N_5O_2$: C, 54.32; H, 3.73; N, 28.79%. Found: C, 54.29; H, 4.00; N, 28.84%.

Synthesis of 4-NPAPH (11). 2-Acetoxymethyl-4-nitropyridine (8): Acetic anhydride (56 cm³) was added to 2-methyl-4-nitropyridine N-oxide (**7**, 14.3 g, 92.8 mmol), which was obtained by nitration of 2-methylpyridine N-oxide (**6**) according to the procedure of Ochiai et al.[3] and the mixture was stirred at 110—120°C for about 20 min. The reaction was stopped with the evolution of nitrogen dioxide. This mixture was evaporated, and acetic anhydride was removed completely by the azeotropic evaporation with ethanol several times. The brown oil obtained was purified in a column of silica gel by elution with chloroform to give pure pale yellow syrup (3.98 g, 21.9%). Bp 110—115°C (at 3 mmHg, 1 mmHg=133.322 Pa), IR (KCl) $\nu_{CH_2COCH_3}$ 1755 cm⁻¹, 1210—1230 cm⁻¹; ν_{NO_2} 1350 cm⁻¹. Anal. Calcd for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28%. Found: C, 48.69; H, 4.01; N, 14.19%.

2-Hydroxymethyl-4-nitropyridine (9): A mixture of 2-acetoxymethyl-4-nitropyridine (**8**, 3.98 g, 20.3 mmol) and 10% hydrochloric acid (23 cm³) was stirred at 70—80°C for 1 h. This solution was concentrated, made alkaline with saturated sodium carbonate, extracted with chloroform, dried over anhydrous sodium sulfate and evaporated to give a pale brown solid, which was recrystallized from benzene (2.89 g, 92.4%). Mp 83.5—84.5°C, IR (KBr) ν_{OH} 3280 cm⁻¹; ν_{NO_2} 1350 cm⁻¹. Anal. Calcd for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18%. Found: C, 46.93; H, 4.20; N, 18.46%.

4-Nitro-2-pyridinecarbaldehyde (10): Manganese dioxide (activated under vacuum at 110°C for 1 d, 16.3 g, 187 mmol) was added to a chloroform solution (250 cm³) of 2-hydroxymethyl-4-nitropyridine (**9**, 2.89 g, 18.8 mmol), and the mixture was refluxed for 16 h. Furthermore manganese dioxide (8 g, 92.0 mmol) was added and the mixture was refluxed for additional 32 h. Before getting cold the mixture was filtered through a Celite pad and evaporated to yield a dark orange oil (2.51 g). This oil was used in the next step without purification because it was very volatile
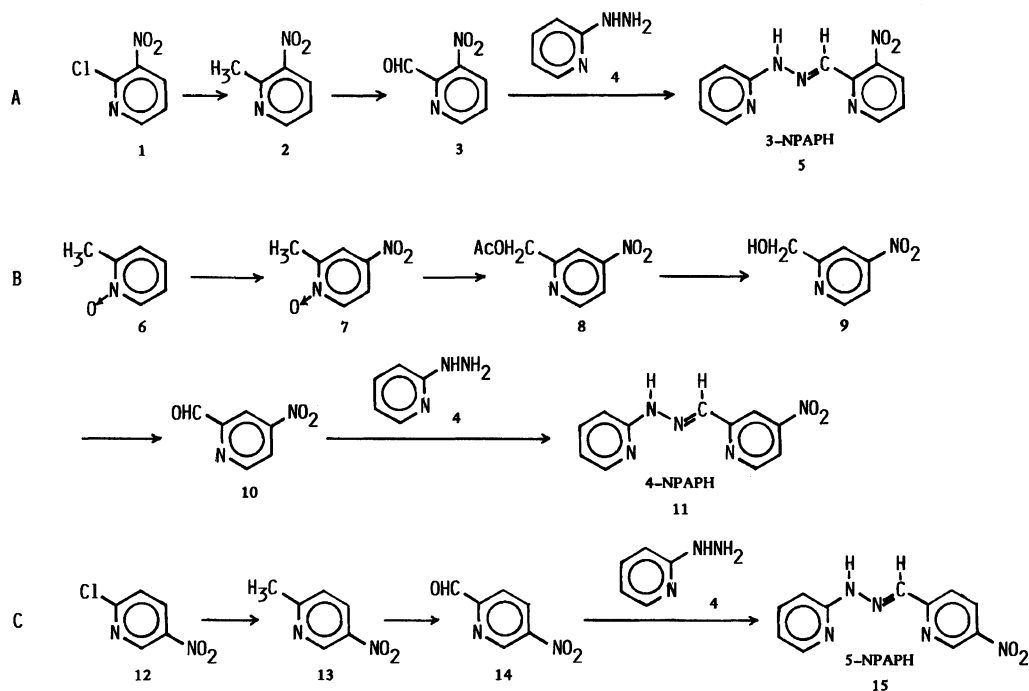
Scheme 1.

