Reaction of Pyridylformazane Derivatives with Transition Metal Ions

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Novel pyridylformazane derivatives have been synthesized by introducing various substituents into a benzene ring. Their characteristics as analytical reagents, such as acid dissociation constants and color reactions with various transition metal ions, have been investigated. A linear relationship has been established between Hammett's substituent constants (σ) and acid dissociation constants (pK_{a1} and pK_{a2}), and between (σ) and stability constants of metal complexes. Introduction of a nitro group into *meta*- or *para*-position of the benzene ring has increased the sensitivity to a great extent; the molar absorption coefficient ($\log \epsilon$) of the zinc complex was 4.91 and the stability constant ($\log K_{ZnA2}$) was 18.97 ± 0.05 .

Keywords Formazane compound, analytical reagent, transition metal complex, stability constant

In order to develop chelating reagents with excellent selectivity, sensitivity and stability, a series of formazane compounds have been investigated; the relationship between their structures and reactivity with metal ions and the possibility of their use as analytical reagents were studied.¹⁻⁵ Generally, the spread of π -electrons in formazane compounds is remarkably enhanced by complex formation with metal ions, yielding bathochromic color changes. Formazane compounds are also of interest as analytical reagents, because their complex formation is easily subject to steric hindrance, so that a relatively limited number of metal ions can react with

formazane compounds.

As a rule, a chelating reagent which can be successfully used in spectrophotometric analysis will have some desirable characteristics: *e.g.*, the high complex formation constants ($>10^{15}$) with metal ions, the high molar absorption coefficients ($\epsilon > 10^4$), and the selectivity of the complex formations with metal ions. Considering these characteristics, we attempted to design formazane derivatives in the present work. The compounds shown in Fig. 1 were synthesized by introducing various substituents into benzene ring to enhance sensitivity and by taking into account some adjustment of the chelate rings. Chemical characteristics of these chelating reagents, including reactivity with transition metal ions, were then investigated in detail.

	X	Y
I :	H	H
II :	H	-CH ₃
III :	-OCH ₃	H
IV :	H	-OCH ₃
V :	-NO ₂	H
VI :	H	-NO ₂

Fig. 1 Formazane compounds.

Experimental

Apparatus

All photometric measurements were made with a double-beam Shimadzu 360 spectrophotometer. Quartz cells (1 cm) were used throughout. A Denki Kagaku Keiki Model HG-3 Digital pH Meter, with a glass and calomel electrode pair, was used for pH measurements.

Reagents

Synthesis of the compounds I-VI (Fig. 1 and Table I). Dissolve 2 g of benzaldehyde-2-pyridyl hydrazone in 500 ml of dioxane-ethanol (1:1) and 50 ml of water (A). Diazotize 1.2-1.5 g of an aniline derivative in the usual way and couple with the A, keeping the temperature at 0-5°C and the pH > 12, to obtain a reddish brown compound. Slightly acidify the solution

Table 1 Analytical results of formazane compounds

Compound	C, %		H, %		N, %		Yield, %
	Calc	Found	Calc	Found	Calc	Found	
I (H)	71.77	71.86	4.98	5.01	23.25	23.36	42
II (<i>p</i> -CH ₃)	72.39	72.51	5.39	5.42	22.22	22.18	58
III (<i>m</i> -OCH ₃)	68.90	69.30	5.13	5.20	21.14	21.10	43
IV (<i>p</i> -OCH ₃)	68.90	69.40	5.13	5.18	21.14	21.08	54
V (<i>m</i> -NO ₂)	65.47	65.56	4.24	4.34	25.45	25.42	43
VI (<i>p</i> -NO ₂)	65.47	65.51	4.24	4.26	25.45	25.38	48

with 1 M acetic acid to precipitate the product. Recrystallize twice from a hot mixture of ethanol and dioxane to obtain reddish brown crystals (42–58% yield). Analytical results of the prepared reagents are given in Table 1.

Metal solutions. Dissolve an appropriate amount of each metal in nitric acid. Add perchloric acid and evaporate up nearly to dryness. Dilute the resulting perchlorate with water to make a 10^{-1} M metal stock solution. Dilute this solution with water to prepare working solutions.

