September, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***60,*** *3269—3275 (1987)* 3269

# Photochromic Behavior of Pyridoxal-α-Amino Acid-Zn(II) Complexes in Methanol

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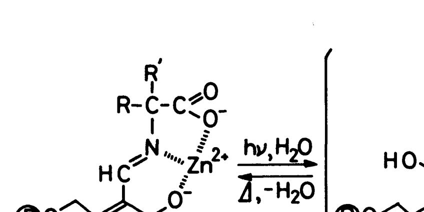
(Received March 13, 1987)

Zn(II) complexes of pyridoxal–α-amino acid Schiff bases showed photochromic behavior in methanol. Spectral studies revealed that intramolecular nucleophilic attack of 5′-hydroxyl group on imine linkage forms cyclic α-amino ether intermediates which thermally return to the original complexes. The photochromism was characteristic of complexes having a 1:1 ligand–metal ratio. Analogous photochromism was also observed with the Cd(II) complex of *N*-pyridoxylidenevaline having a fully occupied d-orbital like the Zn(II) complexes, whereas no photochromism was observed with other transition metal complexes such as Ni(II), Cu(II), Mn(II), and Co(II) complexes.

We have previously reported that Zn(II) complexes of Schiff bases derived from pyridoxal-5′-phosphate and α-amino acids exhibit photochromism in an aqueous solution.[1] The photochromism is caused by photoinduced hydrolysis of the Schiff base ligands, as delineated in Scheme 1. This nucleophilic attack of water on imine carbon made us presume that an intramolecular nucleophilic attack will occur in 5′-hydroxyl group of pyridoxal–α-amino acid–Zn(II) complexes (Scheme 2).

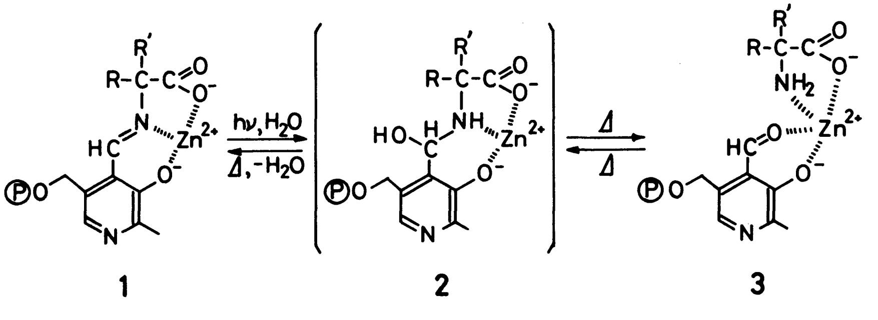
The best-known cyclic ether analogous to the cyclization product **5** is the hemiacetal form of pyridoxal (PL) which is in equilibrium with the aldehyde form in solution and predominant in acidic and neutral methanol solutions.[2] Most metal complexes of PL–α-amino acid Schiff bases, on the other hand, exist exclusively in the imine form.[3] Cyclic isomer **5** is assumed to be thermally unstable so as to return to the original isomer **4**. This report describes spectral examination to confirm the photochromic mechanism. We will further discuss the difference in photochemical behavior between 1:1 (ligand–metal ratio) and 2:1 complexes. The effect of acid on the photochromism will also be examined.



Scheme 2.

## Experimental

PL hydrochloride (Sigma Chem. Co.) was converted to free base in the same manner as described by Christensen.[4] Bis(*N*-pyridoxylidenevalinato)zinc(II) (bis[*N*-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethylene)valinato]zinc(II)) was prepared according to the procedure of Christensen[4] except for the use of zinc perchlorate and KOH instead of chloride and NaOH. 5′-Deoxypyridoxal (3-hydroxy-2,5-dimethyl-4-pyridinecarbaldehyde; 5′-DPL) was prepared by a five-step synthesis[5] starting from pyridoxine hydrochloride (3-hydroxy-4,5-dihydroxymethyl-2-methylpyridine hydrochloride) and was purified by sublimation at 80 °C (mp 108—109 °C). α-Amino acids (Wako Pure Chem. Co.)[6] and metal perchlorates (Kishida Chem. Co.) of the reagent grade or better were used without further purification. Acetonitrile and methanol (Dojin Chem. Co.) of the spectral grade were used as received. UV absorption and fluorescence spectra were recorded on a Shimadzu UV 202 or a JASCO UVIDEC-610A spectrophotometer and a Shimadzu RF-510 spectrometer, respectively. $^1$H NMR spectra were obtained by a Hitachi R-24B spectrometer with tetramethylsilane as an internal standard. IR spectra were obtained by a Hitachi 285S spectrophotometer using KBr disk method.



