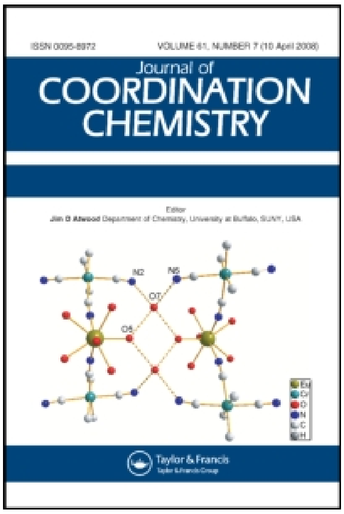

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COORDINATION OF 8-QUINOLINOL-5-SULFONIC ACID TO ALUMINIUM(III) COMPLEXES OF 8-HYDROXY-7- [(6′-SULFO-2′-NAPHTHYL)AZO] -QUINOLINE-5-SULFONATE. EVIDENCE FOR MIXED LIGAND COMPLEX FORMATION

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Studies have been made on the coordination behaviour of the aluminium(III) 8-quinolinol-5-sulfonate (hqs)[1] and aluminium(III) nqs[1] complexes[2] with hqs in 0.1 mol dm^{-3} aqueous sodium chloride solution at 25°. Mixed-ligand complex formation was evidenced by electronic absorption spectral and other spectrophotometric equilibrium studies. Stopped-flow kinetic studies revealed that mixed-ligand complex formation with a *mono*-nqs complex proceeds *via* its reaction with $Hhqs^-$ and hqs^{2-} whereas formation of the *tris*-hqs complex proceeds *via* the reaction of $[Al(H_2O)_6]^{3+}$ with $Hhqs^-$ and hqs^{2-} and also of $[Al(OH)(H_2O)_5]^{2+}$ with H_2hqs and $Hhqs^-$. Coordination mechanisms and structures for the mixed-ligand and the *tris*-hqs complexes are also discussed.

INTRODUCTION

Selectivity of coordination modes in the formation of metal complexes with multidentate ligands is ascribed either to the bulkiness of or to the geometry of the ligands. In the first category belongs the formation of aluminium(III) complexes with 2-methyl-8-quinolinol(mhq),[3] where coordination of the third mhq ligand is hindered sterically by the interaction of the methyl group of the entering species with the coordinated mhq ligands. It is also true of the aluminium(III) complex with 8-hydroxy-7-[(6′-sulfo-2′-naphthyl)azo] -quinoline-5-sulfonate(nqs),[1,2] where coordination of the second and third nqs ligands are hindered sterically by the interaction of the bulky naphthylazo-group of the entering ligand with the coordinated one. To the second category belongs the formation of the aluminium(III) complex with 8-hydroxy-7-[(8′-hydroxy-3′, 6′-disulfo-1′-naphthyl)azo] quinoline-5-sulfonate,[4] whose coordination is limited either to a terdentate or to a bidentate by steric restrictions due to the geometry of the ligand.

In the former case, coordination of ligands less bulky than the initial bulky one would result in the formation of mixed-ligand complexes. This is one of the principal reasons behind the present study in which nqs and 8-quinolinol-5-sulfonic acid (hqs)[1] were chosen as the bulky and compact ligands, respectively. Another reason was to characterize the coordination of two less bulky ligands to the mono nqs complex, $[Al(nqs)(H_2O)_4]$, by comparing the thermodynamics and kinetics of mixed-ligand complex formation with those of the *tris*-hqs complex.

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EXPERIMENTAL

Reagents

The ligand nqs was synthesized by diazotation of 6-aminonaphthalene-2-sulfonic acid followed by coupling with hqs,[2] and was purified by repeated precipitation from dioxane. Calcd. for $C_{19}H_{13}N_3O_7S_2\cdot4.5H_2O$: C, 42.22; H, 4.10; N, 7.77%. Found. C, 41.61; H, 4.02; N, 7.80%.

The ligands hqs (analytical grade) was supplied by the Kanto Chemical Co. Ltd., or the Tokyo Kasei Kogyo Co. Ltd., and used without purification.

An aqueous aluminium(III) solution was prepared from analytical grade nitrate salt from the Wako Pure Chemicals Ind. Co. Ltd., and acidified slightly with a small amount of hydrochloric acid to prevent its hydrolysis. All other chemicals were of analytical or equivalent grade and used without further purification.

Measurements

Complex formation reactions were followed spectrophotometrically in 0.1 mol dm^{-3} aqueous sodium chloride at 25°. For mixed-ligand complex formation, nqs was added in the first place to complete the formation of the *mono*-nqs complex of aluminium(III) quantitatively,[2] and then hqs was added in an appropriate amount. A sodium acetate-acetic acid buffer was used to maintain pH and its concentration was kept below 10^{-2} mol dm^{-3} so that its coordination to the metal ion could be neglected and so that the ionic strength could be maintained practically constant with sodium chloride.

Electronic absorption spectra were measured with a JASCO spectro photometer, model UVIDEC-1. Kinetic measurements were made at 25.0 ± 0.1° with a JASCO spectrophotometer, model SS-25, to which a stopped-flow apparatus, model SFC-5, a data processor, model DP-500, and a WATANABE SOKKI X-Y recorder, model WX-441, were attached. Kinetic runs were performed under pseudo-first-order conditions with respect to hqs. Absorbance changes were followed at 375 nm and 350 nm for mixed-ligand complex and *tris*-hqs complex formation and the pseudo-first-order rate constant, k_{obsd}, was calculated from the relation,

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

where A and A_{eq} stand for absorbances at time t, and at equilibrium, respectively. The pH of the reaction solution was measured using a HORIBA pH meter, model F7-SS, with glass and 3.33 mol dm^{-3} potassium chloride calomel electrodes. Hydrogen ion concentration, $-\log [H^+]$, was 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° and the value of 0.83 was taken from the literature.[5]

RESULTS

Electronic absorption spectra

Figure 1 shows the absorption spectra of the *mono*-nqs complex in the absence (curve 1) and in the presence (curve 2) of two moles of hqs per mole of the *mono*-nqs complex together with the spectrum of the *tris*-hqs complex (curve 3). Curve 2 represents both of the spectral features of curves 1 and 3; an absorption band at 24,000 cm^{-1} due to $\pi \rightarrow \pi^*$ transitions of the azo-group and two absorption bands at 31,000 and 34,000 cm^{-1} due