Reagent solutions. Dissolve an appropriate amount of each reagent in dioxane to make a 10^{-2} M reagent stock solution. Dilute this solution with dioxane to prepare working solutions.

Buffer solutions. Prepare the buffer solutions by mixing the following pairs of solutions: 0.1 M perchloric acid and 0.1 M hexamine solution (pH 1.10–6.90), 0.1 M perchloric acid and 0.05 M borax solution (pH 7.60–9.00), and 0.05 M borax solution and 0.1 M sodium hydroxide solution (pH 9.30–10.80). Use the appropriate dilute sodium hydroxide solutions as the buffer solutions for pH > 10.90.

All other chemicals used were of analytical reagent grade.

Absorption spectra of reagent solutions

To a 25-ml volumetric flask, add 2.5 ml of 1 M sodium perchlorate solution, 2.5 ml of 10^{-4} M reagent solution and 10 ml of dioxane, and then dilute exactly to 25 ml with the buffer solution of an appropriate pH. Measure the absorption spectrum of the resulting solution against a water blank between 350 nm and 700 nm.

Absorption spectra of metal-complex solutions

The absorption spectra of metal-complex solutions were measured under two conditions: one with an excess of metal ion and the other with an excess of reagent. In case of an excess of metal ion, in a 25-ml volumetric flask, add 2.5 ml of 1 M sodium perchlorate solution, 10 ml of dioxane, 1.0 ml of 10^{-2} M metal ion solution and 2.5 ml of 10^{-4} M reagent solution, and then dilute exactly to 25 ml with the buffer solution of an appropriate pH. Measure the absorption spectrum of the solution against a water blank between 500 nm and 800 nm.

In case of an excess of reagent, in a 25 ml volumetric flask take 2.5 ml 1 M sodium perchlorate solution, 10 ml of dioxane, 2.5 ml of 10^{-4} M metal ion solution and 2.5 ml of 10^{-3} M reagent solution, and dilute exactly to 25 ml with the buffer solution of an appropriate pH. Measure the absorption spectrum of the solution against a reagent blank between 500 nm and 800 nm.

Results and Discussion

All the reagents (I–VI) synthesized are insoluble in water but are soluble in organic solvents such as benzene, ethanol and dioxane, yielding orange-yellow color solutions. In dioxane-water mixed solvent media, the neutral and acid solutions of these reagents are orange-yellow (HA) and yellow, respectively, while the alkaline solutions of the reagents I–V are red-purple and that of the reagent VI is blue (Fig. 2). This is probably due to the protonation to the nitrogen atom of pyridine ring (H_2A^+) in acid solution and the deprotonation of the imino group of the formazane nucleus (A^-) in alkaline solution.

In Table 2 are summarized the acid dissociation

Fig. 2 Absorption spectra of the reagent VI (*p*-NO₂) in 50 v/v% dioxane. 1: H_2A^+ , 4.32×10^{-5} M, [VI (*p*-NO₂)]; 2: HA, 4.32×10^{-5} M, [VI (*p*-NO₂)]; 3: A^- , 1.08×10^{-5} M, [VI (*p*-NO₂)]; 1 cm cell.

Table 2 Dissociation constants, molar absorptivities and isosbestic points of formazane compounds

Compound		H ₂ A ⁺	HA	A ⁻
I (H)	pK _a		3.57±0.02	13.32±0.02
	λ _{max} /nm	395	460	490
	log ε (max)	4.20	4.14	4.28
	λ _{isos} /nm		430	436
II (p-CH ₃)	pK _a		3.81±0.03	13.47±0.03
	λ _{max} /nm	400	465	500
	log ε (max)	4.30	4.24	4.39
	λ _{isos} /nm		436	444
III (m-OCH ₃)	pK _a		3.52±0.02	12.91±0.03
	λ _{max} /nm	400	416	510
	log ε (max)	4.29	4.22	4.84
	λ _{isos} /nm		435	443
IV (p-OCH ₃)	pK _a		3.85±0.02	13.32±0.03
	λ _{max} /nm	410	465	510
	log ε (max)	4.41	4.30	4.69
	λ _{isos} /nm		445	448
V (m-NO ₂)	pK _a		2.98±0.02	12.05±0.03
	λ _{max} /nm	405	475	525
	log ε (max)	4.21	4.16	4.85
	λ _{isos} /nm		435	430
VI (p-NO ₂)	pK _a		2.79±0.02	11.73±0.04
	λ _{max} /nm	405	475	610
	log ε (max)	4.43	4.41	4.85
	λ _{isos} /nm		427	503