Scheme 1.

**UV Spectral Studies.** Metal complexes of PL–α-amino acid Schiff bases for UV studies were prepared in situ unless otherwise noted. A methanolic solution of the PL free base was mixed with α-amino acids dissolved in methanol with an equimolar KOH. After 1 h, a solution of a given metal perchlorate in methanol was added to the yellow Schiff base solution. The concentration of amino acids and metal perchlorates was 5 and 10 times as high as that of PL ($1.0\times10^{-4}$ M ($1\,\mathrm{M}=1\,\mathrm{mol\,dm^{-3}}$)), respectively. The use of excess amino acids and metal ions was required to complete the complex formation promptly. Methanolic solutions of the Zn(II) complexes of 5′-DPL–α-amino acid Schiff bases were also prepared in situ in the similar manner. The solutions showed almost the same UV spectra as those of the PL complexes.

The metal complex solutions thus obtained were deaerated by repeated evacuation and flushing with argon three or more times, placed in a 1-cm quartz spectrophotometric cell, and then irradiated with a 500-W super high-pressure mercury lamp (Ushio USH-500D) at room temperature through a filter system composed of a glass filter (Toshiba UV-39) and water in a 5-cm cylindrical cell with quartz windows. After the irradiation, the UV absorption spectra were recorded at appropriate time intervals.

Desired acid or base species of the Zn(II) complexes, when necessary, were obtained by adding standard methanolic solutions of $HClO_4$ or KOH.

**$^1$H NMR Spectral Studies of PL-Valine-Zn(II) System.** A weighed amount of $Zn(ClO_4)_2\cdot6H_2O$ was dissolved in $D_2O$ and the $D_2O$ solution was evaporated to dryness. After this procedure was repeated several times, the residue was dissolved in $CD_3OD$. $CD_3OD$ solution of zinc perchlorate thus obtained (1.0 M, 0.1 cm$^3$) was added to a suspension of 63 mg of bis(*N*-pyridoxylidenevalinato)zinc(II) in 0.5 cm$^3$ $CD_3OD$, and the complex was dissolved completely. The complete dissolution of 2:1 complex by the addition of $Zn^{2+}$ implies that 1:1 complex is more soluble in methanol than 2:1 complex. To the clear solution was added 0.08 cm$^3$ of a $CD_3OD$ solution of KOD (1.0 M) in order to slow down a thermal back reaction; the retardation will be mentioned later. At this time, a small amount of pale yellow precipitate was separated out.[7] After standing for 30 min, the precipitate was filtered out. The resulting clear solution was devided into two parts, and each part was transferred to a Pyrex tube (18 mm diameter) and deaerated by the method described above. The tubes were then dipped in water (20.0±0.5 °C) and irradiated separately with the same Hg lamp as used in the UV studies without any glass filters. In order to ensure efficient mixing, the sample tubes were slanted and rotated while being irradiated. After the irradiation, the photolysates were transferred quickly to NMR sample tubes and NMR spectra were taken at ambient temperature at appropriate time intervals. The spectral changes of two samples in lower and higher magnetic fields were examined. This procedure was required to obtain more unambiguous signals of a photochemically produced intermediate and to follow their momentary changes.

**Isolation of Intermediate.** When the above sample for the NMR measurement was not efficiently agitated during the irradiation, a small amount of precipitate was deposited on the inner wall of Pyrex tube. The precipitate, which is an intermediate formed in the photochromic change as will be described later, disappeared within 10 min on standing at room temperature. In order to isolate it, an analogous $CH_3OH$ solution of the Zn(II) complex was irradiated without agitation at a low temperature (ca. 0 °C) and the photolysate was quickly centrifuged. The precipitate clinging to the bottom of the centrifuge glass tube was dried in vacuo and used for IR measurement in that condition. No attempt to isolate the intermediate was successful.

**Determination of Quantum Yield.** The quantum yield for the disappearance of the starting complex **4** determined by means of an optical-bench system equipped with Ushio USH-500D lamp at 25±1 °C. A beam of 365 nm band isolated with a monochromator (Shimadzu, Baush & Lomb, Grating 1350 grooves/mm) was devided into two beams by a beam splitter, one of which was used to monitor the intensity of incident light. Another beam was used to irradiate the same sample solutions as UV studies in a cylindrical quartz cell of 20×10 mm. The number of photons ($2.2\times10^{15}$ quanta s$^{-1}$) absorbed by the sample solutions was evaluated by subtracting the intensity of transmitted light from that of incident light. The light intensity was determined by the trioxalatoferrate(III) actinometry using 0.006 M potassium trioxalatoferrate(III).[8] The thermal recovery of absorbance at $\lambda_{\mathrm{max}}$ (382—384 nm) obeyed the first-order kinetics. The amount of **4** regenerated during the irradiation was ignored, because it was less than 5% of the amount of **4** reduced by the irradiation.

