Complexations of New Pyridylazo Ligands with Ni(II), Zn(II), and Cd(II)

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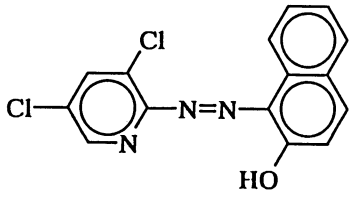
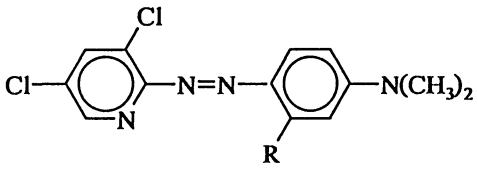
Synopsis. New ligands, 1-(3,5-dichloro-2-pyridyl-azo)-2-naphthol, 2-(3,5-dichloro-2-pyridyl-azo)-5-(dimethylamino) phenol, and 2-(3,5-dichloro-2-pyridyl-azo)-5-(dimethylamino)benzoic acid, were synthesized. Changes in the reduction potentials and electronic spectra of the ligands upon complexation with Ni(II), Zn(II), and Cd(II) were studied. The dissociation constants of the ligands and the stability constants of their metal(II) complexes are discussed.

It is well known for pyridylazo compounds that introduction of halogen or dimethylamino groups on appropriate aromatic ring enhances the sensitivity of photometric determination of a given metal ion, and these substituents are advantageous for metal determination because the absorption peak wavelengths of ligands themselves and those of the complexes are shifted from the ultraviolet to visible region.[1] In view of this, 1-(3,5-dichloro-2-pyridyl-azo)-2-naphthol (abbr. as $Cl_2\beta$PAN), 2-(3,5-dichloro-2-pyridyl-azo)-5-(dimethylamino)phenol (Cl_2DMPAP) and 2-(3,5-dichloro-2-pyridyl-azo)-5-(dimethylamino)benzoic acid (Cl_2PAMB) were newly synthesized in the present work, and their complexing equilibria with Ni(II), Zn(II), and Cd(II) were studied both polarographically and spectrophotometrically.



$Cl_2\beta$PAN



R=OH : Cl_2DMPAP
R=COOH : Cl_2PAMB

Experimental

Preparation of Ligands. $Cl_2\beta$PAN was prepared by coupling 2-naphthol with 3,5-dichloro-2-pyridyldiazonium salt synthesized according to a previous paper.[1c] Yield, 10.8%; mp 191—192 °C. Found: C, 56.83; H, 3.08; N, 13.49%. Calcd for $C_{15}H_9N_3OCl_2$: C, 56.63; H, 2.85; N, 13.21%. IR ($\nu_{N=N}$) 1365 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=6.60 (1H, d, J=9.90 Hz, H-8), 7.40—7.63 (3H, m, H-4, H-5, H-6), 7.66 (1H, d, J=9.90 Hz, H-7), 7.76 (1H, d, J=1.8 Hz, H-4′), 8.41 (1H, d, J=1.8 Hz, H-8′), 8.53 (1H, dd, J=6.3 and 1.4 Hz, H-3), 16.32 (1H, br, s, OH). Cl_2DMPAP was synthesized in a similar manner. Yield, 12.1%; mp 189—191 °C. Found: C, 49.90; H, 4.00; N, 17.80%. Calcd for $C_{13}H_{12}N_4OCl_2$: C, 50.18; H, 3.99; N, 18.01%. IR ($\nu_{N=N}$) 1300 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.32 (6H, s, 2×CH_3), 6.05 (1H, d, J=2.4 Hz, H-6), 6.60 (1H, dd, J=10.2 and 2.4 Hz, H-4), 7.62 (1H, d, J=10.2 Hz, H-3), 7.86 (1H, d, J=3.0 Hz, H-4′), 8.47 (1H, d, J=3.0 Hz, H-6′), 16.11 (1H, br, s, OH). Cl_2PAMB was obtained by a similar procedure. Yield, 5.9%; mp 198—202 °C. Found: C, 49.48; H, 3.45; N, 16.20%. Calcd for $C_{14}H_{12}N_4O_2Cl_2$: C, 49.58; H, 3.57; N, 16.52%. IR ($\nu_{N=N}$) 1296 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=3.23 (6H, s, 2×CH_3), 6.85 (1H, dd, J=9.0 and 3.0 Hz, H-4), 7.68 (1H, d, J=3.0 Hz, H-6), 7.87 (1H, d, J=2.4 Hz, H-4′), 8.06 (1H, d, J=9.0 Hz, H-3), 8.40 (1H, d, J=2.4 Hz, H-6′), 14.35 (1H, br, s, OH). These compounds are slightly soluble in water, methanol, and ethanol, and readily soluble in dioxane, benzene, and chloroform. All the solutions of the ligands and the metal (II) complexes were prepared with aqueous 60% (v/v) dioxane.

