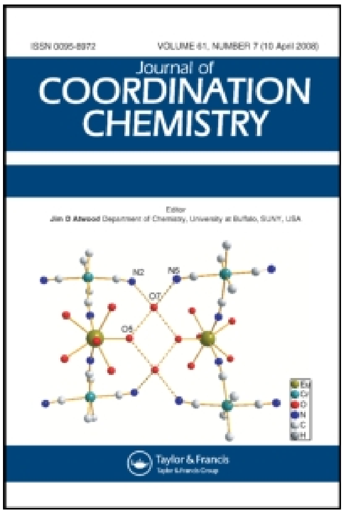
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COORDINATION SELECTIVITY IN THE REACTION OF ALUMINUM(III) WITH 8-HYDROXY-7-[(8 ' -HYDROXY-3 ', 6 ' -DISULFO-1 ' -NAPHTHYL) AZO] QUINOLINE-5-SULFONIC ACID

Hiromi Iwasaki[a]; Ken-Ichi Okamoto[a]; Jinsai Hidaka[a]; Hisahiko Einaga[b]
[a] Department of Chemistry, University of Tsukuba, Niihari, Ibaraki, Japan [b] Institute of Materials Science, University of Tsukuba, Niihari, Ibaraki, Japan

To cite this Article Iwasaki, Hiromi , Okamoto, Ken-Ichi , Hidaka, Jinsai and Einaga, Hisahiko(1983) 'COORDINATION SELECTIVITY IN THE REACTION OF ALUMINUM(III) WITH 8-HYDROXY-7-[(8 ' -HYDROXY-3 ', 6 ' -DISULFO-1 ' -NAPHTHYL) AZO] QUINOLINE-5-SULFONIC ACID', Journal of Coordination Chemistry, 12: 4, 219 — 229
To link to this Article: DOI: 10.1080/00958978308073852
URL: http://dx.doi.org/10.1080/00958978308073852

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1983, Vol. 12, pp. 219–230
0095-8972/83/1204–0219 $18.50/0

COORDINATION SELECTIVITY IN THE REACTION OF ALUMINUM(III) WITH 8-HYDROXY-7-[(8′-HYDROXY-3′, 6′-DISULFO-1′-NAPHTHYL) AZO] QUINOLINE-5-SULFONIC ACID

HIROMI IWASAKI, KEN-ICHI OKAMOTO and JINSAI HIDAKA
Department of Chemistry, University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan

and

HISAHIKO EINAGA†
Institute of Materials Science, University of Tsukuba, Sakura, Niihari, Ibaraki 305, Japan

(Received July 19, 1982)

Studies have been made on the coordination behavior of aluminum(III) with 8-hydroxy-7-[(8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo] quinoline-5-sulfonic acid (H_5hns)[1] which is capable of acting as a bidentate or a terdentate ligand. The ligand serves as an O–N–O terdentate one with coordination of the *azo* nitrogen atom to form a *mono*-hns complex, $[Al(hns)(H_2O)_3]^{2-}$, which involves two fused six-membered chelate rings. Formation of the complex proceeds through three different pathways from a kinetic viewpoint, *i.e.*, reactions of $[Al(H_2O)_6]^{3+}$ with $Hhns^{4-}$, $[Al(OH)(H_2O)_5]^{2+}$ with H_2hns^{3-}, and $[Al(OH)(H_2O)_5]^{2+}$ with $Hhns^{4-}$. The coordination mechanism is discussed.

INTRODUCTION

The selectivity of coordination mode is one of the fundamental functions of coordinating ligands but is not fully and systematically understood at the present time. In our previous paper,[2] octahedral coordination of aluminum(III) ion with 8-hydroxy-7-[(6′-sulfo-2′-naphthyl)azo] quinoline-5-sulfonic acid (nqs, H_3nqs),[1] capable of exhibiting two different coordination modes, was chosen as a relevant model for the investigation of selectivity in coordination. It was found[2] that nqs[1] coordinates to aluminum(III) not with the azophenol but with the quinolinol group to selectively form a *mono*-nqs complex, $[Al(nqs)(H_2O)_4]$, which involves a five-membered chelate ring. The complex further undergoes reaction with 8-quinolinol-5-sulfonic acid (hqs, H_2hqs)[1] to form a mixed-ligand complex, $[Al(nqs)(hqs)_2]^{4-}$, involving quinolinol fragments as the sole coordinated groups.[3]

In the present work, 8-hydroxy-7-[8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo] quinoline-5-sulfonic acid (hns, H_5hns),[1] a ligand capable of exhibiting two different coordination modes either by a dihydroxyazo or a quinolinol fragment, was synthesized and its coordination reaction with the aluminum(III) ion was studied by spectrophotometric methods.

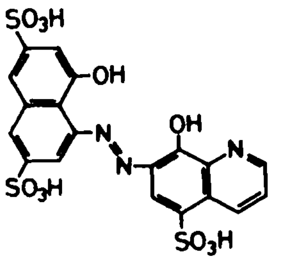
EXPERIMENTAL

Reagents

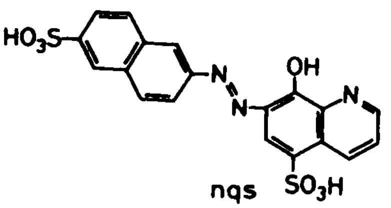
The ligand hns was synthesized by the diazotization of 1-amino-8-naphthol-3, 6-disul-

---

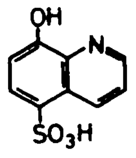
†To whom correspondences should be addressed.