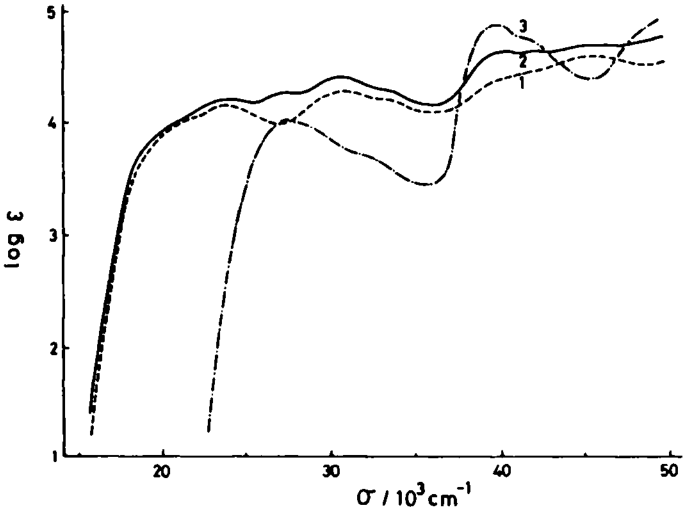

FIGURE 1 Electronic absorption spectra of aluminium(III) complexes. 1: $[Al(nqs)(H_2O)_4]$ (pH 5.05), 2: $[Al(nqs)(hqs)_2]^{4-}$ (pH 5.06), and 3: $[Al(hqs)_3]^{3-}$ (pH 5.00).

to $\pi \rightarrow \pi^*$ transitions of the fused heterocyclic and aromatic rings of the coordinated nqs ligand together with two absorption bands at 27,000 and 39,500 cm^{-1} due to $\pi \rightarrow \pi^*$ transitions of the fused heterocyclic rings of the coordinated hqs ligand. These spectral features demonstrate that hqs coordinates to the *mono*-hqs complex to form a mixed-ligand complex of the type $[Al(nqs)(hqs)_2]^{4-}$. This deduction was checked separately by the mole ratio method.[6] A clear inflexion point was present at the mole ratio of 2, below which a strict linearity was held between the absorbance and the mole ratio. This fact indicates that the mixed-ligand complex is formed without any liberation of the coordinated nqs ligand.

Formation and stability

Based on the above-mentioned results, the formation of the mixed-ligand complex can be expressed as[7] shown in (*1*).

$$[Al(H_2O)_6]^{3+} + Hnqs^{2-} + 2Hhqs^- \overset{K_{eq}}{\rightleftharpoons} [Al(nqs)(hqs)_2]^{4-} + 3H^+$$

$$K_{eq} = [[Al(nqs)(hqs)_2]^{4-}][H^+]^3/[[Al(H_2O)_6]^{3+}]/[Hnqs^{2-}]/[Hhqs^-]^2 \qquad (1)$$

The hydrolysis constant of the aluminium(III) ion, K_{OH}, and the protonation constants of nqs, $k_{a1(nqs)}$ and $k_{a2(nqs)}$, and of hqs, $k_{a1(hqs)}$ and $k_{a2(hqs)}$, have been estimated as in (*2*) – (*6*).

$$K_{OH} = [[Al(OH)(H_2O)_5]^{2+}][H^+]/[[Al(H_2O)_6]^{3+} \qquad (2)$$

$$\log K_{OH} = -4.49^{8}$$

$$k_{a1(nqs)} = [Hnqs^{2-}]/[nqs^{3-}][H^+]$$

$$\log k_{a1(nqs)} = 7.62 \pm 0.05^{2} \qquad (3)$$

$$k_{a2(nqs)} = [H_2nqs^-]/[Hnqs^{2-}][H^+]$$

$$\log k_{a2(nqs)} = 3.00 \pm 0.08^{2} \qquad (4)$$

$$k_{a1(hqs)} = [Hhqs^-]/[hqs^{2-}][H^+]$$

$$\log k_{a1(hqs)} = 8.97 \pm 0.10^{9} \qquad (5)$$

$$k_{a2(hqs)} = [H_2hqs]/[Hhqs^-][H^+]$$

$$\log k_{a2(hqs)} = 4.06 \pm 0.11^{9} \qquad (6)$$

Under the condition that the mixed-ligand complex is mainly present, *i.e.*, $C_{nqs} \gg C_{al}$, $C_{hqs} \gg C_{al}$, and $C_{hqs} > 2C_{nqs}$, where the total concentrations of aluminium(III), nqs and hqs, C_{al}, C_{nqs}, and C_{hqs}, respectively, are defined as

$$C_{al} = [[Al(H_2O)_6]^{3+}] + [[Al(OH)(H_2O)_5]^{2+}] + [[Al(nqs)(hqs)_2]^{4-}] \qquad (7)$$

$$C_{nqs} = [Hnqs^{2-}] + [[Al(nqs)(hqs)_2]^{4-}] \qquad (8)$$

$$C_{hqs} = [H_2hqs] + [Hhqs^-] + 2[[Al(nqs)(hqs)_2]^{4-}] \qquad (9)$$

and that absorbances are measured at a wavelength where Beer's law holds for all the ligand and complex species concerned, equation (*1*) leads to (*10*).

$$1/(A - A_{min}) = 1/\Delta\epsilon C_{al} + (1 + k_{a2(hqs)}[H^+])^2(1 + K_{OH}/[H^+])$$

$$\times [H^+]^3/\Delta\epsilon C_{al} C_{nqs} C_{hqs}{}^2 K_{eq}$$

$$\Delta\epsilon = \epsilon_{112} - \epsilon_{Hnqs} - 2A_{min}/C_{hqs} \cong \epsilon_{112} \qquad (10)$$

In (*10*) the $A - A_{min}$ term is the difference in absorbance between a solution containing both metal ion and ligands and a solution without metal ion; ϵ_{112} and ϵ_{Hnqs} stand for molar absorption coefficients of the mixed-ligand complex $[Al(nqs)(hqs)_2]^{4-}$, and the ligand species $Hnqs^{2-}$, respectively. Experimental results were plotted as shown in Figure 2, from which K_{eq} was found to be 4.46 ± 0.20.

