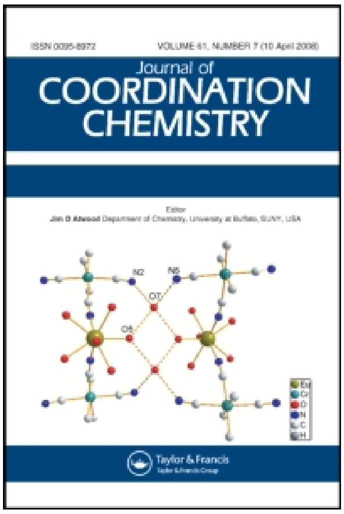

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COMPLEXATION OF A NEW MULTIDENTATE LIGAND 7-[(3,5-DICHLORO-2-CARBOXYPHENYL)AZO]-8-HYDROXYQUINOLINE-5-SULFONIC ACID WITH Ni(II), VO(IV), Zn(II), AND Cd(II)

Masaaki Hirohata[a]; Fumiaki Kai[a]; Kazu Kurosawa[a]; Hu Huang[b]; Kana Ishii[c]; Yasushi Matsuoka[c]; Kenji Komori[c]; Masaaki Nakamura[c]
[a] Graduate School of Natural Science and Technology, Kumamoto University, Kurokami, Kumamoto, Japan [b] Chemicals Research Laboratory, Showa Denko Co. Ltd., Kawasaki-ku, Kawasaki, Japan [c] Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto, Japan

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COMPLEXATION OF A NEW MULTIDENTATE LIGAND 7-[(3,5-DICHLORO-2-CARBOXYPHENYL)AZO]-8-HYDROXYQUINOLINE-5-SULFONIC ACID WITH Ni(II), VO(IV), Zn(II), AND Cd(II)

MASAAKI HIROHATA, FUMIAKI KAI,* KAZU KUROSAWA

Graduate School of Natural Science and Technology, Kumamoto University, Kurokami, Kumamoto 860, Japan

HU HUANG

Chemicals Research Laboratory, Showa Denko Co. Ltd., 5-1 Ohgi-machi, Kawasaki-ku, Kawasaki 210, Japan

KANA ISHII, YASUSHI MATSUOKA, KENJI KOMORI
and MASAAKI NAKAMURA

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860, Japan

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A new title multidentate ligand (CAHQS) containing both carboxyphenylazo and 8-quinolinol fragments has been prepared for the first time. Proton dissociation processes of CAHQS and coordination selectivities of CAHQS toward VO(IV), Ni(II), Zn(II), and Cd(II) have been probed by means of electronic spectroscopy, polarography, and Raman spectroscopy of the complexes in aqueous solutions. It has been shown that the selectivity of CAHQS toward such metal ions is dependent on steric factors in the chelate ring formed, not on HSAB properties of the coordination sites in CAHQS and of such metal ions. Complexing equilibria and stability constants are also reported.

KEYWORDS: Multidentate, coordination selectivity, VO(IV), Ni(II), Zn(II), Cd(II), stability constants

INTRODUCTION

It is generally known that the coordination selectivity of various metal ions toward a multidentate ligand containing more than two groups of potentially chelating donor atoms would be governed by 1) basicity of a donating atom in the ligands,

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* Author for correspondence.

2) the kind of metal ion (HSAB properties), 3) size-match of the chelate ring formed for a metal ion, 4) steric restrictions of the ligands, and so on. This selectivity is, however, not fully and systematically understood at the present time.

In previous papers, the coordination selectivity of the multidentate ligand, 7-[(3,5-dihalo-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (X_2PAHQS,[1-6] Scheme 1), was studied in detail. In this case, it was clearly shown that X_2PAHQS coordinated in aqueous solution selectively by using N,N,O-sites toward Cd(II)[1] as a soft acid, and Fe(II),[6] Ni(II)[1] and Zn(II)[1] as border line acids. By N,N,O-complexation, two five-membered rings, scarcely strained by inspection of molecular models, are formed (Scheme 1). For VO(IV)[2] and VO_2(V)[6] as hard acids, X_2PAHQS coordinated selectively by using N,O-bidentate sites in the 8-quinolinol moiety. In the case of X_2PAHQS, selectivity is mainly governed by HSAB properties. We reported also the coordination selectivity of the analogous multidentate ligand, 7-[(2-hydroxy-5-sulfophenyl)azo]-8-hydroxyquinoline-5-sulfonic acid (SPAHQS,[7] Scheme 1), toward Fe(II), Ni(II), Zn(II), Cd(II), and VO(IV) to investigate effects of variation of ring-members formed by chelation. That is, if SPAHQS acts as an O,N,O-terdentate ligand, the chelate formed is expected to have one five-membered and one six-membered ring as illustrated in Scheme 1. As a result, it was shown that SPAHQS coordinated selectively by N,O-bidentate sites regardless of metal ion hardness.