and labile. IR (KCl) ν_{CHO} 1710 cm^{-1}; ν_{NO_2} 1350 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ=10.2 (s, 1, CHO), 9.16 (d, 1, H$_6$), 8.64 (d, 1, H$_3$), 8.26 (dd, 1, H$_5$).

4-NPAPH (11): 4-Nitro-2-pyridinecarbaldehyde (10, 1.02 g, 6.71 mmol) in ethanol (35 cm^3) was added to a hot ethanol solution (40 cm^3) of 2-pyridylhydrazine (4, 1.02 g, 9.35 mmol), and the mixture was refluxed for 2 h. After cooling overnight a precipitate was collected by filtration and recrystallized from ethanol to give pure orange yellow crystals (1.17 g). Mp 213—214°C, IR (KBr) $\nu_{C=N}$ 1595 cm^{-1}, ν_{NO_2} 1330, 1350 cm^{-1}. Anal. Calcd for C$_{11}$H$_9$N$_5$O$_2$: C, 54.32; H, 3.73; N, 28.79%. Found: C, 54.37; H, 4.10; N, 28.84%.

Synthesis of 5-NPAPH (15).   2-Methyl-5-nitro-pyridine (13).   A modification of the procedure of Dummel and Mosher[4] was used. To a solution of diethyl malonate (25 g, 156 mmol) in anhydrous ether (300 cm^3) was added sodium hydride (contained 60% mineral oil, 6.33 g, 158 mmol) under a nitrogen atmosphere. When the evolution of hydrogen had subsided, 2-chloro-5-nitropyridine (12, 25 g, 158 mmol) was added with stirring, followed by the removal of ether by evaporation. The red, tarry residue was heated with an oil bath to 110°C for 1 h, then refluxed in 6 M (1 M=1 mol dm^{-3}) sulfuric acid (180 cm^3) for 7 h. After cooling to room temperature, the mixture was neutralized with potassium hydroxide under cooling, filtered, and washed with chloroform. The filtrate was transferred to a separate flask and extracted with chloroform. The extract was dried over anhydrous sodium sulfate, and evaporated to give a red-purple solid. This was recrystallized from ethanol twice to yield an almost pure target material (11.4 g, 52.9%). ^{1}H NMR (CDCl$_3$) δ=9.32 (d, 1, H$_6$), 8.36 (dd, 1, H$_4$), 7.36 (d, 1, H$_3$), 2.72 (s, 3, CH$_3$).

5-Nitro-2-pyridinecarbaldehyde (14):   A mixture of 2-methyl-5-nitropyridine (13, 8.55 g, 61.9 mmol), sele-

nium dioxide (8.24 g, 74.3 mmol), 1,4-dioxane (67.5 cm^3) and water (1.5 cm^3) was refluxed for 6.5 h, and then filtered to remove a black precipitate. The filtrate was made alkaline with a saturated sodium hydrogencarbonate solution, filtered again, and extracted with ether (3×100 cm^3). The extract was dried over anhydrous sodium sulfate, and evaporated to give a black-brown oil. This oil was purified in a column of silica gel by elution with 0—2.5% v/v methanol in chloroform to yield crude labile crystals (4.8 g). ^{1}H NMR (CDCl$_3$) δ=10.20 (s, 1, CHO), 9.60 (d, 1, H$_6$), 8.72 (dd, 1, H$_4$), 8.20 (d, 1, H$_3$).

5-NPAPH (15):   5-Nitro-2-pyridinecarbaldehyde (14, 2.5 g, 16.4 mmol) in ethanol (150 cm^3) was added to a hot ethanol solution (90 cm^3) of 2-pyridylhydrazine (4, 1.80 g, 11.8 mmol), and the mixture was refluxed for 1.5 h. After cooling overnight a precipitate was filtered and recrystallized from ethanol to give pure yellow crystals (2.28 g). Mp 235—236°C. IR (KBr) $\nu_{C=N}$ 1595 cm^{-1}, ν_{NO_2} 1330 cm^{-1}. Anal. Calcd for C$_{11}$H$_9$N$_5$O$_2$: C, 54.32; H, 3.73; N, 28.79%. Found: C, 54.79; H, 3.44; N, 28.58%.