Stability constants, β_{112} and $\beta_{11,2}$, were calculated based on the following definitions and relations,

$$\beta_{112} = [[Al(nqs)(hqs)_2]^{4-}]/[[Al(H_2O)_6]^{3+}][nqs^{3-}][hqs^{2-}]^2$$

$$= K_{eq}k_{a1(nqs)}k_{a1(hqs)}{}^2 \qquad (11)$$

$$\beta_{11,2} = [[Al(nqs)(hqs)_2]^{4-}]/[[Al(nqs)(H_2O)_4]][hqs^{2-}]^2$$

$$= \beta_{112}/\beta_{110} \qquad (12)$$

in the light of the K_{eq} value obtained above, the stability constant, β_{110},[2] and the protonation constants, $k_{a1(nqs)}$[2] and $k_{a1(hqs)}$.[9]

$$\beta_{110} = [[Al(nqs)(H_2O)_4]]/[[Al(H_2O)_6]^{3+}][nqs^{3-}]$$

$$\log \beta_{110} = 7.88 \pm 0.18^{2} \qquad (13)$$

The *tris*-hqs complex formation constant can be expressed as shown in (*14*).

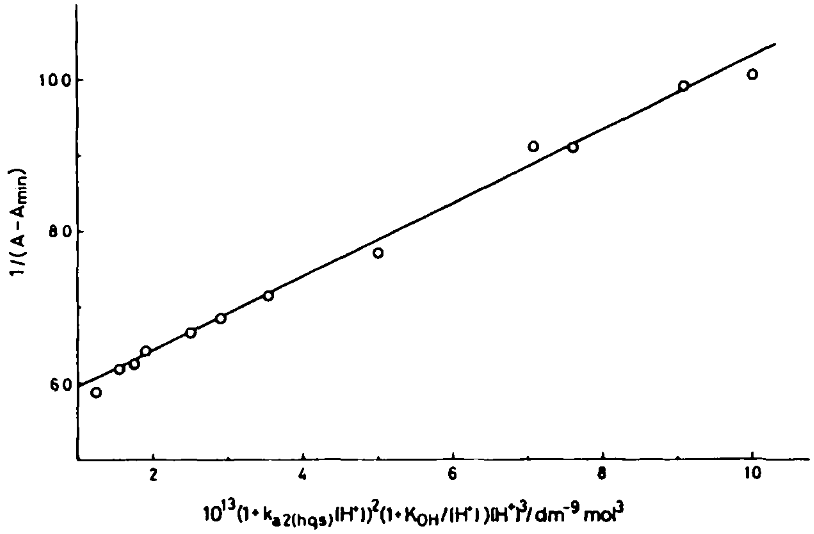

FIGURE 2 Relation between $1/(A - A_{min})$ and $(1 + k_{a2(hqs)}[H^+])^2\ (1 + K_{OH}/[H^+])[H^+]^3$. C_{al}: 4.00×10^{-6} mol dm^{-3}, C_{nqs}: 4.00×10^{-5} mol dm^{-3}, and C_{hqs}: 8.00×10^{-5} mol dm^{-3}; absorbance measurement: 375 nm.

$$[\mathrm{Al(H_2O)_6}]^{3+} + 3\mathrm{Hhqs}^- \xrightleftharpoons{K'_{eq}} [\mathrm{Al(hqs)_3}]^{3-} + 3\mathrm{H}^+$$

$$K'_{eq} = [[\mathrm{Al(hqs)_3}]^{3-}]\,[\mathrm{H}^+]^3/[[\mathrm{Al(H_2O)_6}]^{3+}]\,[\mathrm{Hhqs}^-]^3 \qquad (14)$$

Under the condition that the *tris*-hqs complex is mainly present, *i.e.*, $C'_{hqs} > 3C'_{al}$, where total concentrations of aluminium(*III*) and hqs, C'_{al} and C'_{hqs}, are defined as

$$C'_{al} = [[\mathrm{Al(H_2O)_6}]^{3+}] + [[\mathrm{Al(OH)(H_2O)_5}]^{2+}] + [[\mathrm{Al(hqs)_3}]^{3-}] \qquad (15)$$

$$C'_{hqs} \cong [\mathrm{H_2hqs}] + [\mathrm{Hhqs}^-] + [\mathrm{hqs}^{2-}] \qquad (16)$$

(*20*) can be given from eq. (*14*) - (*16*) and the following absorbance-concentration relations are evident,

$$A' = \epsilon_{Hhqs}[\mathrm{Hhqs}^-] + \epsilon_{2Hhqs}[\mathrm{H_2hqs}] + \epsilon_{103}[[\mathrm{Al(hqs)_3}]^{3-}] \qquad (17)$$

$$\begin{aligned} A'_{max} = {} & (\epsilon_{Hhqs} + \epsilon_{2Hhqs}k_{a2(hqs)}[H^+])/(1 + k_{a2(hqs)}[H^+]) \\ & \times \{C'_{hqs} - 3C'_{al}/(1 + K_{OH}/[H^+])\} + \epsilon_{103}C'_{al}/(1 + K_{OH}/[H^+]) \end{aligned} \qquad (18)$$

$$A'_{min} = \{(\epsilon_{Hhqs} + \epsilon_{2Hhqs}k_{a2(hqs)}[H^+])/(1 + k_{a2(hqs)}[H^+])\}\ C'_{hqs} \qquad (19)$$

$$\begin{aligned} f(A') = {} & \log K'_{eq} - 3\log[H^+] \\ & f(A') \equiv \log(A' - A'_{min})/(A'_{max} - A') - 3\log\{C'_{hqs}/(1 + k_{a2(hqs)}[H^+]) \\ & - 3C'_{al}(A' - A'_{min})/[(1 + K_{OH}/[H^+])(A'_{max} - A'_{min})]\} \end{aligned} \qquad (20)$$

where ϵ_{2Hhqs} and ϵ_{103} stand for molar absorption coefficients of the ligand species H_2hqs, and the *tris*-hqs complex, respectively. Figure 3 shows experimental data for the relation