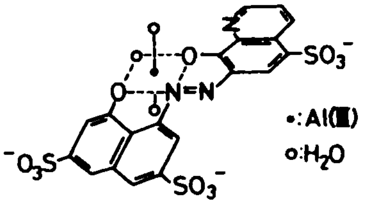
hns



nqs



hqs



mono-hns complex

fonic acid, followed by coupling of the diazonium salt with hqs. The product was extracted with methanol, evaporated to dryness, and applied to a column of Dowex 50W-X8 (100-200 mesh, H^+ form) after being dissolved in water. Calcd. for $C_{19}H_{13}N_3O_{11}S_3 \cdot 4H_2O$: C, 36.36; H, 3.37; N, 6.70%. Found: C, 35.80; H, 3.19; N, 6.38%. The purity of the ligand was examined by potentiometric titration with sodium hydroxide. The ligand 2-[(8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo]-1-naphthol-4-sulfonic acid (dns, H_5dns)[1] was also synthesized by a procedure similar to that for the preparation of hns. An aqueous aluminum(III) nitrate solution was prepared as previously described.[3]

All other chemicals were of analytical or equivalent grade.

Measurements

Spectrophotometric measurements were made with JASCO spectrophotometers, models UVIDEC-1 and SS-25, a stopped-flow apparatus, model SFC-5, a data processor, model, DP-500, and a WATANABE SOKKI X-Y recorder, model WX-441, being attached to the latter. Equilibrium and kinetic measurements were carried out in aqueous media at 25.0 ± 0.1° and $\mu = 0.1$ mol dm^{-3} (NaCl). The protonation and stability constants were determined by measuring absorbances at 300 and 305 nm for the former and at 310 nm for the latter, respectively. For the kinetic runs the metal ion was used in a large excess in order to maintain pseudo-first-order kinetic conditions at controlled hydrogen ion concentrations. The rate constant, k_{obsd}, was calculated according to the following equation.

$$\ln A_{eq}/(A_{eq} - A) = k_{obsd} \cdot t$$

Here, A_{eq} and A refer to absorbances at 310 nm at equilibrium and at time t, respectively. Hydrogen ion concentration was measured with a HORIBA pH meter, model F7-SS, with a combination glass and calomel electrode and calculated according to the relation,

$$-\log\,[H^+] = pH_{meas} + \log f_{H^+}$$

where f_{H^+} is activity coefficient of the hydrogen ion in 0.1 mol dm^{-3} aqueous sodium chloride at 25° with the value of 0.83.[4] Hydrogen ion concentrations were adjusted with buffer solutions; sodium acetate-acetic acid, ammonia-ammonium chloride, sodium borate-hydrochloric acid, and sodium borate-sodium hydroxide were used for determination of the protonation constants of the ligands, sodium acetate-acetic acid for determination of stability and kinetic constants. Concentrations of the buffer solutions were kept as low as possible (usually less than 10^{-2} mol dm^{-3}) so as to maintain constant ionic strength. The acetate buffer at such a low concentration range was confirmed to exert no significant effect on complex formation under the chosen equilibrium and kinetic conditions.

RESULTS

Electronic absorption spectra

Absorption spectra of hns and its aluminum(III) complex are shown in Figures 1 and 2. As the absorption spectra of hns (Fig. 1) indicate, protonation at the naphtholic and phenolic oxygen atoms *peri* and *ortho* to the *azo* group causes a distinct hypsochromic shift of the $\pi \rightarrow \pi^*$ transition due to the *azo* group around 18,000 cm^{-1} and protonation at the phenolic oxygen atom causes a marked spectral change around the 28,000 cm^{-1} region due to perturbation of the $\pi \rightarrow \pi^*$ transitions of the heterocyclic ring. As can be seen from Figures 1 and 2, coordination of the ligand anion (hns^{5-}) to aluminum(III) causes a hypsochromic shift of the $\pi \rightarrow \pi^*$ transition due to the *azo* group from 17,240 cm^{-1} for hns^{5-} to 17,730 cm^{-1} for the complex, and a spectral change due to complex formation around the 28,000 cm^{-1} region is the same as that observed during protonation. Figure 2

