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UV-Visible and ^{1}H NMR Spectroscopic Studies on Direct Chelate Formation between Alkaline Earth Metal Ions and 1-(2-Pyridylazo)-2-naphthol or 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol in Acetonitrile

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In acetonitrile, chelate formation between alkaline earth metal ions and 1-(2-pyridylazo)-2-naphthol (PAN = Hpan) in both the absence and presence of CH_3SO_3H and 1,1,3,3-tetramethylguanidine (1,1,3,3-TMG) was examined by means of UV-visible absorption and ^{1}H NMR spectroscopy at room temperature. Upon the addition of 0.01 mol dm^{-3} or more of $Mg(ClO_4)_2$ to a 5.0×10^{-4} mol dm^{-3} PAN–MeCN solution, the solution color turned from yellow to red. The appearance of a new absorption band with two peaks at 500 and 535 nm indicated 1:1 chelate formation between Mg^{2+} and PAN; the equilibrium constant was evaluated to be 2.5×10^{-3} for the following reaction: $\mathrm{Hpan} + Mg^{2+} \rightleftarrows Mg(pan)^+ + H^+$. The presence of an equivalent amount of the base, 1,1,3,3-TMG, enhanced the chelate formation reaction, while that of the acid (CH_3SO_3H) depressed the reaction remarkably. The ^{1}H NMR results verified the above reaction scheme for Mg^{2+} and PAN. The interaction between the metal ions and PAN in acetonitrile decreased as $Mg^{2+} > Ca^{2+} \simeq Sr^{2+} \gg Ba^{2+}$. In the absence of the base, strange to say, direct chelate formation between Mg^{2+} and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) was much less than that for PAN; however, conversely, it was greater in the presence of a ten-fold amount of the base. The additional interaction between the second Mg^{2+} and the N-atom of the diethylamino group in 5-Br-PADAP was concluded to depress the chelate formation of the first Mg^{2+}. The enhancement of the acidity of CH_3SO_3H (considerably weak acid in MeCN) by the addition of $Mg(ClO_4)_2$ inhibited not only the chelation, but also another interaction between Mg^{2+} and 5-Br-PADAP.

Heterocyclic aza dyestuffs have been utilized in analytical chemistry,[1] especially as "metallochromic" indicators in chelatometric titrations[2,3] as well as photometric determination of trace metal ions.[4] 1-(2-Pyridylazo)-2-naphthol (designated as PAN = Hpan)[5] is one of the most widely used reagents in this class. It is known that PAN forms chelate complexes (usually red color) with many polyvalent metal ions, but does not form colored complexes with the alkaline earth or aluminum ions in aqueous solution, usually, containing some organic solvents.[6] Although Cheng and Bray[7] described that alkaline earth metal ions failed to form detectable precipitates or coloration by adding PAN in methanol to aqueous solutions of metal ions, Shibata[5] included alkaline earth metals in elements reacting with PAN to yield color and/or precipitate from aqueous media. He has also described that, upon the addition of PAN to an ethanolic solution of aluminum salt, an orange-red color develops, and that the same color is observed in other alcohols and acetone. Obviously, in less solvating media, chelation between PAN and Al^{3+} (or some aluminum ion species) may be possible.

By means of electrochemical and spectroscopic methods, we[8] have demonstrated that, in poor solvating media, such as acetonitrile, extraordinary "strong" interactions between alkali metal (Li^+, Na^+) or alkaline earth metal ions and anions can be observed, which would never be operative in aqueous solution at ambient temperature. The effects of the alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates on proton transfer from tropolone[9] and nitrophenols[10] to amine or pyridine bases in acetonirile were interpreted by direct interactions between the metal ions and the tropolonate and nitrophenolate ions. It was found that, with increasing concentration of M^+ or M^{2+}, the values of the Hammett acidity function, Ho, of acids in acetonitrile were altered by direct interactions not only between M^+ or M^{2+} and a acid-base indicator (Ind), "Methyl Yellow" [*p*-(dimethylamino)-azobenzene], but also between M^+ or M^{2+} and the conjugate base from the acids (e.g., CF_3COO^- Mg^{2+}).[11] The color changes of sulfonephthaleins, such as Phenol Red, with the addition of M^+ or M^{2+} in acetonitrile were examined by UV-visible and ^{1}H NMR spectrometry.[12] Very recently, the cleavage of γ-lactone rings of Rhodamine B base and a practical black color former with M^+ and M^{2+} in acetonitrile solution was confirmed by ^{1}H and ^{13}C NMR methods.[13]

In the present work, the chelate formations between alkaline earth metal ions and 1-(2-pyridylazo)-2-naphthol (PAN) and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), cf. Chart 1, in acetonitrile were examined by UV-visible and ^{1}H NMR spectrometry. A stronger chelate formation between Mg^{2+} and PAN than 5-Br-PADAP in the absence of a base was observed, though the opposite tendency occurred in the presence of an appropriate base; the cause of this inconsistency was explored.