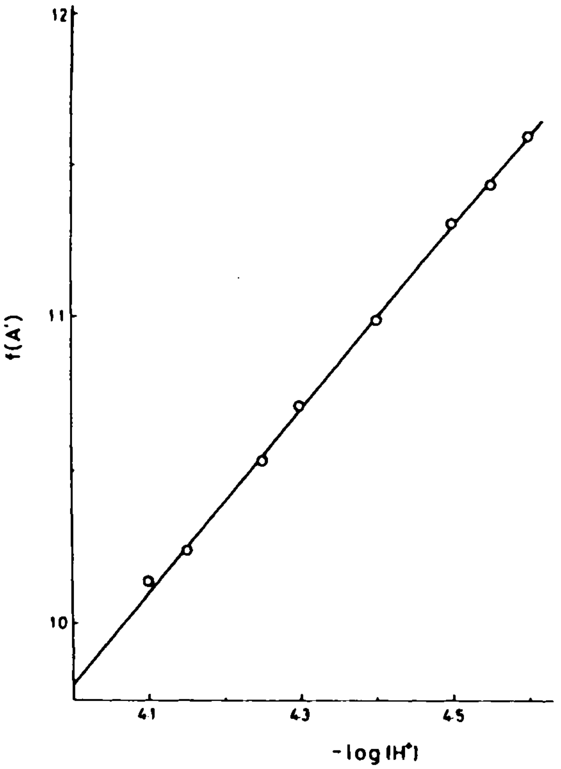

FIGURE 3 Relation between f(A') and – log [H⁺]. C'_{al} : 4.00 × 10^{-5} mol dm^{-3} and C'_{hqs}: 4.00 × 10^{-4} mol dm^{-3}; absorbance measurement: 360 nm.

between f(A′) and – log (H⁺), from which log K_{eq} was calculated to be –2.20 ± 0.04. A stability constant, β_{103}, was calculated using (*21*).

$$\beta_{103} = [[\mathrm{Al(hqs)_3}]^{3-}]/[[\mathrm{Al(H_2O)_6}]^{3+}][\mathrm{hqs}^{2-}]^3$$
$$= K'_{eq}k_{al(hqs)}{}^3 \qquad (21)$$

Stability constants for the intermediate mixed-ligand complex, β_{111}, the *mono*-hqs complex, β_{101}, and the *bis*-hqs complex, β_{102},

$$\beta_{111} = [[\mathrm{Al(nqs)(hqs)(H_2O)_2}]^{2-}]/[[\mathrm{Al(H_2O)_6}]^{3+}][\mathrm{nqs}^{3-}][\mathrm{hqs}^{2-}] \qquad (22)$$
$$\beta_{101} = [[\mathrm{Al(hqs)(H_2O)_4}]^{+}]/[[\mathrm{Al(H_2O)_6}]^{3+}][\mathrm{hqs}^{2-}] \qquad (23)$$
$$\beta_{102} = [[\mathrm{Al(hqs)_2(H_2O)_2}]^{-}]/[[\mathrm{Al(H_2O)_6}]^{3+}][\mathrm{hqs}^{2-}]^2 \qquad (24)$$

were determined or estimated according to the following way. Among them, β_{101} and β_{102} were determined spectrophotometrically by using the known data of β_{103} from the following relation (see Appendix).

$$F = 3 - \{[3(1 + K_{OH}/[H^+]) + 2\beta_{101}[\mathrm{hqs}^{2-}] + \beta_{102}[\mathrm{hqs}^{2-}]^2]/[(1 + K_{OH}/[H^+])$$
$$+ \beta_{101}[\mathrm{hqs}^{2-}] + \beta_{102}[\mathrm{hqs}^{2-}]^2 + \beta_{103}[\mathrm{hqs}^{2-}]^3]\} \qquad (25)$$

TABLE I
Protonation constants of the ligands

Ligand	Log k_{a1}	Log k_{a2}	Remarks*	Reference
hqs	8.35	3.84	0.1 mol dm^{-3} KNO_3 (potentiometry)	
	8.47 ± 0.01	3.98 ± 0.01	0.1 mol dm^{-3} KNO_3 (potentiometry)	
	8.48 ± 0.05	3.92 ± 0.03	0.1 mol dm^{-3} KNO_3 (potentiometry)	†
	8.66	4.09	0.005 mol dm^{-3} $HClO_4$ (potentiometry)	
	8.48	4.19	$\mu = 0.01$, log k_{a3} = 2.04 (potentiometry)	
	8.42 ± 0.07	3.93 ± 0.05	$\mu = 0.1$	
	8.757	4.112	$\mu = 0$	‡
	8.97 ± 0.10	4.06 ± 0.11	0.1 mol dm^{-3} NaCl (spectrophotometry)	present work
nqs	7.62 ± 0.05	3.00 ± 0.08	0.1 mol dm^{-3} NaCl (spectrophotometry)	2

*The data refers to 25°. † L.G. Sillén, G. Schwarzenbach, and A.E. Martell, *Stability Constants of Metal-Ion Complexes*, Sp. Publ. No. 17, p 609 (1964); No. 25, p 592 (1971), The Chemical Society, London. ‡ R.M. Smith and A.E. Martell, *Critical Stability Constants*, **2**, 227 (1975), Plenum Press, New York.

Equation (*25*) can be solved numerically for β_{101} and β_{102} by a curve-fitting method[10] with a normalized curve of

$$Y = 3 - (3 + 2bX + aX^2)/(1 + bX + aX^2 + X^3) \qquad (26)$$

with $\beta_{101} = b\beta_{103}^{1/3}$ and $\beta_{102} = a\beta_{103}^{2/3}$, provided that $K_{OH}/[H^+]$ is negligibly smaller than unity, a condition which can be satisfied by an appropriate choice of experimental conditions. Experiments were carried out at 360 nm for a set of solutions containing total hqs and aluminium(III) concentration ratios (C''_{hqs}/C''_{al}) of 1-3; F and $[hqs^{2-}]$ were calculated using (*A5*) and (*A6*) in the Appendix, and the results are given in Figure 4, from which β_{101} and β_{102} were obtained as shown in Table II.