**Relative Fluorescence Intensity.** The relative fluorescence intensity at 465 nm of the Zn(II) complex of *N*-pyridoxylidenevaline ([PL]=$1.0\times10^{-4}$ M) was measured at 25±1 °C with an excitation wavelength of 385 nm.

## Results and Discussion

**UV Spectral Studies.** Irradiation of a methanolic solution of the Zn(II) complex of *N*-pyridoxylidenevaline with light of wavelengths longer than 390 nm led to an immediate decrease in intensity of absorption bands at 384 and 271 nm and a new absorption band with the maximum wavelength at 314 nm appeared (Fig. 1). When the photolysate was kept in the dark, the UV spectrum returned more than 98% of its initial figure within 60 min at room temperature and showed two isosbestic points at 287 and 333 nm. Almost the same spectral changes were observed with other α-amino acids. The spectral data are summarized in Table 1 together with the quantum yield for photoinduced disappearance of the starting complexes.[9] It is noted that glycine, phenylalanine, homoserine, and serine, in common, gave a weak but discernible shoulder at about 250 nm. In the cases of alanine, valine, α-aminoisobutyric acid, and methionine, this absorption band seems to be buried in an intense band at a shorter wavelength of about 230 nm.

The divalent metal complexes of Schiff bases derived from PL and α-amino acids usually have two characteristic absorption bands in UV region; the longer wavelength band at about 390 nm has been called the $\pi_1$ band and the shorter one at about 270 nm the $\pi_2$ band.[2a)] These bands are assigned as $\pi$–$\pi^*$ transitions of the extended conjugated system formed from pyridine ring, phenolic oxygen and imine linkage. The lack of the conjugated imine linkage, on the other hand, causes shift of these absorption bands to a shorter wavelength. For example, the $\pi_1$ and $\pi_2$ bands of the Zn(II) complex of pyridoxamine (4-aminomethyl-3-hydroxy-5-hydroxymethyl-2-methylpyridine) appear at 301 and 240 nm, respectively;[2a)] those of the Zn(II) complex of an α-hydroxy amine derived from PL and *N*-methylglycine appear at 316 and 248 nm, respectively.[3e)] Thus, the appearance of new absorption bands at about 315 and 250 nm suggests the transformation of imine linkage to a saturated C–N bond. This result seems to agree with the prediction outlined in Scheme 2; however, the formation of an α-amino ether **6** by nucleophilic addition of solvent molecule to imine carbon can also be envisaged.

Table 1. Photochromism of the Zn(II) Complexes of PL-α-Amino Acid Schiff Bases **4** in Methanol[a)]

| α-Amino acid | $\lambda_{max}$/nm Before irradiation | Just after irradiation | Isosbestic points/nm | Quantum yield[b)] |
|---|---|---|---|---|
| Glycine | 384, 270 | 316, ca. 250[c)] | 336, 287 | 0.22 |
| Alanine | 383, 269 | 314 | 334, 285 | 0.17 |
| Valine | 384, 271 | 314 | 333, 287 | 0.19 |
| Phenylalanine | 384, 273 | 316, ca. 250[c)] | 337, 290 | 0.23 |
| AIB[d)] | 382, 270 | 310 | 332, 284 | 0.18 |
| Methionine | 383, 278 | 315 | 335, 290 | 0.05 |
| Homoserine | 382, 281 | 316, ca. 250[c)] | 335, 290 | 0.17 |
| Serine | 382, 279 | 315, ca. 250[c)] | 336, 292 | 0.20 |

a) The initial concentrations of PL, α-amino acids, Zn$^{2+}$, and KOH were $1.0\times10^{-4}$, $5.0\times10^{-4}$, $1.0\times10^{-3}$, and $5.0\times10^{-4}$ M, respectively. b) Quantum yield for the disappearance of **4**.[9)] c) Shoulder. d) α-Aminoisobutyric acid.