constants, wavelengths of maximum absorption, molar absorption coefficients and isosbestic points of each reagent obtained in 50% (v/v) dioxane. The reagents V (*m*-NO₂) and VI (*p*-NO₂) have low pK_{a1} and pK_{a2}, due to an electron-withdrawing nitro group, while the reagent IV (*p*-OCH₃) has a high pK_{a1} due to an electron-repelling methoxyl group. The shift of the absorption maximum wavelength which is observed when each reagent changes from neutral molecule (HA) to anion (A⁻) increases in the following order: reagent I (30 nm)<II (35 nm)<IV (45 nm)<V (50 nm)<III (94 nm)<VI (135 nm).

The molar absorption coefficient of anion (A⁻) increases in the order of reagent I<II<IV<III, V and VI. Thus the anions containing nitro or methoxyl group have high molar absorption coefficients and their absorption maximum wavelengths show red shift. This is probably because the electron system (π*-π) becomes large by the electron-withdrawing and electron-repelling resonance effects of the substituent group. The low molar absorption coefficients for H₂A⁺ forms of all the reagents is attributed to a loss of resonance effect caused by the protonation to the nitrogen atom of the pyridine ring. Figure 2 shows the absorption spectra of cationic (H₂A⁺), neutral (HA) and anionic (A⁻) species of the reagent VI (*p*-NO₂). In Figs. 3 and 4 is illustrated the

Fig. 3 Correlation of the dissociation constant (pK_{a1}) with the Hammett substituent constant.

relationship between Hammett's substituent constants⁶ (σ) and acid dissociation constants (pK_{a1} and pK_{a2}). A linear relationship exists between these constants, so that Hammett's rule is applicable to these formazane compounds. Therefore, it seems that the entire conjugated system of these formazane compounds, like those of

other formazane compounds⁷⁻¹⁰ lie on the same plane. The reagent III (*m*-OCH₃) shows blue shift (max 416 nm) as neutral molecule (HA) and red shift (max 510 nm) as anion (A⁻) when compared with the reagent I (H) under the same conditions, its behavior being different from those of reagents II, IV, V and VI. This is because steric hindrance to the conjugated system in the molecule is caused by the methoxyl group situated in *meta* position in the neutral molecule and the planar structure is slightly distorted, while steric hindrance to the conjugated system is removed by the dissociation imino group of formazane nucleus and then the molecule can take the planar structure. A similar behavior is

known for 2,2'-bipyridyl and its metal complexes.¹¹ Thus, the reagents III, V and VI are supposed to form metal complexes with high molar absorption coefficients.

Absorption spectra of metal complexes

Reactivity of each reagent synthesized with 15 common metal ions (Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Ca²⁺, Mg²⁺, Be²⁺, Pb²⁺, Fe³⁺, Al³⁺, Y³⁺) was examined. Five metal ions, *i.e.*, Co²⁺ (green), Ni²⁺ (deep blue), Cu²⁺ (deep blue), Zn²⁺ (deep blue) and Cd²⁺ (deep blue) (color indicated in parentheses represents the color of each metal complex) showed notable reactivity, but Fe²⁺ and Fe³⁺ (carmine), Hg²⁺ (red) and Pb²⁺ (orange) exhibited weak coloration and the other metal ions did not form colored complexes. Then the reactions of nickel, copper and zinc which showed intense color were quantitatively investigated in mixed dioxane-water solvent media. The absorption coefficients of the complexes, pH ranges suitable for the complex formation and compositions of the complexes (confirmed by mole ratio and continuous variation methods) are summarized in Table 3. As predicted from the results shown in Table 2, the complexes of the reagents, III, V and VI have high molar absorption coefficients. The optimum pH range for complex formation is corresponding to the value of pK_{a1} of each reagent. Large red shifts are observed for complex formations of copper and zinc with the reagent III (209 nm for copper and 194 nm for zinc).