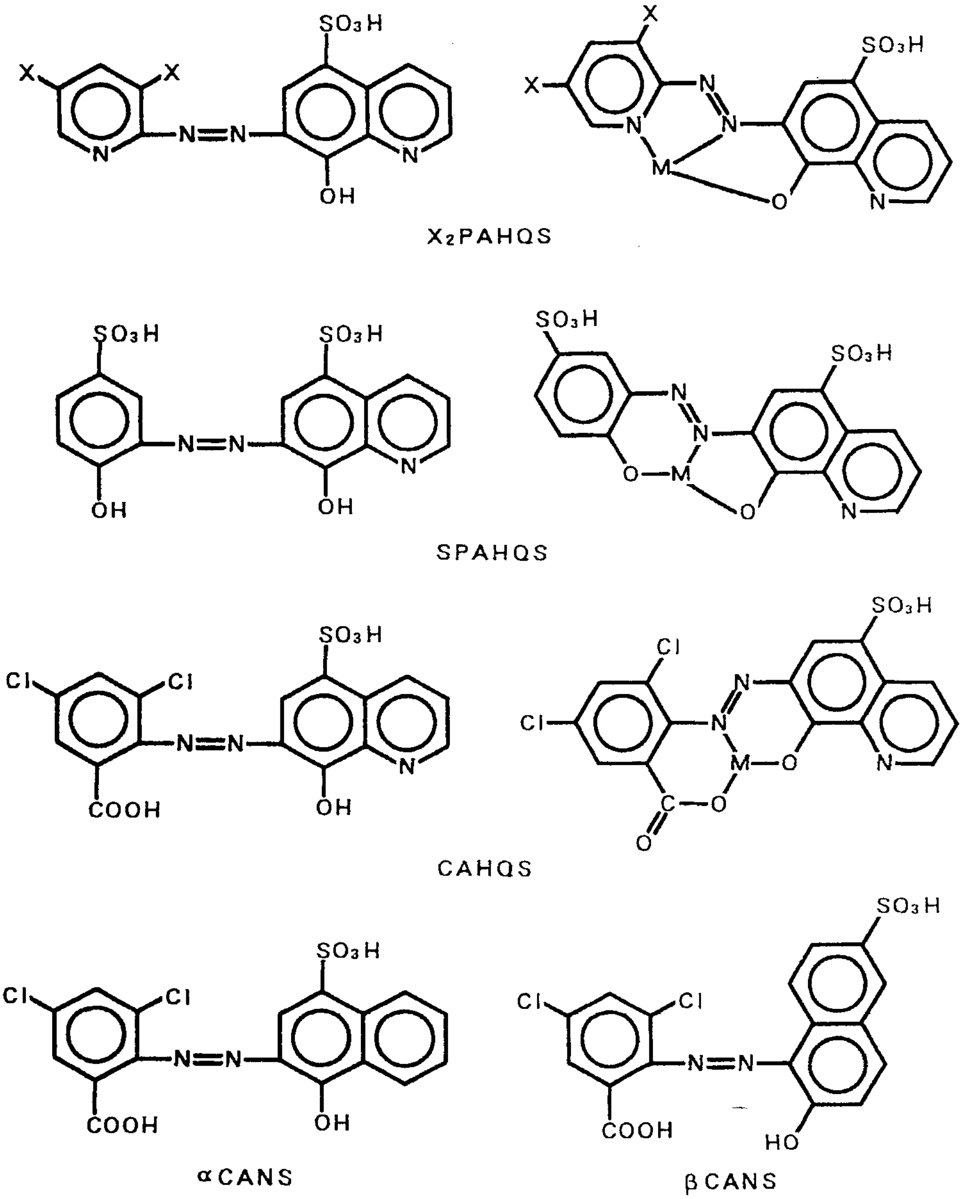
Here we extend our study to a newly prepared multidentate ligand 7-[(3,5-dichloro-2-carboxyphenyl)azo]-8-hydroxyquinoline-5-sulfonic acid (CAHQS, Scheme 1) to judge effects of ring-member variation on selectivity. That is, if CAHQS acts as a terdentate ligand toward metal ions by using O,N,O-sites, two six-membered rings would be expected to form as illustrated in Scheme 1, and thus the study of CAHQS makes clearer the effect of the ring-member formed by complexations on coordination selectivities.

This paper describes, first, proton dissociation processes of CAHQS and of analogous ligands (*vide infra*), then coordination selectivities toward Ni(II), VO(IV), Zn(II), and Cd(II) by means of the electronic spectroscopy, polarography, and Raman spectroscopy. Finally, complexing equilibria and stability constants were analyzed spectrophotometrically. For comparative purposes 2-[(3,5-dichloro-2-carboxyphenyl)azo]-1-hydroxynaphthalene-4-sulfonic acid (α CANS) and 1-[(3,5-dichloro-2-carboxyphenyl)azo]-2-hydroxynaphthalene-6-sulfonic acid (β CANS) as analogues of α CANS were prepared to explore the coordination role of the N-atom in the 8-quinolinol moiety in CAHQS, as shown also in Scheme 1.

EXPERIMENTAL

Reagents

CAHQS was synthesized through a coupling reaction as follows. Commercial 2-amino-3,5-dichlorobenzoic acid (2.06 g, 10 mmol) in MeOH (100 cm^3) acidified with conc. HCl (20 cm^3) was diazotizated at 0°C by the usual method.[8] The MeOH solution containing the diazotizated benzoic acid was added to an equimolar solution of commercial 8-hydroxyquinoline-5-sulfonic acid dissolved in aqueous alkali. Crude product was then obtained by stirring the mixture at 0°C for 2h. The product was purified by recrystallization from aqueous solution, then dried over



Scheme 1 Chemical formulae of new ligands synthesized and assumed ring-members of chelate compounds.

P_2O_5 *in vacuo.* Yield, 54%; mp (decomp.) > 300°C. Found: C, 34.98; H, 2.51; N, 7.49%. Calcd. for $C_{16}H_7N_3O_6SCl_2Na_2 \cdot 3.5H_2O$ (two Na ions in this formula are attached as carboxylate and sulfonate): C, 34.99; H, 2.57; N, 7.65%. IR: 1385

($\nu_{N=N}$); 1694 ($\nu_{C=O}$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 8.08 (1H, d, J = 2.4 Hz), 8.31 (1H, m), 8.34 (1H, d, J = 2.4 Hz), 8.54 (1H, s), 9.34 (1H, dd, J = 1.6, 5.4 Hz), 9.73 (1H, dd, J = 1.6, 8.6 Hz).