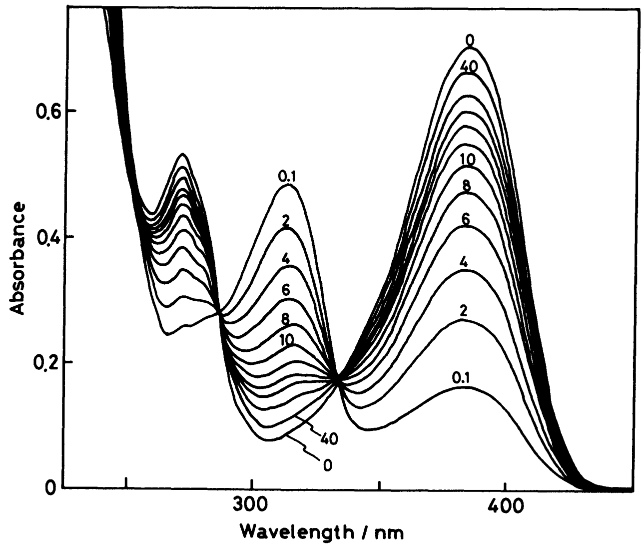
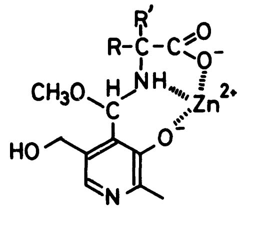


Fig. 1. UV spectral changes of the Zn(II) complex of *N*-pyridoxylidenevaline in methanol. The numeral 0 gives the spectrum before irradiation, and other numerals give the time in minutes after 1-min irradiation at the start of each scan.



**6**

**IR Spectral Studies.** A small amount of precipitate was obtained by irradiating more concentrated solution of the Zn(II) complex of *N*-pyridoxylidenevaline at a low temperature (see Experimental section). When the precipitate was dissolved in methanol again, almost the same thermal UV spectral changes as those in Fig. 1 were observed. This fact suggests that the precipitate is an intermediate of the photochromism.

As shown in Fig. 2(a), the IR spectrum of the intermediate showed a band at 1085 cm$^{-1}$ which can be assigned to the C–O–C stretching vibration. In addition, the intensity of the bands due to the

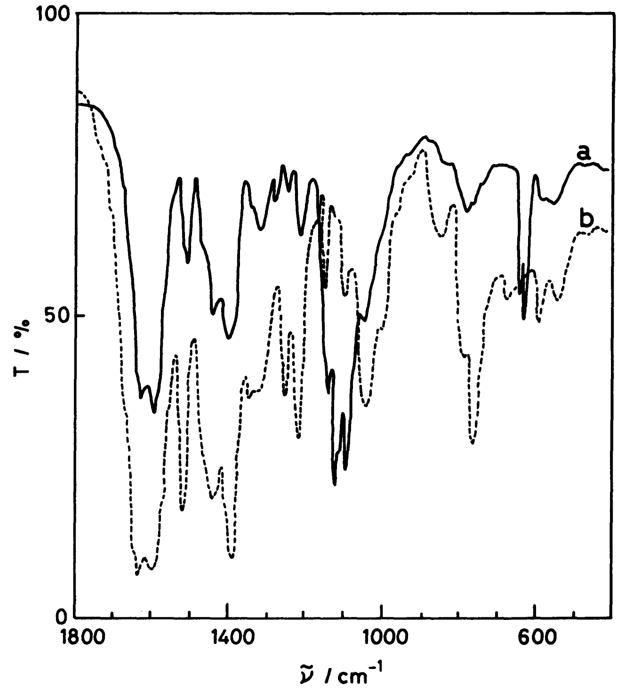


Fig. 2. Comparison of the infrared spectrum of a precipitate obtained through irradiation (a) with that of bis(*N*-pyridoxylidenevalinato)zinc(II) (b).

alcoholic 5′-OH group of bis(*N*-pyridoxylidenevalinato)zinc(II) at 1248, 1045, and 760 cm$^{-1}$ (Fig. 2(b)) decreased remarkably.[10] These facts suggest that the formation of **5** by the intramolecular addition of 5′-OH is predominant over the formation of solvent adduct **6**. This is also supported by the following two facts from UV spectral studies: (1) The Zn(II) complexes of 5′-DPL–α-amino acid Schiff bases without 5′-OH group showed an irreversible slow photoreaction instead of photochromism; (2) almost the same photochromic spectral changes were observed in acetonitrile with low nucleophilicity.[11]

**$^1$H NMR Spectral Studies.** The $^1$H NMR spectrum of the Zn(II) complex of *N*-pyridoxylidenevaline in slightly alkaline $CD_3OD$ showed five prominent signals (Fig. 3, 0: before irradiation), which were readily assigned on the basis of data reported for several Schiff base metal complexes:[3b,7b,12] δ 8.80 (1H, s, HC=N–), 7.50 (1H, s, 6-H), 3.82 (1H, d, α-H of valine moiety), 2.55 (3H, s, 2-$CH_3$), and 1.08 and 0.99 (6H, d and d, $CH_3$ of isopropyl group). The signal of methylene proton of 5-hydroxymethyl group is probably obscured by the solvent absorption.