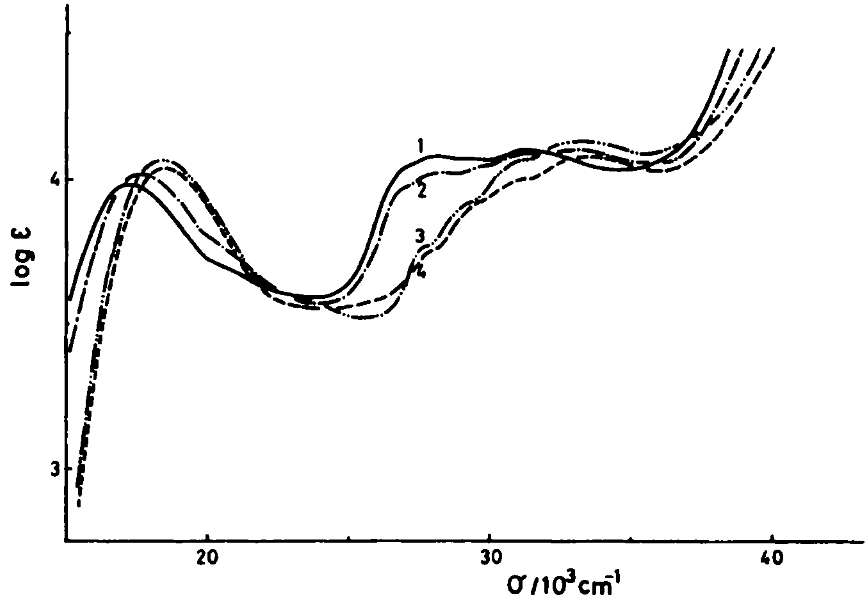


FIGURE 1 Absorption spectra of hns. 1, hns^{5-}(pH 11.89); 2, $Hhns^{4-}$(pH 10.22); 3, H_2hns^{3-}(pH 5.21); and 4, H_3hns^{2-}(pH 2.42).

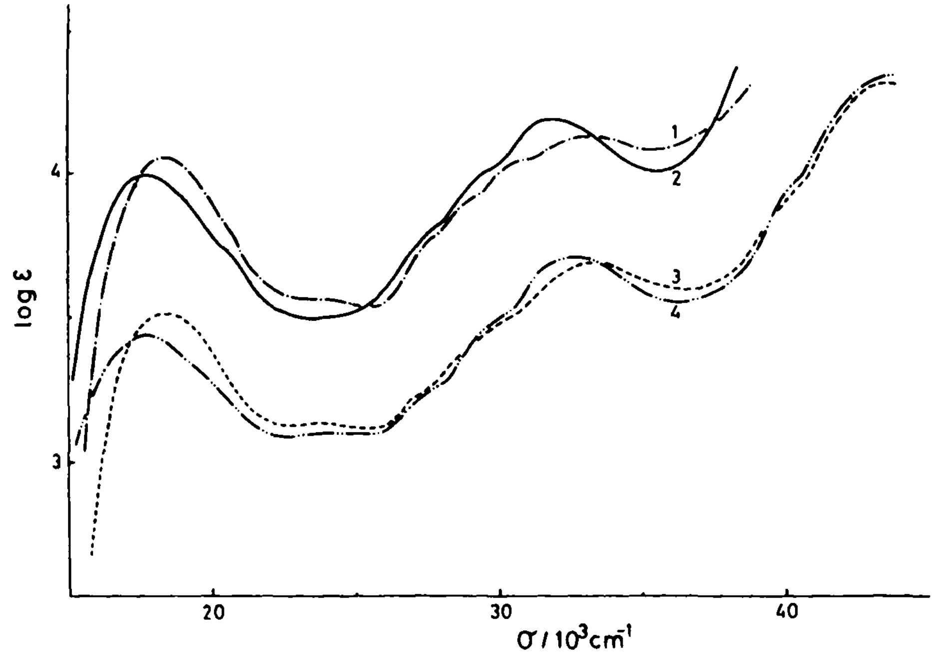


FIGURE 2 Absorption spectra of hns and dns and their aluminum (III) complexes. 1, hns (H_2hns^{3-}) (pH 4.78); 2, $[Al(hns)(H_2O)_3]^{2-}$(pH 4.35); 3, dns (H_2dns^{3-}) (pH 5.14); and $[Al(dns)(H_2O)_3]^{2-}$ (pH 4.97). Curves 3 and 4 were shifted 0.500 unit downward along the log ϵ axis in order to make comparison of the spectra of 1 and 2 with those of 3 and 4 easy.

reveals that the absorption spectrum of the aluminum(III) complex with hns bears a close resemblance to that with dns, the latter ligand acting as a terdentate. These spectral features demonstrate that hns coordinates to the aluminum(III) ion not with its quinolinol group, as nqs does,[2] but selectively with its dihydroxyazo group as an O-N-O type ligand to form two fused six-membered chelate rings.

The composition of the complex was estimated by the methods of continuous variations and molar ratio.[5] Changes in absorbances at 310 and 560 nm with mole fraction of metal ion or with ligand-to-metal ratio gave a maximum or a distinct inflection at the point corresponding to a *mono*-hns complex. Hence the result is consistent with the formation of the hns complex, $[Al(hns)(H_2O)_3]^{2-}$. The difficulty of forming a *bis*-hns complex may be attributed to steric factors, especially bulkiness, of the ligand itself.

Figure 3 shows that the absorption spectrum changes steadily with increasing metal-to-ligand ratio, showing isosbestic points at 266, 298, 394, and 572 nm, and that the spectrum remains practically unchanged beyond the ratio of unity. Hence the *mono*-hns complex is the sole complex formed in the reaction of aluminum(III) ion with hns.