The stability constant, β_{111}, could not be obtained directly from the experimental data due in part to difficulty in the reliable determination of the molar absorption coefficients of the intermediate mixed-ligand complex species and in part to the complexity of the equilibria to which it refers. Hence β_{111} was estimated from the known data for β_{101}, β_{102}, β_{103}, β_{110}, and β_{112} by taking into account similarities in the co-ordination modes of the ligands nqs and hqs and in the thermodynamic characteristics of the mixed-ligand and hqs complexes. Results are given in Table II. Furthermore, a stability constant, $\beta_{11,1}$, defined by (*27*)

$$\beta_{11,1} = [[Al(nqs)(hqs)(H_2O)_2]^{2-}]/[[Al(nqs)(H_2O)_4]][hqs^{2-}] = \beta_{111}/\beta_{110} \qquad (27)$$

was calculated from the known data. These stability constants together with the corresponding Gibbs standard free energy change ($-\Delta G^\circ_{ij}$) are summarized in Table II.

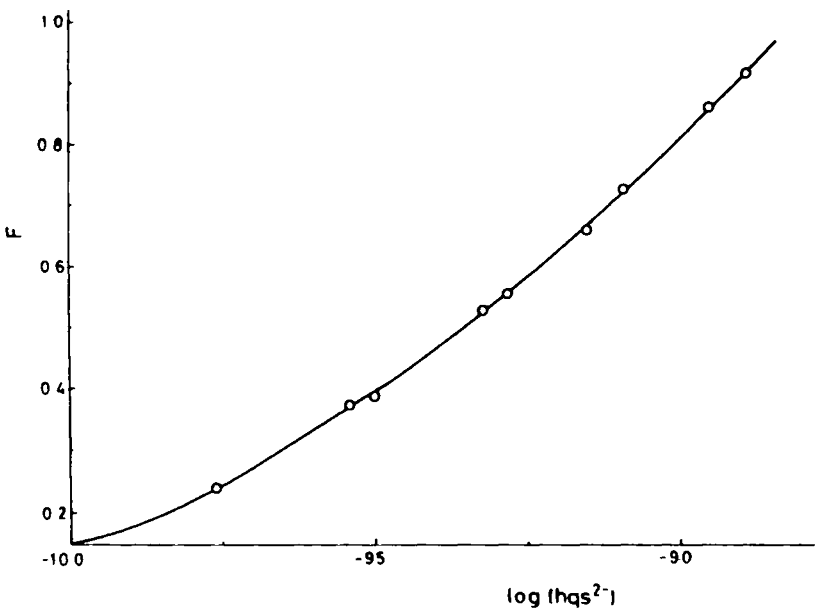

FIGURE 4 Relation between F and log $[hqs^{2-}]$. C''_{al} : 4.00×10^{-5} mol dm^{-3}, C'''_{hqs}/C''_{al} : 1 - 3; absorbance measurement: 360 nm. The line is the theoretical equation $Y = 3 - (3 + 2 \times 10^{9.24} [hqs^{2-}] + 10^{17.61} [hqs^{2-}]^2)/(1 + 10^{9.24} [hqs^{2-}] + 10^{17.61} [hqs^{2-}]^2 + 10^{24.70} [hqs^{2-}]^3)$.

Kinetics and mechanism.

It seems reasonable from the foregoing results that the formation of the mixed-ligand complex from the *mono*-nqs complex proceeds *via* intermediate formation of the species $[Al(nqs)(hqs)(H_2O)_2]^{2-}$. The rate-determining step should lie either in the formation of the intermediate mixed-ligand complex (stage I) or in the reaction of the intermediate complex with the second hqs ligand (stage II). For both of the cases, the coordinating ligand species may be H_2hqs or hqs^{2-} together with the predominant species $Hhqs^-$. Therefore three reaction pathways are anticipated for each stage. For stage I,

TABLE II
Stability constants and related data

Complex	(lij)*	Log β_{lij}	$-\Delta G^\circ_{lij}$/kJ mol^{-1} **	Remarks
$[Al(nqs)(H_2O)_4]$	(110)	7.88 ± 0.18	45.0 ± 1.0	Ref. no. 2
$[Al(nqs)(hqs)(H_2O)_2]^{2-}$	(111)	17.6 ± 0.6	100 ± 3	a
$[Al(nqs)(hqs)(H_2O)_3]^{2-}$	(11,1)	9.7 ± 0.7	55 ± 4	b
$[Al(nqs)(hqs)_2]^{4-}$	(112)	26.21 ±	149.6 ± 2.5	
$[Al(nqs)(hqs)_2]^{4-}$	(11, 2)	18.3 ± 0.6	105 ± 4	c
$[Al(hqs)(H_2O)_4]^+$	(101)	9.24 ± 0.14	52.7 ± 0.8	
$[Al(hqs)_2(H_2O)_2]^-$	(102)	17.61 ± 0.24	100.5 ± 1.4	
$[Al(hqs)_3]^{3-}$	(103)	24.70 ± 0.35	141.0 ± 2.0	

*$[Al(nqs)_i(hqs)_j(H_2O)_{6-2(i+j)}]^{(3-2i-2j)}$. ** Calculated by the relation $-\Delta G^\circ_{lij} = RT \ln \beta_{lij}$ with no correction for the activity coefficient to zero ionic strength. [a]Estimated from β_{101}, β_{102}, β_{103}, β_{110}, and β_{112}. [b]Calculated from β_{110} and β_{111}. [c]Calculated from β_{110} and β_{112}. All the data relate to 0.1 mol dm^{-3} aqueous sodium chloride solution at 25°.