Fig. 4 Correlation of the dissociation constant (pK_{a2}) with the Hammett's substituent constant.

Stability constants of metal complexes

The stability constants of metal complexes were

Table 3 Spectral data for metal complexes

Compound	Metal ion	$\lambda_{\max}/\text{nm}$	$\log \epsilon$	pH range	Composition metal:ligand
I (H)	Cu(II)	620	4.34	4.5-9.5	1:1
	Zn(II)	600	4.76	8.0-9.5	1:2
	Ni(II)	610	4.70	5.0-9.5	1:2
II (<i>p</i> -CH ₃)	Cu(II)	620	4.34	4.5-9.5	1:1
	Zn(II)	600	4.84	8.2-9.5	1:2
	Ni(II)	600	4.73	5.2-9.5	1:2
III (<i>m</i> -OCH ₃)	Cu(II)	625	4.36	3.5-9.5	1:1
	Zn(II)	610	4.80	7.6-9.5	1:2
IV (<i>p</i> -OCH ₃)	Cu(II)	635	4.37	4.5-9.5	1:1
	Zn(II)	610	4.80	7.8-9.5	1:2
V (<i>m</i> -NO ₂)	Cu(II)	620	4.31	3.0-9.0	1:1
	Zn(II)	620	4.91	7.3-9.0	1:2
	Ni(II)	620	4.78	4.0-9.0	1:2
VI (<i>p</i> -NO ₂)	Cu(II)	635	4.35	2.7-9.0	1:1
	Zn(II)	635	4.91	7.0-8.7	1:2
	Ni(II)	625	4.80	3.8-9.0	1:2

measured spectrophotometrically. The calculation method previously reported¹² can be simplified, because under this experimental condition the side reaction of metals with hydroxide ion is small.

When complex MA_n , in which the ratio of metal (M) to ligand (A) is 1:n, is exclusively formed, the following equation can be written with regard to the total concentration of ligand $[A]_T$:

$$[A]_T = \Sigma[H_2A] + [A] + n[MA_n] \quad (1)$$

The concentration of free ligand $[A]$ may be represented as

$$[A] = \frac{[A]_T - n[MA_n]}{P}, \quad (2)$$

where

$$P = 1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1}K_{a2}}$$

and K_{a1} and K_{a2} are the dissociation constants of ligand. The total concentration of metal ion $[M]_T$ may be written as

$$[M]_T = [M] + [MA_n]. \quad (3)$$

The absorbance of a mixture of complex and ligand measured with a 1-cm cell at given pH and wavelength can be written as

$$A = \varepsilon_1[H_2A^+] + \varepsilon_2[HA] + \varepsilon_3[A^-] + \varepsilon_4[MA_n] + \varepsilon_5[M] \quad (4)$$

where ε_1 , ε_2 , ε_3 , ε_4 and ε_5 are the molar absorption coefficients for cation of ligand, neutral ligand, anion of ligand, complex and metal ion, respectively. Substituting Eqs. (2) and (3) into Eq. (4) and rearranging, we get

$$[MA_n] = \frac{A - \frac{Q}{P}[A]_T - \varepsilon_5[M]_T}{\varepsilon_4 - \varepsilon_5 - n \frac{Q}{P}}, \quad (5)$$

where

$$Q = \frac{\varepsilon_1[H^+]^2}{K_{a1}K_{a2}} + \frac{\varepsilon_2[H^+]}{K_{a2}} + \varepsilon_3.$$

Thus the stability constant K_{MA_n} can be obtained from

$$K_{MA_n}^n = \frac{[MA_n]}{[M][A]^n} = \frac{[MA_n]P^n}{([M]_T - [MA_n])([A]_T - n[MA_n])^n}. \quad (6)$$

