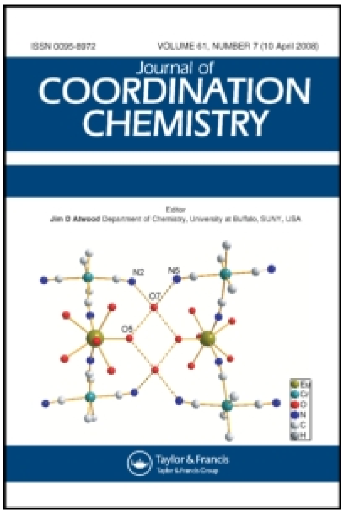

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COORDINATION SELECTIVITY AND LIGAND SUBSTITUTION REACTIONS OF AN ALUMINUM(III) COMPLEX WITH 8-HYDROXY-7-[(2 ' -CARBOXY-1 ' -PHENYL)-AZO]QUINOLINE-5-SULFONIC ACID

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COORDINATION SELECTIVITY AND LIGAND SUBSTITUTION REACTIONS OF AN ALUMINUM(III) COMPLEX WITH 8-HYDROXY-7-[(2′-CARBOXY-1′-PHENYL)-AZO]QUINOLINE-5-SULFONIC ACID

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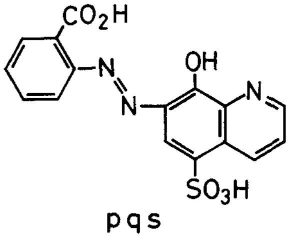
The coordination behavior of aluminum(III) with 8-hydroxy-7-[(2′-carboxy-1′-phenyl)azo]quinoline-5-sulfonic acid (H_3pqs) was examined. This quinolinol derivative functions as a terdentate ligand of the O-N-O type to form *mono*- and *bis*-(O-N-O) complexes by way of the reaction of $[Al(H_2O)_6]^{3+}$ with $Hpqs^{2-}$ and pqs^{3-} and of $[Al(OH)(H_2O)_5]^{2+}$ with H_2pqs^- and $Hpqs^{2-}$. The ligand substituion reaction of $[Al(pqs)_2]^{3-}$ with 8-quinolinol-5-sulfonic acid was also studied in connection with its reaction mechanism.

INTRODUCTION

In our previous studies,[1-3] the aluminum(III) ion was found to form octahedral complexes with 8-hydroxy-7-[(6′-sulfo-2′-naphthyl)azo]-quinoline-5-sulfonic acid (H_3nqs)[4] and with 8-hydroxy-7-[(8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo]quinoline-5-sulfonic acid ($H_5(hns)$,[4] the selective coordination sites of these ligands being the quinolinol group for the former and the dihydroxyazo group for the latter.

In the present work, 8-hydroxy-7-[(2′-carboxy-1′-phenyl)azo]-quinoline-5-sulfonic acid (H_3pqs),[4] a ligand capable of exhibiting two different coordination modes either by a carboxyhydroxyazo group or a quinolinol one, was synthesized, and the formation of an aluminum(III) complex with the ligand was studied kinetically. Furthermore, the ligand substitution reaction of the aluminum(III) complex with 8-quinolinol-5-sulfonic acid (H_2hqs)[4] was studied in order to characterize the specific features of the coordination of aluminum(III) with pqs.[4]



pqs

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EXPERIMENTAL

Reagents.

The diazotization of *o*-aminobenzoic acid and the coupling of the resulting diazonium salt with hqs[4] afforded pqs. The product was purified by repeated recrystallization from weakly acidic aqueous solution and dried *in vacuo*. Purity of the ligand was checked by elemental analysis. 2-[(2'-Carboxyl-1'-phenyl)azo]-1-naphthol-4-sulfonic acid (H_3pns)[4] was synthesized by a procedure similar to that for pqs. An aqueous aluminum(III) nitrate solution was prepared as described elsewhere.[3] All the chemicals used were of analytical or equivalent grade.

Measurements.

Spectrophotometric measurements were made on JASCO spectrophotometers as described previously.[3] Equilibrium and kinetic measurements were carried out at 25.0 ± 0.1° in 0.1 mol dm^{-3} aqueous sodium chloride. The protonation and stability constants were determined spectrophotometrically by measuring absorbances at 330 and 495 nm for the former and at 320 nm for the latter, respectively. The rate constants for the formation of the aluminum(III) complex with pqs were obtained from the absorbance change at 320 nm under the pseudo-first-order kinetic conditions with respect to the metal ion, while those for the ligand substitution reaction were obtained from the absorbance change at 500 nm under pseudo-first-order kinetic conditions with respect to hqs. The rate constant, k_{obsd}, was calculated according to the following equation.

