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Selectivity of Coordination Sites in Ni(II), Zn(II), and Cd(II) Complexes with 7-[(3,5-Dichloro(or bromo)-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic Acid

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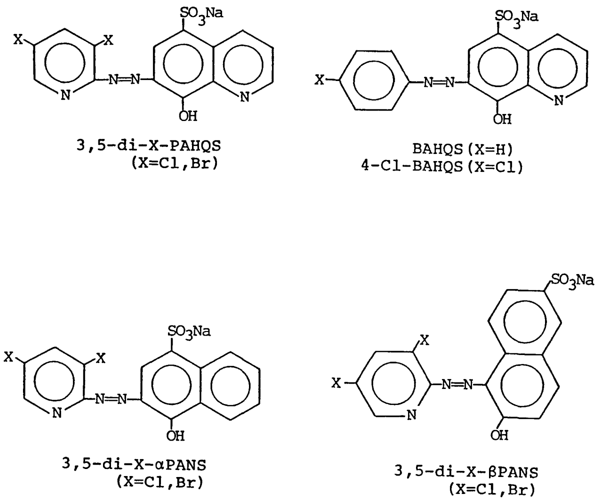
A new multidentate ligand, 7-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (sodium salt, abbr. as 3,5-di-X-PAHQS, X=Cl or Br) which contains pyridylazonaphthol (PAN) and 8-quinolinol skeletons, was prepared for the first time in order to investigate its coordination behavior toward metal(II) ions. For comparative studies, the ligands (2-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-1-hydroxynaphthalene-4-sulfonic acid (sodium salt, abbr. as 3,5-di-X-αPANS, X=Cl or Br), 1-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-2-hydroxynaphthalene-6-sulfonic acid (sodium salt, abbr. as 3,5-di-X-βPANS, X=Cl or Br), and 7-[(4-chloro or unsubstituted phenyl)azo]-8-hydroxyquinoline-5-sulfonic acid(sodium salt, abbr. as 4-Cl-BAHQS for chloro substituted phenyl and BAHQS for unsubstituted phenyl, respectively)) were also prepared. The coordination modes of the synthesized multidentate ligands with Ni(II), Zn(II), and Cd(II) ions were investigated both spectrophotometrically and polarographically, in aqueous solution. Judging from the variations of the reduction potentials of the azo group with metal complexations, in the case of the ligands of BAHQS systems, the azo group did not participate in complexation. On the contrary, for the ligands of the PAN and PAHQS systems, the azo group in these ligands clearly participated in metal-complexation. On the basis of the results of polarographic studies and of spectral data, the complexing equilibria of these complexes were analyzed and the stability constants calculated. The dissociation constants and the reduction potentials of these new ligands are also discussed.



3,5-di-X-PAHQS (X=Cl,Br)

BAHQS (X=H)
4-Cl-BAHQS (X=Cl)

3,5-di-X-αPANS (X=Cl,Br)

3,5-di-X-βPANS (X=Cl,Br)

Scheme 1. Chemical formula of new ligands synthesized.

The selectivity of the coordination modes[1] in metal complexes is one of the fundamental functions of multidentate ligands, because of their steric restrictions, and is ascribed either to the bulkiness of the ligands or to the basicity of an atom contained in the ligands. However, the selectivity is not considered to be fully and systematically understood at the present time. Accordingly, a study of multidentate ligands is of interest for metal complexation from the viewpoint of the selectivity of coordination sites against various metal ions. For example, it is well-known that, in aqueous solutions, the Ni(II) ion coordinates with *N,N,O*-terdentate pyridylazophenolic or naphtholic ligands (such as 4-[(2-pyridyl)azo]resorcinol or 1-[(2-pyridyl)azo]-2-hydroxynaphthalene) to form *N,N,O*-terdentate complexes.[2–4] On the other hand, the formation of the *N,N*-bidentate complex of an *N,N,O*-terdentate ligand (4-[4-methyl-2-pyridyl)azo]resorcinol) with Ni(II) perchlorate in an aprotic solvent, such as thoroughly dehydrated neat 1,4-dioxane,[5] was also reported. Further, it is known that a ligand (8-hydroxyquinoline-5-sulfonic acid (abbr. as HQS)) coordinates with various metal ions involving a representative metal ion, such as Al(III), to form stable *N,O*-bidentate complexes.[6,7] In the present study, as is shown in Scheme 1, 7-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (sodium salt, abbr. as 3,5-di-X-PAHQS, X=Cl,or Br), which is expected to coordinate to metal(II) ions either with *N,N,O*-(N-atom in pyridine ring, N-atom of adjacent one in azo group to 8-hydroxyquinoline ring, O-atom of quinolinolate) to form two five-membered fused chelate rings, or with *N,O*- of the 8-hydroxyquinoline moiety to form a five-membered chelate ring, was prepared for the first time in order to investigate its coordination behavior toward metal(II) ions. For the sake of comparative studies, ligands 2-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-1-hydroxynaphthalene-4-sulfonic acid (sodium salt, abbr. as 3,5-di-X-αPANS, X=Cl or Br), 1-[(3,5-dichloro(or bromo)-2-pyridyl)azo]-2-hydroxynaphthalene-6-sulfonic acid (sodium salt, abbr. as 3,5-di-X-βPANS, X=Cl or Br), 7-[(4-chloro or unsubstituted phenyl)azo]-8-hydroxyquinoline-5-sulfonic acid (sodium salt, abbr. as 4-Cl-BAHQS for chloro substituted phenyl and BAHQS for unsubstituted phenyl, respectively), were also prepared, since these ligands were also expected to act as an *N,N,O*-(N-atom in the pyridine ring, an N-atom of the azo group, an O-atom of naphtholate) terdentate ligands or *N*,*O*-(HQS moiety) bidentate ligands in aqueous solutions, as described above.

