

Acid–Base Behavior of Substituted Hydrazone Complexes Controlled by the Coordination Geometry

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A new series of substituted hydrazone complexes, [Cu(Hpbph)] (1), [Cu(Hpbph)PPh₃](PF₆) (2-PF₆), [NiCl(Hpbph)]Cl (3-Cl), [PtCl(Hpbph)]ClO₄ (4-ClO₄), and [PtCl(pbph)] (4b) (Hpbph = 2-(diphenylphosphino)benzaldehyde 2-pyridylhydrazone) have been synthesized and characterized. X-ray crystallography revealed that the copper(I) complexes adopt pseudo-tetrahedral geometry, while the nickel(II) and platinum(II) complexes provide square-planar forms. All the complexes exhibit distinct color changes on the basis of the deprotonation/protonation on the ligand although their acid/base behaviors are largely different. The acidity constants (pK_a) in methanol were determined to be 11.4 (1), 12.5 (2), 7.7 (3), and 6.7 (4). The results indicate that the dissociation of the proton on the ligand strongly depends on the ligand deformation controlled by the coordination geometry of the complexes and ancillary ligands also somewhat affect the acidity.

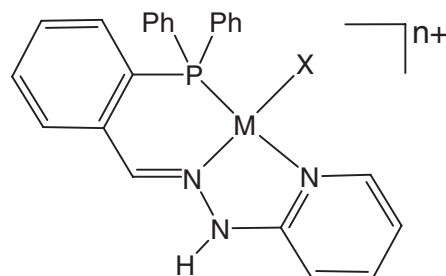
Metal complexes with substituted hydrazones, R¹HC=NNHR² (R¹, R² = alkyl, aryl, acyl, etc.) have attracted much attention for their chromic behavior,^{1,2} catalytic properties,^{3–5} and biological applications.^{6–8} Such characteristics of hydrazone complexes are often related to the deprotonation/protonation behavior of the hydrazone ligands, and thus it is important to control the behavior from the viewpoints of the construction of new materials having proton conductivity and sensing and catalytic abilities. In order to control the deprotonation/protonation behavior, the geometry and ligand field strength of hydrazone complexes should be important because the deprotonation of uncoordinated hydrazones occurs only in highly basic conditions. For example, the acidity constant (pK_a) of pyridine-2-aldehyde-2-pyridylhydrazone (i.e., R¹, R² = pyridine) was estimated to be ca. 14.5 in water, while the metal complexes were reported to provide colored deprotonated forms as well as a colorless protonated form.^{1,9} In the case of a palladium complex with 2-(diphenylphosphino)benzaldehyde 2-pyridylhydrazone (Hpbph), it was found that both protonated and deprotonated forms coexist in the crystal as the composition of [PdCl(Hpbph)][PdCl(pbph)]Cl·2H₂O.¹⁰ Thus various types of hydrazone complexes have been prepared until now. However, the acidity constants of hydrazone complexes have not been determined exactly and the protonation/deprotonation properties and their control have not been studied clearly.

In this study, we focus on the coordination geometry of hydrazone complexes. Monovalent copper ion with d¹⁰ electronic configuration preferentially adopts tetrahedral coordination geometry, while the divalent nickel and platinum ions with d⁸ configuration take square-planar geometry. We have prepared a series of new complexes, [Cu(Hpbph)] (1), [Cu(Hpbph)PPh₃](PF₆) (2-PF₆), [NiCl(Hpbph)]Cl (3-Cl), [PtCl(Hpbph)](ClO₄) (4-ClO₄), and the deprotonated form,

[PtCl(pbph)] (4b) (Scheme 1) and investigated their acid–base properties as well as their structures.

Experimental

Materials. The ligand Hpbph was prepared by a slightly modified method reported in the literature.¹⁰ A suspension of 2-(diphenylphosphino)benzaldehyde (199 mg, 0.68 mmol) and 2-hydrazinopyridine (79 mg, 0.72 mmol) in methanol (10 mL) was stirred for 2 h at room temperature. After 2 h, white-yellow precipitate was filtered, washed with methanol and diethyl ether, and dried in vacuum. Yield 60%, ¹H NMR (dmsd-*d*₆): δ 10.98 (s, 1H, –NH), 8.58 (d, *J* = 4.3 Hz, 1H), 8.06 (d, *J* = 4.0 Hz, 1H), 7.95 (dd, *J* = 6.8, 4.3 Hz, 1H), 7.53 (t, *J* = 8.6 Hz, 1H), 7.45–7.35 (m, 7H), 7.30–7.10 (m, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.85–6.65 (m, 2H). Other chemicals were used as those commercially available.