$$\begin{aligned}
&d[[\mathrm{Al(nqs)(hqs)(H_2O)_2}]^{2-}]/dt\ (= d[[\mathrm{Al(nqs)(hqs)_2}]^{4-}]/dt)\\
&\quad = (k_{00}[\mathrm{H_2hqs}] + k_{01}[\mathrm{Hhqs^-}] + k_{02}[\mathrm{hqs^{2-}}])[[\mathrm{Al(nqs)(H_2O)_4}]]\\
&\quad - (k_{-00}[\mathrm{H^+}]^2 + k_{-01}[\mathrm{H^+}] + k_{-02})[[\mathrm{Al(nqs)(hqs)(H_2O)_2}]^{2-}] \qquad (28)
\end{aligned}$$

and for stage II,

$$\begin{aligned}
&d[[\mathrm{Al(nqs)(hqs)_2}]^{4-}]/dt\\
&\quad = (k_{20}[\mathrm{H_2hqs}] + k_{21}[\mathrm{Hhqs^-}] + k_{22}[\mathrm{hqs^{2-}}])[[\mathrm{Al(nqs)(hqs)(H_2O)_2}]^{2-}]\\
&\quad - (k_{-20}[\mathrm{H^+}]^2 + k_{-21}[\mathrm{H^+}] + k_{-22})[[\mathrm{Al(nqs)(hqs)_2}]^{4-}] \qquad (29)
\end{aligned}$$

where k_{ij} is the forward rate constant for the pathway involving $[\mathrm{Al(nqs)(hqs)_{i/2}(H_2O)_{4-i}}]^{i-}$ ($i = 0$ and 2) and $\mathrm{H_{2-j}hqs^{j-}}$ ($j = 0 \cdot 2$) and k_{-ij} is the reverse rate constant. In these cases, protolytic processes were assumed to be always at equilibrium since they are very fast compared to the coordination processes.[11]

Under pseudo-first-order kinetic conditions with respect to hqs concentration, the following relations can be deduced for each stage by use of total hqs concentration, C'''_{hqs}:

$$C'''_{\mathrm{hqs}} \cong [\mathrm{H_2hqs}] + [\mathrm{Hhqs^-}] + [\mathrm{hqs^{2-}}] \qquad (30)$$

$$k'_{\mathrm{obsd}} = k_{i0}k_{a1(\mathrm{hqs})}k_{a2(\mathrm{hqs})}[\mathrm{H^+}]^2 + k_{i1}k_{a1(\mathrm{hqs})}[\mathrm{H^+}] + k_{i2} \qquad (31)$$

where, for stage I ($i = 0$),

$$\begin{aligned}
k'_{\mathrm{obsd}} \equiv\ & k_{\mathrm{obsd}}[C'''_{\mathrm{hqs}}/(1 + k_{a1(\mathrm{hqs})}[\mathrm{H^+}] + k_{a1(\mathrm{hqs})}k_{a2(\mathrm{hqs})}[\mathrm{H^+}]^2)]/\{1/\beta_{11,2}\\
& + (C'''_{\mathrm{hqs}}/(1 + k_{a1(\mathrm{hqs})}[\mathrm{H^+}] + k_{a1(\mathrm{hqs})}k_{a2(\mathrm{hqs})}[\mathrm{H^+}]^2))^2\} \qquad (31')
\end{aligned}$$

and for stage II ($i = 2$),

$$\begin{aligned}
k'_{\mathrm{obsd}} \equiv\ & (k_{\mathrm{obsd}}/\beta_{11,1})/\{1/\beta_{11,2} + (C'''_{\mathrm{hqs}}/(1 + k_{a1(\mathrm{hqs})}[\mathrm{H^+}]\\
& + k_{a1(\mathrm{hqs})}k_{a2(\mathrm{hqs})}[\mathrm{H^+}]^2))/\beta_{11,1}\} \qquad (31'')
\end{aligned}$$

Hence the reaction mechanism can be deduced by plotting k'_{obsd} derived from the experimentally obtained k_{obsd} data for either (*31'*) or (*31''*) against $[\mathrm{H^+}]$ as a best fit for (*31*). A series of k_{obsd} data was recorded by a stopped-flow technique. Reasonable results were obtained when k'_{obsd} was calculated using (*31'*) and a linear relation was found between k'_{obsd} and $[\mathrm{H^+}]$ (*c.f.* Figure 5). It can be concluded that the rate-determining step is in stage I and that the reaction proceeds through the interaction of the *mono*-nqs complex with the species $\mathrm{Hhqs^-}$(k_{01}) and $\mathrm{hqs^{2-}}$(k_{02}).

Analogously, *tris*-hqs complex formation may proceed stepwise through the *mono*-and *bis*-hqs complex species. If the rate-determining step involves the coordination of the first hqs ligand to the aluminium(III) ion, which was found to be the case, six reaction pathways are anticipated by taking K_{OH}, $k_{a1(\mathrm{hqs})}$ and $k_{a2(\mathrm{hqs})}$ into account, and

$$\begin{aligned}
&d[[\mathrm{Al(hqs)(H_2O)_4}]^{+}]/dt\ (= d[[\mathrm{Al(hqs)_3}]^{3-}]/dt)\\
&\quad = (k_{30}[\mathrm{H_2hqs}] + k_{31}[\mathrm{Hhqs^-}] + k_{32}[\mathrm{hqs^{2-}}])[[\mathrm{Al(H_2O)_6}]^{3+}]\\
&\quad + (k_{20}[\mathrm{H_2hqs}] + k_{21}[\mathrm{Hhqs^-}] + k_{22}[\mathrm{hqs^{2-}}])[[\mathrm{Al(OH)(H_2O)_5}]^{2+}]\\
&\quad - \{k_{-30}[\mathrm{H^+}]^2 + (k_{-31} + k_{-20})[\mathrm{H^+}] + (k_{-32} + k_{-21}) + k_{-22}[\mathrm{OH^-}]\}\ [[\mathrm{Al(hqs)}\\
&\quad \mathrm{(H_2O)_4}]^{+}] \qquad (32)
\end{aligned}$$