Reagents.   All reagents used were of analytical grade and all solutions were prepared with distilled, deionized water, unless stated otherwise.

Hydrazone Solutions: Prepared by dissolving the synthesized hydrazones in 1,4-dioxane or benzene.

Buffer Solutions: The following buffers were used, and adjusted to the pH required: 0.2 M acetic acid–0.2 M sodium acetate, 0.2 M tris(hydroxymethyl) aminomethane (Tris)–0.2 M nitric acid, 0.2 M glycine–0.2 M hydrochloric acid, 0.2 M glycine–0.2 M sodium hydroxide, 0.2 M boric acid–0.2 M sodium borate or 0.2 M sodium hydrogencarbonate–0.2 M sodium carbonate.

Apparatus.   The following apparatus were used: a Hitachi 3200 automatic recording spectrophotometer, a JASCO A-3 infrared (IR) spectrometer, a Toa HM-20B pH

meter, an Iwaki KM shaker and a Haake FK-2 thermoelectric circulating bath. All extractions were performed by shaking samples in 50-cm³ centrifuging tubes in a constant-temperature room kept at 25±1°C.

Procedures. Acid Dissociation Constant: The acid dissociation constants of the synthesized hydrazones were determined spectrophotometrically[5] in aqueous 1,4-dioxane solutions of various concentrations (8—28% v/v) at 25±0.1°C and an ionic strength of 0.2 adjusted with sodium chloride. The pH was adjusted with glycine buffer.

Partition Coefficient: A 20-cm³ portion of an aqueous solution containing acetate buffer to adjust the pH to a required value between 3 and 5 and sodium chloride to keep the ionic strength at 0.2 was placed in a 50-cm³ centrifuging tube together with 20 cm³ of 3.0×10^{-4} M hydrazone solution in benzene. The tube was shaken for 2 h, which was sufficient for equilibration. After phase separation by centrifuging, a 10-cm³ portion of the aqueous phase was transferred into a 25-cm³ calibrated flask, to which are added 5 cm³ of 1,4-dioxane, 2 cm³ of borate buffer to adjust the pH to a required value between 8 and 10 and a required volume of 2.5 M sodium chloride solution to keep the ionic strength at 0.2 and then diluted to the mark with water. The absorbance of the solution was measured at the maximum-absorption wavelength of the hydrazone against 20% v/v aqueous 1,4-dioxane solution, the concentration of the hydrazone being obtained from a calibration graph for HL prepared under the identical conditions. The equilibrium concentration of the hydrazone in the organic phase was calculated by subtracting the aqueous equilibrium concentration from the initial concentration.

Distribution of Nickel: The distribution of nickel between benzene and aqueous phases was determined as a function of the hydrogen ion concentration.

A 10-cm³ portion of an aqueous solution containing a fixed amount of nickel(II), acetate buffer to adjust the pH to a required value and a sufficient amount of sodium chloride to keep the ionic strength at 0.2 was placed in a 50-cm³ centrifuging tube along with 10 cm³ of benzene containing the hydrazone. The tube was shaken for 12 h, which was sufficient for equilibration. After phase separation by centrifuging, the absorbance of the extract was measured at the maximum-absorption wavelength of the complex against a reagent blank prepared under the same conditions. The equilibrium concentration of the nickel(II) in the organic phase was determined by using a calibration graph prepared as follows: 10-cm³ aqueous solutions containing a different volume of a standard nickel(II) solution, 1 cm³ of 0.2 M borate buffer (pH 8.5) and 1 cm³ of 2 M sodium chloride solution were shaken with 10 cm³ of benzene containing the hydrazone for 2 h. The equilibrium concentration of the nickel(II) in the aqueous phase was calculated by subtracting the organic equilibrium concentration from the initial concentration.

Results and Discussion

Identification of Hydrazones. The identification of the synthesized hydrazones was performed by elemental analysis and IR spectra measured with potassium bromide tablets. The results are summarized in Table 1 together with data of their melting points, in-

Table 1. Properties of Synthesized Hydrazones

Hydrazone	Mp/°C	$\nu_{C=N}$/cm^{-1}	Analysis (%)[a]		
			C	H	N
3-NPAPH	185–186	1600	54.29	4.00	28.84
			(54.32)	(3.73)	(28.79)
4-NPAPH	213–214	1595	54.37	4.10	28.84
			(54.32)	(3.73)	(28.79)
5-NPAPH	235–236	1595	54.79	3.44	28.58
			(54.32)	(3.73)	(28.79)

a) Figures in parentheses indicate calculated values.

dicating that the target hydrazones are synthesized and there is no problem in their purity.