- M = Cu⁺, X = I[–], n = 0 (1)
M = Cu⁺, X = PPh₃, n = 1 (2)
M = Ni²⁺, X = Cl[–], n = 1 (3)
M = Pt²⁺, X = Cl[–], n = 1 (4)

Scheme 1.

Table 1. Crystallographic Data

	1·CH ₂ Cl ₂	2-PF ₆	3-Cl	4b
Formula	C ₂₅ H ₂₂ N ₃ PCl ₂ ICu	C ₄₂ H ₃₅ N ₃ P ₃ F ₆ Cu	C ₂₄ H ₂₀ N ₃ PCl ₂ Ni	C ₂₄ H ₁₉ N ₃ PClPt
Formula weight	656.80	852.18	511.01	610.95
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> /Å	8.800(6)	11.689(1)	11.563(4)	7.431(2)
<i>b</i> /Å	10.703(8)	12.577(4)	12.435(4)	10.031(3)
<i>c</i> /Å	14.23(1)	13.952(4)	15.291(6)	14.797(5)
α /°	89.68(3)	109.302(4)	90.00	101.098(4)
β /°	74.92(2)	93.545(4)	90.687(2)	95.702(4)
γ /°	82.30(2)	93.649(4)	90.00	98.763(4)
<i>V</i> /Å ³	1282(2)	1924(1)	2198(1)	1060.2(6)
<i>Z</i>	2	2	4	2
<i>T</i> /K	150	150	150	150
GOF on <i>F</i> ²	1.059	1.053	1.040	1.006
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.087	0.050	0.036	0.058
<i>wR</i> ₂ ^b	0.240	0.143	0.098	0.150

a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. b) $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$.

Synthesis of Complexes. **[Cu(Hpbph)I]·CH₂Cl₂ (1·CH₂Cl₂):** To Hpbph (65 mg, 0.17 mmol) in dichloromethane (10 mL) was added solid CuI (32 mg, 0.17 mmol). The mixture was stirred for an hour and orange precipitate was filtered. The product was washed with diethyl ether and dried in vacuum. Yield: 105 mg (94%). Anal. Calcd for C₂₅H₂₂N₃PCl₂ICu: C, 45.72; H, 3.38; N, 6.40%. Found: C, 45.35; H, 3.38; N, 6.47%. IR (KBr): 3192 ν(N–H), 3052 ν(C–H, aromatic) cm^{−1}. ¹H NMR (dms-*d*₆): δ 11.68 (s, 1H, –NH), 8.34 (d, *J* = 5.9 Hz, 1H), 7.89 (s, 1H), 7.73 (t, *J* = 7.0 Hz, 2H), 7.60–7.30 (m, 12H), 6.97 (t, *J* = 6.4 Hz, 1H), 6.80 (m, 4H).

[Cu(Hpbph)PPh₃]PF₆ (2-PF₆): A mixture of AgPF₆ (6.2 mg, 0.25 mmol) and 1·CH₂Cl₂ (14 mg, 0.25 mmol) in dichloromethane (30 mL) was stirred for 30 min at room temperature. The precipitate of AgI was removed by filtration. After adding PPh₃ (6.4 mg, 0.25 mmol), the mixture was stirred for an hour and the solution was kept at room temperature. Yellow crystals were formed after a few days. The crystals were washed with diethyl ether and dried in vacuum. Yield: 202 mg (95%). Anal. Calcd for C₄₂H₃₅N₃P₃F₆Cu: C, 59.19; H, 4.14; N, 4.93%. Found: C, 59.41; H, 4.18; N, 4.78%. IR (KBr): 3322 ν(N–H), 3059 ν(C–H, aromatic) cm^{−1}. ¹H NMR (dms-*d*₆): δ 11.95 (s, 1H, –NH), 8.24 (d, *J* = 5.2 Hz, 1H), 8.02 (s, 1H), 7.77–7.62 (m, 3H), 7.45 (t, *J* = 7.3 Hz, 7H), 7.29 (t, *J* = 7.8 Hz, 9H), 7.07 (t, *J* = 9.0 Hz, 7H), 6.79 (m, 6H).