These calculations were carried out with a FACOM 230-30 computer. The results obtained are summarized in Table 4. The stability constants involved are appreciably high, so that the reagents tested might react with the metal ions as tridentate ligands, quinoyl, imino and azo groups. The order of the magnitude of $\log K_{MA}$ is $Cu > Ni > Zn$, corresponding to Irving-William series while that of $\log K_{MA2}$ is $Ni > Cu > Zn$. $\delta \log K$ ($\log K_{MA} - \log K_{MA2}$) is positive for copper complexes, but negative for nickel complexes, among which the complexes with the reagents V and VI have the most negative value

Table 4 Stability constants of metal complexes in 50 v/v % dioxane

Compound	Metal ions	$\log K_{MA}^A$	$\log K_{MA2}^A$	$\log K_{MA2}^{2A}$
I (H)	Cu(II)	17.38±0.02	12.18±0.02	29.56±0.02
	Zn(II)	10.02±0.05	10.44±0.04	20.46±0.05
	Ni(II)	14.38±0.02	16.06±0.02	30.44±0.02
II (p-CH ₃)	Cu(II)	16.46±0.02	11.26±0.02	27.72±0.02
	Zn(II)	10.28±0.05	9.27±0.04	19.55±0.05
	Ni(II)	14.18±0.02	15.86±0.02	30.04±0.02
III (m-OCH ₃)	Cu(II)	16.78±0.02	11.58±0.02	28.38±0.02
	Zn(II)	9.90±0.05	10.39±0.04	20.29±0.05
IV (p-OCH ₃)	Cu(II)	16.70±0.02	11.50±0.02	28.20±0.02
	Zn(II)	9.75±0.05	10.23±0.04	19.98±0.05
V (m-NO ₂)	Cu(II)	16.19±0.02	10.99±0.02	27.18±0.02
	Zn(II)	9.42±0.05	10.48±0.04	19.90±0.05
	Ni(II)	13.54±0.02	15.33±0.02	28.87±0.02
VI (p-NO ₂)	Cu(II)	15.92±0.02	10.72±0.02	26.64±0.02
	Zn(II)	9.84±0.05	9.13±0.04	18.97±0.05
	Ni(II)	13.54±0.02	15.33±0.02	28.87±0.02

Fig. 5 Correlation of the stability constants of metal complexes with the Hammett's substituent constant. 1 ●, $\log K_{\text{CuA}}$; 2 ○, $\log K_{\text{NiA}}$; 3 ◐, $\log K_{\text{NiA2}}$.

Fig. 6 Proposed structure of Zn, Ni-formazane complexes.

(−1.79). This result indicates the large contribution of the increased electron-withdrawing resonance effect. Figure 5 depicts the relationship between Hammett's substituent constants (σ)⁶ and the stability constants, showing a linear relationship. Figure 6 illustrates the estimated structure for the metal complex of reagent VI. Thus copper(II) appears to assume square planar dsp^2

configuration^{7-10,13}, and nickel(II) and zinc(II) octahedral d^2sp^3 configuration.

In summary, new pyridylformazane derivatives were synthesized by taking into account the balance among selectivity and sensitivity of color reactions, and the stability of complexes. Three kinds of derivatives: 1-(2-pyridyl)-3-phenyl-5-(3-methoxyphenyl) formazane, 1-(2-pyridyl)-3-phenyl-5-(3-nitrophenyl) formazane and 1-(2-pyridyl)-3-phenyl-5-(4-nitrophenyl) formazane, were found to be excellent in selectivity (smaller number of metal ions Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pd^{2+} , form colored complex with these reagents), sensitivity and stability of complexes. The reagents V ($m\text{-NO}_2$) and VI ($p\text{-NO}_2$) look especially promising as analytical reagents for zinc because of the high molar absorption coefficient ($\log \epsilon = 4.91$) and the high stability constant ($\log K_{\text{ZnA2}} = 18.97 \pm 0.05$).

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