In acidic solutions, the pyridine-N atom of PAN is protonat-

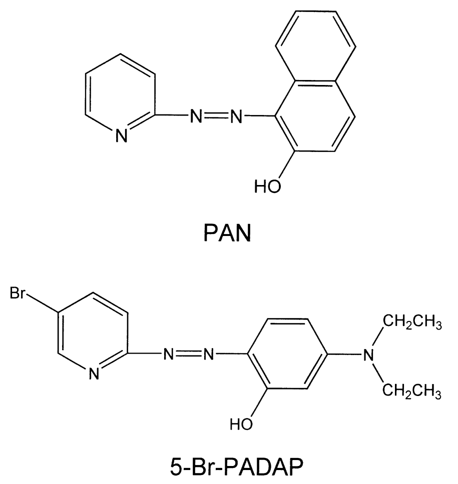
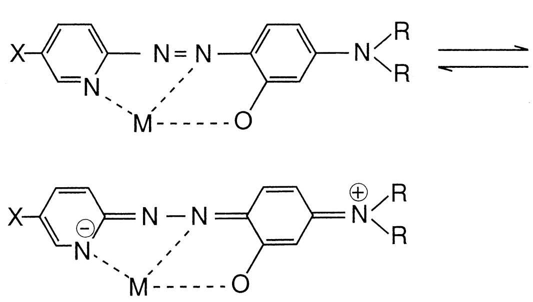


Chart 1.



Scheme 1. "Charged quinone" strucuture of pyridylazo compounds.

ed; and in basic solutions, the H of the OH group is ionized: the acidity constants of PAN are reported to be $pK_1 = 2.9$ and $pK_2 = 11.5$ in aqueous solution;[14] which were given by extrapolation from 1,4-dioxane-water mixed media. The values vary with the contents of the organic solvent and the measurement methods employed.[5] The metal chelates of PAN consist of metal cations bounded to O^- of the OH group (after deprotonation), to pyridine-N and aza-N, constructing double five-membered rings.[4]

Metal chelates of pyridylazo compounds, possessing both electron-donating and withdrawing groups at the ends of the azobenzene, give larger absorptivities than those without the groups, which can be attributed to a "charged quinone" structure,[15,16] as shown in Scheme 1. Recently, PAN was used as a metal collector in a solvent sublation-spectrophotometric determination of trace Ni^{2+} in drinking water.[17] PAN had been utilized for the solvent extraction of Ca^{2+}, Sr^{2+}, and Ba^{2+} with a 1:1 mixture of CCl_4 and tributyl phosphate.[18] Transition metals were determined with a more sensitive derivative, 5-Br-PADAP, spectrophotometrically.[19] Liquid chromatography[20] and potentiometry[21] were used to determine of trace metal ions as chelates with 5-Br-PADAP. Ohashi et al.[22] have reported the isomer recognizing adsorption of the Pd(II)-5-Br-PADAP complex at the toluene–water interface.

Experimental

1-(2-Pyridylazo)-2-naphthol (A. C. S. reagent) and 2-(5-bromo-2-pyridylazo)- 5-diethylaminophenol (97%) were purchased from Aldrich and used as received. Me_4NOH (25 wt% methanol solution) and Et_4NOH (20 wt% aqueous solution) were obtained from Aldrich. Anhydrous perchlorate salts and other chemicals were used as mentioned previously.[10–13] UV-visible spectra were measured using a Hitachi double-beam spectrophtometer (Model U-2000) in a 0.1 cm quartz cuvette at room temperature. ^1H NMR measurements were carried out with a JEOL FT-NMR spectrometer (Model JNM-LA400) in 5 mm sample tubes at 25 °C. Acetonitrile-d_3 (99.6 atom% D, containing 0.03% TMS) from Aldrich was used for the NMR measurements. TMS was used as the internal standard for the chemical shift.

Results and Discusion

UV-Visible Absorption Spectra of PAN in the Presence of Mg^{2+}. In acetonitrile, the UV-visible absorption spectra of PAN gave absorption bands at 225, 300, and 465 nm; the molar absorptivity at 465 nm was found to be $\varepsilon/(cm^{-1}\ mol^{-1}\ dm^3) = 1.8 \times 10^4$. The addition of 0.01 mol dm^{-3} or more of $Ca(ClO_4)_2$ or $Sr(ClO_4)_2$ to 5.0×10^{-4} mol dm^{-3} PAN caused the solution color to turn from yellow to red, whereas almost no color change was caused by the addition of $LiClO_4$ and $Ba(ClO_4)_2$. The effects of $Mg(ClO_4)_2$ were stronger than those of $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$. The color change occurred immediately upon mixing solutions of Mg^{2+} and PAN. On the other hand, Nakagawa and Wada[23] examined the rate of the ligand substitution reaction of Cu^{2+}-PAN with EDTA in aqueous and 5 vol% 1,4-dioxane-aqueous solutions at 25 °C. Note that the rates of the ligand substitution reactions between PAN and EDTA, i.e., M^{n+}–PAN + EDTA → M^{n+}–EDTA + PAN, are not very fast in chelatometric titrations at room temperature.

Figure 1 shows the changes in the UV-visible absorption spectra of PAN with increasing concentration of $Mg(ClO_4)_2$ in acetonitrile; a new absorption band with two peaks at ca. 500

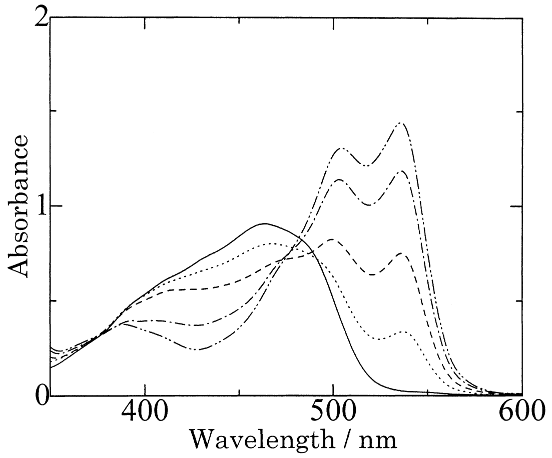


Fig. 1. Changes in UV-visible absorption spectra ($l = 0.1$ cm) of 5.0×10^{-4} mol dm^{-3} PAN with increasing concentration of $Mg(ClO_4)_2$ in acetonitrile: (———) 0; (- - - - -) 0.01; (– – – –) 0.1; (— - —) 0.5; (— - - —) 1.0 mol dm^{-3} $Mg(ClO_4)_2$.