[NiCl(Hpbph)]Cl (3-Cl): To Hpbph (24 mg, 0.06 mmol) in methanol (10 mL) was added solid NiCl₂·6H₂O (15 mg, 0.06 mmol). The mixture was stirred for an hour and orange precipitate was filtered. The product was washed with methanol and dried in vacuum. Yield: 28 mg (90%). Anal. Calcd for C₂₄H₂₀N₃PCl₂Ni: C, 56.41; H, 3.95; N, 8.22%. Found: C, 56.42; H, 3.93; N, 8.27%. ¹H NMR (CDCl₃): δ 14.96 (s, 1H, –NH), 9.14 (s, 1H), 8.19 (d, *J* = 5.7 Hz, 1H), 7.78 (m, 10H), 7.54 (m, 4H), 7.32 (m, 2H), 6.86 (t, *J* = 6.8 Hz, 1H). IR (KBr): 3182 ν(N–H), 3049 ν(C–H, aromatic) cm^{−1}.

[PtCl(Hpbph)]ClO₄ (4-ClO₄) and [PtCl(pbph)] (4b): The starting material, [PtCl₂(PhCN)₂] (PhCN = benzonitrile) was prepared by refluxing a mixture of PtCl₂ and PhCN.¹¹ A mixture of [PtCl₂(PhCN)₂] (142 mg, 0.3 mmol) and Hpbph

(115 mg, 0.3 mmol) in acetonitrile (30 mL) with a drop of triethylamine was refluxed for 3 h. By concentration of the solution, red crystals of [PtCl(pbph)] (4b) were deposited. The crystals were collected by filtration, washed with diethyl ether, and dried in vacuum. Next, 4b (61 mg, 0.1 mmol) was dissolved in acetonitrile and after adding a drop of perchloric acid (60%), yellow needle crystals of 4·ClO₄ were deposited on standing for several days. For 4·ClO₄, Yield: 37 mg (52%). Anal. Calcd for C₂₄H₂₀N₃O₄PCl₂Pt·1.3H₂O: C, 39.23; H, 3.10; N, 5.72; Cl, 9.65%. Found: C, 38.98; H, 2.81; N, 5.69; Cl, 9.63%. ¹H NMR (CDCl₃): δ 12.16 (t, *J* = 21 Hz, 1H, –NH), 9.04 (t, *J* = 48 Hz, 1H), 8.75 (m, 1H), 7.96 (m, 1H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.70–7.35 (m, 13H), 7.09 (t, *J* = 6.7 Hz, 1H). IR (KBr): 3059 ν(C–H) (aromatic), 1121 ν(ClO₄) cm^{−1}. MS (ESI⁺): *m/z* = 612 [M]⁺. For 4b, Yield: 147 mg (80%). Anal. Calcd for C₂₄H₁₉N₃ClPPt: C, 47.18; H, 3.13; N, 6.88; Cl, 5.80%. Found: C, 47.33; H, 3.32; N, 7.11; Cl, 6.12%. ¹H NMR (CDCl₃): δ 8.36 (m, 1H), 8.27 (t, *J* = 48 Hz, 1H), 7.85–7.25 (m, 15H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.35 (t, *J* = 6.7 Hz, 1H). IR (KBr): 3051 ν(C–H) (aromatic) cm^{−1}. MS (ESI⁺): *m/z* = 612 [M + H]⁺.

X-ray Crystallography. All of the X-ray diffraction data were collected on a Rigaku AFC-8/Mercury CCD system. All structures were solved by direct methods and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included and refined using a riding model. The crystallographic data and final *R* indices are summarized in Table 1. Calculations were carried out using the program packages, Crystal Structure and SHELXL-97.¹² Crystallographic data have been deposited with Cambridge Crystallographic Data Center: Deposition numbers CCDC-766424–766427 for complexes, 2-PF₆, 1·CH₂Cl₂, 3-Cl, and 4b in the order.

Determination of Acidity Constants. Acid–base behavior of the complexes was investigated in methanol solution (2.3 × 10^{−5} M) by the titration of 2.3 mM methanolic potassium hydroxide or 2.3 mM perchloric acid. The absorption spectral changes were measured monitoring the pH values with a EUTECH pHScanWP2 pH meter. The pH values were