α CANS was synthesized by a procedure similar to that for CAHQS, except that 1-naphthol-4-sulfonic acid was used instead of 8-hydroxyquinoline-5-sulfonic acid as coupling component. Yield, 28%; mp (decomp.) > 300°C. Found: C, 36.39; H, 1.86; N, 5.04%. Calcd. for $C_{17}H_8N_2O_6SCl_2Na_2 \cdot 2HCl$ (Cl^- from HCl was determined by titration with Ag^+): C, 36.58; H, 1.81; N, 5.02%. IR: 1370 ($\nu_{N=N}$); 1711 ($\nu_{C=O}$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.93–8.23 (3H, m), 8.10 (1H, s), 8.35 (1H, d, J = 2.4 Hz), 8.78 (1H, dd, J = 1.6, 7.0 Hz), 9.05 (1H, dd, J = 1.6, 7.0 Hz).

β CANS was also synthesized by the same procedure for CAHQS and α CANS by using 2-naphthol-6-sulfonic acid instead of 8-hydroxyquinoline-5-sulfonic acid for CAHQS. Yield, 70%; mp (decomp.) > 300°C. Found: C, 42.26; H, 1.86; N, 5.56%. Calcd. for $C_{17}H_8N_2O_6SCl_2Na_2$: C, 42.08; H, 1.66; N, 5.77%. IR: 1374 ($\nu_{N=N}$); 1711 ($\nu_{C=O}$) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 7.00 (1H, d, J = 9.0 Hz), 7.70 (1H, d, J = 2.4 Hz), 7.94 (1H, d, J = 7.6 Hz), 8.07 (1H, d, J = 9.0 Hz), 8.10 (1H, d, J = 1.0 Hz), 8.30 (1H, d, J = 7.6 Hz).

Aqueous Ni(II), VO(IV), Zn(II), and Cd(II) solutions were prepared as perchlorates. The concentrations of the metal ions were determined by the usual EDTA titration. All other chemicals used were of analytical or equivalent grade.

Measurements

^{1}H NMR spectra were obtained on a JEOL PMX60-SI NMR spectrometer. IR spectra were recorded on a JASCO A-102 spectrometer (KBr disk). Dissociation constants of the ligands and stability constants of the complexes were measured spectrophotometrically on a Hitachi 220A recording spectrophotometer. Polarograms were recorded on a Yanaco P-1100 polarographic analyzer in an aqueous solution containing 0.1 mol dm^{-3} KNO_3 as supporting electrolyte, and 0.01% gelatin as maximum suppressor. A three-electrode cell was used, 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 = 1.00 s/drop at −0.5 V *vs* SCE, in electrolytic solution at pH 7.0. Raman spectra were recorded on a JASCO R-800 spectrometer equipped with an NEC GLG 3200 Ar^+ laser as exciting light source. The pH values of the sample solutions for both spectrophotometric and polarographic measurements were adjusted by an appropriate buffer solution, and were read instantly after the measurements on a Hitachi-Horiba F-13 pH meter.

RESULTS AND DISCUSSION

Electronic spectra and dissociation constants of CAHQS

Figure 1 shows the electronic spectra of CAHQS at various pH values. The fully protonated ligand species (curve a) gives two dominant peaks at 19,500 cm^{-1} corresponding to the $\pi^* \leftarrow \pi$ transition of the azo group[9,10] and around 28,000 cm^{-1} due to the quinoline ring.[11,12] The absorption bands are shifted hypsochromically

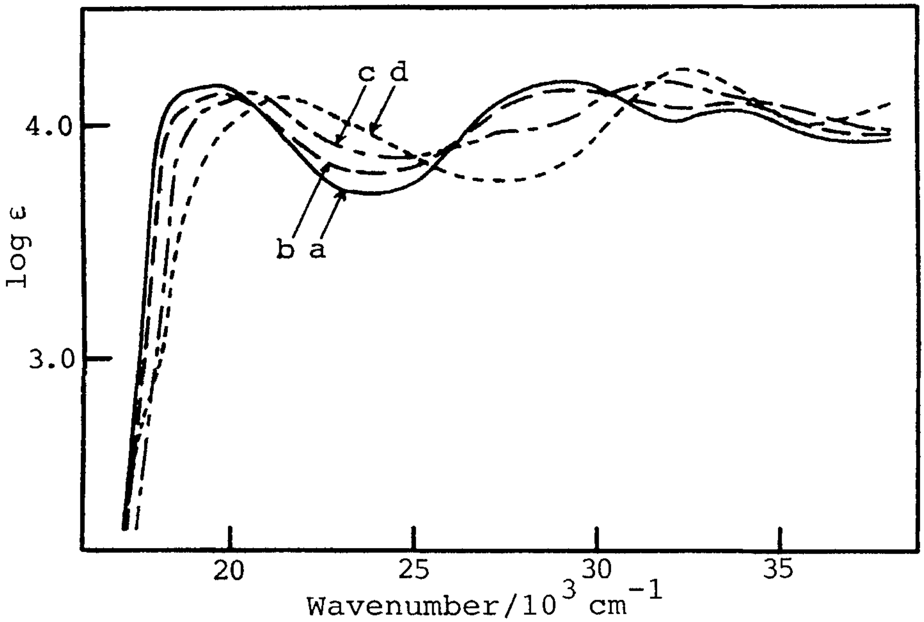


Figure 1 Absorption spectra of CAHQS in aqueous solution at various pH values; pH: a = 0.01 (species H_3L); b = 2.23 (species H_2L); c = 5.14 (species HL); d = 9.64 (species L); [CAHQS] = 1.00×10^{-5} mol dm^{-3}, 25.0 ± 0.5°C.

upon deprotonation (curves b–d). Among them, the shift in the 19,500–21,500 cm^{-1} region reflects deprotonation at the quinolinolate oxygen atom, whereas the shift in the 28,000–34,500 cm^{-1} region reflects protonation at the quinoline nitrogen atom as well as protonation at the quinolinolate oxygen atom. Proton dissociation processes of CAHQS are shown in Scheme 2. The sequence of the dissociations is first that from –COOH, then from HN^+-, and finally from HO–, on the basis of the basicity of the ligating groups which decreases in the order[13] quinolinolate > quinoline > carboxylate > azo group. The dissociation constants obtained are listed in Table 1 together with those of α CANS and β CANS.