Properties and Characteristics of Hydrazones. The synthesized hydrazones are insoluble in water, but soluble in common organic solvents such as ethanol, 1,4-dioxane, benzene, and chloroform, these solutions being stable for a long period. According to a qualitative test, a decrease in solubility in the organic solvent due to the introduction of a nitro group was observed, but the degree of decrease was not so large as when it was introduced to the pyridine ring in the hydrazine moiety of PAPH.[6] Among the synthesized hydrazones, 4-NPAPH showed the largest solubility in benzene, followed by 3- and 5-NPAPH. These hydrazones are also soluble in aqueous acidic or alkaline solutions as a result of protonation or deprotonation, respectively.

Absorption Spectra: Figure 1 shows absorption spectra of 5-NPAPH in aqueous 20% v/v 1,4-dioxane solutions of various pH values. Three clear isosbestic points are observed, which suggests that 5-NPAPH exists in solution in any of four species, depending on pH and its acid dissociation equilibria obey Eq. 1 shown below. The other two hydrazones also gave similar spectra to those shown in Fig. 1. The maximum-absorption wavelength and the molar absorptivity of each species of the synthesized hydrazones are summarized in Table 2. The absorption maxima of 5-NPAPH, especially that of the species HL is considerable red-shifted compared with not only those of the others but also that of PA-5-NPH in which a nitro group is introduced to the pyridine ring in the hydrazine moiety.

Acid Dissociation Constants: As is clear from their structures and absorption spectra shown in Fig. 1, the probable acid-dissociation equilibria of the synthesized hydrazones may be written as follows:

$$H_3L^{2+} \overset{K_{a1}}{\rightleftharpoons} H_2L^{+} \overset{K_{a2}}{\rightleftharpoons} HL \overset{K_{a3}}{\rightleftharpoons} L^{-}, \quad (1)$$
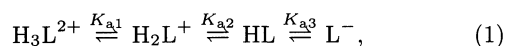
where K_{a1}, K_{a2}, and K_{a3} are the acid dissociation constants. K_{a1} values were determined spectrophotometrically in aqueous solution, while K_{a2} values were estimated by extrapolating the plot of apparent pK_{a2} values determined spectrophotometrically in aqueous 8—28% v/v 1,4-dioxane solutions versus the 1,4-dioxane concentration to the intercept. Values of pK_{a1} and pK_{a2} of the synthesized hydrazones thus obtained are given
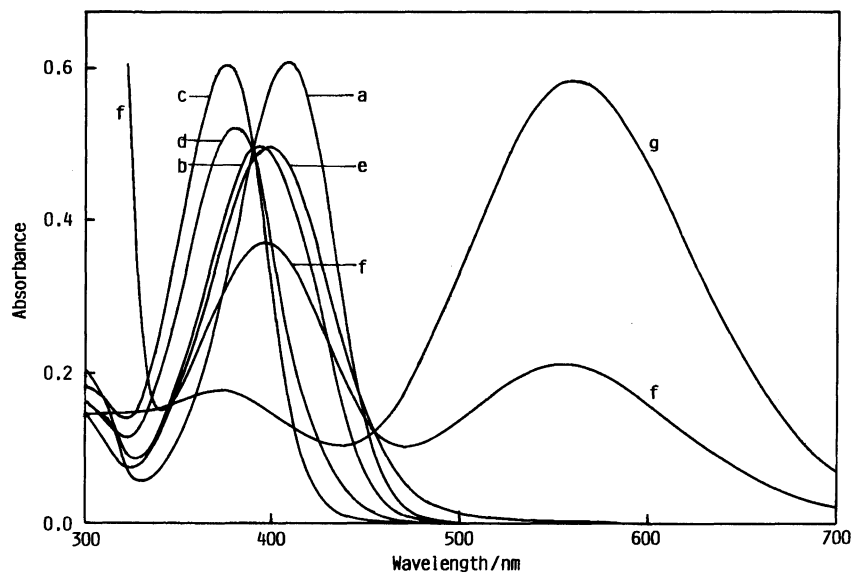
Fig. 1. Absorption spectra of 5-NPAPH in aqueous 20% v/v 1,4-dioxane solutions of various pHs. 5-NPAPH, 2.0×10^{-5} M; reference, water; pH: a, <0 (in 4.8 M HCl); b, <0 (in 2.4 M HCl); c, 0.8—2.7; d, 4.5; e, 7.0—11.0; f, 13.0; g, 13.8.