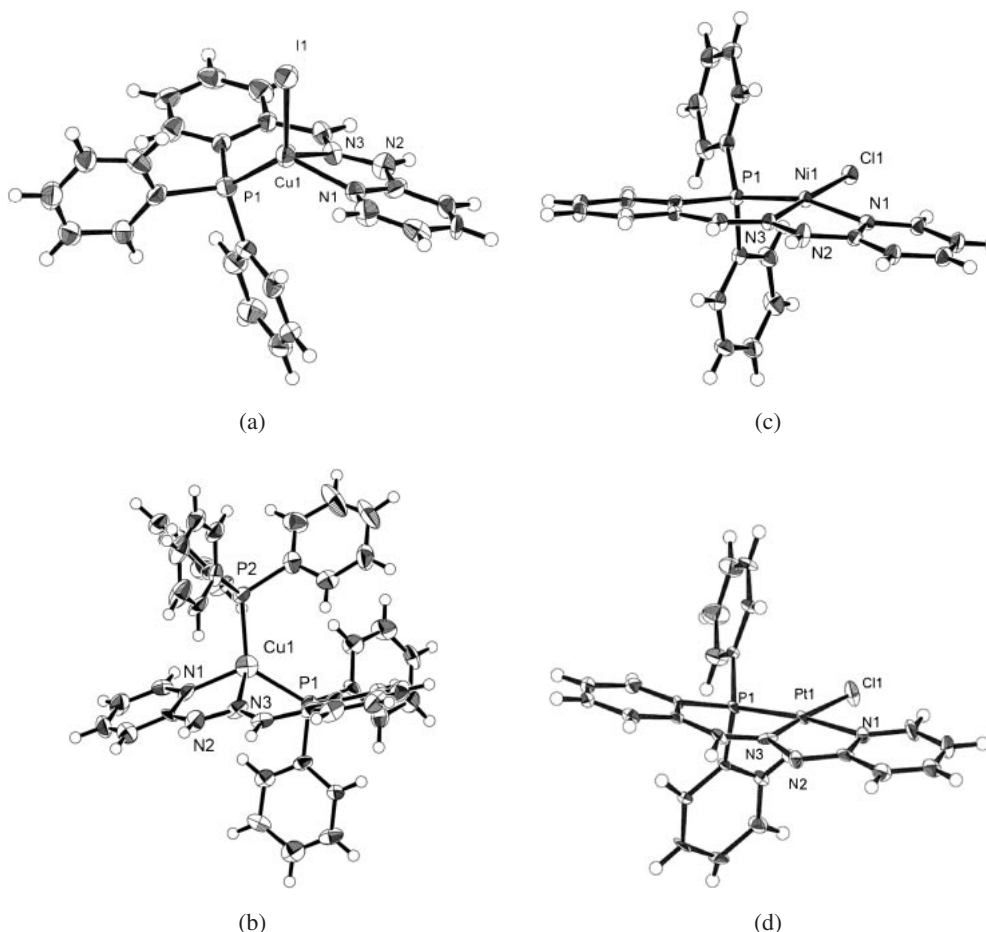


Figure 1. Molecular structures of (a) $[\text{Cu}(\text{Hpbph})\text{I}]$ (**1**), (b) $[\text{Cu}(\text{Hpbph})\text{PPh}_3]^+$ (**2**), (c) $[\text{NiCl}(\text{Hpbph})]^+$ (**3**), and (d) $[\text{PtCl}(\text{pbph})]$ (**4b**). The thermal ellipsoids are drawn as the 50% probability level for non-hydrogen atoms.

corrected by using the eq 1 to the values in methanol, where pH_{corr} and pH_{obs} stand for the corrected and observed values, respectively. Corrected coefficient value $\delta = -2.24$ was used for methanol solution.^{13,14}

$$\text{pH}_{\text{corr}} = \text{pH}_{\text{obs}} - \delta \quad (1)$$

On the basis of the pH dependence of the absorbance data, the limiting absorbance method was employed to determine the acidity constants ($\text{p}K_{\text{a}}$) of the complexes.¹⁵ The $\text{p}K_{\text{a}}$ values were determined from the intercepts of the least-square lines of the plots of $\log\{(A - A_{\text{min}})/(A_{\text{max}} - A)\}$ versus pH, where the slopes were adjusted to be 1.00 (Figure S1). These $\text{p}K_{\text{a}}$ values are consistent with those estimated by another method, the half height method.¹⁵

Other Measurements. ^1H NMR spectra were measured on a JEOL JNM-EX270 spectrophotometer. IR spectra were measured as KBr pellets with a JASCO FT/IR-4100 spectrophotometer. UV-vis absorption and emission spectra were recorded on Shimadzu UV-2500 and JASCO F6000 spectrophotometers, respectively.