and 535 nm appeared upon the addition of $Mg(ClO_4)_2$. It must be a good trial to compare the absorption spectrum of Mg–PAN in MeCN with that of Mg–EBT (EBT = Eriochrome Black T) in aqueous solution.[24] The spectrum of Mg–EBT gives a band around 520–560 nm (ε = ca. 1.8×10^4). In the presence of 1.0 mol dm^{-3} $Mg(ClO_4)_2$, the absorbances at 505 and 536 nm increased up to 1.31 and 1.49 (i.e., $\varepsilon = 2.6 \times 10^4$ and ca. 3.0×10^4), respectively. Therefore, the appearance of two peaks around 500 and 535 nm seemed to suggest the direct formation of a 1:1 chelate complex between Mg^{2+} and PAN. However, the complexity in the isosbestic points, appearing in the spectra, may suggest some difficulty in completely removing H^+ from the PAN molecule in the presence of lower concentrations of $Mg(ClO_4)_2$.

The effects of an acid or base on the spectrum of PAN in acetonitrile were examined. The addition of CH_3SO_3H to 5.0×10^{-4} mol dm^{-3} PAN gave an absorption band around 420 nm with increasing concentration of the acid; at 0.1 mol dm^{-3}, the absorbance reached its maximum value of 0.87 (λ_{max} = 423 nm). On the other hand, a relatively strong base, 1,1,3,3-TMG, caused a PAN solution to turn red color at higher concentrations of the base ($\geq$ 0.01 mol dm^{-3}), while no spectrum change occurred in the presence of the lower concentrations of the base. We may mention that the presence of an equivalent amount of a strong base, Et_4NOH (5.0×10^{-4} mol dm^{-3}), caused complete deprotonation from OH of PAN.

Figure 2 shows the increase in the absorbances at ca. 535 nm from 5.0×10^{-4} mol dm^{-3} PAN with increasing concentration of Mg^{2+} in the absence or presence of 5.0×10^{-4} mol dm^{-3} 1,1,3,3-TMG; a distinct isosbestic point had been observed at 483 nm in the spectra. The presence of the base caused enhanced-increases at around 500 and 535 nm. At 2.5×10^{-4} mol dm^{-3} Mg^{2+}, the absorbances at 501 and 538 nm were already 0.882 and 0.827, respectively; based on the molar ratio, we suppose that the 1:2 chelate ($Mg(pan)_2$) can be formed at this point. In the presence of 0.1 mol dm^{-3} Mg^{2+}, the absorbances reached maximum values of 1.31 (λ_{max} = 503 nm) and 1.50 (λ_{max} = 536 nm). Upon finding the maximum values, the equilibrium constant, $K = [Mg\ (pan)^+][H^+]/([Hpan][Mg^{2+}])$, was estimated to be 2.5×10^{-3} for the following equation:

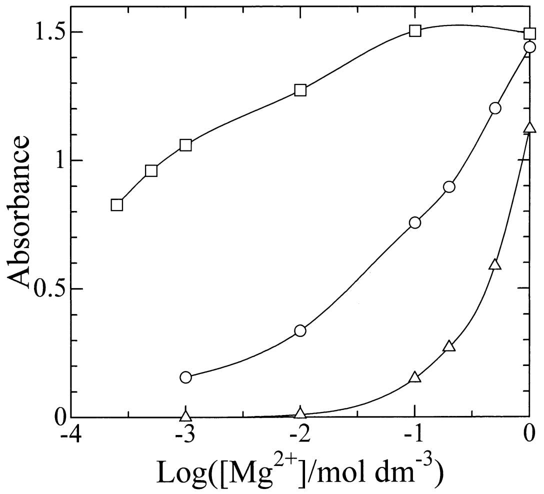


Fig. 2. Increases of absorbance at λ_{max} (ca. 535 nm) of 5.0×10^{-4} mol dm^{-3} PAN in the absence and the presence of the equivalent amount of CH_3SO_3H or 1,1,3,3-TMG by the addition of $Mg(ClO_4)_2$: (○) absence of the acid or the base; (△) CH_3SO_3H; (□) 1,1,3,3-TMG.

$$\mathrm{Hpan} + \mathrm{Mg}^{2+} \rightleftarrows \mathrm{Mg(pan)}^+ + \mathrm{H}^+. \tag{1}$$

An approximate value of the chelate formation constant for the reaction $pan^- + Mg^{2+} \rightleftarrows Mg(pan)^+$ could be estimated as $\sim 10^{20}$, assuming the dissociation constant of OH proton in PAN to be $pK_2 \sim 23$ (cf. pK_a = 20.7 and 26.6 for p-nitrophenol and phenol, respectively, in MeCN).[25] The extremely weak acidity of PAN in MeCN brings about a rather large formation constant. Pease and Williams[26] have reported on the equilibrium constant for 1:1 chelation between Cu^{2+} and PAN in a 20 vol% 1,4-dioxane-aqueous solution to be 6.4×10^3, and the stability constant for the chelate to be approximately 10^{16}. The equilibrium constant for Mg^{2+} in the present system was found to be much smaller than that for Cu^{2+} in the medium.