$$\ln A_{eq}/(A_{eq} - A_t) = k_{obsd} \cdot t \qquad (1)$$

Here, A_{eq} and A_t refer to absorbances at equilibrium and at time t, respectively. Hydrogen ion concentration was measured with the pH meter as described elsewhere[3] and calculated according to the relation,

$$-\log [H^+] = pH_{meas} + \log f_{H^+} \qquad (2)$$

where f_{H^+} is the activity coefficient of hydrogen ion in 0.1 mol dm^{-3} aqueous sodium chloride at 25° ($f_{H^+} = 0.83^5$). The hydrogen ion concentration was adjusted with aqueous buffer solutions as specified in the previous paper.[3]

RESULTS AND DISCUSSION

Electronic Absorption Spectra.

Figure 1 shows absorption spectra of pqs at various pH's. The fully deprotonated ligand species, pqs^{3-}, gives three dominant peaks corresponding to $\pi \rightarrow \pi^*$ transitions at 21,500 cm^{-1} due to the *azo* group and at 31,800 cm^{-1} and around 40,000 cm^{-1} due to the quinoline and benzene rings. These absorption bands are shifted bathochromically upon protonation. Among them, the spectral shifts in the 18,000–21,000 and 36,000–40,000 cm^{-1} regions reflect protonation at the quinolinolate oxygen atom, whereas the shift in the 28,000–32,000 cm^{-1} region reflects protonations at the quinoline nitrogen atom and the carboxylate group as wel as the protonation at the quinolinolate oxygen atom, because the basicity of the ligating groups decreases in the order[1,2,6] quinolinolate > quinoline > carboxylate

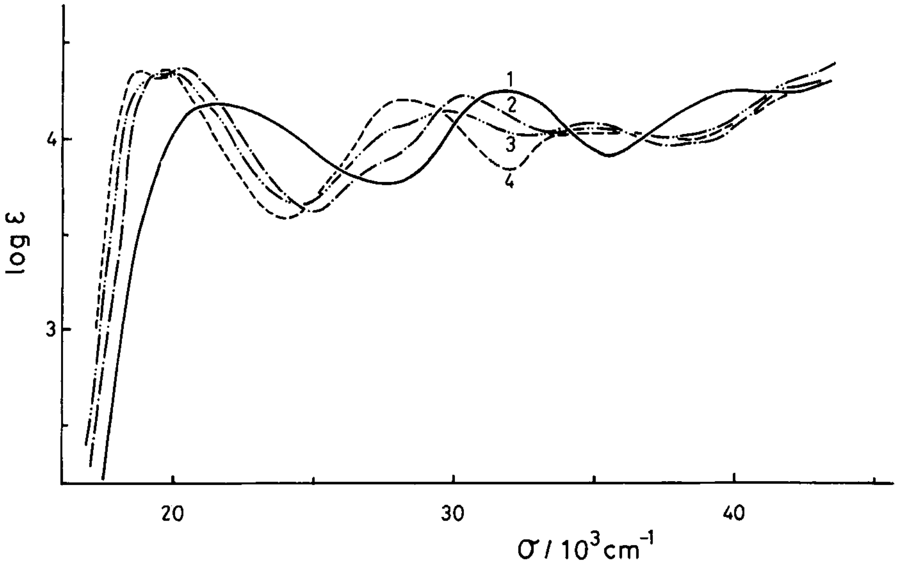

FIGURE 1 Absorption spectra of pqs: 1, pH 11.86 (pqs^{3-}); 2, pH 6.40 ($Hpqs^{2-}$); 3, pH 3.56; and 4, pH 2.04 (H_3pqs).