Measurements. ^{1}H NMR spectra were recorded on a JEOL JNM-EX90 FT NMR spectrometer. IR spectra were recorded on a JASCO A-102 spectrometer (KBr disk). Electronic spectra were recorded on a Hitachi 220A recording spectrophotometer. Polarograms were obtained on a Yanaco Polarographic Analyzer P-1100 as described previously,[2] in an aqueous 60% (v/v) dioxane solution.

Results and Discussion

Protonation Constants of Ligands. All of the dissociation constants of the ligands were obtained by the Hildebrand-Reilly's method.[3] The values are summarized in Table 1 together with those of analogous ligands for comparison. The larger pK_{ai} values of hydroxyl groups in $Cl_2\beta$PAN and Cl_2DMPAP than

Table 1. Dissociation Constants of the Ligands

Ligand	pK_{a1}	pK_{a2}	pK_{a3}	Ref
$Cl_2\beta$PAN	<0[a]	10.91[b]		This work
Cl_2DMPAP	<0[a]	1.05[c]	11.29[d]	This work
Cl_2PAMB	<0[a]	0.21[c]	4.59[e]	This work
βN	9.31[b]			Ref. 8
AP	9.83[d]			Ref. 8
MAB	2.57[c]	5.00[e]		Ref. 8

Aq 60% (v/v) dioxane soln, μ=0.1 (KNO_3), 25.0± 0.5 °C. All the experimental errors are within ±0.05 in pK_a unit in this work. The dissociations of proton are from: a) nitrogen atom in pyridine moiety; b) HO- in naphthol moiety; c) nitrogen atom in dimethylamino group; d) HO- in phenol moiety; e) HOOC-. βN=2-naphthol; AP=3-aminophenol; MAB=4-dimethylaminobenzoic acid.

those of βNS and AP indicate the presence of strong intramolecular hydrogen bonding[2] between the azo and hydroxyl groups in Cl_2βPAN and Cl_2DMPAP. The ^{1}H NMR data for these ligands are in line with this speculation, namely, the signal of the proton of the hydroxyl groups in these ligands appears in very low magnetic fields (δ=16.32 for Cl_2βPAN and 16.11 for Cl_2DMPAP). On the other hand, the pK_{ai} value of the carboxyl group in Cl_2PAMB is lower than that of MAB. This may reflect a strong electron-attractive ability of the dichloropyridylazo group rather than weak intramolecular hydrogen bonding between the azo and carboxyl group in Cl_2PAMB, which has a highly distorted six-membered ring by forming the intramolecular hydrogen bonding as speculated from a molecular model.

Coordination Modes in Metal (II) Complexes. Figure 1 shows the relation between the pH and the reduction potential of the azo group. For Cl_2βPAN and Cl_2DMPAP, it is particularly noteworthy that the half-wave potentials are markedly shifted toward positive potentials region at pH=10.9 and 11.3, respectively, where the proton in the hydroxyl group at an ortho position to the azo group will be dissociated (see Table 1). This means that a very strong hydrogen bond formed between the proton of the hydroxyl group and the N atom in the azo group is abruptly destroyed at this pH; the azo group is thus easily reduced at this pH by a positive shift effect.[4] In Cl_2PAMB, however, the reduction potential of the azo group is only dependent on pH, but independent of the kinds of the ligand species, since the hydrogen bonding is very weak. The reduction potentials of the ligands in Ni(II) complexes are markedly negative of those of free ligands at the same pH, showing stabilization by a negative shift effect.[5,6] This means that, for these complexes, stable chelate rings involving the azo group are formed. The magnitude of the shift for the metal (II) complexes was in the order of Ni(II)>Zn(II)>Cd(II).