Formation and Stability

The protonation constants of hns were determined spectrophotometrically in the first instance at the conditions specified earlier. Analysis of absorbance data at 305 nm was performed by the aid of (*1*).

$$\log (A_{(i-1)hns} - A)/(A - A_{ihns}) = \log K_{ai} + \log [H^+] \qquad (1)$$

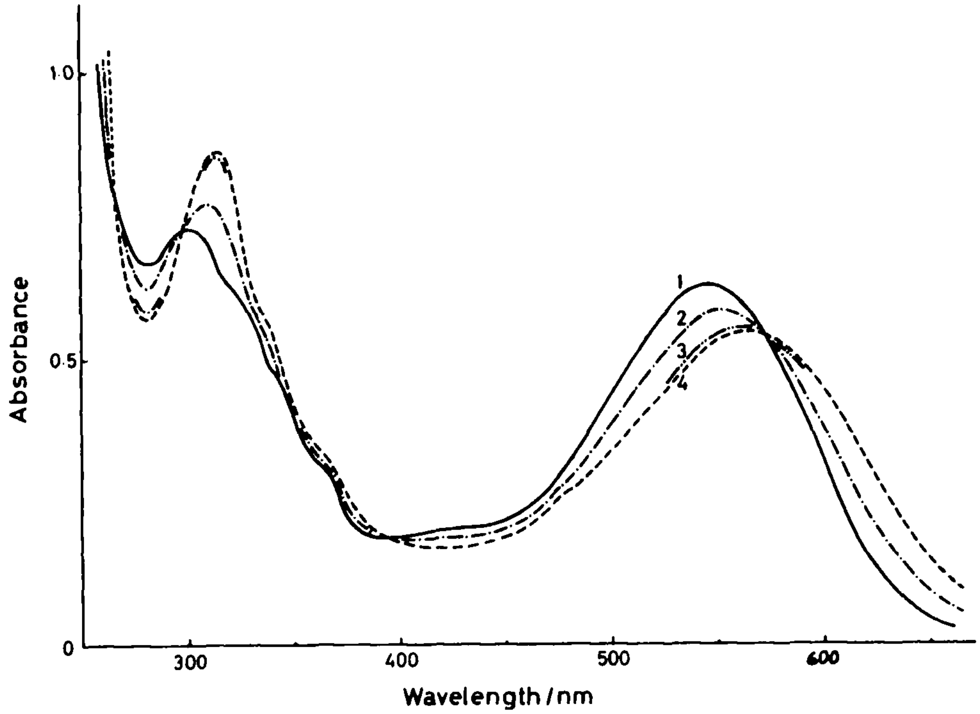


FIGURE 3 Absorption spectra of the aluminum(III)-hns system at different metal-to-ligand ratios. [Al(III)]/[hns] molar ratio: 1, 0; 2, 0.5; 3, 1.0; and 4, 1.5 ∿ 2.0. Ligand concentration: 6.00×10^{-5} mol dm^{-3}. pH 4.60.

Here, i (= 1 ∿ 3) refers to number of protons associated with the ligand species. Equation (*1*) can be derived from (*2*) ∿ (*4*) and Beer's law in conjunction with $A_{(i-1)hns}$, A_{ihns}, and A, which refer to absorbances of solutions containing species $H_{i-1}hns^{(6-i)-}$ alone, $H_ihns^{(5-i)-}$ alone, and both of them, respectively; K_{a1} is an equilibrium constant for the protonation at the naphtholic oxygen atom (i = 1), K_{a2} is that at the phenolic oxygen atom (i = 2), and K_{a3} is that at the heterocyclic nitrogen atom (i = 3).

$$K_{a1} = [Hhns^{4-}]/[hns^{5-}]\ [H^+] \quad (2)$$

$$K_{a2} = [H_2hns^{3-}]/[Hhns^{4-}]\ [H^+] \quad (3)$$

$$K_{a3} = [H_3hns^{2-}]/[H_2hns^{3-}]\ [H^+] \quad (4)$$

The protonation constants are summarized in Table I together with those of related ligands.

From the characteristic spectral features of the *mono*-hns complex, the protonation constants of hns, and the hydrolysis constant of aluminum(III) ion, K_{OH},

$$\begin{aligned} K_{OH} &= [[Al(OH)(H_2O)_5]^{2+}]\ [H^+]/[[Al(H_2O)_6]^{3+}] \\ \log K_{OH} &= -4.49^6 \end{aligned} \quad (5)$$

the *mono*-hns complex formation is expressed by

TABLE I
Protonation constants of the ligands.

Ligand	Protonation constants[a]			Reference
	Log K_{a1}	Log K_{a2}	Log K_{a3}	
hns	11.46 ± 0.06	8.33 ± 0.04	3.81 ± 0.05	present work
		Log K_{a1}	Log K_{a2}	
hqs		8.97 ± 0.10	4.06 ± 0.11	3
nqs		7.62 ± 0.05	3.00 ± 0.08	2

[a] The data are for 0.1 mol dm^{-3} aqueous sodium chloride at 25°.

$$[Al(H_2O)_6]^{3+} + H_2hns^{3-} \overset{K_{eq}}{\rightleftharpoons} [Al(hns)(H_2O)_3]^{2-} + 2H^+ \tag{6}$$

$$K_{eq} = [[Al(hns)(H_2O)_3]^{2-}]] [H^+]^2/[[Al(H_2O)_6]^{3+}] [H_2hns^{3-}]$$

and additionally, with increased acidity, by

$$[Al(H_2O)_6]^{3+} + H_3hns^{2-} \overset{K'_{eq}}{\rightleftharpoons} [Al(hns)(H_2O)_3]^{2-} + 3H^+ \tag{7}$$

$$K'_{eq} = [[Al(hns)(H_2O)_3]^{2-}] [H^+]^3/[[Al(H_2O)_6]^{3+}] [H_3hns^{2-}] = K_{eq}/K_{a3}$$