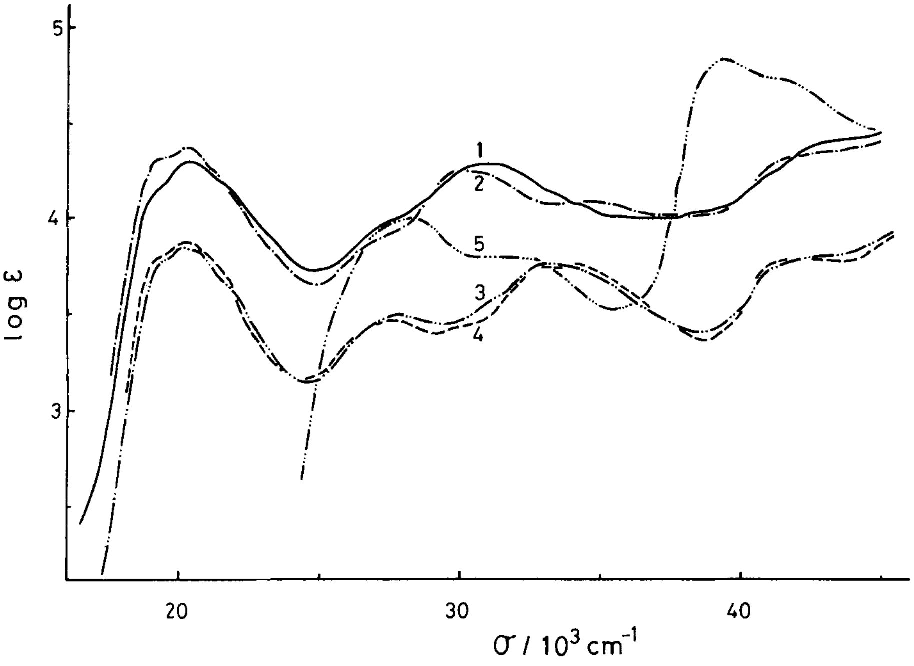

FIGURE 2 Absorption spectra of aluminum(III) complexes with pqs, pns, and hqs: 1, $[Al(pqs)_2]^{3-}$ (pH 4.25); 2, $Hpqs^{2-}$ (pH 5.83); 3, $[Al(pns)_2]^{3-}$ (pH 4.30); 4, $Hpns^{2-}$ (pH 5.85), and 5, $[Al(hqs)_3]^{3-}$ (pH 5.80). Curves 3 and 4 were shifted by 0.5 units downward vertically.

> *azo* group. Figure 2 shows absorption spectra of the aluminum(III) complexes with pqs and related ligands. Coordination of pqs^{3-} to aluminum(III) causes similar bathochromic shifts as is seen in Figures 1 and 2. Furthermore, it is evident from Figure 2 that the carboxyhydroxyazo group of pqs coordinates to aluminum(III) selectively because the absorption spectrum characteristic of the pqs complex is comparable to that of the pns complex but not to that of the hqs complex. Hence, pqs functions as an O-N-O type terdentate ligand toward aluminum(III).

The composition of the pqs complex was estiamted by the method of continuous variation. A sharp and single maximum was observed clearly at 0.67 ligand mole fraction, indicating that the *bis*-pqs complex is formed. This is in contrast with complexes of nqs[1,2] and hns[3] having a naphthalene ring. This indicates that the benzene ring in the 8-hydroxy-7-phenylazoquinoline ligand does not cause any steric hindrance in the formation of the *bis* (terdentato)aluminum(III) complex.

Formation and Stability.

The protonation constants, K_{ai} ($i = 1$–3), of pqs are correlated with absorbance by equation (*3*)

$$\log (A_{(i-1)pqs} - A_x)/(A_x - A_{ipqs}) = \log K_{ai} + \log [H^+] \qquad (3)$$

Here, i refers to the number of protons associated with the ligand species; $A_{(i-1)pqs}$, A_{ipqs}, and A_x are absorbances of solutions containing the ligand species $H_{i-1}pqs^{(4-i)-}$ alone, $H_ipqs^{(3-i)-}$ alone, and both of them together, respectively. Inspection of the pH dependence of the absorption spectrum of the ligand (*cf* Figure 1) together with our previous results[1-3] revealed that K_{a1}, K_{a2}, and K_{a3} correspond to protonations at the quinolinolate oxygen, the heterocyclic nitrogen, and the carboxylate oxygen atoms, respectively, and that K_{a1} and K_{a2} can be determined from absorbance changes at 495 nm and K_{a3} from that at 330 nm. The protonation constants are summarized in Table I.

In slightly acidic aqueous solution, aluminum(III) ($K_{OH} = [[Al(OH)(H_2O)_5]^{2+}][H^+]/[[Al(H_2O)_6]^{3+}]$, $\log K_{OH} = -4.49$[7]) and pqs are present mainly in the forms of $[Al(H_2O)_6]^{3+}$ and $Hpqs^{2-}$ respectively. The formation equilibria for the pqs complex are expressed as follows.

$$[Al(H_2O)_6]^{3+} + Hpqs^{2-} \xrightleftharpoons{K_{eq1}} [Al(pqs)(H_2O)_3] + H^+$$

$$[Al(pqs)(H_2O)_3] + Hpqs^{2-} \xrightleftharpoons{K_{eq2}} [Al(pqs)_2]^{3-} + H^+$$

TABLE I
Protonation constants of ligands.