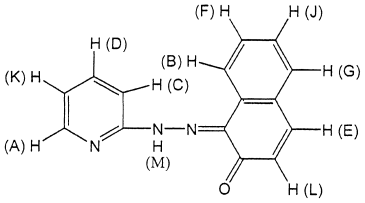
In the presence of 5.0×10^{-4} mol dm^{-3} 1,1,3,3-TMG, $Ca(ClO_4)_2$ or $Sr(ClO_4)_2$ caused spectrum changes similar to those in Fig. 1, i.e., the effects of $Mg(ClO_4)_2$ in the absence of a base. These spectrum changes suggested that Ca^{2+} and Sr^{2+} can form chelate complexes with PAN in the presence of the base in acetonitrile. However, distinct chelate formation between Ba^{2+} and PAN could not be observed even in the presence of a base. The interaction between PAN and M^{2+} decreased as $Mg^{2+} > Ca^{2+} \simeq Sr^{2+} \gg Ba^{2+}$. The interaction seems to depend upon the metal ion size as well as the "coordination" abilities of the alkaline earth metal ions in the aprotic solvent.

The addition of 1.0×10^{-3} mol dm^{-3} $Mg(ClO_4)_2$ to 5.0×10^{-4} mol dm^{-3} PAN in the presence of 5.0×10^{-4} mol dm^{-3} CH_3SO_3H caused an increase of the absorbance at ca. 420 nm. A similar increase at 420 nm was caused by the increasing concentration of the acid without $Mg(ClO_4)_2$, as mentioned above. Apparently, the acidity of CH_3SO_3H in acetonitrile seemed to be enhanced by the addition of Mg^{2+} as follows:

$$\mathrm{CH_3SO_3H} + \mathrm{Mg}^{2+} \rightleftarrows \mathrm{H}^+ + \mathrm{CH_3SO_3Mg}^+. \tag{2}$$

Although methanesulfonic acid may behave as a strong acid ($pK_a = -1.2$)[27] in aqueous solution, the acidity of CH_3SO_3H is much weakened in an aprotic solvent; the pK_a value is reported to be ca. 8.4 or 10.0 in acetonitrile.[28,29] The enhancement of the acidity of acids in the presence of Li^+ and alkaline earth metal ions has been reported;[11,12] this matter will be discussed in detail in the final section of the present paper. By the addition of a large excess of Mg^{2+} (> 0.1 mol dm^{-3}) to the PAN solution in the presence of the acid, a band with two peaks at 500 and 535 nm appeared, which indicated that the Mg^{2+} ion formed a 1:1 chelate complex with PAN. However, the extent of the complex formation was remarkably depressed in the presence of acid, as clearly shown in Fig. 2. In the presence of a higher concentration of CH_3SO_3H (0.01 mol dm^{-3}), even 1.0 mol dm^{-3} $Mg(ClO_4)_2$ was not able to form the $Mg(pan)^+$ chelate; only the acid form of PAN (H_2pan^+) was observed.

^{1}H NMR Study of the Chelate Formation between Mg^{2+} and PAN. The ^{1}H NMR method was employed in order to



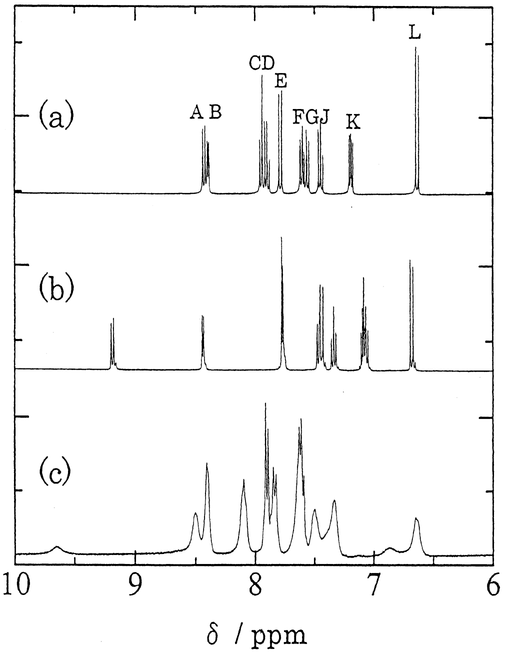


Fig. 3. ^{1}H NMR spectra of 0.01 mol dm^{-3} PAN in CD_3CN in the presence of Et_4NOH or $Mg(ClO_4)_2$: (a) 0; (b) 0.01 mol dm^{-3} Et_4NOH; (c) 0.05 mol dm^{-3} $Mg(ClO_4)_2$.

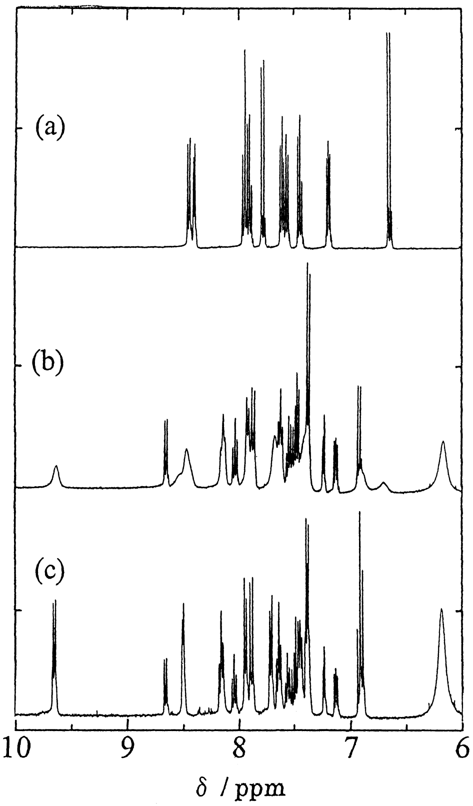


Fig. 4. Changes in ^{1}H NMR spectra of 0.01 mol dm^{-3} PAN with increasing concentration of $Mg(ClO_4)_2$ in the presence of 0.01 mol dm^{-3} 1,1,3,3-TMG in CD_3CN: (a) 0; (b) 0.1; (c) 0.2 mol dm^{-3} $Mg(ClO_4)_2$.