On the basis of equations (*8*) ∿ (*11*), the following relations are derived.

$$C_{Al} = [[Al(H_2O)_6]^{3+}] + [[Al(OH)(H_2O)_5]^{2+}] + [[Al(hns)(H_2O)_3]^{2-}] \tag{8}$$

$$C_{hns} = [H_3hns^{2-}] + [H_2hns^{3-}] + [[Al(hns)(H_2O)_3]^{2-}] \tag{9}$$

$$A = \epsilon_{3Hhns}[H_3hns^{2-}] + \epsilon_{2Hhns}[H_2hns^{3-}] + \epsilon_{11}[[Al(hns)(H_2O)_3]^{2-}] \tag{10}$$

$$A_{min} = \{(\epsilon_{2Hhns} + \epsilon_{3Hhns}K_{a3}[H^+])/(1 + K_{a3}[H^+])\} C_{hns} \tag{11}$$

Here, ϵ_{2Hhns}, ϵ_{3Hhns}, and ϵ_{11} are the molar absorption coefficients of species H_2hns^{3-}, H_3hns^{2-}, and the *mono*-hns complex, respectively. Eq. (*12*) can be derived from Eq. (*6*). This equation concerns the hydrogen ion dependence of absorbance difference between a solution containing both metal ion and ligand and a solution without metal ion ($A - A_{min}$), provided that the *mono*-hns complex is present in such a concentration that its quadratic concentration term can be neglected relative to the total concentrations of aluminum(III) (C_{Al}) and of hns (C_{hns}).

$$1/(A - A_{min}) = (C_{Al} + C_{hns})/(\epsilon_{11} - A_{min}/C_{hns})C_{Al}C_{hns} + (1 + K_{a3}[H^+])$$
$$\times (1 + K_{OH}/[H^+]) [H^+]^2/K_{eq}(\epsilon_{11} - A_{min}/C_{hns})C_{Al}C_{hns} \tag{12}$$

Experimental data were plotted as shown in Figure 4, from which log K_{eq} was determined to be − 3.92 ± 0.05.

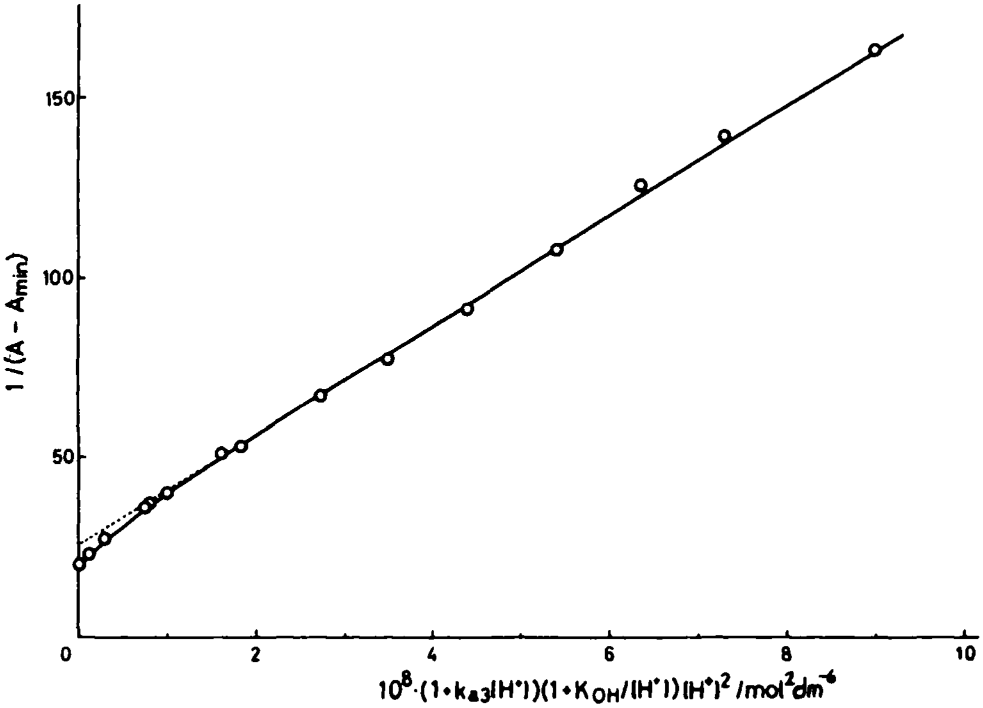


FIGURE 4 Relation between $1/(A - A_{min})$ and $(1 + K_{a3}[H^+])(1 + K_{OH}/[H^+])[H^+]^2$. C_{Al}: 1.50×10^{-5} mol dm^{-3} and C_{hns}: 3.00×10^{-5} mol dm^{-3}. Absorbance at 310 nm.

TABLE II
Stability constants and related data.