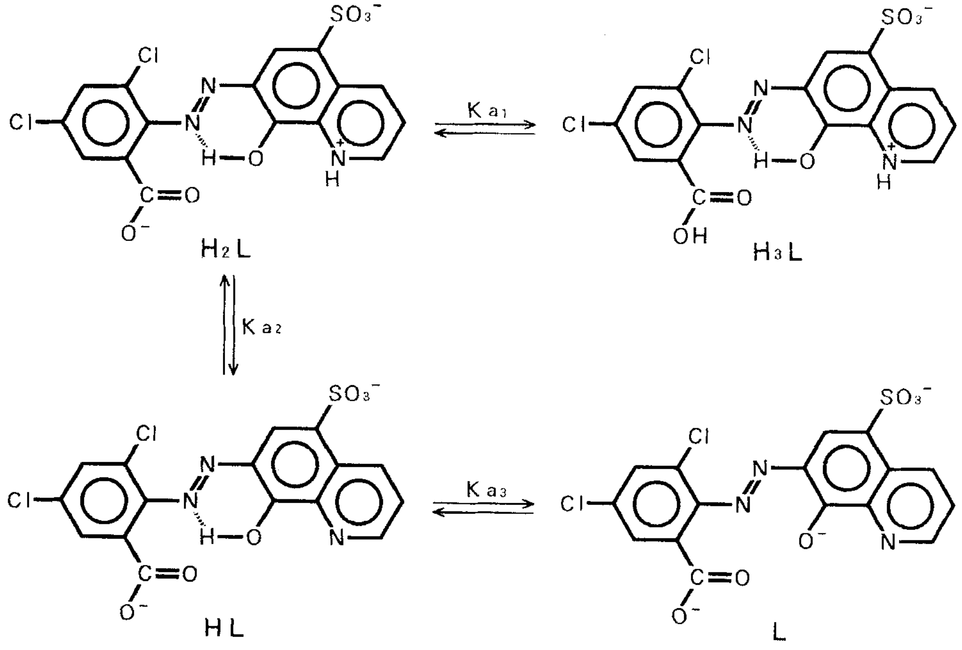
Electronic spectra of metal complexes

Figure 2 shows the electronic spectra of free CAHQS and related ligands, and of the metal complexes with them. The peak of the species H_2L of CAHQS at 19,100 cm^{-1}

Table 1 Dissociation Constants.[a]

Ligand	pK_{a1}	pK_{a2}	pK_{a3}
CAHQS	1.20	2.82	7.56
α CANS	2.20[b]	8.74[c]	
β CANS	2.17[b]	11.32[c]	

[a] Aqueous solution, μ = 0.1 (KNO_3), 25.0 ± 0.5°C. [b] Carboxylate. [c] Naphtholate; The errors are within ±0.05 in pK_{ai} units.



Scheme 2 Dissociation processes of CAHQS.

due to the $\pi^* \leftarrow \pi$ transition of the azo group (curve a) was shifted to 23,200 cm^{-1} upon VO(IV) -CAHQS complexation (curve b). Here, only VO(IV) among the metal ions studied reacts with the species in the H_2L form as summarized in Table 1. The frequency difference between the peak of the species H_2L and that of the VO(IV) -CAHQS complex amounts to *ca* 4,000 cm^{-1}. Likewise, the absorption maximum at 20,500 cm^{-1} for free CAHQS in the HL form (curve c) was shifted to 21,400 cm^{-1} by Ni(II) complexation (curve d) and to 21,600 cm^{-1} by Cd(II) (curve e). These shifts toward higher frequencies strongly suggest that CAHQS coordinates to these metal ions only with the 8-quinolinolate moiety as an N,O-bidentate ligand.[2,6] Although a spectrum of the CAHQS-Zn(II) complex is not shown in Figure 2, both of the above features, and trends of shifts are the same as those for other complexes (see Table 2). On the other hand, the peaks of the $\pi^* \leftarrow \pi$ transitions of the azo groups for the species HL of free α CANS and β CANS (curves f and i, 20,000 cm^{-1}) were shifted to lower frequencies, where the shifts are not so large compared with those of CAHQS complexations but amount to *ca* 700 cm^{-1} accompanying complexation with VO(IV) (curves g and j), and with Ni(II) (curves h and k). These inverse shifts upon complexation with α CANS and β CANS strongly indicate that α CANS and β CANS act as O,N,O (O atom of carboxylate, one of the N atoms in the azo group, O atom in 8-quinolinolate) terdentate ligands.[2,6] The spectra for the sets of α CANS and β CANS with Cd(II) and Zn(II) have not been shown in Figure 2 because neither colour changes due to complexation nor isosbestic points attributed to complexation equilibria were observed at any pH.