Figure 3 also shows that new signals appeared on irradiation and then disappeared within 10 min at ambient temperature. The UV spectral changes simultaneously observed were almost the same as those in Fig. 1.

NMR spectra by imine proton showed a marked shift with irradiation from δ 8.80 to a higher magnetic field at δ 5.85. It has been reported[13] that the imine proton resonance of *N*-pyridoxylidenehistidine at δ 8.33 shifts to a higher magnetic field at δ 5.81 by cyclization forming a tetrahydropyridine derivative. Moreover, the 4-CH signal of an α-hydroxy amine formed from PL and *N*-methylglycine appears at δ 6.09,[14] and the signals of methine protons at 2 position of various 2-phenyloxazolidine compounds appear at about δ 5.8.[15] Thus, the photocyclization to **5** described above was further confirmed by the singlet signal induced at δ 5.85 as well as by other newly-induced signals which can be readily assigned to pyridine ring proton (δ 7.62, s), the valine moiety α-proton (δ 3.48, d), the 2-methyl protons (δ 2.53, s), and the methyl protons of the isopropyl group (δ 1.12—0.94, m) of **5**.

**Effects of Acid and Base on Photochromism.** UV spectra of the metal complexes of PL–α-amino acid Schiff bases have two characteristic bands, i.e., the $\pi_1$ and $\pi_2$ bands described above. These bands were affected by the addition of $HClO_4$ or KOH. For example, the $\pi_1$ band (382 nm) of the Zn(II) complex of *N*-pyridoxylidenevaline in an acidic solution shifted to a longer wavelength (385 nm) with a decrease in absorbance by the addition of KOH,

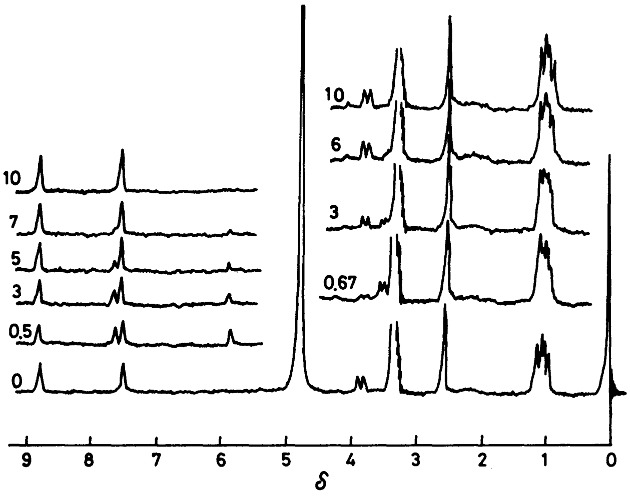


Fig. 3. $^1$H NMR spectra of a $CD_3OD$ solution of the Zn(II) complex of *N*-pyridoxylidenevaline. The numeral 0 gives the spectrum before irradiation and other numerals give the time in minutes after irradiation at the start of each scan. The spectra in lower and higher magnetic fields were separately taken using two samples.