Results and Discussion

Synthesis of the Complexes. The ligand Hpbph was coordinated to metal ions such as Cu^+ , Ni^{2+} , and Pt^{2+} with different geometries as a tridentate ligand to form a series of

mononuclear complexes proving the flexibility of the ligand. Only protonated forms of Hpbph were isolated for copper(I) complexes (**1**· CH_2Cl_2 and **2**· PF_6). It is remarkable that both copper(I) complexes are very stable in air. On the other hand, the nickel(II) and platinum(II) complexes were obtained as protonated forms in organic solvents in the presence of a base such as triethylamine, while the protonated forms were able to be isolated from the acidic solution. Though the synthesis of the deprotonated form of the nickel(II) complex, $[\text{NiCl}(\text{pbph})]$ has been reported previously,¹⁰ the protonated form **3** and both forms of the platinum(II) complexes **4** and **4b** were obtained and characterized in this work.

Structural Descriptions. Figure 1 shows ORTEP drawings of molecular structures of complexes **1–3** and **4b**.¹⁶ Relevant geometric parameters of the complexes are listed in Table 2.

As shown in Figures 1a and 1b, the geometry around copper(I) ion is a pseudo-tetrahedron for both **1** and **2**. It is interesting to note that the P1, N1, and I1 atoms for the structure of **1** are located almost in a plane including Cu1. Similar tendency can be seen also for **2**. The deviations of the four atoms (P1, N1, I1, and Cu1 for **1**, and P1, N1, P2, and Cu1 for **2**) from the least-square plane are within 0.17 Å for **1** and 0.16 Å for **2**. The sum of the three angles formed by these atoms around Cu1 is calculated to be 359.6(2)° for **1** and

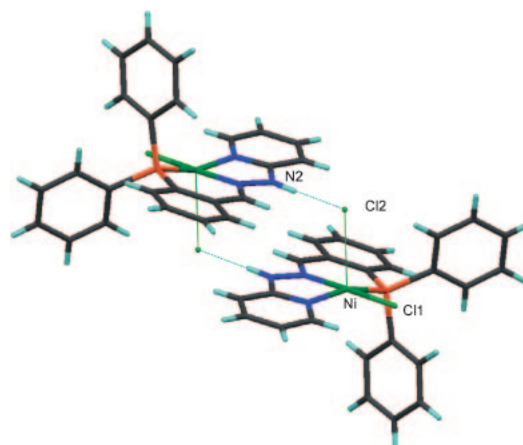
Table 2. Selected Bond Lengths/Å, Bond Angles/°, and Dihedral Angles/°^{a)}

	1 ·CH ₂ Cl ₂	2 ·PF ₆	3 ·Cl	4b
M–N1	2.045(8)	2.065(2)	1.946(2)	2.051(7)
M–N3	2.273(8)	2.127(2)	1.886(2)	1.965(9)
M–P1	2.193(3)	2.237(1)	2.162(7)	2.219(2)
M–X	2.555(1)	2.230(1)	2.167(8)	2.297(3)
N1–M–N3	75.7(3)	78.06(9)	83.81(7)	79.3(3)
N1–M–P1	125.1(2)	121.55(7)	162.97(6)	173.0(2)
N1–M–X	102.2(2)	110.98(7)	94.36(5)	94.1(2)
N3–M–P1	80.6(2)	84.37(6)	94.54(5)	95.8(2)
N3–M–X	120.6(2)	120.33(7)	178.11(5)	173.4(2)
P1–M–X	132.31(8)	125.82(3)	87.07(3)	90.80(9)
Dihedral angle ^{b)}	21.9(4)	19.1(1)	12.12(7)	13.2(4)

a) M = CuI for **1** and **2**, NiI for **3**, PtI for **4b**; X = I[−] for **1**, P₂ for **2**, Cl[−] for **3** and **4b**. b) The dihedral angles denote those between least-squares planes for phenylene and pyridine rings of the ligands Hpbph or pbph[−].

358.4(1)° for **2**, respectively. Therefore, the coordination geometry of these hydrazone copper(I) complexes can be said to be an inclined trigonal pyramid rather than a distorted tetrahedron. It would be due to the structural restraint of this PNN tridentate ligand, Hpbph, which prefers planar coordination for its conjugated structure (phenyl–HC=NNH–pyridyl) even for the protonated form. In fact, the CuI–N3 bond distance is elongated largely for **1** and **2** (2.273(8) and 2.127(2) Å, respectively) compared with those for the complexes having planar geometry (Table 2). The dihedral angle between pyridine and phenylene rings in Hpbph (or pbph[−]) also indicates the deformation of the ligand due to the coordination to the monovalent copper ion (Table 2). Nevertheless, it is noteworthy that these copper(I) complexes are stable in air. In the crystal structure of **1**, the intermolecular hydrogen bond between the secondary amine (N2–H) and the I[−] ligand in the adjacent complex was found (N2–H2···I1 = 2.85, N2···I1 = 3.723(8) Å).¹⁷ In the case of **2**, the amine proton interacts with one of the fluorine atoms of PF₆[−] (N2–H2···F1 = 2.09, N2···F1 = 2.940(9) Å).