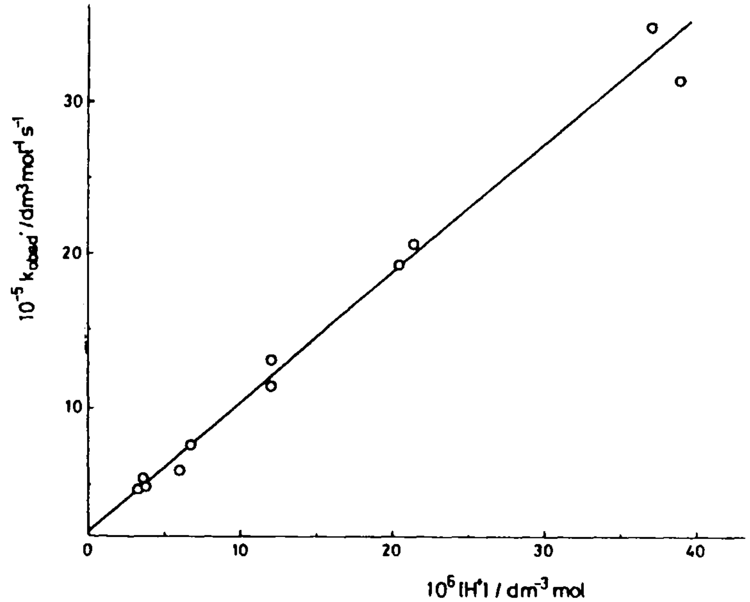

FIGURE 5 Relation between k'_{obsd} and [H$^+$]. C'''_{al}: 8.00 × 10^{-6} mol dm^{-3}, C'''_{nqs}: 8.00 × 10^{-5} mol dm^{-3}, and C'''_{hqs}: 8.00 × 10^{-5} - 4.00 × 10^{-4} mol dm^{-3}; absorbance measurement: 375 nm.

where k_{mn} is the forward rate constant for the reaction of $[Al(OH)_{3-m}(H_2O)_{3+m}]^{m+}$ (m = 2 and 3) and $H_{2-n}hqs^{n-}$ (n = 0 - 2) and k_{-mn} is the reverse rate constant. The following relation can be deduced under pseudo-first-order kinetic conditions with respect to hqs concentration.

$$k''_{obsd} = k_{30}k_{a1(hqs)}k_{a2(hqs)}[H^+]^2 + (k_{31} + k_{20}k_{a2(hqs)}K_{OH})\,k_{a1(hqs)} \times [H^+] + (k_{32} + k_{21}k_{a1(hqs)}K_{OH}) + k_{22}K_{OH}[H^+]^{-1} \tag{33}$$

$$k''_{obsd} \equiv k_{obsd}(C'''_{hqs}/(1 + k_{a1(hqs)}[H^+] + k_{a1(hqs)}k_{a2(hqs)}[H^+]^2))^2/\{1/\beta_{103} + (C_{hqs}/(1 + k_{a1(hqs)}[H^+] + k_{a1(hqs)}k_{a2(hqs)}[H^+]^2))^3\} \tag{33'}$$

$$C'''_{hqs} \cong [H_2hqs] + [Hhqs^-] + [hqs^{2-}] \tag{34}$$

A series of k_{obsd} data were recorded under the conditions shown in Figure 6. Reasonable results were obtained when k''_{obsd} was calculated from k_{obsd} assuming that (*33'*) should hold, and a linear relation was found between k''_{obsd} and [H$^+$] (*c.f.* Figure 6). It can be deduced that the rate-determining step involves the co-ordination of the first hqs to the metal ion and that the reaction proceeds through the reactions of $[Al(H_2O)_6]^{3+}$ with $Hhqs^-$ (k_{31}) and hqs^{2-} (k_{32}) and of $[Al(OH)(H_2O)_5]^{2+}$ with H_2hqs (k_{20}) and $Hhqs^-$ (k_{21}). All the kinetic and related data are summarized in Table III.

DISCUSSION

Formation of the mixed-ligand complex is evidenced by an absorption spectrum which shows features characteristic of coordinated nqs and hqs. The related stability constants,[12] kinetic, and thermodynamic data are given in Tables II and III. These results

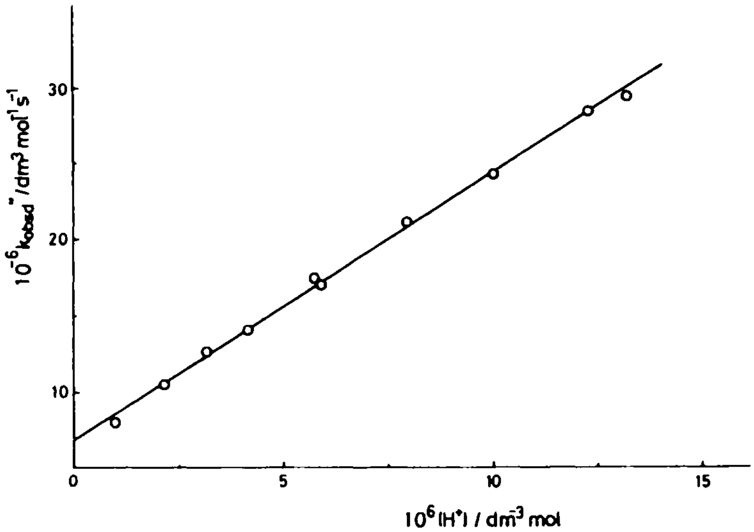

FIGURE 6 Relation between k''_{obsd} and $[H^+]$. C'''_{Al}: 2.00×10^{-5} mol dm^{-3} and C'''_{hqs}: 6.00×10^{-4} - 1.00×10^{-3} mol dm^{-3}; absorbance measurement: 350 nm.

indicate that the mixed-ligand complex is formed from the *mono*-nqs complex and hqs. Examination of molecular models suggests that two hqs units can be accommodated by *mono*-nqs complex to form mixed-ligand complexes, and either the facial or the meridional configuration with respect to the co-ordinated donor atoms is possible. The mixed-ligand complex may be present preferentially in either of these two geometrical isomers, but it was not possible to assign a structure experimentally due to the lability of the complex in solution.

The present kinetic results indicate that the rate-determining step for the formation of the *tris*-hqs complex concerns the co-ordination of the first hqs ligand to the aluminium(III) ion and that of the mixed-ligand complex is likewise involves the co-ordination of the first hqs ligand to the *mono*-nqs complex. This means that in the formation of the *tris*-bidentate complex the rate is slowest in the coordination of the first ligand and fastest in that of the third ligand. Hence it may be argued that the co-ordinated water molecules around the metal ion are increasingly labilized by substitutional introduction of the ligands in the primary co-ordination sphere.