The metal ions studied in this work are Ni(II), Zn(II), and Cd(II), since they form stable complexes with PAN and HQS ligands. The present work describes the coordination modes of the synthesized multidentate ligands with these metal(II) ions focussing on the coordiantion selectivity of the chelate rings, using both spectrophotometric and polarographic methods.

Experimental

Preparation of Ligands. 3,5-di-X-PAHQS (X=Cl or Br): The diazotization[8] of 2-amino-3,5-di-X-pyridine and the azo coupling of the resulting diazonium salt with commercially obtained 8-hydroxyquinoline-5-sulfonic acid (sodium salt) in a methanol solution by passing CO_2 gas at 60—65 °C for 36 hours afforded 3,5-di-X-PAHQS. The crude product was purified twice by recrystallization from an aqueous solution, and then dried in vacuo (yield 15%, mp (decomp)>300 °C).

3,5-di-X-αPANS (X=Cl or Br): The ligand was also synthesized by a procedure similar to that for 3,5-di-X-PAHQS, but with a reaction time of 24 hours (yield 25%, mp (decomp) >300 °C).

3,5-di-X-βPANS (X=Cl or Br): The ligand was synthesized by a similar procedure for 3,5-di-X-αPANS, but with a reaction time of 12 hours (yield 25%, mp (decomp)>300 °C).

BAHQS: Aniline was diazotizated by the usual method.[9] To a slightly basic (pH 8—10) aqueous solution containing diazotizated aniline, commercially obtained 8-hydroxyquinoline-5-sulfonic acid (sodium salt) was added; a crude product was then obtained by refluxing the solution under an N_2 atmosphere for about 5 hours. The crude product was purified by recrystallization from a mixed solvent of dimethylformamide and chloroform (yield 81%, mp (decomp)>300 °C).

4-Cl-BAHQS: This ligand was synthesized by a procedure similar to that for BAHQS (yield 83%, mp (decomp)>300 °C).

The purities of all the ligands were checked by elemental analysis. ^{1}H NMR spectra were obtained on a JEOL PMX60-SI spectrometer. The IR spectra were recorded on a JASCO A-102 spectrometer (KBr disk).

Aqueous Ni(II), Zn(II), and Cd(II) solutions were prepared as perchlorates, in which Zn(II) perchlorate was obtained by dissolving metallic zinc (Wako, 99.999%) in perchloric acid; Ni(II) and Cd(II) perchlorates were prepared by dissolving their nitrates in perchloric acid. In order to avoid hydrolysis, a small excess of acid was added. The concentrations of the metal(II) ions were determined by titration with EDTA, using the usual methods. All of the other chemicals used were of analytical or equivalent grade and were used without further purification.

Measurements. The dissociation constants of the ligands and the formation constants of the complexes were obtained spectrophotometrically on a Hitachi 220A recording spectrophotometer. All measurements were carried out under the following conditions; ligand concentration=1.00×10^{-5} mol

Table 1. Elemental Analyses and Spectral Data of Ligands

Ligand	Mol form	C/%	H/%	N/%	^{1}H NMR	IR
		Found (Calcd)	Found (Calcd)	Found (Calcd)	δ_{CF_3COOH}	$\nu_{N=N}$/cm^{-1}
3,5-di-Cl-PAHQS	$C_{14}H_7N_4O_4SCl_2Na\cdot2H_2O$	36.42 (36.78)	2.41 (2.42)	12.11 (12.25)	9.88 (1H, d), 9.19 (1H, d), 8.76 (1H, d, *J*=2 Hz), 8.59 (3H, m)	1374
3,5-di-Br-PAHQS	$C_{14}H_7N_4O_4SBr_2Na\cdot2H_2O$	30.57 (30.79)	1.98 (2.03)	10.09 (10.25)	9.86 (1H, d), 9.25 (1H, d), 8.89 (1H, d, *J*=2 Hz), 8.79 (1H, d, *J*=2 Hz), 8.49 (2H, m)	1359
3,5-di-Cl-αPANS	$C_{15}H_8N_3O_4SCl_2Na\cdot H_2O$	40.78 (41.11)	2.34 (2.30)	9.41 (9.59)	8.42 (4H, m), 7.82 (3H, m)	1374
3,5-di-Br-αPANS	$C_{15}H_8N_3O_4SBr_2Na\cdot1.5H_2O$	33.60 (33.60)	1.98 (2.07)	7.72 (7.84)	8.66 (1H, d, *J*=2 Hz), 8.53 (1H, d, *J*=2 Hz), 8.37 (2H, m), 7.73 (3H, m)	1355
3,5-di-Cl-βPANS	$C_{15}H_8N_3O_4SCl_2Na\cdot H_2O$	41.00 (41.11)	2.29 (2.30)	9.46 (9.59)	8.63 (1H, d, *J*=2 Hz), 8.55 (1H, d, *J*=10.2 Hz), 8.46 (1H, d, *J*=2 Hz), 7.96 (3H, m), 6.78 (1H, d, *J*=10 Hz)	1366
3,5-di-Br-βPANS	$C_{15}H_8N_3O_4SBr_2Na\cdot2H_2O$	33.20 (33.05)	1.92 (2.22)	7.69 (7.71)	8.62 (1H, d, *J*=2 Hz), 8.59 (1H, d, *J*=2 Hz), 8.46 (1H, d, *J*=6 Hz), 7.83 (3H, m), 6.71 (1H, d, *J*=10 Hz)	1358
4-Cl-BAHQS	$C_{15}H_9N_3O_4SClNa\cdot DMF\cdot1/3CHCl_3$	43.94 (44.16)	3.08 (3.03)	11.00 (11.24)	9.40 (3H, m), 8.76 (1H, s), 8.41 (2H m), 7.75 (2H, d, *J*=9.6 Hz)	1386
BAHQS	$C_{15}H_{10}N_3O_4SNa\cdot DMF\cdot1/3CHCl_3$	47.80 (47.44)	3.61 (3.76)	12.18 (12.07)	9.86 (1H, *J*=7.8 Hz), 9.05 (1H, s), 8.86 (1H, s), 8.38 (1H, s), 7.82 (2H, m), 7.61 (3H, m)	1388

dm^{-3}, metallic ion concentration=1.00×10^{-4} mol dm^{-3}, μ=0.1 (KNO$_3$), 25.0±0.5 °C.