In contrast to the copper(I) complexes, the nickel(II) and platinum(II) complexes, **3** and **4b**, take square-planar structures as is usual for d⁸ metal complexes (Figures 1c and 1d). As shown in Table 2, it is clear that the deformations of the hydrazone ligand in **3** and **4b** are much less than those for the copper(I) complexes on the basis of the M–N bond lengths and the dihedral angles between pyridine and phenylene rings in the ligand. Comparing **3** with **4b**, the planarity of the coordination plane is better for the neutral platinum(II) complex **4b**. The maximum deviation from the least-square plane made by five atoms (C11, P1, N1, N3, and Metal ion (NiI or PtI)) is 0.162(9) Å for **4b** while 0.488(2) Å for **3**. The larger deviation for the nickel(II) complex would be due to the formation of a dimeric structure linked by the chloride ions as shown in Figure 2. In the crystal structure of the nickel(II) complex **3**·Cl, the amine proton makes a strong hydrogen bond with the counter anion, Cl[−] (N2–H2···Cl2 = 2.18, N2···Cl2 = 3.030(2) Å),¹⁷ which is also located just on the axial position of the Ni atom of the adjacent complex related by the inversion

**Figure 2.** Dimeric structure of **3**·Cl: Ni···Cl2 = 2.9115(6), N2···Cl2 = 3.030(2), N2–H2···Cl2 = 2.18 Å.

center in the crystal (Ni···Cl2 = 2.9115(6) Å). For the corresponding palladium(II) complex, which was found to be a co-crystal of the protonated and deprotonated forms, such dimeric structure was not formed though there was the hydrogen bond between the amine proton and the Cl[−] ion in the crystal.¹⁰

Absorption Spectra and Acid–Base Behavior. The electronic absorption spectra at various pH values in methanol are shown in Figure 3 and the data are summarized in Table 3. All the complexes exhibit characteristic absorption bands arising from the intraligand transition of the pbph ligand in the visible region.^{2,18} The copper(I) complexes **1** and **2** in methanol exhibited similar spectra with the maximum at 289 nm and a shoulder around 350 nm. By the titration of a methanolic KOH solution, the decrease in the bands and the appearance of new bands occurred at 420 and 453 nm for **1** and **2**, respectively, showing the color change from yellow to orange. On the other hand, the nickel(II) and platinum(II) complexes **3** and **4** exhibit red color in methanol and spectral changes occurred by adding perchloric acid showing the color change from red to yellow. The absorption bands for the deprotonated form of **3** and **4** appear at much longer wavelength (500 nm) compared with those of copper(I) complexes. This would be related to the planarity of the Hpbph ligand in the complex (vide infra). The intraligand transitions must be lowered in the square-planar complexes because of the extension of π -conjugation. All the spectral changes gave the isosbestic points indicating the equilibrium between two components. The initial spectrum recovered completely by returning the pH values to the original points (Figure 3). These results indicate that the deprotonation/protonation of the complexes occurs reversibly in the different pH regions (Scheme 2). For the platinum complex **4**, luminescence spectra with maxima at 602 and 465 nm were also observed for both deprotonated and protonated forms, respectively (Figure S2), though other complexes exhibit no luminescence at room temperature.¹⁹

Figure 4 shows the plots of absorbance changes against pH at 409, 460, 500, and 505 nm for **1**, **2**, **3**, and **4**, respectively. The acidity constants (pK_a) of the complexes determined by the limiting absorbance method are listed in Table 3. Considering that the free Hpbph ligand never dissociates its proton even under very highly basic conditions in methanol (Figure S3),