verify direct chelate formation between Mg^{2+} and PAN in acetonitrile. Figure 3 shows the changes in the ^{1}H NMR spectra of PAN by the addition of $Mg(ClO_4)_2$ in CD_3CN. Upon the addition of 0.05 mol dm^{-3} Mg^{2+} to 0.01 mol dm^{-3} PAN, a broad signal appeared at ca. 9.62 ppm (vs TMS). Considering the results based on the UV-visible absorption spectra, the changes in ^{1}H NMR signals seemed to correspond to the formation of a 1:1 chelate between Mg^{2+} and PAN. The assignments of the signals of PAN, itself, were made, based on the Research Information Data Base (SDBS Compound Information) of National Institute of Advanced Industrial Science and Technology.

Upon the addition of an equivalent amount of a strong base, Et_4NOH, a 0.01 mol dm^{-3} PAN–CD_3CN solution gave a sharp signal (doublet) at 9.18 ppm. It was found that the appearance of the signal shows complete deprotonation from PAN, because the further addition of a strong base caused no further changes in the spectrum.

Figure 4 shows the changes in the ^{1}H NMR signals of 0.01 mol dm^{-3} PAN in the presence of 0.01 mol dm^{-3} 1,1,3,3-TMG with increasing concentration of $Mg(ClO_4)_2$. Almost no spectrum changes by the addition of 1,1,3,3-TMG (cf., Figs. 3(a) and 4(a)) indicated that the OH proton of PAN remained in the compound. Upon the addition of 0.1 mol dm^{-3} $Mg(ClO_4)_2$, a new signal appeared at 9.63 ppm, although the whole spectrum showed very complicated signals. The signal at 9.63 ppm turned very sharp and to be a doublet peak at 0.2 mol dm^{-3} $Mg(ClO_4)_2$. The ^{1}H NMR spectrum changes suggested deprotonation from PAN and chelation with Mg^{2+} in acetonitrile.

Interaction between 5-Br-PADAP and Alkaline Earth Metal Ions in the Absence and Presence of Bases. In acetonitrile, 5-Br-PADAP (H(5-Br-padap)) gave a UV-visible absorption band at 450 nm (molar absorptivity, $\varepsilon = 3.33 \times 10^4$). Upon the addition of $Mg(ClO_4)_2$, the solution color changed from red-brown to red, giving another band with two peaks at 515 and 545 nm (cf. Fig. 5). The addition of $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, or $Ba(ClO_4)_2$ caused a minor, or almost no-color change. A distinct color change with the addition of magnesium salt suggested direct chelate formation between Mg^{2+} and 5-Br-PADAP. However, the extent of the reaction for 5-Br-PADAP was apparently smaller than that for PAN, as shown Fig. 1. The following experiments were performed to explore the cause of the smaller interaction for 5-Br-PADAP.

Figure 6 shows the spectral changes of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP in the presence of a ten-fold amount of base, 5.0 $\times$ 10^{-3} mol dm^{-3} 1,1,3,3-TMG, with increasing concentration of $Mg(ClO_4)_2$. Before discussing the effects of Mg^{2+}, we just mention that almost no spectral change for 5-Br-PADAP upon the addition of 1,1,3,3-TMG (cf. Figs. 5 and 6(1)) indicates that the OH proton of the ligand is not deprotonated by a ten-fold amount of the base. The addition of even $\leq 2.5 \times 10^{-4}$ mol dm^{-3} $Mg(ClO_4)_2$ caused a solution containing a base to

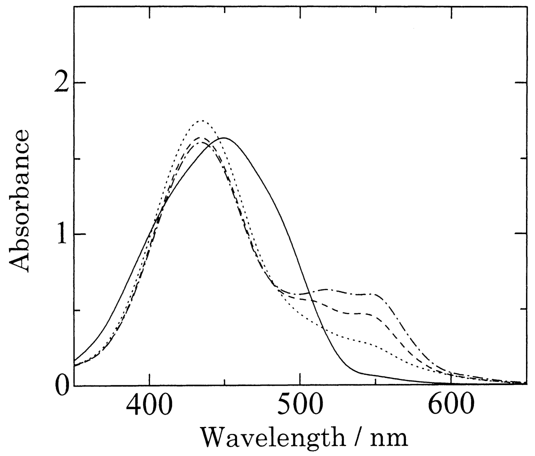


Fig. 5. Effects of $Mg(ClO_4)_2$ on the UV-visible absorption spectra (l = 0.1 cm) of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP in acetonitrile: (———) 0; (- - - - -) 0.01; (– – – –) 0.1; (— - —) 1.0 mol dm^{-3} $Mg(ClO_4)_2$.