Table 2. Absorption Maxima, λ_{max}, Molar Absorptivities, ε, in Aqueous 20% v/v 1,
4-Dioxane, Acid Dissociation Constants and Partition Coefficients of Synthesized
Hydrazones between Benzene and Water

Hydrazone	Species	λ_{max}/nm	$\varepsilon/10^4 \text{ M}^{-1}\text{cm}^{-1}$	pK_{a1} and pK_{a2} [a]	$\log K_D$
	H_2L^+	361	2.3	$pK_{a1}=0.33$	
3-NPAPH	HL	344	1.7	$pK_{a2}=5.42-0.024\ C$	2.00
	L^-		Not determined		
	H_2L^+	360	2.2	$pK_{a1}=0.22$	
4-NPAPH	HL	337	2.0	$pK_{a2}=5.47-0.024\ C$	2.44
	L^-		Not determined		
	H_2L^+	376	2.9	$pK_{a1}=0.28$	
5-NPAPH	HL	399	2.5	$pK_{a2}=5.24-0.020\ C$	2.33
	L^-	ca. 562	—		
	H_2L^+	350	2.6	$pK_{a1}=3.01$ [b]	
PAPH	HL	337	2.6	$pK_{a2}=5.75$ [b]	1.58 [b]
	L^-		Not determined		

a) pK_{a2} values were shown as functions of 1,4-dioxane concentration, C.   b) Determined in an earlier work.[1]

in Table 2, indicating that the inductive effect of the nitro group on the pyridine ring reflects the pK_a values of the hydrazones, that is, the acid dissociation of the hydrazones is considerably stimulated by the introduction of a nitro group. Values of pK_{a3} were not determined because they were too large (above 14) to measure. K_{a1} and K_{a2} are considered to correspond to the deprotonation of the protonated pyridine-nitrogens in the aldehyde and hydrazine moieties of the hydrazones, respectively, contrary to the assignment in the hydrazone, e.g., PA-5-NPH, in which a nitro group was introduced to the hydrazine moiety. K_{a3} corresponds to the deprotonation of the secondary amino group.

Partition Coefficients of Hydrazones: In the pH region 3—5 where the experiments were carried out, the distribution ratio, D_{HL}, of the synthesized hydrazo-

nes between an aqueous and a benzene phase can be expressed by Eq. 2 and is rewritten as Eq. 3 by employing the acid dissociation constant, K_{a2}, and the partition coefficient, K_D, of the hydrazones.

$$D_{HL} = \frac{[HL]_{org}}{[H_2L^+] + [HL]}, \tag{2}$$

$$D_{HL} = \frac{K_D}{\dfrac{[H^+]}{K_{a2}} + 1}, \tag{3}$$

where the subscript org represents the concentration in the organic phase. Equation 3 is further rewritten as Eq. 4:

$$\log D_{HL} = \log K_D - \log\left(\frac{[H^+]}{K_{a2}} + 1\right). \tag{4}$$

Equation 4 means that the plot of $\log D_{HL}$ versus

$\log \{([H^+]/K_{a2})+1\}$ gives straight lines with a slope of -1, the value of K_D being obtained from the intercept of this line. Such the relation was experimentally obtained for the synthesized hydrazones as shown in Fig. 2. The values of $\log K_D$ are given in Table 2, indicating that the introduction of a nitro group increases the K_D value in the following sequence: PAPH< 3-NPAPH<5-NPAPH<4-NPAPH.

Color Reactions with Metal Ions and Extractabilities of Metal Complexes. The color reactions of the synthesized hydrazones with metal ions were examined in aqueous 40% v/v 1,4-dioxane at apparent pH 5, 7, and 10. The results revealed that every hydrazone reacts rapidly with cadmium(II), cobalt(II), copper(II), iron(II), nickel(II), palladium(II), zinc(II), etc. to form colored complexes with large molar absorptivities in weakly and/or alkaline media.