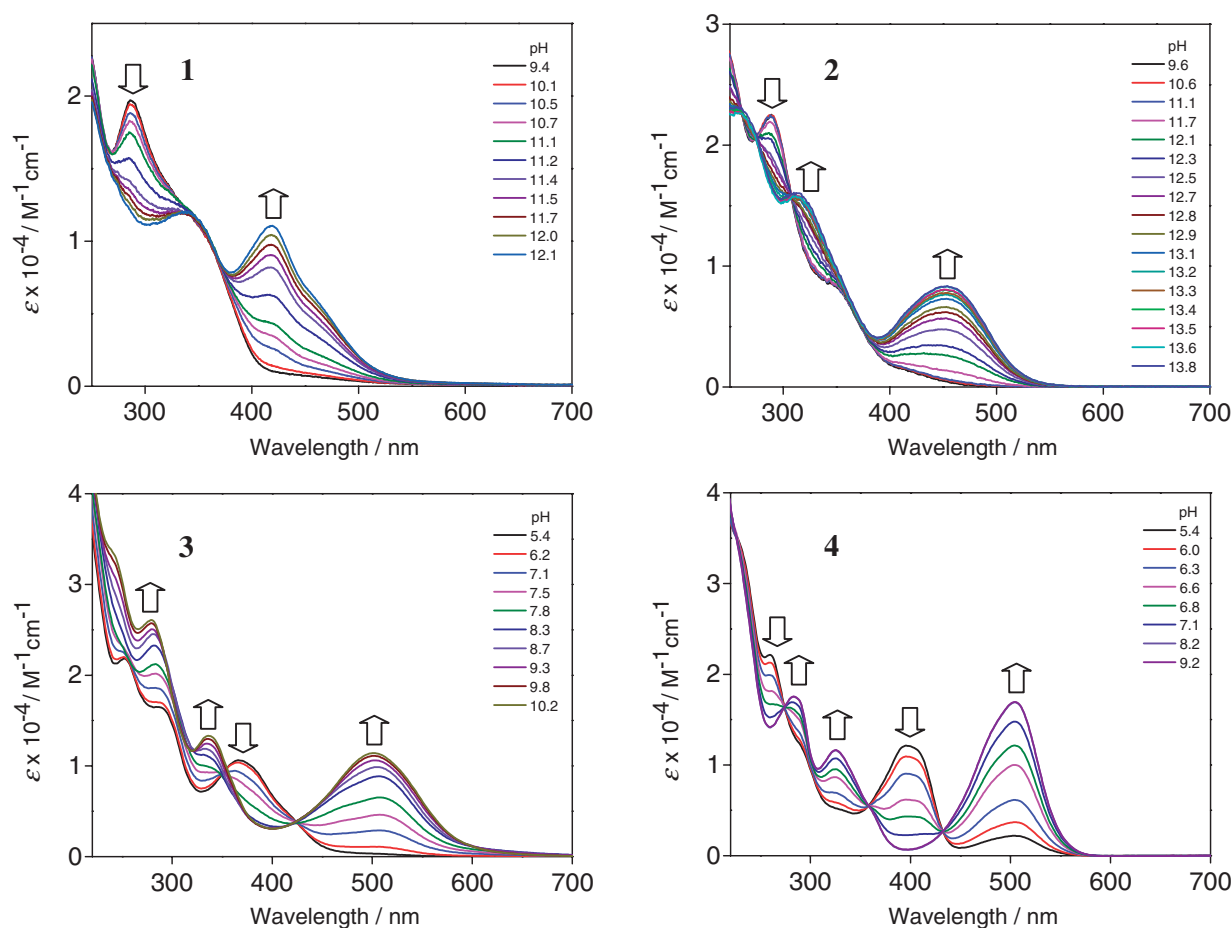
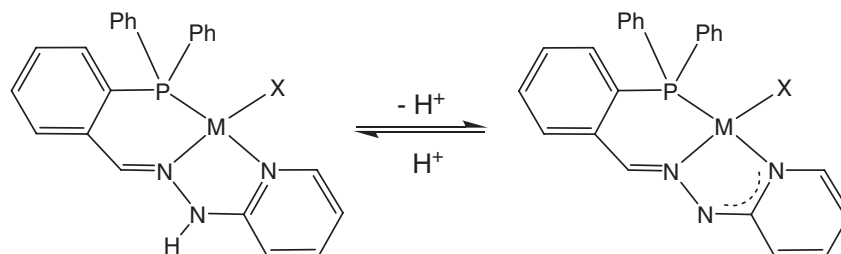


Figure 3. Absorption spectral changes of 1–4 at various pH values in methanol at room temperature.

Table 3. Absorption Data and the pK_a Values in Methanol

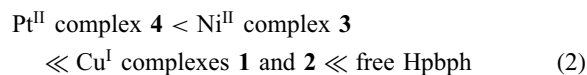
Compounds	$\lambda_{\max}/\text{nm}$ ($\epsilon \times 10^{-4}/\text{M}^{-1} \text{cm}^{-1}$)		pK_a^a
	Protonated form	Deprotonated form	
Hpbph	337 (2.72)		—
1	289 (1.95), 350sh (1.11)	338 (1.20), 420 (1.10), 460sh (0.60)	11.4
2	289 (2.25), 350sh (0.83)	316 (1.60), 453 (0.83)	12.5
3	252 (2.18), 291sh (1.63), 365 (1.06)	279 (2.61), 336 (1.33), 502 (1.14)	7.7
4	260 (2.21), 291sh (1.20), 396 (1.21)	283 (1.75), 325 (1.16), 506 (1.69)	6.7

a) The estimated errors are ± 0.1 .