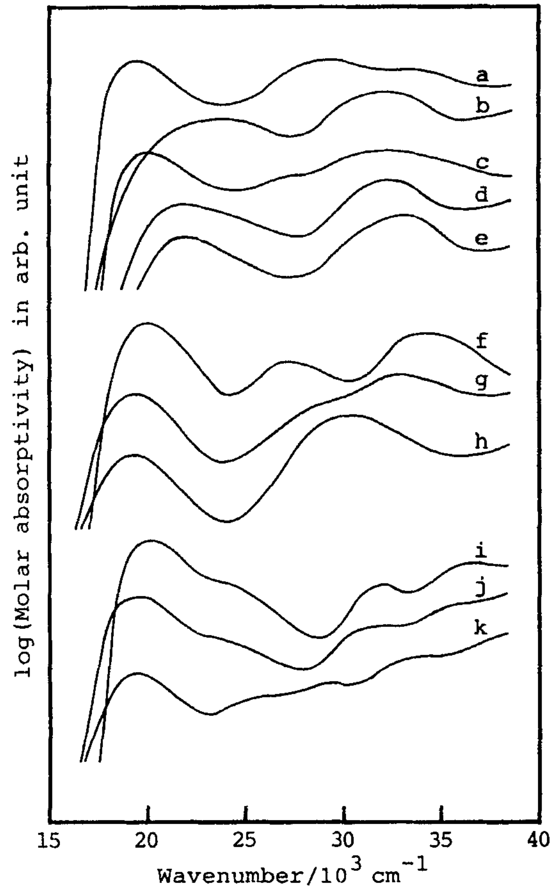


Figure 2 Absorption spectra of mixture of metal ions and ligands in aqueous solution at various pH values; a = free CAHQS at pH 2.23 (H_2L); b = CAHQS + VO(IV) at pH 2.25; c = free CAHQS at pH 5.14 (HL); d = CAHQS + Ni(II) at pH 5.42; e = CAHQS + Cd(II) at pH 5.21; f = free α CANS at pH 4.97 (HL); g = α CANS + VO(IV) at pH 5.13; h = α CANS + Ni(II) at pH 5.46; i = free β CANS at pH 6.86 (HL); j = β CANS + VO(IV) at pH 5.00; k = β CANS + Ni(II) at pH 6.50; [ligand] = 1.00×10^{-5} mol dm^{-3}, [metal] = 1.00×10^{-4} mol dm^{-3}, $\mu = 0.1$ (KNO_3), 25.0 ± 0.5°C.

Table 2 Complexing pH range, equilibrium mode, and stability constants for complexes.[a]

Ligand	pH Range	Equilibrium	$\tilde{\nu}_{max}/10^3(\varepsilon_{max}/10^4)^b$	$\log\beta_1$
CAHQS	1.21-3.15	$VO + H_2L \Leftrightarrow VOL + 2H$	23.2(1.02)	15.94
″	2.89-4.86	$Ni + HL \Leftrightarrow NiL + H$	21.4(1.14)	10.71
″	3.54-5.74	$Zn + HL \Leftrightarrow ZnL + H$	21.0(1.10)	10.35
″	4.20-6.52	$Cd + HL \Leftrightarrow CdL + H$	21.6(1.06)	8.93
α CANS	2.86-4.52	$VO + HL \Leftrightarrow VOL + H$	19.3(1.18)	14.68
″	4.75-6.17	$Ni + HL \Leftrightarrow NiL + H$	19.3(1.06)	11.43
β CANS	2.24-5.09	$VO + HL \Leftrightarrow VOL + H$	19.4(1.27)	19.17
″	4.82-7.71	$Ni + HL \Leftrightarrow NiL + H$	19.4(1.07)	13.75

[a] Aqueous solution, $\mu = 0.1$ (KNO_3), 25.0 ± 0.5°C. [b] $\pi^* \leftarrow \pi$ absorption of azo group; All errors are within ±0.05 in $\log\beta_1$ units.

Polarograms of ligands and their metal complexes

To investigate the coordination mode of the multidentate ligands containing azo groups against metal ions, comparison of reduction potentials for the azo group in the free ligand and in the metal complex is quite useful to judge whether the N atom in the azo group coordinates to metal ion or not.[1,2,6,7] Figure 3 shows the relation between pH and reduction potentials of the azo groups for free CAHQS and its VO(IV), Ni(II), Zn(II), and Cd(II) complexes over pH 2–12. It is seen to hold a linear relation for free CAHQS (solid line, $E_{1/2} = -0.07\text{pH} + 0.15$, $r = 0.999$) and its complexes through the pH range studied.

The potential variations with pH for free αCANS (solid line, $E_{1/2} = -0.07\text{pH} + 0.10$, $r = 0.999$) and its VO(IV) and Ni(II) complexes are shown in Figure 4. The potentials for the VO(IV) complex at $\text{pH} < 3$ are almost the same as those of free α CANS, and at pH 3–6 they are shifted to a negative region, showing stabilization by a negative shift effect.[1,14–16] At $\text{pH} > 6$ the potentials lie again on the line of the free ligand. This means that the VO(IV) complex is dissociated at

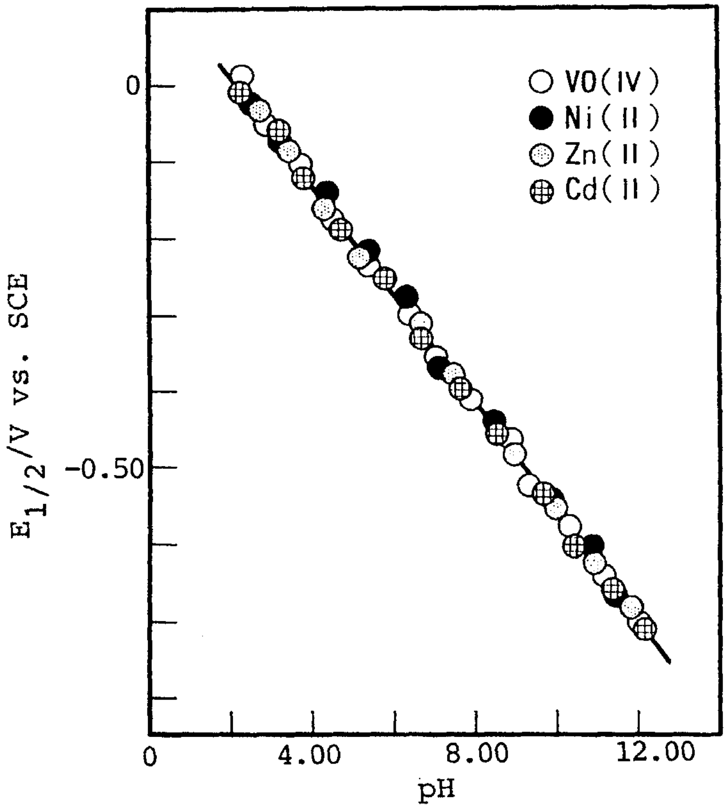


Figure 3 Relation between pH and half-wave potentials of CAHQS and its metal complexes with VO(IV), Ni(II), Zn(II), and Cd(II). The solid line is the potential variation of free CAHQS. [CAHQS] = [metal] = 2.50×10^{-4} mol dm^{-3}, $\mu = 0.1$ (KNO_3), 0.01% gelatin, 24 ± 2°C.