These complexes except the cobalt complexes were extracted into organic solvents such as benzene, chloroform and 4-methyl-2-pentanone. Table 3 shows absorption maxima and apparent molar absorptivities of the complexes extracted into benzene from aqueous solutions of pH 4, 7, and 10. Absorption maxima of 5-NPAPH and 4-NPAPH complexes, which have nearly the same wavelengths, are red-shifted more than those of 3-NPAPH complexes. Apparent molar absorptivities of 5-NPAPH complexes are the largest among the three hydrazone complexes, followed by 3-NPAPH complexes, and those of 4-NPAPH complexes are smaller than those of complexes of PAPH, the mother compound.[1,6] These results reveal that the introduction of a nitro group into the 5-position of the pyridine ring in the aldehyde moiety of PAPH brings about fairly large increases in molar absorptivities of complexes of the resultant hydrazone, 5-NPAPH, as well as bathochromic shifts of their ab-
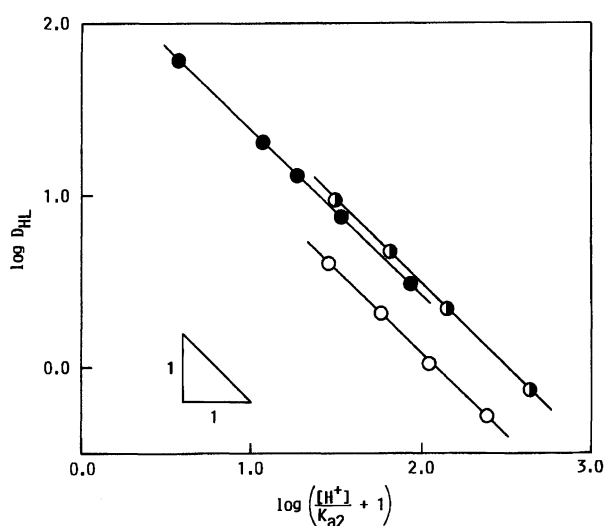
Table 3. Absorption Maxima, λ_{max}, and Apparent Molar Absorptivities, ε', of Metal Complexes of Hydrazones Extracted into Benzene

Complex	pH 4		pH 7		pH 10	
	λ_{max} nm	ε' $M^{-1}cm^{-1}$	λ_{max} nm	ε' $M^{-1}cm^{-1}$	λ_{max} nm	ε' $M^{-1}cm^{-1}$
3-NPAPH						
Cd(II)	—	—	—	—	519	61200
Co(II)[a]	513	39700	513	40900	513	35100
Cu(II)	—	—	526	54700	526	55600
Fe(II)	478	43700	478	43700	—	—
Ni(II)	532	9300	527	47000	527	48200
Pd(II)	605	25400	—	—	572	23100
Zn(II)	—	—	520	49300	520	57600
4-NPAPH						
Cd(II)	—	—	—	—	567	4000
Co(II)[a]	531	19500	531	19500	531	14800
Cu(II)	—	—	562	17800	562	22200
Fe(II)	491	26000	491	25200	—	—
Ni(II)	—	—	566	17500	566	20500
Pd(II)	619	10100	619	7100	619	7500
Zn(II)	—	—	—	—	551	16400
5-NPAPH						
Cd(II)	—	—	—	—	564	44700
Co(II)[a]	538	35600	538	35800	538	27000
Cu(II)	—	—	557	86200	557	94500
Fe(II)	504	51900	504	50300	—	—
Ni(II)	567	10700	567	80700	567	96000
Pd(II)	625	23000	—	—	583	15000
Zn(II)	—	—	557	15900	558	66000

a) Measured in aqueous solutions.

sorption spectra. The degree of bathochromic shifts was larger but that of increases in molar absorptivities was somewhat smaller than when a nitro group was introduced to the corresponding position in the hydrazine moiety.[1,6]

Extraction and Characterization of Nickel Complexes. As may be seen from the above results, as the synthesized hydrazones form complexes with large molar absorptivities with copper(II), nickel(II), and zinc(II), they, especially 5-NPAPH, seem to be useful extractive spectrophotometric reagents for these metals. So, the complexation of the synthesized hydrazones with nickel(II), which forms complexes with the largest molar absorptivities among these metal ions, and the extraction of the nickel complexes into benzene were investigated somewhat in detail and compared with one another in the subsequent work.

Absorption Spectra of Nickel Complexes and the Effect of pH on Extraction of Nickel: Figure 3 shows absorption spectra of nickel complexes of the synthesized hydrazones, and Fig. 4 the effect of pH on the extraction of the nickel complexes, which also reveals that the 5-NPAPH complex has the largest apparent molar absorptivity.