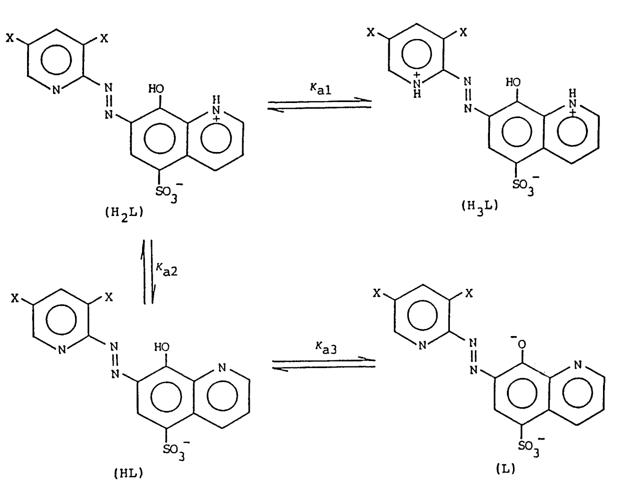
Polarograms were recorded on a Yanaco Polarographic Analyzer P-1100 in an aqueous solution containing 0.1 mol dm^{-3} KNO$_3$ as the supporting electrolyte, and 0.01% gelatin as the maximum suppressor. A three-electrode cell was used for measurements, in which the working electrode was a dropping mercury electrode (DME); the auxiliary electrode was a platinum coil. A saturated calomel electrode (SCE) was used as the reference electrode. The DME had the following characteristics: m=2.02 mg s^{-1}, t=1.00s/drop at −0.5 V vs. SCE, in electrolytic solution at pH=7.0.

The pH values of the sample solutions for both spectrophotometric and polarographic measurements, which were adjusted by an appropriate buffer solution, were read instantly on a Hitachi-Horiba F-13 pH meter after measurements had been carried out.

Results and Discussion

In Table 1, the data of elemental analyses, ^{1}H NMR and IR spectra are listed. As can be seen in this table, the spectral data of ^{1}H NMR for eight ligands can be reasonably assigned to protons in each ligand. Further, all of the ligands show IR spectra in the region 1350—1390 cm^{-1} due to a stretching vibration of the azo group. These data show that the objective ligands were clearly prepared. As described above, the melting points of all the ligands (>300 °C) suggest that the obtained azo dyes were in the form of sodium salts (-SO$_3$Na).

Protonation Constants of Ligands. As a typical example, the dissociation process of 3,5-di-X-PAHQS is shown in Scheme 2, in which the charges of species are omitted for simplicity. All of the dissociation constants were calculated using Hildebrand's method.[10)] The obtained values are summarized in Table 2, together with those of 3,5-di-X-αPANS and 3,5-di-X-βPANS. For a comparison, the dissociation constants of 8-hydroxyquinoline-5-sulfonic acid (HQS), 1-hydroxynaphthalene-4-sulfonic acid (αNS) and 2-hydroxynaphthalene-6-sulfonic acid (βNS) are also listed in this Table. As can be seen from Table 2, the pK_{ai} values of the BAHQS system, PAHQS systems and 3,5-di-X-αPANS ligands were smaller than those of ligands HQS and αNS, which had no pyridylazo-group (meaning of pK_{ai} was presented in the footnote in Table 2). These results could be explained in terms of an electron-attractive ability of the pyridylazo group. In addition, no differences in the pK_{a2} and pK_{a3} values of the chloro- and bromo-derivatives of 3,5-di-X-PAHQS systems were observed. In other words, the effects on the dissociation by chlorine and bromine introduced into the pyridine ring were almost the same. The same basicities of the chloro- and bromo-derivatives may be considered as a reflection of Hammette's constants (σ_p: Cl=0.23, Br=0.23; σ_m: Cl=0.37, Br=0.39); furthermore, it was demonstrated that a conjugated system was formed between 3,5-di-X-pyridine and 8-hydroxyquinoline via the azo group. On the other hand, the pK_{ai} value of the ligand, 3,5-di-

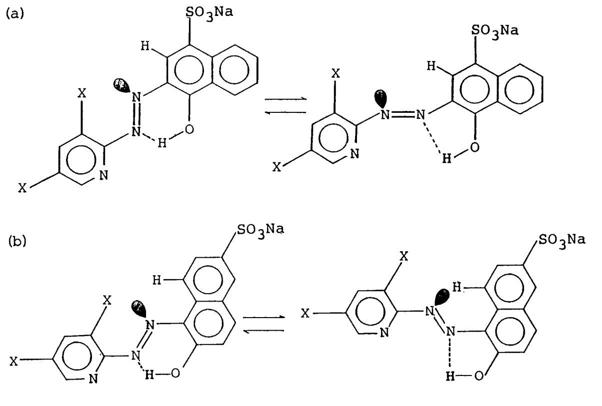


Scheme 2. Dissociation processes of 3,5-di-X-PAHQS as typical example.