It is seen in Fig. 2 that the absorption for the π→π* transition[7] in the metal (II) complexes markedly shift to lower wavenumbers compared with those of the HL species. In addition, the absorption band of the complexes is split into two peaks, although this splitting is not very clear for the Cl_2PAMB complexes. Similar shifts upon complexation were reported in metal (II) complexes of analogous ligands forming *N,N,O*-terdentate chelate rings.[7] Accordingly, the above mentioned changes in the reduction potentials and absorption spectra of the azo group by complexation strongly suggest that these ligands coordinate to metal (II) ions with *N,N,O*-(N atom in the pyridine ring, N atom in the

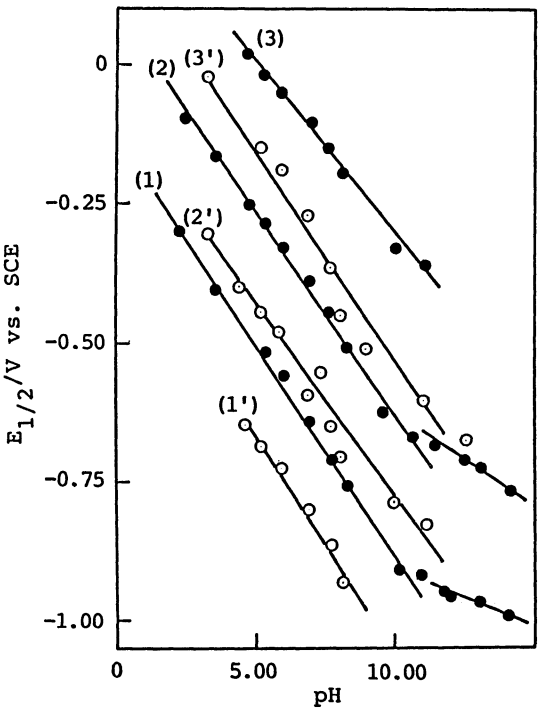


Fig. 1. Relation between pH and half-wave potential of ligands and their Ni(II) complexes.
(1): Cl_2βPAN, (1'): Cl_2βPAN+Ni(II), (2): Cl_2DMPAP, (2'): Cl_2DMPAP+Ni(II), (3): Cl_2PAMB, (3'): Cl_2PAMB+Ni(II), $C_L=C_{Ni}=1.25\times10^{-4}$ mol dm^{-3}, μ=0.1 (KNO_3), 0.01% gelatin, 24±2°C. Curves (1) and (1') are shifted 0.20 unit downward, and (3) and (3') are shifted 0.10 unit upward for clarity.

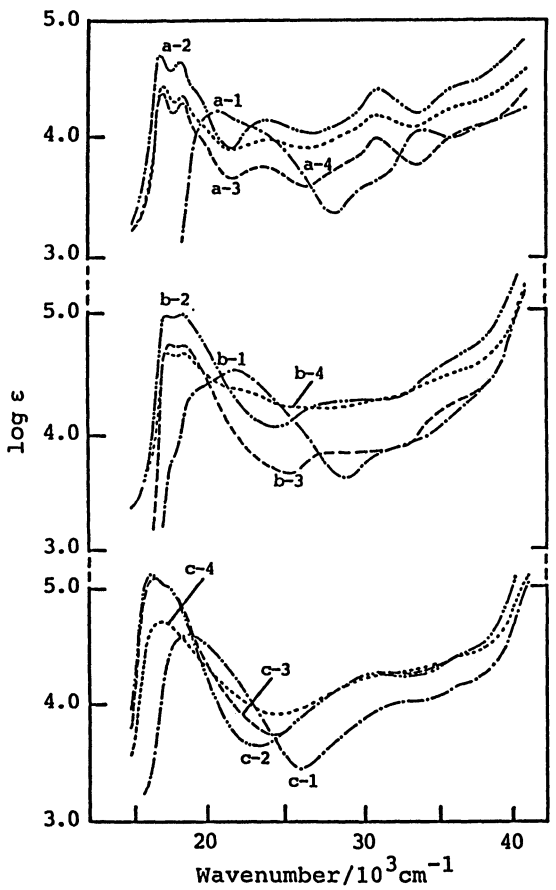


Fig. 2. Absorption spectra of Cl_2βPAN (a-series), Cl_2DMPAP (b-series) and Cl_2PAMB (c-series), and their metal(II) complexes.
a-1: HL (pH 8.18); a-2: NiL(7.67); a-3: ZnL(9.28); a-4: CdL(9.65); b-1: HL (7.16); b-2: NiL (9.07); b-3: ZnL (9.70); b-4: CdL (9.21); c-1: HL (1.67); c-2: NiL (7.40); c-3: ZnL (6.52); c-4: CdL (7.08). $C_L=1.00\times10^{-5}$ mol dm^{-3}, $C_{Me}=1.00\times10^{-4}$ mol dm^{-3}, 25.0±0.5 °C.