Extraction Constants of the Nickel Complexes: The overall reaction in the extraction of
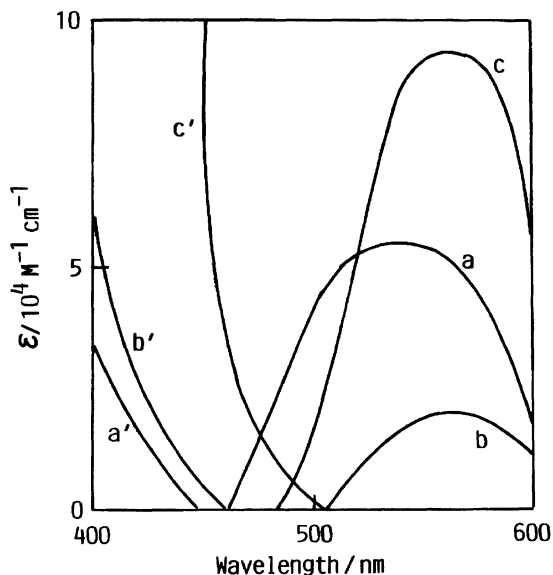

Fig. 2. Plots of $\log D_{HL}$ vs. $\log \{([H^+]/K_{a2})+1\}$. Hydrazones, 2.0×10^{-5} M; $V_{aq}=V_{org}=20$ cm^3; temperature, $25\pm1°C$; ionic strength, 0.2 (NaCl); shaking time, 1 h; O, 3-NPAPH; ◑, 4-NPAPH; ●, 5-NPAPH.

Fig. 3. Absorption spectra of nickel complexes of synthesized hydrazones. Hydrazones, 1.5×10^{-4} M; Ni-(II), 5.7×10^{-6} M; pH, 8.4; $V_{aq} = V_{org} = 10$ cm^3; shaking time, 12 h; reference: a, b, c, reagent blank; a', b', c', benzene; a, 3-NPAPH complex; b, 4-NPAPH complex; c, 5-NPAPH complex; a', 3-NPAPH; b', 4-NPAPH; c', 5-NPAPH.
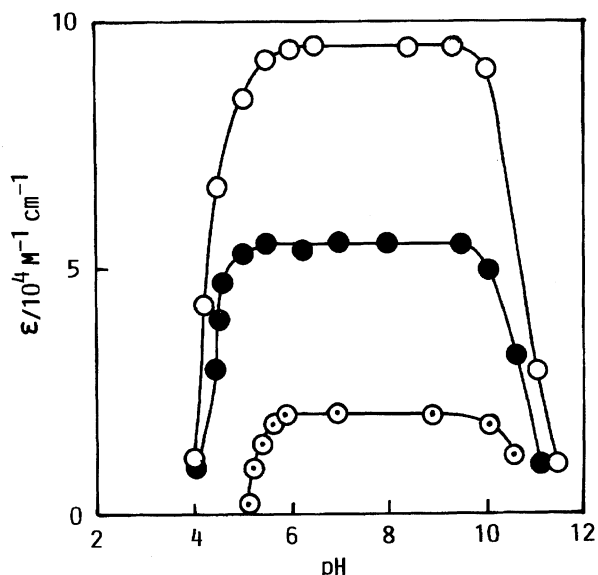

Fig. 4. Effect of pH on extraction of nickel complexes. Hydrazones, 1.5×10^{-4} M; shaking time, 12 h; $V_{aq} = V_{org} = 10$ cm^3; reference, reagent blank.

	Complex	Wavelength/nm
○	5-NPAPH complex	567
●	3-NPAPH complex	527
⊙	4-NPAPH complex	566

nickel(II) with each hydrazone, HL, may be expressed

as

$$Ni^{2+} + (n + m)HL_{org} \rightleftharpoons NiL_n(HL)_{m,org} + nH^+. \quad (5)$$

The extraction constant, K_{ex}, is defined as Eq. 6 and is rewritten as Eq. 7 by using the distribution ratio, D_{Ni}, of nickel.

$$K_{ex} = \frac{[NiL_n(HL)_m]_{org}[H^+]^n}{[Ni^{2+}][HL]_{org}^{n+m}}, \quad (6)$$

$$\log D_{Ni} = \log K_{ex} + (n + m) \log[HL]_{org} + npH. \quad (7)$$

The plots of $\log D_{Ni}$ versus pH at constant concentrations of the hydrazones give straight lines with a slope of 2 in all the extraction systems, as shown in Fig. 5. Likewise, plots of $\log D_{Ni}$ versus $\log [HL]_{org}$ at constant pH values yield also straight lines with a slope of 2. These results reveal that $n=2$ and $m=0$ in Eq. 7, i.e., only a 1:2 complex, NiL_2, is extracted into benzene in each extraction system, which was in accord with the results obtained separately by the continuous variation method. The $\log K_{ex}$ values for 3-NPAPH-, 4-NPAPH- and 5-NPAPH-nickel(II) systems calculated from the intercept of each line in Fig. 5 were -1.13, -2.91, and -1.58, respectively, indicating that the introduction of a nitro group to the aldehyde moiety scarcely affects the K_{ex} values of nickel complexes.