Table 2. Dissociation Constants of Ligands

Ligand	pK_{a1}	pK_{a2}	pK_{a3}	Ref.
3,5-di-Cl-PAHQS		2.23	7.23	This work[a)]
3,5-di-Br-PAHQS		2.21	7.25	This work[a)]
HQS	3.84[c)]	8.35[d)]		b)
3,5-di-Cl-αPANS		7.99[e)]		This work[a)]
3,5-di-Br-αPANS		7.91[e)]		This work[a)]
3,5-di-Cl-βPANS		10.70[e)]		This work[a)]
3,5-di-Br-βPANS		10.73[e)]		This work[a)]
αNS	8.01			b)
βNS	8.86			b)
BAHQS	2.93[c)]	7.40[d)]		This work[a)]
4-Cl-BAHQS	2.77[c)]	7.32[d)]		This work[a)]

All the experimental errors are within ±0.05 in pK_a unit in this work. a) Aq soln, μ=0.1 (KNO$_3$), 25.0±0.5 °C. b) R. M. Smith and A. E. Martell, "Critical Stability Constants," Plenum Press, New York (1982). HQS: 8-hydroxyquinoline-5-sulfonic acid; αNS: 1-hydroxynaphthalene-4-sulfonic acid; βNS: 2-hydroxynaphthalene-6-sulfonic acid. c) Dissociation of proton from heterocyclic nitrogen atom in HQS. d) Dissociation of proton from HO- in HQS. e) Dissociation of proton from HO- in hydroxynaphthalene moiety.



Scheme 3. Tautomerism equilibria of intramolecular hydrogen bonding of ligands. (a): 3,5-di-X-αPANS, (b): 3,5-di-X-βPANS.

X-βPANS, was larger than that of βNS, showing strong hydrogen bonding between the azo and hydroxyl groups. The pK_{ai} values of 3,5-di-X-βPANS were larger than those of 3,5-di-X-αPANS by a factor of about 3 in pK_{ai} units, as listed in Table 2. This can be explained in terms of Scheme 3: tautomerism equilibria are considered to be present in these ligands, as illustrated in this Scheme. Regarding the results for 3,5-di-X-βPANS, a six-membered ring by a dipole–dipole interaction between the naphtholate ring hydrogen atom and a lone pair electron of the N-atom in the azo group should be formed, owing to the direction of the lone pair electron against the naphtholate ring hydrogen atom, as well as to a suitable distance between the N-atom of the azo group and the hydrogen atom. Accordingly, the hydrogen bond should be stabilized in 3,5-di-X-βPANS. Whereas, for 3,5-di-X-αPANS, no stabilization by a dipole–dipole interaction should be expected as a result of the direction of the lone pair electron of the N-atom and distance between the N-atom and the ring hydrogen atom, as shown in the Scheme.

Polarograms of Ligands and Their Metal(II) Complexes. Figure 1 shows the relations between the pH values vs. the reduction potentials of the azo groups in ligands 3,5-di-Cl-αPANS, 3,5-di-Cl-βPANS, 3,5-di-Cl-PAHQS, and BAHQS. As can be seen from Fig. 1 fine linear relations are obtained in all cases involving the ligands. However, it is noteworthy that, in the case of the ligand of the βPANS system, the values of the half-wave potentials are markedly shifted toward the positive potential region at pH=10.73, where a dissociation of the proton in the hydroxyl group at an ortho position to the azo group will occur. This means that very strong hydrogen bonding formed between the proton of the hydroxyl group and the nitrogen atom in the azo group, which is additionally stabilized by the dipole–dipole interaction shown in Scheme 3, is abruptly destroyed at this pH; thus, the azo group is easily reduced at this pH by a positive shift effect.[11] On the other three ligands, since the hydrogen bonding is very weaker than that of βPANS ligands, the reduction potentials of the azo groups were only dependent on the pH values, but independent of the kinds of ligand species.

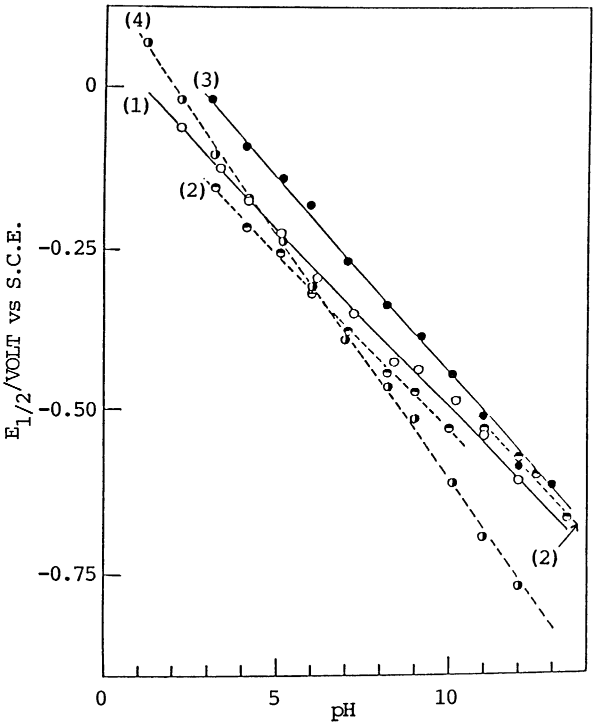


Fig. 1. Relation between pH and half-wave potential of ligand. (1): 3,5-di-Cl-αPANS, $E_{1/2}$=0.048−0.055 pH (r=0.999); (2): 3,5-di-Cl-βPANS, $E_{1/2}$=0.007−0.055 pH (pH=3—10, r=0.999); $E_{1/2}$=0.074−0.056 pH (pH=11—13, r=0.987); (3): 3,5-di-Cl-PAHQS, $E_{1/2}$=0.157−0.061 pH (r=0.999); (4): BAHQS, $E_{1/2}$=0.138−0.076 pH (r=0.999), [ligand]=2.50×10^{-4} mol dm^{-3}, μ=0.1 (KNO$_3$), 0.01% gelatin, 24±2 °C.