Complex	Log β	$-\Delta G°$/kJ mol^{-1},[a]	Remarks
$[Al(hns)(H_2O)_3]^{2-}$	16.03 ± 0.10	91.5 ± 0.6	present work, $\beta = \beta_{11}$
$[Al(nqs)(H_2O)_4]$	7.88 ± 0.18	45.0 ± 1.0	ref. no. 2, $\beta = \beta_{110}$
$[Al(hqs)(H_2O)_4]^+$	9.24 ± 0.14	52.7 ± 0.8	ref. no. 3, $\beta = \beta_{101}$

[a] Calculated by the relation, $-\Delta G° = RT \ln \beta$, without extrapolation to the zero ionic strength. All the data are for 0.1 mol dm^{-3} aqueous sodium chloride at 25°.

The stability constant β_{11} was calculated using the following definition and relation,

$$\beta_{11} = [[Al(hns)(H_2O)_3]^{2-}]/[[Al(H_2O)_6]^{3+}][hns^{5-}] = K_{s1}K_{s2}K_{eq} \qquad (13)$$

and results are summarized in Table II together with the related data.

Kinetics and Mechanism

Based on the foregoing results, the *mono*-hns complex is formed by the reaction of $[Al(H_2O)_6]^{3+}$ and $[Al(OH)(H_2O)_5]^{2+}$ with H_3hns^{2-}, H_2hns^{3-}, and $Hhns^{4-}$. Hence six reaction pathways are anticipated and the corresponding rate equation is given as follows.

$$
\begin{aligned}
&d[[\mathrm{Al(hns)(H_2O)_3}]^{2-}]/dt \\
&= (k_{32}[\mathrm{H_3hns^{2-}}] + k_{33}[\mathrm{H_2hns^{3-}}] + k_{34}[\mathrm{Hhns^{4-}}])[[\mathrm{Al(H_2O)_6}]^{3+}] + (k_{22}[\mathrm{H_3hns^{2-}}] \\
&\quad + k_{23}[\mathrm{H_2hns^{3-}}] + k_{24}[\mathrm{Hhns^{4-}}])[[\mathrm{Al(OH)(H_2O)_5}]^{2+}] - \{k_{-32}[\mathrm{H^+}]^3 \\
&\quad (k_{-33} + k_{-22})[\mathrm{H^+}]^2 + (k_{-34} + k_{-23})[\mathrm{H^+}] + k_{-24}\}\,[[\mathrm{Al(hns)(H_2O)_3}]^{2-}]
\end{aligned}
\tag{14}
$$

Here, k_{ij} is the forward rate constant for the reaction pathway of $[\mathrm{Al(OH)_{3-i}(H_2O)_{3+i}}]^{i+}$ ($i = 2$ and 3) with $\mathrm{H_{5-j}hns^{j-}}$ ($j = 2 \sim 4$) and k_{-ij} is the corresponding reverse rate constant. In these cases, protolytic processes were assumed to be always at equilibrium since they are very fast compared with coordination processes.[7]

Under the pseudo-first-order kinetic conditions with respect to the aluminum(III) concentration, Eq. (*15*), which provides a correlation between hydrogen ion conentration and modified rate constant k'_{obsd}, can be deduced from Eq. (*14*).

$$
\begin{aligned}
k'_{\mathrm{obsd}} &= k_{32}K_{a1}K_{a2}K_{a3}[\mathrm{H^+}]^3 + (k_{33} + k_{22}K_{a3}K_{\mathrm{OH}})K_{a1}K_{a2}[\mathrm{H^+}]^2 + \\
&\quad (k_{34} + k_{23}K_{a2}K_{\mathrm{OH}})K_{a1}[\mathrm{H^+}] + k_{24}K_{a1}K_{\mathrm{OH}}
\end{aligned}
\tag{15}
$$

$$
\begin{aligned}
k'_{\mathrm{obsd}} &\equiv k_{\mathrm{obsd}}/\{1/\beta_{11} + C'_{\mathrm{Al}}/[(1 + K_{a1}[\mathrm{H^+}] + K_{a1}K_{a2}[\mathrm{H^+}]^2 + \\
&\quad K_{a1}K_{a2}K_{a3}[\mathrm{H^+}]^3)(1 + K_{\mathrm{OH}}/[\mathrm{H^+}])]\}
\end{aligned}
\tag{16}
$$

Here, the total concentration of aluminum(III) C'_{Al} is given as follows.

$$
C'_{\mathrm{Al}} \doteqdot [[\mathrm{Al(H_2O)_6}]^{3+}] + [[\mathrm{Al(OH)(H_2O)_5}]^{2+}]
\tag{17}
$$

Hence, actual reaction pathways can be deduced on the basis of best-fit treatments of experimental data to k'_{obsd} *vs.* $[\mathrm{H^+}]$ correlations compared with theoretical ones. Figure 5 shows a linear relation between k'_{obsd} and $[\mathrm{H^+}]$. Consequently, the *mono*-hns complex is formed by the reactions of $[\mathrm{Al(H_2O)_6}]^{3+}$ with $\mathrm{Hhns^{4-}}$ (k_{34}) and of $[\mathrm{Al(OH)(H_2O)_5}]^{2+}$ with $\mathrm{H_2hns^{3-}}$ (k_{23}) and $\mathrm{Hhns^{4-}}$ (k_{24}). Kinetic data are summarized in Table III together with those for related complexes.