Conclusion

Three new hydrazones derived from PAPH were synthesized. Their properties and reactivities with metal ions and the extraction of the resultant complexes, especially nickel complexes have been investigated and compared with one another. As the result, it has been found that (1) the introduction of a nitro group to the
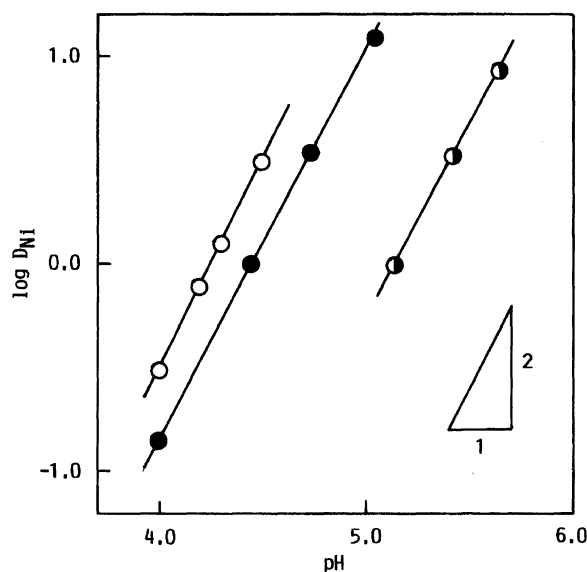

Fig. 5. Plots of $\log D_{Ni}$ vs. pH. Hydrazones, 2.0×10^{-4} M; Ni(II), 5.7×10^{-6} M; $V_{aq} = V_{org} = 10$ cm^3; temperautre, $25 \pm 1°C$; ionic strength, 0.2 (NaCl); shaking time, 12 h. ○, 3-NPAPH; ◑, 4-NPAPH; ●, 5-NPAPH.

pyridine ring in the aldehyde moiety of PAPH loweres the pK_a values, increases the log K_D values, causes remarkable bathochromic shifts in absorption spectra of the hydrazone and its metal complexes, but scarcely affects the K_{ex} values of nickel complexes (presumably those of other metal complexes), (2) the introduction to the 5- or 3-position of the pyridine ring brings about increases in molar absorptivities of metal complexes, but the introduction to the 4-position causes decreases in them, and (3) among the synthesized hydrazones, 5-NPAPH is the most sensitive for metal ions, especially for nickel(II). Furthermore, taking into consideration the results reported already,[1,6] it is concluded concerning the molecular design of the highly sensitive hydrazone reagent that (1) the introduction of a nitro group to the 5-position of the pyridine ring in either the hydrazine or aldehyde moiety of PAPH is very effective for increasing its sensitivity for metal ions, and the introduction to the hydrazine moiety is preferable to the aldehyde moiety for increasing the molar absorptivity of metal complexes, (2) as for the bathochromic shifts of absorption spectra of the hydrazone and its metal complexes and the minimization of the decrease in their solubilities in organic solvents, the introduction to the aldehyde moiety is more effective than that to the hydrazine moiety, and (3) the introduction to the aldehyde moiety scarcely affects the K_{ex} values of nickel complexes, but the introduction to the hydrazine moiety increases them remarkably.

References

1) H. Ishii, T. Odashima, and T. Hashimoto, *Anal. Sci.*, **3**, 347 (1987).

2) G. E. Dunn and H. F. Thimm, *Can. J. Chem.*, **55**, 1342 (1977).

3) E. Ochiai, K. Arima, and M. Ishikawa, *Yakugaku Kaishi*, **63**, 79 (1943).

4) R. J. Dummel and H. S. Mosher, *J. Org. Chem.*, **24**, 1007 (1959).

5) G. P. Hildebrand and C. N. Reilley, *Anal. Chem.*, **29**, 258 (1957).

6) T. Odashima and H. Ishii, *Anal. Chim. Acta*, in press.