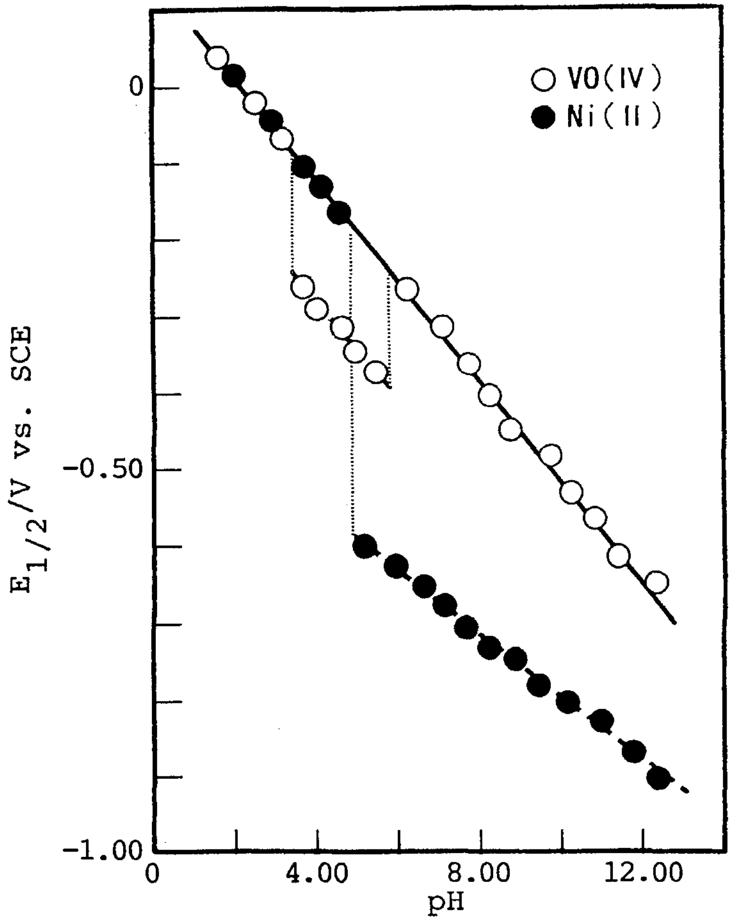


Figure 4 Relation between pH and half-wave potentials of α CANS and its metal complexes with VO(IV) and Ni(II). The solid line indicates the potential variation of free α CANS. Experimental conditions are the same as those in Figure 3.

pH > 6 by the hydrolysis of the VO(IV) ion.[2,6,17] Likewise, the potential variations for the Ni(II) complex with α CANS at pH > 4 are also largely shifted to the negative side by the same effect.[1,14-16]

The potential variations for free β CANS (solid line, $E_{1/2} = -0.07\text{pH} + 0.08$, $r = 0.999$) and its VO(IV) and Ni(II) complexes are given in Figure 5. The trends are quite close to those of the α CANS systems shown in Figure 4.

These polarographic results strongly indicate that the azo group in the ligand CAHQS does not coordinate to the metal ions regardless of their hardness. In other words, the metal ions coordinate selectively to the 8-quinolinol moiety in CAHQS as an N,O-bidentate, whereas the ligands α CANS and β CANS act as terdentates by using O,N,O-ligating sites.[1,2,6,7]

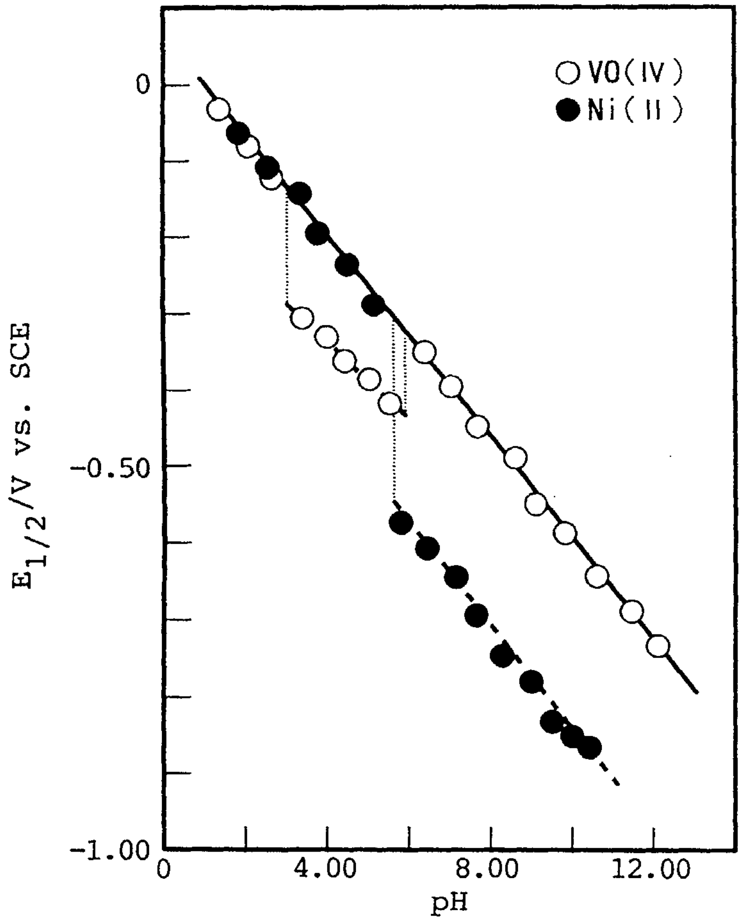


Figure 5 Relation between pH and half-wave potentials of β CANS and its metal complexes with VO(IV) and Ni(II). The solid line shows potential variation of free β CANS. All experimental conditions are the same as those in Figure 3.