Ligand	Protonation constants[a]				References
		Log K_{a1}	Log K_{a2}	Log K_{a3}	
pqs		9.02 ± 0.04	3.63 ± 0.11	3.34 ± 0.05	present work
nqs		7.62 ± 0.05	3.00 ± 0.08		1
hqs		8.92 ± 0.10	4.06 ± 0.11		2
	Log K_{a1}	Log K_{a2}	Log K_{a3}		
hns	11.46 ± 0.06	8.33 ± 0.04	3.81 ± 0.05		3

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

Under the conditions that a total concentration of aluminum(III), C_{Al}, is in large excess over that of the ligand, C_{pqs}, the following relation can be derived for the first stage.

$$(A_{ML} - A_L)/(A - A_L) = 1 + (1/K_{eq1}C_{Al})\{(1 + K_{a2}[H^+] + K_{a2}K_{a3}[H^+]^2)(1 + K_{OH}/[H^+])\}[H^+] \qquad (4)$$

Here, A_{ML} and A_L refer to absorbances of the *mono*-pqs complex and the ligand, respectively. A_{ML} was estimated from molar absorption coefficient of the *mono*-pqs complex.

Likewise, the following relation is derived for the *bis*-pqs complex under the condition $2C_{Al} = C_{pqs}$.

$$3\log(A_{ML2} - A) - \log(A - A_L) = \log(A_{ML2} - A_L)^2/4K_{eq1}K_{eq2}C_{Al}^2 + \log\{[H^+]^2(1 + K_{a2}[H^+] + K_{a2}K_{a3}[H^+]^2)^2(1 + K_{OH}/[H^+])\} \qquad (5)$$

Here, A_{ML2} refers to the absorbance of the *bis*-pqs complex.

Experimental data obtained under these conditions were plotted as shown in Figures 3 and 4, from which $\log K_{eq1} = 0.84 \pm 0.04$ and

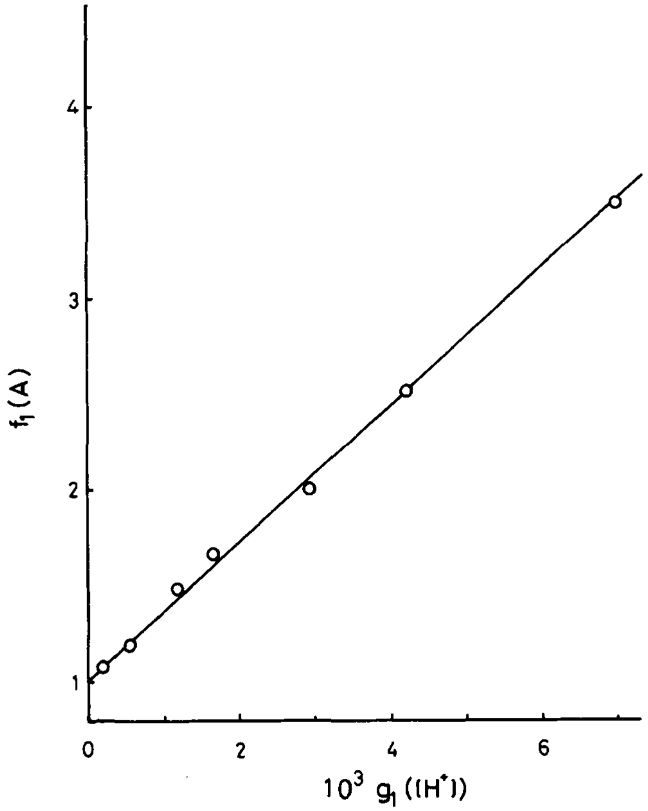

FIGURE 3 Correlation between $f_1(A)$ and $g_1([H^+])$. $f_1(A) \equiv (A_{ML} - A_L)/(A - A_L)$ and $g_1([H^+]) \equiv (1 + K_{a2}[H^+] + K_{a2}K_{a3}[H^+]^2)(1 + K_{OH}/[H^+])[H^+]$. C_{Al}: 4.00×10^{-4} mol dm^{-3}, C_{pqs}/C_{Al}: 1/20, and absorbance at 320 nm.