DISCUSSION

In the present work, a new multidentate ligand, hns, was synthesized to investigate its coordination behavior toward the aluminum(III) ion and to compare it with the behavior of nqs,[2] in order to gain more information about selectivity in coordination mode as regards multidentate azoquinolinol and related ligands. The present ligand can assume either of two different coordination modes; as an *O-N* type bidentate involving the quinolinol group or as an *O-N-O* type tertendate with the dihydroxyazo group. The absorption spectra indicate that hns serves as a terdentate ligand *via* donation of the *azo* nitrogen atom, the coordinate bond of which is weaker than that of the heterocyclic nitrogen atom as illustrated in the case of nqs.[2] Comparison of the stability constants and related data for the hns complex with those for the nqs and the hqs complexes (Table II) indicates that an increase in the number of chelate rings contributes predominantly to the

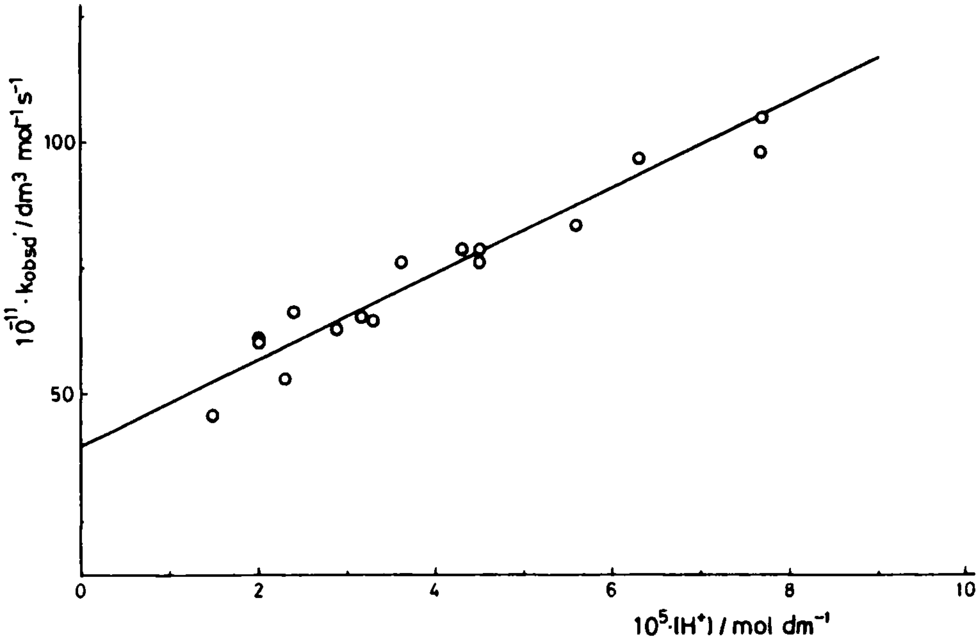


FIGURE 5 Relation between k'_{obsd} and $[H^+]$. C'_{Al}: $1.00 \times 10^{-3} \sim 2.00 \times 10^{-3}$ mol dm^{-3} and C'_{hns}: 1.00×10^{-4} mol dm^{-3}. Absorbance at 310 nm.

enhancement of stability of the aluminum(III) complexes in the first place and, consequently, the lower donor ability (basicity) of the *azo* nitrogen atom relative to that of the heterocyclic nitrogen atom is compensated for by the formation of fused chelate rings. Hence it can be suggested that the change from monohydroxyazo to dihydroxyazo character in the multidentate ligands is effective for selective coordination, the latter being capable of exhibiting a coordination mode different from that of the former.

TABLE III
Kinetic constants for the formation of the aluminum(III) complexes.

Pathway[a]	Kinetic constant/$dm^3\ mol^{-1}\ s^{-1}$,[b]	Remarks[c]	Reference
$Al^{3+} + Hhns^{4-} (k_{34})$ and $AlOH^{2+} + H_2hns^{3-} (k_{23})$	$k_{34} + k_{23} K_{a2} K_{OH}$: $(2.96 \pm 0.40) \times 10^5$	$K_{a2} = K_{a2(hns)}$	present work
$AlOH^{2+} + Hhns^{4-} (k_{24})$	k_{24}: $(4.28 \pm 0.30) \times 10^5$	$\Delta G^{\neq}_{24}$: 40.9 ± 0.2	present work
$Al^{3+} + nqs^{3-} (k_{33})$ and $AlOH^{2+} + Hnqs^{2-} (k_{22})$	$k_{33} + k_{22} K_{a1} K_{OH}$: $(19.8 \pm 0.6) \times 10^5$	$K_{a1} = K_{a1(nqs)}$	2
$AlOH^{2+} + nqs^{3-} (k_{23})$	k_{23}: $(1.2 \pm 0.7) \times 10^5$	$\Delta G^{\neq}_{23}$: 44 ± 1	2
$Al^{3+} + hqs^{2-} (k_{32})$ and $AlOH^{2+} + Hhqs^{-} (k_{21})$	$k_{32} + k_{21} K_{a1} K_{OH}$: $(6.9 \pm 0.6) \times 10^6$	$K_{a1} = K_{a1(hqs)}$	3

[a] Abbreviations: Al^{3+}, $[Al(H_2O)_6]^{3+}$; $AlOH^{2+}$, $[Al(OH)(H_2O)_5]^{2+}$. [b] The data are for 0.1 mol dm^{-3} aqueous sodium chloride at 25°. [c] $\Delta G^{\neq}_{ij}$ for the condition specified[b] was calculated by the relation, $-\Delta G^{\neq}_{ij} = RT(\ln k_{ij} - \ln kT/h)$, where R is the gas constant, T the temperature, k the Boltzmann constant, and h the Planck constant, respectively, in kJ mol^{-1}.