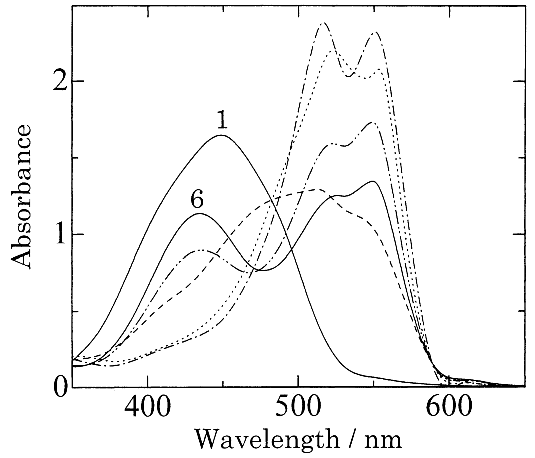


Fig. 6. Effects of $Mg(ClO_4)_2$ on the UV-visible absorption spectra (l = 0.1 cm) of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP in the co-existence of 5.0×10^{-3} mol dm^{-3} 1,1,3,3-TMG in acetonitrile: (1 ———) 0; (- - - - -) 2.5×10^{-4}; (– – – –) 1.0×10^{-3}; (— - —) 0.01; (— - - —) 0.5; (6 ———) 1.0 mol dm^{-3} $Mg(ClO_4)_2$.

turn a strong red color (two peaks at around 520 and 550 nm), suggesting the formation of a 1:2-type complex ([Mg^{2+}]:[5-Br-PADAP] = 1:2). Our independent experiment of the molar ratio method with 2.0×10^{-4} mol dm^{-3} Mg^{2+} and one- to six-fold concentration of the ligand (containing an equivalent amount of Me_4NOH) suggested the formation of the 1:2-type complex. However, a further addition of Mg^{2+} caused a sudden decrease in the absorbance of the peaks. With > 1.0×10^{-3} mol dm^{-3} Mg^{2+}, a different band with two peaks, which should be based on the 1:1 complex, appeared, and the absorbance increased with increasing Mg^{2+} concentration (up to ~0.01 mol dm^{-3} Mg^{2+}). It is known that MInd and $M(Ind)_2$ type complexes give similar spectra and the molar absorptivity of $M(Ind)_2$ is twice as large as that of MInd for PAN and its derivatives (Ind).[30] Therefore, we can well understand that the spectra for 2.5×10^{-4} and 0.01 mol dm^{-3} Mg^{2+} are very similar to each other.

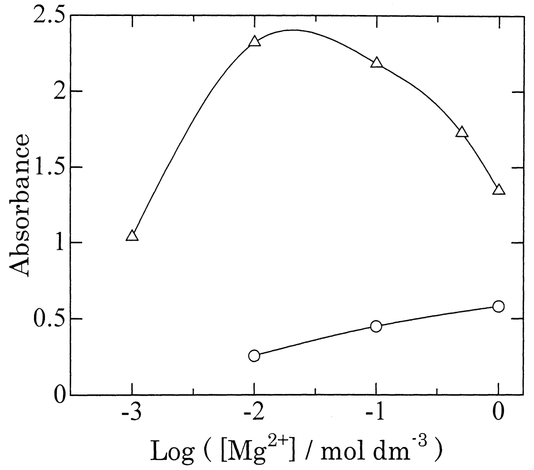
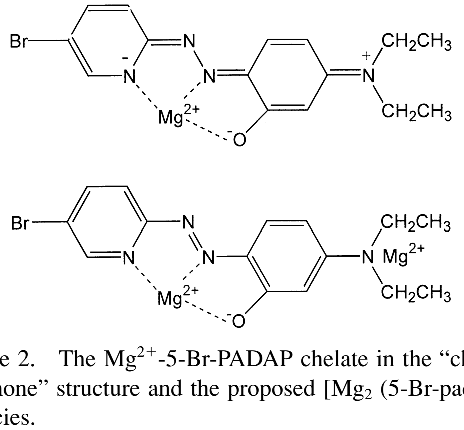


Fig. 7. Changes of absorbance at λ_{max} (ca. 550 nm) of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP in the absence and the presence of the base by the addition of $Mg(ClO_4)_2$: (○) 0; (△) 5.0×10^{-3} mol dm^{-3} 1,1,3,3-TMG.

Strange to say, the intensity of the peaks decreased with increasing concentration of Mg^{2+} (> 0.01 mol dm^{-3}), as clearly displayed in Fig. 7. The decrease in the absorbance may suggest a further interaction between Mg^{2+} and 5-Br-PADAP, setting aside the 1:1 chelate formation. The second Mg^{2+} can interact with the N-atom of the diethylamino group ($-NEt_2$) in 5-Br-PADAP. This interaction should prevent the chelate from taking a "charged quinone" structure (cf. Scheme 1).[15,16] The appearance of a band at 435 nm with 1.0 mol dm^{-3} $Mg(ClO_4)_2$ (cf. Fig. 6) was assigned to the partial structure, $-NEt_2Mg^{2+}$ (vide infra). The strong intensity of absorption for the present chelate complex seemed to owe much to the "charged quinone" structure, since the molar absorptivity of the 1:1-type chelate complex of 5-Br-PADAP and Mg^{2+} in MeCN was much larger (4.8×10^4 at λ_{max} = 520 nm) than that of PAN (ε = 2.8 $\times$ 10^4 at λ_{max} = 503 nm). Note that the absorbance around 550 nm of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP containing a ten-fold amount of 1,1,3,3-TMG and 1.0 mol dm^{-3} $Mg(ClO_4)_2$ was found to be less than 1.5; this may suggest that the molar absorptivity of a non-"charged-quinone" structure species, "$[Mg_2(5\text{-Br-padap})]^{3+}$" (Scheme 2), is very close to that of



Scheme 2. The Mg^{2+}-5-Br-PADAP chelate in the "charged quinone" structure and the proposed $[Mg_2\ (5\text{-Br-padap})]^{3+}$ species.

$[Mg(pan)]^+$.