Table 2. Composition, Maximum Wavenumber (Molar Absorptivity), and Stability Constant of the Ni(II), Zn(II), and Cd(II) Complexes[a]

Metal ion		$Cl_2\beta$PAN	Cl_2DMPAP	Cl_2PAMB
	b)	NiL_2	NiL_2	NiL_2
Ni (II)	c)	17.4, 18.6 (6.0, 5.3)	17.7, 18.7 (11.1, 11.4)	16.5, 17.5_{sh} (13.2, 10.1)
	d)	$\log\beta_2=35.33$	$\log\beta_2=35.48$	$\log\beta_2=16.99$
	b)	ZnL	ZnL	ZnL_2
Zn(II)	c)	17.4, 18.7 (2.9, 2.4)	17.7, 18.9 (6.3, 6.0)	16.7, 17.5_{sh} (12.3, 11.0)
	d)	$\log\beta_1=19.80$	$\log\beta_1=20.07$	$\log\beta_2=13.34$
	b)	CdL	CdL	CdL
Cd(II)	c)	17.4, 18.7 (3.3, 2.8)	17.7, 18.9 (5.3, 5.2)	17.2 (5.3)
	d)	$\log\beta_1=16.09$	$\log\beta_1=17.00$	$\log\beta_1=6.28$

a) Aq 60% (v/v) dioxane soln, μ=0.1 (KNO_3), 25.0±0.5 °C. b) Chemical form of complex (L: fully deprotonated ligand.). c) Maximum wavenumber/10^3 cm^{-1} (maximum molar absorptivity, $\varepsilon_{max}/10^4$). sh: shoulder. d) $\beta_{1,2}$ mean over-all stability constants. Experimental errors are within ±0.10 in log β unit.

azo group adjacent to the naphthol, phenol, or benzoic acid ring, O atom of the naphtholate, phenolate, or benzoate)terdentate. In these ligands, no formation of tetrahedral complexes is anticipated in view of the steric restriction since the three coordination sites (*N,N,O*) lie on the same plane. The structure of these complexes may be a six-coordinated octahedron. In the case of 1 : 1 complexes three water molecules as solvent would be coordinated as $ML(H_2O)_3$, and in 1 : 2 complexes two *N,N,O*-terdentate ligands coordinated to a metal (II) ion.

Stability Constants of Metal (II) Complexes. For all the metal (II)-ligand combinations, pH variation of the complex solution led to a spectral change with a clear isosbestic point due to the presence of an equilibrium. The complexing equilibria could thus be analyzed as described previously.[2]

Table 2 summarizes the results. The complexes formed were very stable in a wide pH range up to about pH=12. The maximum molar absorptivity exceeds 10^5 for the Ni(II) complexes with Cl_2DMPAP and Cl_2PAMB, and the Zn(II) complex with Cl_2PAMB. Therefore Cl_2DMPAP and Cl_2PAMB are useful as highly sensitive spectrophotometric reagents. The stability constants, after a final correction for the side-reaction coefficients of ligands using the values in Table 1 and the values for metal (II) ions,[8] are listed in Table 2. The β_1 values of Zn(II) and Cd(II), having filled *d* shells, with $Cl_2\beta$PAN and Cl_2DMPAP are significantly larger than those of other complexes with inorganic or amino acid ligands[8] having no π conjugated system. Namely, this can be contributed to the strong π back-donation in these complexes, since all the ligands have conjugated system which is formed between the pyridine ring and the phenol, naphthol, or benzoic acid ring via the azo group. On the other hand, the magnitude of β for the Cl_2PAMB complex is very small. This probably reflects the situation that Cl_2PAMB forms a metal (II) complex involving a five-membered ring and a highly distorted six-membered ring as suggested by molecular model. As noted in Table 1, the pK_a (4.59) of Cl_2PAMB is much smaller than those of the other two ligands (10.91 for $Cl_2\beta$PAN and 11.29 for Cl_2DMPAP).

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