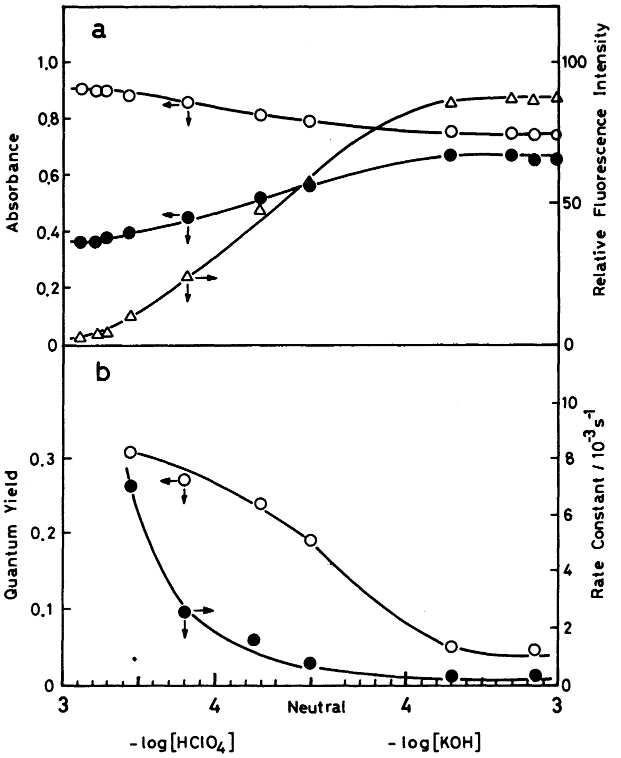


Fig. 4. (a) UV absorbance changes at 385 nm (○) and 272 nm (●) and fluorescence intensity changes (△) of the Zn(II) complex of *N*-pyridoxylidenevaline as a function of $HClO_4$ or KOH concentration in methanol. (b) Quantum yields for the disappearance of the Zn(II) complex of *N*-pyridoxylidenevaline (○) and rates of the thermal back reaction (●) as a function of $HClO_4$ or KOH concentration.

whereas the $\pi_2$ band at 280 nm shifted to a shorter wavelength (272 nm) with an increase in absorbance. Plots of the absorbances at 272 and 385 nm vs. the negative common logarithm of concentration of the added $HClO_4$ or KOH (Fig. 4(a)) gave titration curves similar to those in $H_2O$,[16] and can be well explained by the proton equilibrium on pyridine nitrogen. The relative fluorescence intensity also varied with adding $HClO_4$ or KOH and the resulting titration curve had an inflection point similar to that of UV absorbance (Fig. 4(a)).[17] This fact indicates that the p$K$ value for the proton equilibrium of pyridine nitrogen in the excited singlet state is nearly equal to that in the ground state.

All solutions used for preparing the titration curves in Fig. 4(a) showed photochromic spectral changes, and the $\pi_1$ band of the intermediate occurred at 300 nm in a slightly alkaline solution (the concentration of KOH added, $5.0\times10^{-5}$ M), whereas the band in solutions acidified with $HClO_4$ occurred at 314 nm. This difference can also be explained by the proton equilibrium on pyridine ring of the intermediate. A similar proton equilibrium has been reported for the Cu(II) complex of *N*-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridylmethyl)valine:[18] The deprotonation of the complex causes a blue shift of the absorption maximum from 315 to 300 nm.

The quantum yield for disappearance of the Zn(II) complex of *N*-pyridoxylidenevaline became greater with an increase in the concentration of $HClO_4$ and the titration curve (Fig. 4(b)) showed an inflection point similar to those observed in UV and fluorescence spectral studies. The photocyclization seems, therefore, to be accelerated by protonation of pyridine nitrogen in the excited singlet state or in the ground state. The rate of thermal back reaction increased with an increase in the amount of $HClO_4$ added, and inversely decreased as the amount of KOH added increased (Fig. 4(b)). The rate change can be interpreted in terms of proton catalysis in a ring cleavage reaction of **5**.

**Difference in Photochemical Behavior between 2:1 and 1:1 Complex.** Addition of much larger amount of KOH (e.g., $1.05\times10^{-2}$ M) caused the disappearance of photochromism, and instead, a slow irreversible spectral change took place to give a band of product with $\lambda_{max}$ at 322 nm. The irreversible change was also observed in systems containing less than equimolar amount of $Zn^{2+}$: for example, in a system containing $Zn^{2+}$ of $0.6\times10^{-4}$ M and PL, valine, and KOH of $1.0\times10^{-4}$ M.

The Zn(II) complexes of PL-α-amino acid Schiff bases exist as 2:1 form in solid state.[4,7b,15b] Gansow and Holm,[7b] on the other hand, showed by NMR analyses that 2:1 and 1:1 species co-exist in an aqueous PL-alanine-Zn(II) system and that the extent of formation of 2:1 species increases with an increase in pH. The 2:1 species is also formed in aqueous solutions containing appreciably smaller amounts of $Zn^{2+}$ (0.016—0.05 M) than those of PL and alanine (0.1 M). These facts made us infer that the irreversible change is induced by excitation of 2:1 species, whereas the photochromism is induced by excitation of 1:1 species.