Figure 7 also indicates that the presence of a mere ten-fold amount of 1,1,3,3-TMG caused a remarkable enhancement of the chelate formation for 5-Br-PADAP. In the absence of a base, the apparent equilibrium constant for 5-Br-PADAP (HL) was found to be much smaller than that for PAN (vide supra). It is of interest to note that the apparent equilibrium constant for the reaction $HL + Mg^{2+} \rightleftarrows MgL^+ + H^+$ decreased with increasing concentration of $Mg(ClO_4)_2$; e.g., $K = 2.6 \times 10^{-4}$ and 4.5×10^{-5} at 0.1 and 1.0 mol dm^{-3} Mg^{2+}, respectively. The decrease in the apparent equilibrium constant also supports that the other interaction can occur between HL and Mg^{2+} in addition to 1:1 chelate formation.

With a careful re-examination of Fig. 5, a strong interaction between Mg^{2+} and N-atom of $-NEt_2$ was recognized by the appearance of the peak at 435 nm for 5-Br-PADAP in both the absence and presence of 1,1,3,3-TMG (cf. also Fig. 6(6)). We are confident that the second Mg^{2+} interaction with 5-Br-PADAP causes a small chelate formation constant for 5-Br-PADAP in the absence of an appropriate proton-acceptor or base. Another possibility of the small chelate formation constant for 5-Br-PADAP is as follows: the recombination between the diethylamino-N atom and H^+, which had been deprotonated from an OH group by chelation with Mg^{2+}, should interfere with any further chelation between Mg^{2+} and 5-Br-PADAP.

Figure 8 shows spectral changes of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP with increasing concentration of $Ba(ClO_4)_2$ in the presence of a ten-fold amount of 1,1,3,3-TMG. Differing from Mg^{2+}, the presence of a half amount of Ba^{2+} made no 1:2-type complex (ML_2). At higher Ba^{2+} concentrations (0.01–1.0 mol dm^{-3}), the formation of the 1:1 chelate complexes was indicated by the appearance of a band at around 520–550 nm. For $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$, the formation of only the 1:1- and not the 1:2-type chelate complex was able to be distinctly observed in acetonitrile. With increasing concentrations of Ca^{2+}, Sr^{2+}, or Ba^{2+}, a decrease in the absorbance of the 1:1-type chelate complex was not observed, which indicates that these metal ions do not interact with the diethylamino-N atom as much as does Mg^{2+}. Thus, the presence of a small amount of an appropriate base, which never affects the absorption spectrum of 5-Br-PADAP (HL), can act as a good proton acceptor when metal ions are added:

$$HL + M^{2+} + B \rightleftarrows ML^+ + BH^+. \qquad (3)$$

In the next section, the effects of acids on chelate formation of 5-Br-PADAP are discussed.

In the Presence of Acids and Mg^{2+}. The addition of an equivalent amount of a "strong" acid, CF_3SO_3H, caused a 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP solutin to turn deep red color, giving a band with triple peaks around 530 nm (cf. Fig. 9), which should suggest the formation of an acid form (H_2L^+). However, with a further addition of the acid, the solution returned to have a red-brown color; the wavelength of the band peak (ca. 450 nm) was, apparently, quite close to that of the original 5-Br-PADAP solution. At this point, the diprotonated species (H_3L^{2+}) should be formed.

Figure 10 shows the Mg^{2+} effects on the UV-visible spectrum of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP containing 5.0×10^{-4} mol dm^{-3} CH_3SO_3H in acetonitrile. The acidity of methanesulfonic acid is so weak in acetonitrile (vide supra) that the peak at 530 nm of the monoprotonated species (H_2L_+) did not developed very much. Upon the addition of a small amount of $Mg(ClO_4)_2$ (5.0×10^{-4} mol dm^{-3}), the absorbance of the peak at 530 nm increased up to ca. 2.0. However, by a further addition of Mg^{2+}, the absorbance at 530 nm decreased, and a (new) peak at 435 nm appeared instead. The first increase at 530 nm should have been caused by a quantitative formation of the H_2L^+ species. The increase in the acidity of the CH_3SO_3H solution by the addition of $Mg(ClO_4)_2$ can be explained by Eq. 2, as mentioned. Secondly, the appearance of the peak at 435 nm

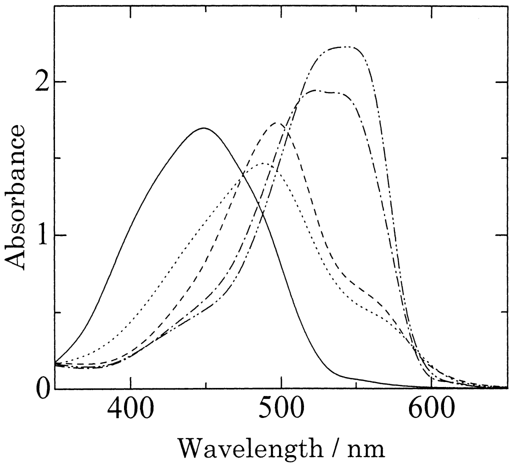


Fig. 8. Effects of $Ba(ClO_4)_2$ on the UV-visible absorption spectra ($l = 0.1$ cm) of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP in the co-existence of 5.0×10^{-3} mol dm^{-3} 1,1,3,3-TMG in acetonitrile: (———) 0; (- - - - -) 2.5×10^{-4}; (– – – –) 1.0×10^{-3}; (— - —) 0.1; (— - - - —) 1.0 mol dm^{-3} $Ba(ClO_4)_2$.