Resonance Raman Spectra

The Raman bands due to stretching vibrations of an azo group in various azo compounds are known to appear in the 1,200–1,700 cm^{-1} region.[7,18] In a previous paper,[7] the Raman bands of SPAHQS in this region were carefully measured in either D_2O or H_2O medium, and the spectra observed in both solutions were evidently attributed to the azo group stretching vibrations. Figure 6 depicts the Raman spectra of the free ligands and their metal complexes in aqueous solution at several pH values. The spectrum of free CAHQS at pH 8.33 (a-1) shows bands at 1,390, 1,420, 1,470, and 1,595 cm^{-1}. The bands of the complexes CAHQS-VO(IV) at pH 3.96 (a-2) and CAHQS-Ni (II) at pH 6.25 (a-3) are almost the same. This result evidently indicates that there is no participation of the N atoms of the azo group in CAHQS in coordination with VO(IV) and Ni(II). In other words, CAHQS

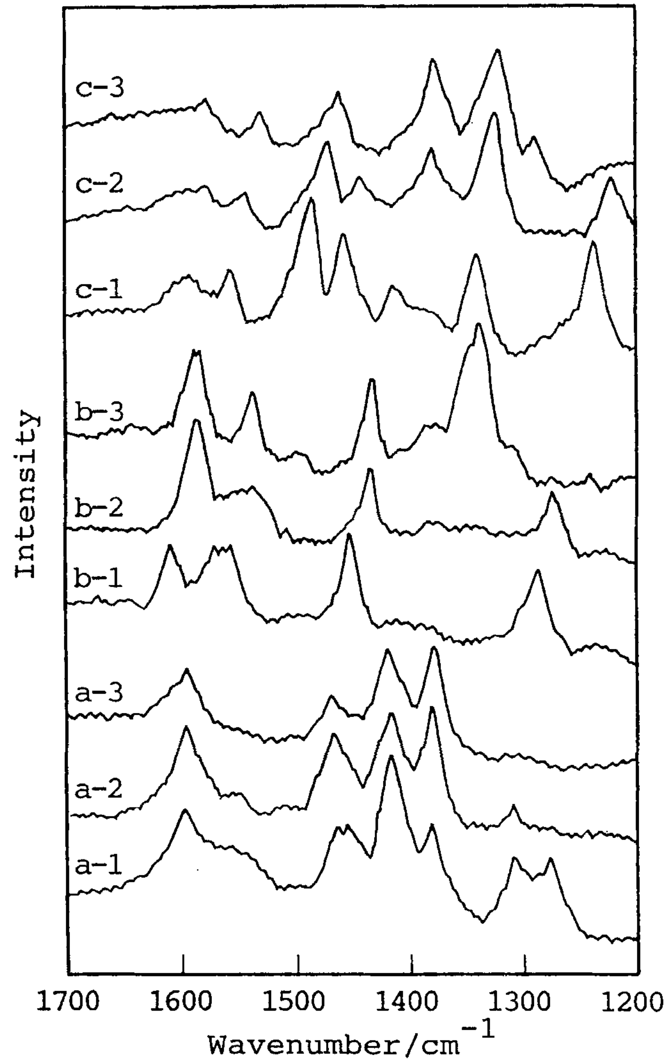


Figure 6 Resonance Raman spectra of ligands and their VO(IV) and Ni(II) complexes in aqueous solution. a-1 = free CAHQS at pH 8.33; a-2 = CAHQS + VO(IV) at pH 3.96; a-3 = CAHQS + Ni(II) at pH 6.25; b-1 = free αCANS at pH 9.98; b-2 = αCANS + VO(IV) at pH 4.96; b-3 = αCANS + Ni(II) at pH 6.25; c-1 = free β CANS at pH 12.35; c-2 = β CANS + VO(IV) at pH 4.85; c-3 = β CANS + VO(IV) at pH 8.06. A wavelength of 476.5 nm was used for the CAHQS and αCANS systems, and 457.9 nm for the β CANS systems, as excitation light source.

coordinates with only the 8-quinolinolate moiety[7] regardless of the hardness of the metal ions. The bands for free α CANS at pH 9.98 (b-1) observed at 1,286, 1,458, around 1,560, and 1,610 cm^{-1} are shifted toward lower frequency regions upon complexations with VO(IV) at pH 4.96 (b-2) and with Ni(II) at pH 6.25 (b-3). The frequency difference between free α CANS and its metal complexes amounts to

8–23 cm^{-1}. Likewise, the bands for free *β* CANS at pH 12.35 (c-1) at 1,240, 1,340, 1,414, 1,458, 1,480, 1,560 cm^{-1} are shifted by 12–32 cm^{-1} toward the lower frequency region by complexations with VO(IV) at pH 4.85 (c-2) and with Ni(II) at pH 8.06 (c-3). These results for *α* CANS and *β* CANS systems clearly show (as well as those from the spectroscopic and polarographic studies) that both ligands coordinate with VO(IV) and Ni(II) by O,N,O-sites as terdentate ligands. Thus for CAHQS, which has an electronegative N atom in 8-quinolinol, it seems that metal ions coordinate to N,O-sites in 8-qunolinol to avoid steric restriction by O,N,O-chelation. For *α* CANS and *β* CANS, which have no electronegative N atoms of an 8-quinolinol moiety, it seems likely that O,N,O-sites must be used for coordination toward VO(IV) and Ni(II).

Complexing equilibria and calculation of stability constants

Except for the sets of Zn(II) and Cd(II) with *α* CANS and *β* CANS, the solutions containing the ligands and metal ions (ligand: metal ion = 1:10) showed spectroscopic changes with pH variation, having clear isosbestic points in the pH ranges as shown in Table 2. The stability constants were calculated by the following equations, where C_M stands for the initial concentrations of metal ions.