The half-wave potentials of 3,5-di-Cl-PAHQS were in the positive region compared with those of 3,5-di-Cl-αPANS and of BAHQS. This can be explained by an electronegative rule[12] for a reduction of organic compounds.

Figure 2 shows plots of the pH vs. the reduction potentials of the azo groups of free 3,5-di-Cl-αPANS, 3,5-di-Cl-βPANS, and their Ni(II) complexes. It can apparently be seen from this figure that the reduction potentials of the ligands in Ni(II) complexes at the same pH values were markedly shifted to the negative side, compared with those of the ligands themselves, showing stabilization by a negative-shift effect.[13–15]

Figure 3 shows plots of the pH vs. the reduction potentials of the azo groups in BAHQS and 3,5-di-Cl-PAHQS, themselves, and of their Ni(II) complexes. It was found from this figure, in the case of the ligand BAHQS, that the reduction potentials of BAHQS itself and that of the Ni(II) complex were almost similar to each other, suggesting that the azo group did not

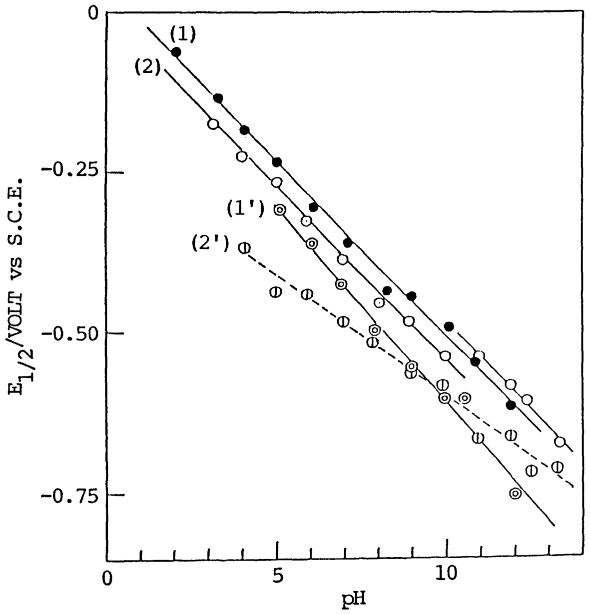


Fig. 2. Relation between pH and half-wave potential of ligand and its nickel(II) complex. (1): 3,5-di-Cl-αPANS, $E_{1/2}=0.048-0.055$ pH ($r=0.999$); (1′): 3,5-di-Cl-αPANS+Ni(II), $E_{1/2}=0.007-0.061$ pH ($r=0.992$); (2): 3,5-di-Cl-βPANS, $E_{1/2}=0.007-0.055$ pH (pH=3—10, $r=0.999$); $E_{1/2}=0.074-0.056$ pH (pH=11—13, $r=0.987$); (2′): 3,5-di-Cl-βPANS+Ni(II), $E_{1/2}=-0.214-0.038$ pH ($r=0.986$); [ligand]=2.50×10^{-4} mol dm^{-3}, [Ni^{2+}]=2.50×10^{-4} mol dm^{-3}, $\mu=0.1$ (KNO_3), 0.01% gelatin, 24±2 °C.

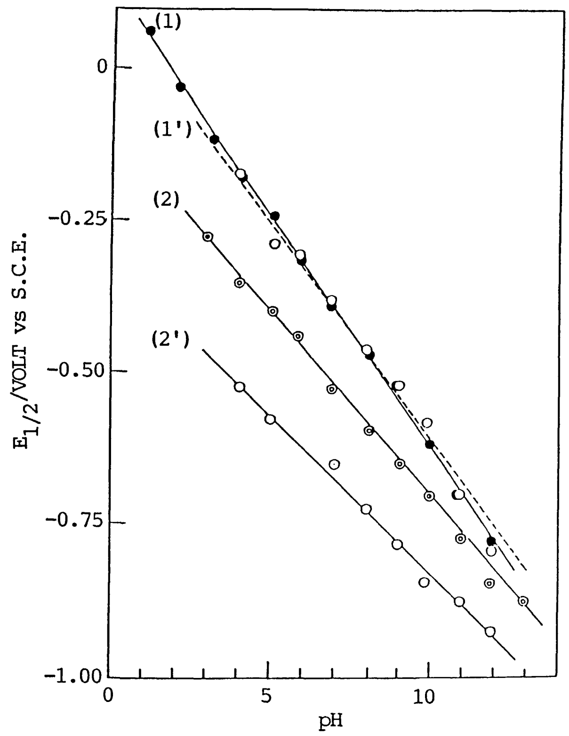


Fig. 3. Relation between pH and half-wave potential of ligand and its nickel(II) complex. (1): BAHQS, $E_{1/2}=0.138-0.076$ pH ($r=0.999$); (1′): BAHQS+Ni(II), $E_{1/2}=0.105-0.071$ pH ($r=0.995$); (2): 3,5-di-Cl-PAHQS, $E_{1/2}=0.157-0.061$ pH ($r=0.999$); (2′): 3,5-di-Cl-PAHQS+Ni(II), $E_{1/2}=-0.062-0.052$ pH ($r=0.997$); Curves (2) and (2′) are shifted 0.25 unit downward for clarity. [ligand]=2.50×10^{-4} mol dm^{-3}, [Ni^{2+}]=2.50×10^{-4} mol dm^{-3}, $\mu=0.1$ (KNO_3), 0.01% gelatin, 24±2 °C.

participate, in this case, in the complexations. In other words, complexation occurred by using only the hydroxyquinoline moiety in the ligand.[16] On the other hand, in the case of the ligand 3,5-di-Cl-PAHQS, it was similar to the PAN systems; thus, the reduction potentials of the ligand in the Ni(II) complex were considerably shifted toward the negative potential region at the same pH values. This means, for a ligand of the PAHQS system, that a stable Ni(II)-complexation should occur by forming chelate rings containing the azo group.