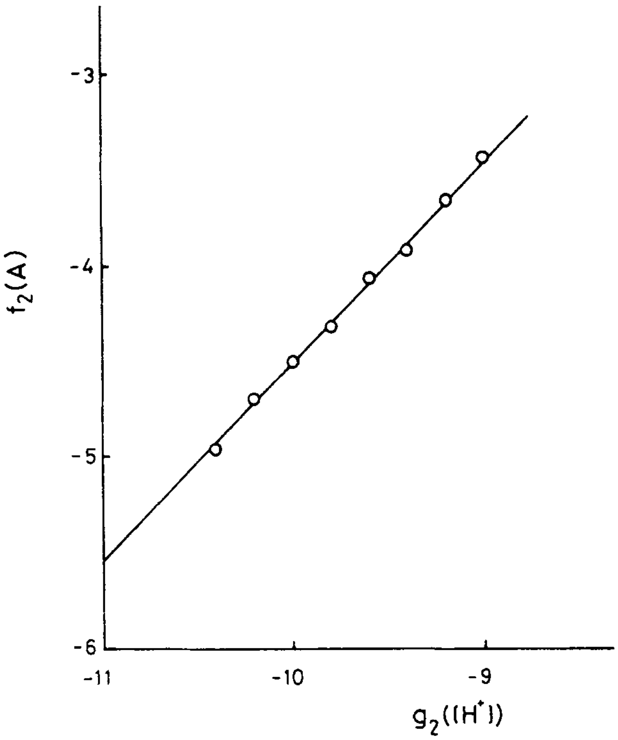

FIGURE 4 Correlation between $f_2(A)$ and $g_2([H^+])$. $f_2(A) \equiv 3\log(A_{ML_2} - A) - \log(A - A_L)$ and $g_2([H^+]) \equiv \log\{[H^+]^2(1 + K_{a2}[H^+] + K_{a2}K_{a3}[H^+]^2)^2(1 + K_{OH}/[H^+])\}$. C_{Al}: 4.92 × 10^{-5} mol dm^{-3}, C_{pqs}: 9.84 × 10^{-5} mol dm^{-3}, and absorbance at 320 nm.

$\log K_{eq1}K_{eq2} = -1.20 \pm 0.05$ were obtained. Stability constants, β_{11} ($= K_{eq1}K_{a1}$) and β_{12} ($= K_{eq1}K_{eq2}K_{a1}^2$), were calculated therefrom and are summarized in Table II.

TABLE II
Thermodynamic parameters for coordination equilibria.

Complex	Log β	$-\Delta G^\circ$ kJ mol$^{-1,a}$	Remarks
$[Al(pqs)(H_2O)_3]$	9.86 ± 0.08	56.3 ± 0.5	present work, $\beta = \beta_{11}$
$[Al(pqs)_2]^{3-}$	16.84 ± 0.13	96.1 ± 0.8	present work, $\beta = \beta_{12}$
$[Al(hns)(H_2O)_3]^{2-}$	16.03 ± 0.10	91.5 ± 0.6	ref. no. 3, $\beta = \beta_{11}$
$[Al(nqs)(H_2O)_4]$	7.88 ± 0.18	45.0 ± 1.0	ref. no. 1, $\beta = \beta_{110}$
$[Al(hqs)(H_2O)_4]^+$	9.24 ± 0.14	52.7 ± 0.8	ref. no. 2, $\beta = \beta_{101}$
$[Al(hqs)_2(H_2O)_2]^-$	17.61 ± 0.24	100.5 ± 1.4	ref. no. 2, $\beta = \beta_{102}$
$[Al(hqs)_3]^{3-}$	24.70 ± 0.35	141.0 ± 2.0	ref. no. 2, $\beta = \beta_{103}$

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

Formation Kinetics.

In the light of our previous results,[1-3] the rate-determining step in the formation of aluminum(III) complexes with arylazoquinolinol ligands is the coordination of the first ligand to the aquaaluminum(III) ion. Furthermore, based on the foregoing results, the pqs complex is formed kinetically by the reactions of $[Al(H_2O)_6]^{3+}$ and

$[Al(OH)(H_2O)_5]^{2+}$ with H_3pqs, H_2pqs^-, $Hpqs^{2-}$, pqs^{3-}. Hence, eight reaction pathways are proposed here with the rate equation given below.

$$
\begin{aligned}
&d[[Al(pqs)(H_2O)_3]]/dt \\
&= (k_{30}[H_3pqs] + k_{31}[H_2pqs^-] + k_{32}[Hpqs^{2-}] + k_{33}[pqs^{3-}]) \\
&\quad \times [[Al(H_2O)_6]^{3+}] + (k_{20}[H_3pqs] + k_{21}[H_2pqs^-] + k_{22}[Hpqs^{2-}] \\
&\quad + k_{23}[pqs^{3-}]) [[Al(OH)(H_2O)_5]^{2+}] \\
&\quad - (k_{-30}[H^+]^3 + (k_{-31} + k_{-20})[H^+]^2 + (k_{-32} + k_{-21})[H^+] \\
&\quad + (k_{-33} + k_{-22}) + k_{-23}[OH^-])[[Al(pqs)(H_2O)_3]] \qquad (6)
\end{aligned}
$$