In equilibria for CAHQS of the type $M + HL \Leftrightarrow ML + H^+$ (M = Ni(II), Zn(II), and Cd(II)), equation (*1*) was used.

$$\log\beta_1 = \log([ML]/[M][L]) = \log([ML]/[HL]) \\ -pH - \log C_M + pK_{a3} \qquad (1)$$

In the case of $VO + H_2L \Leftrightarrow VOL + 2H^+$ for CAHQS, equation (*2*) was applied for the calculation.

$$\log\beta_1 = \log([VOL]/[VO][L]) = \log([VOL]/[H_2L]) \\ -2pH - \log C_{VO} + pK_{a2} + pK_{a3} \qquad (2)$$

For the complexation of *α* CANS and *β* CANS with VO(IV) and Ni(II) in the type $M + HL \Leftrightarrow ML + H^+$, equation (*3*) was used.

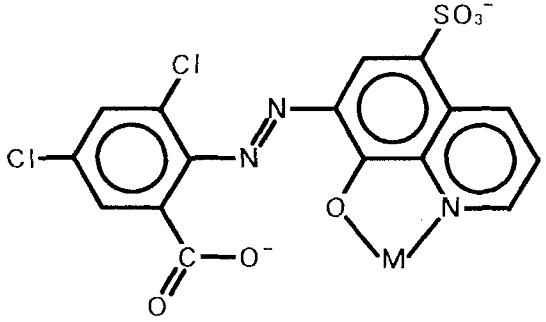
$$\log\beta_1 = \log([ML]/[M][L]) = \log([ML]/[HL]) \\ -pH - \log C_M + pK_{a2} \qquad (3)$$

K_{a2} in equation (*3*) corresponds to the proton dissociation of naphtholate HO- (see Scheme 2 and Table 1). In any case, the released proton numbers upon complexations were determined graphically from the slope of the straight line between pH *vs* the first term of the right hand side in each equation. All compositions of the complexes (M:L) were confirmed by the continuous variation method.

The stability constants, which are corrected finally by the side reaction coefficients[19] of metal ions, are listed in Table 2. For the stability constants of the Ni(II) complexes with the three ligands, it can be seen that the constants decrease in the order *β* CANS>> *α* CANS> CAHQS. This can be interpreted by the chelate effect, *i.e.*, the CAHQS complex has only one chelate ring from N,O-bidentate chelation, and for the *α* CANS and *β* CANS complexes two chelate rings are formed by O,N,O-complexations. Furthermore, the sequence *β* CANS >> *α* CANS ($\Delta\log\beta_1$ = 2.32) is interpreted by the pK_{a2} values for *α* CANS (8.74) and *β* CANS

(11.32), *i.e.*, the difference in pK_{a2} value between α CANS and β CANS (ΔpK_{a2} = 2.58) reflects directly on the stability constants defined in equation (*3*).

In summary, the electronic spectra,[2,6] polarograms,[1,2,6,7] and Raman spectra[7] show that CAHQS selectively coordinates to VO(IV) (hard acid), Ni(II) (border line acid), Zn(II) (border line acid), and Cd(II) (soft acid) at only the 8-quinolinol moiety as one of the fragments of CAHQS, regardless of the HSAB properties of the metal ions and ligating atoms (Scheme 3). Accordingly, selectivity is governed by steric restrictions in the complexes formed.



Scheme 3 N,O-chelation of CAHQS.

References

1. H. Huang, H. Chikushi, M. Nakamura and F. Kai, *Bull. Chem. Soc. Jpn.*, **63**, 1985 (1990).
2. H. Huang, Y. Asai, M. Hirohata, M. Nakamura and F. Kai, *Nippon Kagaku Kaishi*, 1348 (1990).
3. H. Huang, F. Kai, Y. Asai, M. Hirohata and M. Nakamura, *Bull. Chem. Soc. Jpn.*, **64**, 2464 (1991).
4. H. Huang, F. Kai, Y. Asai, M. Hirohata and M. Nakamura, *Chem. Lett.*, 65 (1991).
5. H. Huang, F. Kai, Y. Asai, M. Hirohata, M. Nakamura and T. Tokii, *J. Coord. Chem.*, **25**, 357 (1992).
6. H. Huang, F. Kai, T. Shoda and M. Nakamura, *J. Coord. Chem.*, **28**, 155 (1993).
7. H. Huang, F. Kai, M. Hirohata, M. Nakamura, S. Matsuzaki, K. Komori and Y. Tsunematsu, *J. Coord. Chem.*, in press.
8. S.F. James, J.L. William and S.B. Ann, Anal. Chem., **29**, 821 (1957).
9. F. Gerson and E. Heibronner, *Helv. Chim. Acta*, **45**, 42 (1962).
10. J.P. Hart and W.F. Smyth, *Spectrochim. Acta*, **A36**, 279 (1980).
11. S.L. Srivastava and M. Prasad, *Spectrochim. Acta*, **A40**, 681 (1984).
12. J. Mason, B.S. Saraswat and R.C. Mehrotra, *Polyhedron*, **4**, 2089 (1985).
13. A. Albert and E.P. Serjeant, "Ionization Constants of Acids and Bases", (Methuen, London, 1962), Chap. 8.
14. L. Holleck, J.M. Abd El Kader and A.M. Shams El Din, *J. Electroanal. Chem.*, **20**, 287 (1969).
15. G.W. Latimer, Jr., *Talanta*, **15**, 1 (1968).
16. S. Koide, "Kagakuno Ryouiki Zoukan No. 69", Ed. T. Fujinaga and M. Maruyama (Nankoudou, Tokyo, 1965), Vol. 3, p. 83.
17. F.J.C. Rossotti and H.S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).
18. J. Brandmüller, H. Hacker and H.W. Schrötter, *Chem. Ber.*, **99**, 765 (1966).
19. R.M. Smith and A.E. Martell, "Critical Stability Constants", *Chem. Soc.*, (London, 1964).