Scheme 2.

the effect of coordination is clear. The pK_a values of the compounds increase in the following order:



As a result, a distinct difference can be seen in the pK_a values between the complexes containing the much distorted ligand 1 and 2 and the complexes containing the planar geometry 3 and 4. The easiness of deprotonation would be closely related to the electron density on the secondary amine of the ligand Hpbph.

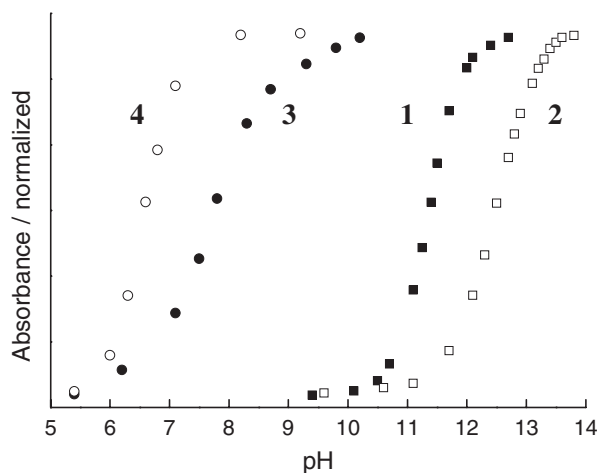


Figure 4. Absorbance–pH curves for **1–4** monitored at 409, 460, 500, and 505 nm, respectively: **1** (■), **2** (□), **3** (●), and **4** (○).

As mentioned in the section of Structural Descriptions, the deformed geometries of Hpbph for **1** and **2** result in weaker coordination, where the effect of the donation from the ligand to metal would be small compared with that for the complexes containing Hpbph with planar geometry. In fact, the chemical shifts of the ^1H NMR for **1** and **2** (δ 10.50 and 10.25 in CDCl_3 , respectively) appear at higher magnetic field compared with those for **3** and **4** (δ 14.06 and 12.16 in CDCl_3 , respectively). In comparison of two square-planar complexes, the $\text{p}K_{\text{a}}$ value of the Pt^{II} complex **4** is slightly smaller than that of the Ni^{II} complex **3**. The higher acidity for the Pt^{II} complex would be ascribed to the higher stability of the planar geometry due to the stronger ligand field compared with the Ni^{II} complex. Furthermore, for the Cu^{I} complexes, the $\text{p}K_{\text{a}}$ value of **2** is somewhat larger than that of **1** (Table 3). This can be explained by the difference of the ligand field strength between I^- and PPh_3 : The electron density on the Hpbph ligand would increase for **2** containing the stronger ligand, PPh_3 compared with that for **1** containing the weaker ligand, I^- , which results in the suppression of the deprotonation of the ligand for **2**. Thus the effect of ancillary ligands on the acidity of the hydrazone ligands is clarified.

Conclusion

All of the complexes containing a substituted hydrazone exhibit acid–base behavior followed by remarkable color changes. The dissociation of proton in the hydrazone ligand is induced by the coordination to metal ions. However, the acidity strongly depends on the coordination geometry characteristic of the metal ions. The copper(I) complexes in pseudo-tetrahedral conformation stabilize the protonated forms compared with the corresponding nickel(II) and platinum(II) complexes with square-planar geometry. One of the main reasons would be the distorted coordination structures by the rigid PNN tridentate ligand where the coordination of N atom in the middle of the ligand weakens. In addition, for the deprotonated form, the planar geometry would be more favorable to get an extended π -conjugation. In conclusion, we elucidated that the acidity of the substituted hydrazone ligand can be controlled by using the characteristics of coordination

geometry of metal ions. The findings would be useful for biological and catalytic application. In fact, we found that the substituted hydrazone ligand dimerized forming a covalent bond on copper(I) complexes by controlling the acidity. The reactions are now under investigation.

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Supporting Information

The absorbance vs. pH curves with the plots for the limiting absorbance method, luminescence spectra of **4**, UV–vis spectra of free Hpbph in basic methanol (Figures S1–S3). This material is available free of charge on the Web at: <http://www.csj.jp/journals/bcsj/>.

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- 19 However, the platinum complex was found to be sensitive to the visible light. The luminescence properties will be reported elsewhere.