Here, k_{ij} refers to the rate constant for the forward reaction pathway of $[Al(OH)_{3-i}(H_2O)_{3+i}]^{i+}$ ($i = 2$ and 3) with $H_{3-j}\,pqs^{j-}$ ($j = 0$–3) and k_{-ij} to that for the corresponding reverse reaction. In these cases, protolytic processes were assumed to be always at equilibrium.[1-3] Under the pseudo-first-order kinetic conditions with respect to the aluminum(III) ion, Eq. (*7*) is deduced from Eq. (*6*).

$$
\begin{aligned}
k'_{obsd} &= k_{30}K_{a1}K_{a2}K_{a3}[H^+]^3 + (k_{31} + k_{20}K_{a3}K_{OH})K_{a1}K_{a2}[H^+]^2 \\
&\quad + (k_{32} + k_{21}K_{a2}K_{OH})K_{a1}[H^+] + (k_{33} + k_{22}K_{a1}K_{OH}) \\
&\quad + k_{23}K_{OH}[H^+]^{-1} \qquad (7)
\end{aligned}
$$

$$
\begin{aligned}
k'_{obsd} &\equiv k_{obsd}/ \{ 1/\beta_{11} + C'_{Al}/(1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2 \\
&\quad + K_{a1}K_{a2}K_{a3}[H^+]^3)(1 + K_{OH}/[H^+]) \} \qquad (8)
\end{aligned}
$$

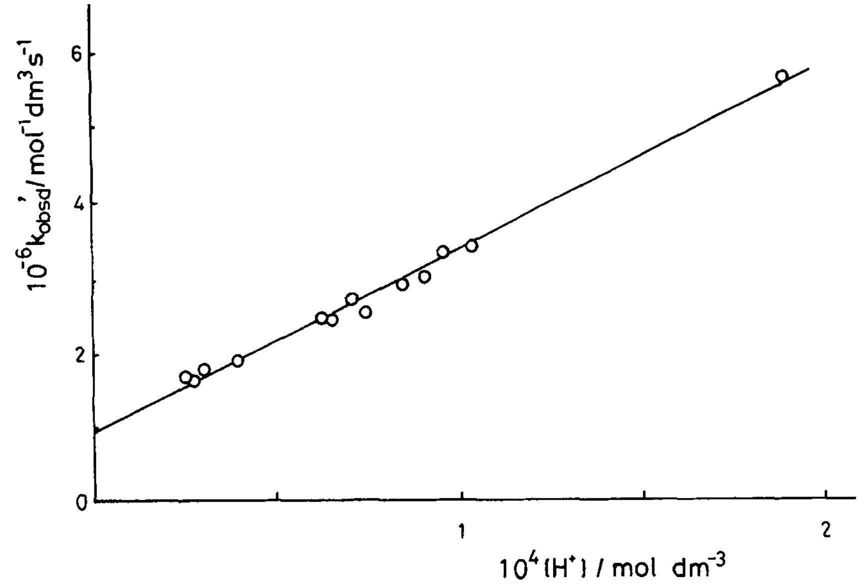

FIGURE 5 Correlation between k'_{obsd} and $[H^+]$. C'_{Al}: $(3.09–4.64) \times 10^{-3}$ mol dm^{-3}, c'_{pqs}: 6.18×10^{-5} mol dm^{-3}, and absorbance at 320 nm.

TABLE III
Kinetic constants for various coordination reactions.

Pathway[a]	Kinetic constant $mol^{-1}\ dm^3\ s^{-1,b}$		Remarks	References
$Al^{3+} + Hpqs^{2-}(k_{32})$ and $AlOH^{2+} + H_2pqs^{-}(k_{21})$	$k_{32} + k_{21}K_{a2}K_{OH}$:	$(2.38 \pm 0.30) \times 10$	$K_{a2} = K_{a2(pqs)}$	present work
$Al^{3+} + pqs^{3-}(k_{33})$ and $AlOH^{2+} + Hpqs^{2-}(k_{22})$	$k_{33} + k_{22}K_{a1}K_{OH}$:	$(9.26 \pm 0.30) \times 10^5$	$K_{a1} = K_{a1(pqs)}$	present work
$Alpqs + pqs^{3-}(k_{03})$	k_{03}:	$(2.9 \pm 0.6) \times 10^5$	$k_{-03} = (3.00 \pm 0.43) \times 10^{-2}\ s^{-1}$	present work
$Al^{3+} + Hhns^{4-}(k_{34})$ and $AlOH^{2+} + H_2hns^{3-}(k_{23})$	$k_{34} + k_{23}K_{a2}K_{OH}$:	$(2.96 \pm 0.40) \times 10^5$	$K_{a2} = K_{a2(hns)}$	3
$Al^{3+} + nqs^{3-}(k_{33})$ and $AlOH^{2+} + Hnqs^{2-}(k_{22})$	$k_{33} + k_{22}K_{a1}K_{OH}$:	$(19.8 \pm 0.6) \times 10^5$	$K_{a1} = K_{a1(nqs)}$	1
$Alnqs + hqs^{2-}(k_{02})$	k_{02}:	$(1.75 \pm 0.30) \times 10^5$		2
$Al^{3+} + hqs^{2-}(k_{32})$ and $AlOH^{2+} + Hhqs^{-}(k_{21})$	$k_{32} + k_{21}K_{a1}K_{OH}$:	$(6.9 \pm 0.6) \times 10^6$	$K_{a1} = K_{a1(hqs)}$	2