In order to ascertain this idea, the influence of $Zn^{2+}$ on $^1$H NMR spectra of the Zn(II) complex of *N*-pyridoxylidenevaline was investigated and the results are depicted in Fig. 5. A saturated solution of the Zn(II) complex in alkaline $CD_3OD$ (0.12 M KOD) prepared by dissolving 2:1 complex showed, as a whole, upfield-shifted signals compared to those of solutions containing extraneous $Zn^{2+}$, indicating that the signals of 2:1 species appear in higher magnetic fields than 1:1 species. It seems important that the solution without extraneous $Zn^{2+}$ failed to show the photochromic spectral changes as observed in a solution containing excess $Zn^{2+}$ (Fig. 3). These results support the idea that the presence of 1:1 species is a prerequisite for the photochromism.

**Irradiation of Other Metal Complexes.** Photochemical behavior of *N*-pyridoxylidenevaline complexes with other divalent metal ions such as $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$, and $Cd^{2+}$ was investigated in

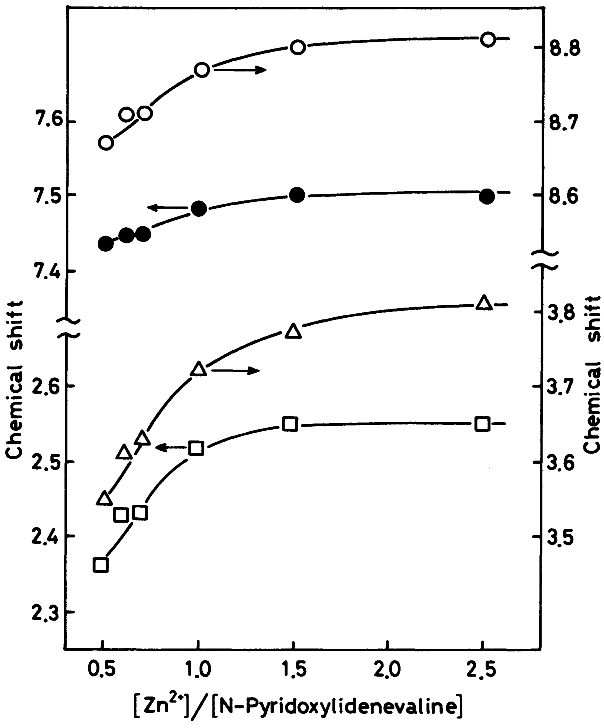


Fig. 5. $^1$H NMR chemical shifts as a function of the concentration of $Zn^{2+}$ in a methanolic solution of the Zn(II) complex of *N*-pyridoxylidenevaline ([*N*-pyridoxylidenevaline]=$4.0\times10^{-2}$ M, [KOH]=0.12 M): ○; -CH=N-, ●; ArH, △; α-H of valine moiety, □; Ar-$CH_3$.

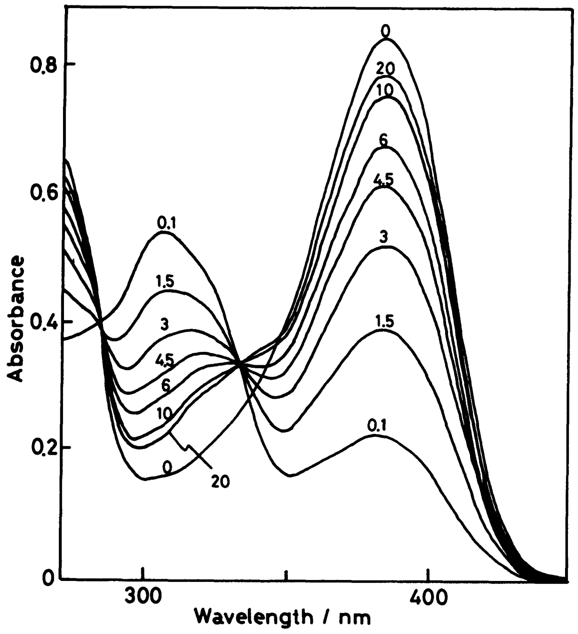


Fig. 6. UV spectral changes of the Cd(II) complex of *N*-pyridoxylidenevaline in methanol. The numeral 0 gives the spectrum before irradiation, and other numerals give the time in minutes after 3-min irradiation at the start of each scan.

methanol containing excess metal ions. The Cd(II) complex having the $d^{10}$ electronic structure like the Zn(II) complexes showed photochromism (Fig. 6), whereas the Cu(II) and Ni(II) complexes were exceedingly photostable. For the Co(II) and Mn(II) complexes, only a slight irreversible decrease was observed in the absorbance of intraligand $\pi$-$\pi^*$ bands at about 385 nm: less than 5% decrease after irradiation for 3 min. In addition, fluorescence intensity of the complexes showing no photochromism was negligibly weak in comparison with those of the photochromic Zn(II) and Cd(II) complexes. Thus, lack of photochromism in the transition-metal complexes with unfilled d-shells appears to be attributed to the presence of nonradiative processes from the intraligand $\pi$-$\pi^*$ singlet state to d–d or charge-transfer excited state, although it is not yet clear whether the singlet state is photoreactive or not in the cases of the Zn(II) and Cd(II) complexes.