The same results described above were observed in the cases of Zn(II)- and Cd(II)-complexation. Namely, in the Ni(II), Zn(II), and Cd(II) complexes formed with PAN and PAHQS, it was clearly observed that the azo groups were coordinated to these metal(II) ions. In the metal(II) complexes formed with BAHQS, however, it was found that the azo group did not participate in metal(II)-complexations.

Spectrophotometric Data of Metal(II) Complexes: Table 3 shows the compositions (metal to ligand), complexing pH ranges, maximum absorption wavenumbers and molar absorptivities of the complexes. Though the compositions were mainly determined by Hildebrand's method,[10] they were confirmed by the continuous variation method (Job's method). As can be seen from the Table, so far as the Ni(II)-3,5-di-X-PAHQS complexes were concerned, the compositions were 1:2 by using the HL' species of 3,5-di-X-PAHQS judging from the polarographic results which showed that the azo group should participate in metal-complexations and from the complexing pH ranges.

It is noteworthy that the ligands of the PAHQS system coordinates at a lower pH than in either the PAN or BAHQS system. Similar results were found by Busev et al. in their study on compleximetric determination with 7-(2-pyridylazo)-8-hydroxy-quinoline (PAHQ).[17]

For the complexes formed between Ni(II), Zn(II), and Cd(II) and the four PANS ligands systems, the complexing modes seemed to be similar to each other on the basis of the features of the absorption spectra, compositions and complexing pH ranges of the complexes.[2—4] Accordingly, it was thought that the metal ions studied in this experiments reacted with these 3,5-di-X-αPANS and 3,5-di-X-βPANS to form the *N*,*N*,*O*-terdentate mode (N-atom in pyridine ring, N-atom of adjacent one in azo group to hydroxy-

Table 3. Composition, Complexing pH Range, Maximum Wavenumber, and Molar Absorptivity of Ni(II), Zn(II), and Cd(II) Complexes[a)]

Metal ion		3,5-di-Cl-PAHQS	3,5-di-Br-PAHQS	3,5-di-Cl-αPANS	3,5-di-Br-αPANS	3,5-di-Cl-βPANS	3,5-di-Br-βPANS	BAHQS	4-Cl-BAHQS
Ni(II)	b)	1 : 2	1 : 2	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
	c)	$Ni(HL')_2$[f)]	$Ni(HL')_2$[f)]	NiL	NiL	NiL	NiL	NiL	NiL
	d)	0—2.00	0—2.00	0.71—5.05	0.85—5.06	0.45—5.28	0.55—5.28	0.53—5.25	0.06—5.02
	e)	18.9(2.3)	18.8(2.2)	17.1(2.8) 18.2(3.0)	16.9(2.9) 18.2(3.0)	17.5(2.8) 18.8(2.6)	17.4(2.9) 18.7(2.6)	22.7(1.8)	22.2(1.9)
Zn(II)	b)	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
	c)	Zn(HL′)[f)]	Zn(HL′)[f)]	ZnL	ZnL	ZnL	ZnL	ZnL	ZnL
	d)	0—2.10	0—2.10	2.96—6.48	2.96—6.42	3.09—6.37	3.09—6.37	0.06—5.68	0.20—5.57
	e)	20.0(2.0)	20.0(2.0)	17.5(2.8) 18.5(3.2)	17.4(3.0) 18.5(3.2)	18.0(2.8) 19.1(2.6)	17.8(2.8) 19.1(2.5)	23.2(1.8)	23.2(1.7)
Cd(II)	b)	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1	1 : 1
	c)	Cd(HL′)[f)]	Cd(HL′)[f)]	CdL	CdL	CdL	CdL	CdL	CdL
	d)	0—2.10	0—2.10	3.88—6.68	3.76—6.60	4.66—9.01	4.66—9.01	0.07—5.67	0.07—5.67
	e)	20.0(1.8)	20.0(1.6)	17.4(2.9) 18.5(3.2)	17.2(3.0) 18.4(3.3)	17.8(2.6) 19.0(2.3)	17.8(2.6) 19.0(2.3)	23.2(1.5)	23.2(1.5)

a) Aq soln, μ=0.1 (KNO_3), 25.0+0.5 °C. b) Composition (metal: ligand). c) Chemical form of complex. d) Complexing pH range. e) Maximum wavenumber/10^3 cm^{-1} (maximum molar absorptivity, $\varepsilon_{max}/10^4$), in visible region. f) HL′ is ligand which has still conjugated proton combined with nitrogen atom in quinoline moiety, but its phenolic proton has been released, judging from pK_a values.

naphthalene ring, O-atom of naphtholate). Therefore, from the fact of the 1 : 1 composition of the complexes, if the structures of the complexes are assumed to be a six-coordinated octahedron, three water molecules as a solvent are coordinated as $[ML(H_2O)_3]$, which has two five-membered fused chelate rings. In this ligand systems, the formation of a tetrahedral structure for the complexes, is not anticipated because of the sterical restriction, since three coordination sites in the PANS ligands lie on the same plane.