[a] Abbreviations: Al^{3+}, $[Al(H_2O)_6]^{3+}$; $AlOH^{2+}$, $[Al(OH)(H_2O)_5]^{2+}$; Alpqs, $[Al(pqs)(H_2O)_3]$; and Alnqs, $[Al(nqs)(H_2O)_4]$. [b] The data are for 0.1 mol dm^{-3} aqueous sodium chloride at 25°.

Here, C'_{Al} is total concentration of aluminum(III). Figure 5 indicates that a linear relation apparently holds between the modified rate constant, k'_{obsd}, and $[H^+]$. The kinetic parameters are summarized in Table III.

Substitution Kinetics.

A preliminary study by electronic spectroscopy revealed that a large excess of hqs causes a ligand substitution reaction of $[Al(pqs)_2]^{3-}$ with hqs to form $[Al(hqs)_3]^{3-}$. This substitution reaction was followed under pseudo-first-order kinetic conditions with respect to hqs.

The observed rate constant is generally expressed by (*9*).

$$k_{obsd} = \sum_{0}^{2} k_p\,[H_{2-p}hqs^{p-}]^m \qquad (9)$$

where p is a variable and m is a constant (m = 0 or 1). The value of k_{obsd} depends neither on the concentration of hqs nor on that of hydrogen ion as is clearly seen from Figure 6. This means that the ligand substitution reaction proceeds by a dissociative mechanism to form the *mono*-pqs complex and the rate-determining step is the liberation of one of the coordinated pqs species, as follows.

$$[Al(pqs)_2]^{3-} \underset{k_{03}}{\overset{k_{-03}}{\rightleftharpoons}} [Al(pqs)(H_2O)_3] + pqs^{3-}$$

$$[Al(pqs)(H_2O)_3] + 3H_{2-p}hqs^{p-} \xrightarrow{\text{rapid}} [Al(hqs)_3]^{3-} + pqs^{3-} + 3(2-p)H^+$$

$$pqs^{3-} + (3-j)H^+ \overset{\text{equil.}}{\rightleftharpoons} H_{3-j}pqs^{j-}$$

$$-d[[Al(pqs)_2]^{3-}]/dt = k_{-03}[[Al(pqs)_2]^{3-}] - k_{03}[[Al(pqs)(H_2O)_3]]\,[pqs^{3-}] \qquad (10)$$

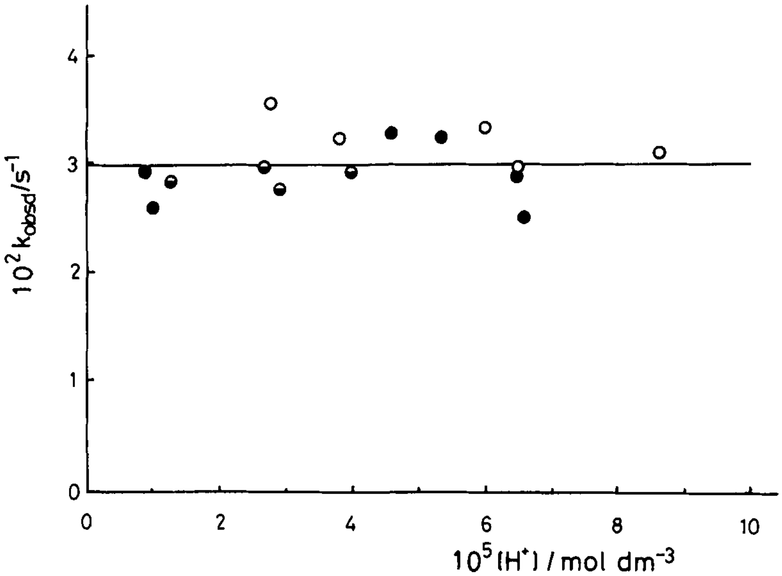

FIGURE 6 Correlation between k_{obsd} and $[H^+]$. $C_{Al(pqs)_2}$: 3.16×10^{-5} mol dm^{-3}, C_{hqs}: ◒, 1.26×10^{-3}; ●, 1.58×10^{-3}, and ○, 1.90×10^{-3} mol dm^{-4}, and absorbance at 500 nm.