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3) a) It is well-known that alternative cyclization takes place thermally in the cases of Schiff bases or their metal complexes having highly nucleophilic functional groups at $\beta$ or $\gamma$ position of the amino acid moieties.[3b–e] For example, the Schiff base of cysteine gives a thiazolidine derivative.[3b] Such cyclization products are not formed with any one of amino acids employed in the present study (listed in Table 1); b) E. H. Abbot and A. E. Martell, *J. Am. Chem. Soc.*, **92**, 1754 (1970); c) D. Heyl, S. A. Harris, and K. Folkers, *J. Am. Chem. Soc.*, **70**, 3429 (1948); d) Y. Matsushima, *Chem. Pharm. Bull.*, **16**, 2046 (1968); e) *ibid.*, **16**, 2143 (1968).

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6) Optically-active amino acids were of L-configuration.

7) a) The precipitate appears to be a mixture of 2:1 complex, $Zn(OD)_2$, and $KClO_4$, because the IR spectrum of the precipitate was similar to that of 2:1 complex and because the addition of KOD possibly leads to deposition of $Zn(OD)_2$ and $KClO_4$. The precipitation of the complex is in harmony with the formation of a 2:1 complex at high pH in an aqueous PL–alanine–Zn(II) system,[7b] as will be discussed later in detail; b) O. A. Gansow and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 5629 (1968); *ibid.*, **91**, 573 (1969).

8) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

9) As will be described later, the Zn(II) complex of *N*-pyridoxylidenevaline existed as the 1:1 form rather than 2:1 form when the concentration of $Zn^{2+}$ was 1.5 times or above as high as that of the Schiff base ligand (see Fig. 5). Since the solutions used here contained excess $Zn^{2+}$ ($[Zn^{2+}]/[\text{ligand}]=10$, see Experimental section), all the starting complexes probably exist as 1:1 forms.

10) Careful inspection of IR spectrum of the precipitate (Fig. 2(a)) revealed that the intermediate was contaminated with a small amount of starting complex and $Zn(ClO_4)_2$. A new band at $1110\,cm^{-1}$ is attributed to the stretching vibration of a perchlorate anion which was added to the sample solution as zinc perchlorate.

11) a) Acetonitrile solution was prepared by mixing the crystalline 2:1 complex and zinc perchlorate at a 1:5 molar ratio. At this time, the addition of a small amount of water (2%) was required to dissolve two components. The direct participation of water in the photochromism, if any, would give an $\alpha$-hydroxy amine analogous to **2** which has a UV spectrum similar to those of the cyclic ethers **5**. However, this type of $\alpha$-hydroxy amine has not yet been detected,[11b] and thus is expected to be readily transformed into a mixed complex analogous to **3**.[1] Careful inspection of the spectrum just after the irradiation revealed the absence of the mixed complex which probably has a similar spectrum to that of PL, dismissing the possibility of the photohydrolysis; b) D. Hopgood and D. L. Leussing, *J. Am. Chem. Soc.*, **91**, 3740 (1969); D. L. Leussing and C. K. Stanfield, *J. Am. Chem. Soc.*, **88**, 5726 (1966).

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15) H. Aoyama, M. Sakamoto, K. Kuwabara, K. Yoshida, and Y. Omote, *J. Am. Chem. Soc.*, **105**, 1958 (1983).

16) a) Davis et al.[16b)] reported an increase in the absorbance of the $\pi_1$ band and a decrease in the $\pi_2$ band in $H_2O$ by lowering pH, and obtained the $pK_a$ value of 6.5 for the proton dissociation on the pyridine nitrogen. b) L. Davis, F. Roddy, and D. E. Metzler, *J. Am. Chem. Soc.*, **83**, 127 (1961).

17) Although the absorbances at the excitation wavelength (385 nm) decreased with a decrease in the $HClO_4$ concentration and an increase in the KOH concentration (Fig. 4(a)), the fluorescence intensity inversely increased. Thus the acid and base effects on the fluorescence intensity are somewhat underestimated.

18) H. N. Christensen, *J. Am. Chem. Soc.*, **81**, 6495 (1959).