Stability Constants of the Metal(II) Complexes. All of the aqueous solutions containing Ni(II), Zn(II), and Cd(II) complexes with the eight ligands synthesized in this experiments showed spectral changes having clear isosbestic points, due to pH variations. As can be seen from the structure of the PANS ligand systems among the eight ligands, they have a possibility for only one coordination mode, namely by using *N*,*N*,*O*-terdentate ring-formations. In this case, a released proton number in an equilibrium attained should be one from the naphtholic hydroxyl group for a 1 : 1 complexation for a metal : ligand. Accordingly, the stability constants for these complexes could be obtained by calculations using simple equilibrium equations, as described previously,[18)] and Hildebrand's method.[10)] However, the complexation equilibria for the ligands of the PAHQS system which have coordination sites of *N*,*N*,*O*- or *N*,*O*- and for BAHQS system which have coordination sites of *O*,*N*-(O-atom of quinolinolate, N-atom of adjacent one in azo group to quinolinol ring) or *N*,*O*-(HQS moiety) are considered to be very complicated. However, judging from the variations of the reduction potentials of the azo group with the metal-complexations described above, no participation of azo group in the metal complexations was observed for the ligands of the BAHQS system. On the contrary, for the ligands of the PAHQS system, azo group in this ligand clearly participated in metal complexations, judging from the results of polarography. In this case, the complexation equilibria are simplified and, thus, analyses of the equilibria were carried out easily. For example, in the cases of complexations between 3,5-di-X-PAHQS and Zn(II) or Cd(II):

$$M + H_2L \overset{K_1}{\rightleftharpoons} M(HL') + H, \tag{1}$$

where charges of the species are omitted for simplicity, and HL' is a ligand which still has a conjugated proton combined with a nitrogen atom in the quinoline moiety; however, its phenolic proton has been released by the complexing reaction with metal(II) ion,

$$K_1 = [M(HL')][H]/[M][H_2L]. \tag{2}$$

When the total metal concentrations were denoted as C_{Me},

$$C_{Me} = [M] + [M(HL')], \quad (3)$$

the total ligand concentrations, C_L, were

$$C_L = [H_2L] + [HL] + [M(HL')]. \quad (4)$$

The stability constant, β_1, of the complex, [M(HL')], is calculated by using the pK_{a3} values of the ligands as follows:

$$\beta_1 = [M(HL')]/[M][HL'] = K_1/K_{a3}. \quad (5)$$

In this complexing reaction, K_{a3}=[HL'][H]/[H$_2$L]. Then, Eq. 6 can be derived from Eqs. 1—5 as

$$\log\beta_1 = \log([M(HL')]/[H_2L]) - pH$$
$$- \log(C_{Me} + [HL]/2 - C_L/2) + pK_{a3}. \quad (6)$$

For the Ni(II) complex with 3,5-di-X-PAHQS,

$$Ni + 2H_2L \rightleftharpoons Ni(HL')_2 + 2H. \quad (7)$$

In this case, Eq. 8 can be derived as in the cases of Zn(II) and Cd(II) complexes:

$$\log\beta_2 = \log([M(HL')_2]/[H_2L]) - 2pH$$
$$- \log(C_{Me} + [HL]/3 - C_L/3)$$
$$- \log(C_L/3 - [HL]/3) + 2pK_{a3}. \quad (8)$$

In Eqs. 6 and 8, $[HL]=C_L/(1+[H]/K_{a2}+K_{a3}/[H])$.

On the other hand, for the metal(II) complexes with BAHQS, the equilibrium is given as

$$M + H_2L \rightleftharpoons ML + 2H. \quad (9)$$

The stability constants of the complexes ML are given as

$$\log\beta_1 = \log([ML]/[H_2L]) - 2pH$$
$$- \log(C_{Me} + [HL]/2 - C_L/2)$$
$$+ 2pK_{a1} + 2pK_{a2}. \quad (10)$$

In Eq. 10, $[HL]=(1+[H]/K_{a1}+K_{a2}/[H])$. By using Eqs. 6, 8, and 10, log([M(HL')]/[H$_2$L]) vs. pH from Eq. 6, log([M(HL')$_2$]/[H$_2$L]) vs. pH from Eq. 8 and log([ML]/[H$_2$L]) vs. pH from Eq. 10 should give straight lines with slopes of 1, 2, and 2, respectively, and then, each stability constant is obtained from the intercepts of the lines. As typical examples, Figs. 4 and 5 show the relations for the complexations of 3,5-di-Cl-PAHQS-Zn(II) using Eq. 6, and of 3,5-di-Cl-PAHQS-Ni(II) by Eq. 8, respectively. The formation constants, corrected by the side reaction coefficients of ligands and metal(II) ions with the data in Table 2 and in the reference 19, are listed in Table 4. From these results, in the case of the BAHQS system, 1:1 complexations are considered, by a magnitude of β_1, to occur with ring formation using *N,O*- sites in the hydroxyquinoline moiety. On the other hand, in the 1:1 complexations of Zn(II) and Cd(II) with the ligand of the PAHQS system, *N,N,O*-terdentate chelate ring formations by using the N-atom in the azo group are considered to occur as well as complexations of the PANS ligand systems, judging from larger stability constants of the Zn(II) and Cd(II) complexes with the PAHQS ligands, compared with those of the α- and

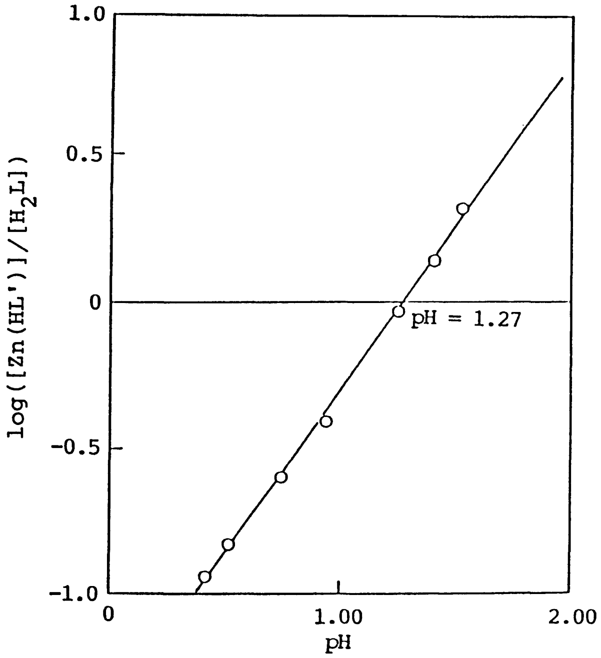


Fig. 4. Plots of log([Zn(HL')]/[H$_2$L]) vs. pH of Zn-3,5-di-Cl-PAHQS complex at 540 nm (25.0+0.5 °C). log([Zn(HL']/[H$_2$L])=−1.43+1.13 pH (r=0.999).