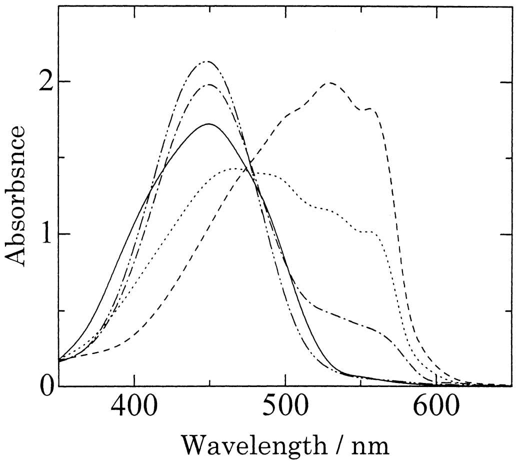


Fig. 9. Changes in UV-visible absorption spectra ($l = 0.1$ cm) of 5.0×10^{-4} mol dm^{-3} 5-Br-PADAP with increasing concentration of a strong acid in acetonitrile: (———) 0; (- - - - -) 2.5×10^{-4}; (– – – –) 5.0×10^{-4}; (— - —) 1.0×10^{-3}; (— - - - —) 2.0×10^{-3} mol dm^{-3} CF_3SO_3H.

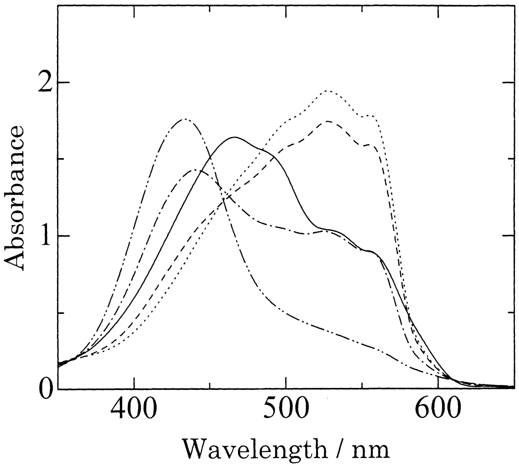
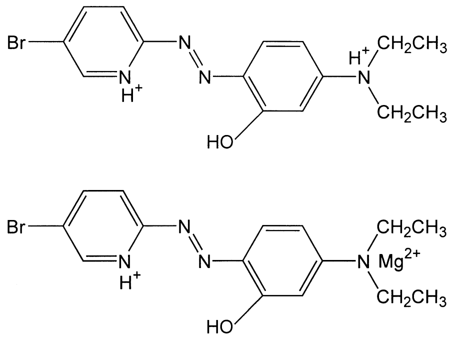


Fig. 10. Effects of $Mg(ClO_4)_2$ on the UV-visible absorption spectra (l = 0.1 cm) of 5.0 × 10^{-4} mol dm^{-3} 5-Br-PADAP in the co-existence of 5.0 × 10^{-4} mol dm^{-3} CH_3SO_3H in acetonitrile: (———) 0; (- - - - -) 5.0 × 10^{-4}; (– – – –) 0.01; (— - —) 0. 1; (— - - —) 0.5 mol dm^{-3} $Mg(ClO_4)_2$.



Scheme 3. Non-chelating interaction of 5-Br-PADAP with H^+ and Mg^{2+}.

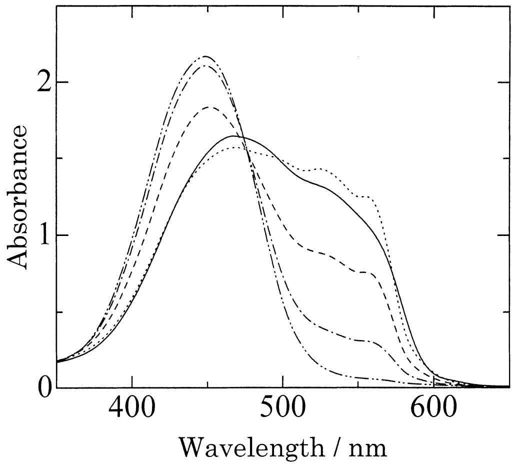


Fig. 11. Effects of $Mg(ClO_4)_2$ on the UV-visible absorption spectra (l = 0.1 cm) of 5.0 × 10^{-4} mol dm^{-3} 5-Br-PADAP in the co-existence of 5.0 × 10^{-3} mol dm^{-3} CH_3SO_3H in acetonitrile: (———) 0; (- - - - -) 2.5 × 10^{-4}; (– – – –) 5.0 × 10^{-4}; (— - —) 1.0 × 10^{-3}; (— - - —) 0.01 mol dm^{-3} $Mg(ClO_4)_2$.

is not caused by a diprotonated species (H_3L^{2+}: λ_{max} = 450 nm), but by a species such as "$H_2L^+Mg^{2+}$," i.e., the Mg^{2+} ion interacts with the diethylamino-N atom and the normal chelate does not form because of the strong acidity (cf. Scheme 3).

In the presence of a ten-fold amount of CH_3SO_3H, the Mg^{2+} ion caused somewhat different effects on 5-Br-PADAP (cf. Fig. 11), compared with the case in the presence of an equivalent amount of CH_3SO_3H. With increasing concentration of Mg^{2+}, the increase in the absorbance at 530 nm was hardly observed, but a decrease of the absorbance at 530 nm and an increase of the peak at 450 nm occurred. The peak at 450 nm should be caused by the diprotonated species (H_3L^{2+}). A clear isosbestic point, observed at 478 nm, with increasing concentration of Mg^{2+} supported the simple protonation scheme from H_2L^+ into H_3L^{2+}. Thus, in the presence of a higher concentration of CH_3SO_3H (5.0 × 10^{-3} mol dm^{-3}), neither chelation nor an interaction between Mg^{2+} and $-NEt_2$ was observed. The above results verify that the acidity of a "weak" acid (CH_3SO_3H) is strengthened by the interaction between Mg^{2+} and the conjugate anion ($CH_3SO_3^-$) in acetonitrile, following Eq. 2.

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