$$k_{obsd} = k_{-03}[1 + (\beta_{12}/\beta_{11}) \; \{C'_{pqs}/(1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2 + K_{a1}K_{a2}K_{a3}[H^+]^3)\}] \doteqdot k_{-03} \text{ (under the experimental conditions)} \qquad (11)$$

Here, C'_{pqs} refers to the total concentration of pqs. The rate constants k_{-03} and k_{03}, which are calculated by the relation,

$$k_{03} = k_{-03}\beta_{12}/\beta_{11} \qquad (12)$$

are given in the Table III.

As observed with hns,[3] pqs can function either as an O-N type bidentate or as an O-N-O type terdentate ligand. The present spectroscopic studies indicate that pqs coordinates to aluminum(III) specificially as a terdentate ligand due to the chelate effect brought about by the carboxylate group *ortho* to the *azo* group.

Formation of the pqs complex proceeds through the reactions of $[Al(H_2O)_6]^{3+}$ with $Hpqs^{2-}$ and pqs^{3-} and those of $[Al(OH)(H_2O)_5]^{2+}$ with H_2pqs^- and $Hpqs^{2-}$, to give the *mono*-pqs complex, which undergoes rapid coordination with the second pqs ligand to yield the *bis*-pqs complex. Comparison of the kinetic parameters shows that the fully deprotonated pqs ligand coordinates to aluminum(III) faster than the singly and doubly protonated species. As is seen from Table III, magnitudes of the kinetic parameters for the pqs complex are comparable to those for aluminum(III) complexes with related ligands.[1-3] Therefore, the kinetic rate-determining step must remain the same irrespective of the nature of all these ligands; *i.e.*, donation *via* the quinolinolate oxygen atom to the aquaaluminum(III) ion. This rate-determining step is followed by interactions of the carboxylate and *azo* groups with the cationic aluminum(III) -unidentate pqs complex to complete the formation of the *mono*-pqs complex with two six-membered chelate rings.

In order to obtain further information on the kinetic behavior of the second pqs ligand resulting in the formation of the *bis*-pqs complex, a ligand substitution reaction with hqs was studied. The substitution (aquation) of the *bis*-pqs complex was found to proceed through a dissociative mechanism. Besides those studies by ^{1}H-, ^{17}O-, ^{27}Al-, and ^{31}P-NMR methods,[8-10] this may be the first kinetic evidence supporting the notion that chelated aluminum(III) complexes with octahedral coordination spheres utilise a dissociative (or dissociative interchange) substitution mechanism with a multidentate ligand. The rate constant for the coordination of the second pqs ligand is $(2.9 \pm 0.5) \times 10^5$ mol^{-1} dm^3 s^{-1}, which is close to that for the coordination of hqs to the *mono*-nqs complex, $(1.75 \pm 0.30) \times 10^5$ mol^{-1} dm^3 s^{-1}.[2] This implies that the coordination of the second ligand to the *mono*-(O-N-O or O-N) complex (anation) is little influenced by the nature of the coordinated ligand and that it proceeds in the same way as in coordination to the aqua-aluminum(III) ion.

In conclusion, the k_{22} process contributes much to the overall reaction relative to the k_{33} process on the basis of the fact that $k_{22}K_{a1}K_{OH}$ is greater than k_{33}, because k_{33} should not exceed k_{03}.[2]

REFERENCES AND NOTES

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4. Abbreviations: pqs, 8-hydroxy-7-[(2′-carboxyl-1′-phenyl)azo]-quinoline-5-sulfonic acid (H_3pqs); pns, 2-[(2′-carboxy-1′-phenyl)azo]-1-naphthol-4-sulfonic acid (H_3pns); nqs, 8-hydroxy-7-[(6′-sulfo-2′-naphthyl)azo]quinoline-5-sulfonic acid (H_3nqs); hns, 8-hydroxy-7-[(8′-hydroxy-3′,6′-disulfo-1′-naphthyl)azo]-quinoline-5-sulfonic acid (H_5hns); and hqs, 8-quinolinol-5-sulfonic acid (H_2hqs). $H_{3-j}pqs^{j-}$, $H_{3-j}pns^{j-}$ and $H_{3-j}nqs^{j-}$ ($j = 0$–3), $H_{5-j'}hns^{j'-}$ ($j' = 0$–5), and $H_{2-j''}hqs^{j''-}$ ($j'' = 0$–2) indicate the ionic species of the individual ligands.
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