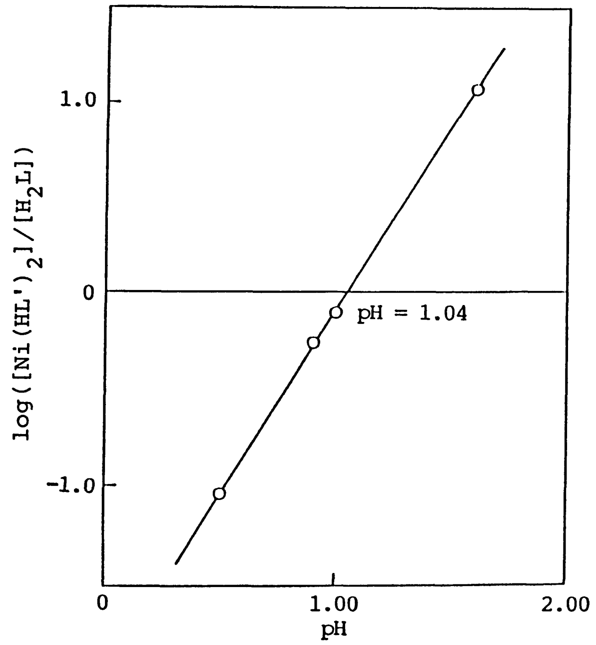
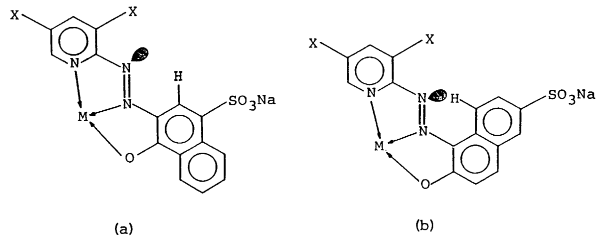


Fig. 5. Plots of log([Ni(HL')$_2$]/[H$_2$L]) vs. pH of Ni-3,5-di-Cl-PAHQS complex at 570 nm (25.0+0.5 °C). log([Ni(HL']$_2$)/[H$_2$L])=−1.98+1.90 pH (r=0.999).

Table 4. Stability Constants of Ni(II), Zn(II), and Cd(II) Complexes[a)]

Metal ion	3,5-di-Cl-PAHQS		3,5-di-Br-PAHQS		3,5-di-Cl-αPANS		3,5-di-Br-αPANS		3,5-di-Cl-βPANS		3,5-di-Br-βPANS		BAHQS		4-Cl-BAHQS	
	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$
Ni(II)	—	27.04	—	27.11	16.55	—	15.61	—	20.87	—	21.05	—	12.38	—	12.50	—
Zn(II)	15.96	—	16.01	—	10.38	—	9.86	—	15.19	—	15.33	—	12.07	—	(12.4)[b)]	—
Cd(II)	15.93	—	15.98	—	9.31	—	9.19	—	(11.5)[b)]	—	(11.9)[b)]	—	11.61	—	(11.5)[b)]	—

a) Aq soln, μ=0.1 (KNO_3), 25.0+0.5 °C. Experimental errors are within ±0.10 in $\log\beta$ unit. For metal complexes with PAHQS, β_1=[M(HL′)]/[M][HL′] and β_2=[M(HL′)$_2$]/[M][HL′]^2, respectively. For metal complexes with PANS and BAHQS, β_1=[ML]/[M][L] and β_2=[ML$_2$]/[M][L]^2, respectively. b) Tentatively estimated values because of an obscure isosbestic point of absorption curves varying with pH changes, but showing exactly straight line with a slope of unity by treating with the Hildebrand's method.



Scheme 4. Probable structures of metal complexes. (a): Complex with 3,5-di-X-αPANS, (b): Complex with 3,5-di-X-βPANS. In which, M denotes Ni(II), Zn(II), and Cd(II).

βPANS ligands. Regarding the degree of the complexation equilibria of Ni(II) complexes, however, no exact argument can be made because of the different compositions of Ni(II): ligands (1:2 for PAHQS and 1:1 for PANS); it might, however, be considered that the *N,N,O*-chelate rings are formed in these complexes, judging from very large values of β_2. Nevertheless, these considerations seemed to be closely associated with the results of the polarographic studies described above, that the reduction potentials of the azo group in the metal complexes fromed with ligands of the PAHQS system were shifted markedly toward the negative region, compared with those of free ligands at the same pH. Moreover, the degree of this shift was larger than that of the PANS ligand systems.

In all complexations of the metal(II) ions studied, the stability constants with 3,5-di-X-βPANS were always larger than those with 3,5-di-X-αPANS in about 2—5 in $\log\beta_1$ unit, as listed in Table 4. This difference might be attributed to a stabilization effect brought about by a six-membered ring formation by a dipole–dipole interaction between the naphtholate ring hydrogen atom and the N-atom of the azo group of the 3,5-di-X-βPANS complexes, as shown in Scheme 4. Finally, the values of $\log\beta_1$ of the 1:1 metal(II) complexes formed with the PANS and BAHQS systems were in the order Ni(II)>Zn(II)>Cd(II).

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