We were unable to detect the formation of the *bis*-hns complex even with a large excess of hns. Examination of molecular models reveals that hns assumes a planar structure with the meridional configuration in octahedral coordination. Incapability of forming the *bis*-hns complex can be attributed to the bulkiness of the coordinated hns, which inhibits coordination of the second hns by steric interference and/or repulsive interactions between the anionic *mono*-hns complex and the higher anionic species H_2hns^{3-} and $Hhns^{4-}$.

There remains an ambiguity as to the donor atom in the *azo* group. The terdentate hns can afford either two six-membered chelate rings by donation of the nitrogen atom bound to the naphthalene ring or five- and seven-membered chelate rings by donation of the nitrogen atom bound to the quinoline ring. It has been reported[8] that the aluminum(III) complex of the terdentate ligand 1-[(2′-hydroxy-5′-sulfo-1′-phenyl)azo] -2-naphthol (Solochrome Violet R, H_3hpn), $[Al(hpn)(H_2O)_3]$, with five- and six-membered chelate rings has the stability constant $\log \beta = 18.4$ ($-\Delta G^\circ = 105$ kJ mol^{-1}; $\mu = 0, 25^\circ$). Since the six-membered chelate ring is nearly as stable as the five-membered one and more stable than the seven-membered one[9] for the complex with planar coordination, it can be argued that hns forms two six-membered rather than five- and seven-membered chelate rings in its complex. This is also supported by examination of molecular models.

In accordance with the kinetic data, the *mono*-hns complex is formed through the reaction pathways of $[Al(H_2O)_6]^{3+}$ with $Hhns^{4-}$ and $[Al(OH)(H_2O)_5]^{2+}$ with H_2hns^{3-} and $Hhns^{4-}$. In our previous studies,[2,3] it was concluded that the deprotonated phenolic oxygen atom[10] of the quinolinol group coordinates in the first place to the metal ion upon substitution of a coordinated water molecule and acts initially as a unidentate ligand (this refers to the rate-determining step) and the nitrogen atom then undergoes coordination to complete the formation of a five-membered chelate ring in the following step. Comparison of the kinetic constants for the hns complex with those for the nqs and the hqs complexes (Table III) indicates that the rate-determining step for the formation of the hns complex is identical to that for the nqs and the hqs complexes. Moreover, the naphtholic oxygen atom[10] of hns in the *mono*- and *di*-protonated states is blocked by protons. Hence it may be presumed that the deprotonated phenolic oxygen atom of the dihydroxyazo group coordinates to the metal ion as a unidentate ligand, which process may be assigned to the rate-determining step. Then, the nitrogen atom of the azo group may coordinate to the metal atom to form a six-membered chelate ring, followed by coordination of the naphtholic oxygen atom upon liberation of its proton to complete the formation of fused two six-membered chelate rings with meridional configuration.

The assignment of the rate-determining step was supported by kinetic parameters k_{23} and k_{24} for the hns complex. As Table III shows, k_{23} is 40 dm^3 mol^{-1} s^{-1} at most since $K_{a2(hns)}K_{OH}$ is about 7×10^3; hence k_{23} is 10^4 times smaller than k_{24}. This means that, in the k_{23} pathway, the phenolic oxygen atom is blocked by proton with respect to its access and coordination to the metal atom.

REFERENCES AND NOTES

1. Abbreviations: hns, 8-hydroxy-7-[(8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo]quinoline-5-sulfonic acid (H_5hns); nqs, 8-hydroxy-7-[(6′-sulfo-2′-naphthyl)azo]quinoline-5-sulfonic acid (H_3nqs); hqs, 8-quinolinol-5-sulfonic acid (H_2hqs). dns, 2-[(8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo]-1-naphthol-4-sulfonic acid (H_5dns). H_3hns^{2-}, H_2hns^{3-}, $Hhns^{4-}$, hns^{5-}, and H_2dns^{3-} indicate the protonated species of the individual ligands.
2. K. Hayashi, K. Okamoto, J. Hidaka, and H. Einaga, *J. Chem. Soc., Dalton Trans.*, 1377 (1982).
3. K. Hayashi, T. Ohsawa, K. Okamoto, J. Hidaka, and H. Einaga, *J. Coord. Chem.*, in press.
4. J. Kielland, *J. Amer. Chem. Soc.*, 59, 1675 (1937).

5. H.L. Schläfer, *Komplexbildung in Lösung;* Springer Verlag, Berlin, 1961, pp. 233, 253.
6. L.P. Holmes, D.L. Cole, and E.M. Eyring, *J. Phys. Chem.*, **72**, 301 (1968).
7. M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).
8. E. Coates and B. Rigg, *Trans. Faraday Soc.*, **58**, 2058 (1962).
9. G. Anderegg, *Coordination Chemistry*, ed. by A.E. Martell, Van Nostrand Reinhold, New York, 1971, Vol. 1, pp. 470–6.
10. A phenolic oxygen atom on the quinoline ring is placed *ortho* to the azo group and a naphtholic oxygen atom on the naphthalene ring *peri* to the azo group, respectively.