Comparison of the kinetic data concerning the reactions of $[Al(H_2O)_6]^{3+}$ with nqs^{3-} (k_{33}) and of $[Al(OH)(H_2O)_5]^{2+}$ with Hqs^{2-} (k_{22}) with those of $[Al(H_2O)_6]^{3+}$ with hqs^{2-} (k_{32}) and of $[Al(OH)(H_2O)_5]^{2+}$ with $Hhqs^-$ (k_{21}) indicates that both nqs and hqs behave kinetically in a similar manner and that the co-ordination mechanism can be discussed in terms of the quinolinol group. There are two possible ways for the order of the donor atoms, *N* and *O*, in the co-ordination of the quinolinol group in the fully deprotonated state to the aluminium(III) ion. The present results (Table III) show that the rates concerning the fully deprotonated ligand species are substantially faster than those concerning the singly protonated ligand species. Furthermore, the aluminium(III) ion generally forms more stable bonds with oxygen donor atoms than with nitrogen donor atoms. It may be inferred that the oxygen atom of the deprotonated ligand co-ordinates substitutionally for the water molecule at the metal ion as a uni-dentate ligand, and that this process will be the rate-determining step. The nitrogen atom may then co-ordinate to the metal atom to complete the five-membered chelate ring. For the quino-

TABLE III
Kinetic constants for aluminium(III) complex formation

Reaction*	Kinetic constant†/$dm^3 mol^{-1} s^{-1}$		Remarks‡	Reference
$Al^{3+} + nqs^{3-}(k_{33})$ and $AlOH^{2+} + Hnqs^{2-}(k_{22})$	$k_{33} + k_{22} K_{a1(nqs)} K_{OH}$	: $(19.8 \pm 0.6) \times 10^5$		2
$AlOH^{2+} + nqs^{3-}(k_{23})$	k_{23}	: $(1.2 \pm 0.7) \times 10^5$	$\Delta G^{\ddagger}_{23}$: 44 ± 1	2
$Alnqs + Hhqs^{-}(k_{01})$	k_{01}	: $(9.10 \pm 0.30) \times 10^1$	$\Delta G^{\ddagger}_{01}$: 61.8 ± 0.1	present work
$Alnqs + hqs^{2-}(k_{02})$	k_{02}	: $(1.75 \pm 0.30) \times 10^5$	$\Delta G^{\ddagger}_{02}$: 43.1 ± 0.4	present work
$Al^{3+} + Hhqs^{-}(k_{31})$ and $AlOH^{2+} + H_2hqs\ (k_{20})$	$k_{31} + k_{20} K_{a2(hqs)} K_{OH}$	: $(18.5 \pm 0.6) \times 10^3$		present work
$Al^{3+} + hqs^{2-}(k_{32})$ and $AlOH^{2+} + Hhqs^{-}(k_{21})$	$k_{32} + k_{21} K_{a1(hqs)} K_{OH}$	: $(6.9 \pm 0.6) \times 10^6$		present work

*The following abbreviations were used: $Al^{3+} \equiv [Al(H_2O)_6]^{3+}$, $AlOH^{2+} \equiv [Al(OH)(H_2O)_5]^{2+}$, and $Alnqs \equiv [Al(nqs)(H_2O)_4]$. †The data are for 0.1 mol dm^{-3} aqueous sodium chloride solution at 25°. ‡$\Delta G^{\ddagger}_{ij}$ for the condition specified †was calculated by the relation, $-\Delta G^{\ddagger}_{ij} = RT(\ln k_{ij} - \ln kT/h)$, where R is the gas constant, T the temperature, k the Boltzmann constant, and h the Planck constant, respectively; unit : kJ mol^{-1}.

linol group in the singly protonated state, the nitrogen atom may donate first because the phenolic oxygen atom is protonated. This may be followed by the interaction of the phenolic oxygen atom with the central metal atom to form the chelate ring with the loss of a proton.

Mechanistically, the co-ordination proceeds by an associative (or associative interchange) or a dissociative (or dissociative interchange) mechanism, or more specifically, the Eigen-Tamm dissociative, stepwise co-ordination mechanism,[13] to which the reaction of aluminium(III) ion with sulfate,[14] salicylate,[15] 5-sulfosalicylate,[16] formate,[17] semi-sylenol orange and semi-methyl-thymol blue[18] belong. If the co-ordination of the quinolinol group proceeds by the dissociative, stepwise co-ordination mechanism,[13] then the observed rate constant (k_f), which is defined as the product of the outer-sphere association constant (K_{os}) and the dissociation rate constant of the co-ordinated water molecule (k_{-H_2O}), should vary with K_{os} and should be little influenced by the nature of the entering ligands. Our tentative estimation of k_{-H_2O} from K_{os} calculated by the Fuoss equation[19-22] with the assumption of the distance of closest approach of the metal cation and the anionic ligand species to be about 5×10^{-10} m, a dielectric constant for the solvent medium of 78.3, the ionic strength (μ) of the solution being 0.1 mol dm^{-3}, the temperature at 298 K, and from our kinetic data (k_f) in Table III, gave values of k_{-H_2O} several orders of magnitudes higher than those from the kinetic constants (k_f) cited above[14-18] and those measured directly as the exchange rate constant for the co-ordinated water molecule with bulk solvent molecules.[11,23] Of course some of the assumptions involved in the estimation of k_{-H_2O} given here may be invalid and it may be necessary to take into account thermo dynamic properties related to the activated state in order to deduce the reaction mechanism conclusively. Nevertheless, it should be pointed out that the complex formation behaviour of the aluminium(III) ion can not always be satisfactorily explained simply by a mechanism in which the dissociation of the water molecule from the primary co-ordination sphere of the metal ion is the ultimate rate-determining step.

REFERENCES AND NOTES

1. In this paper, abbreviations of nqs and hqs were used to mean the ligands 8-hydroxy-7-[6'-sulfo-2'-naphthyl)azo]quinoline-5-sulfonic acid (H_3nqs) and 8-quinolinol-5-sulfonic acid (H_2hqs), respectively, and those of H_2nqs$^-$, Hnqs^{2-}, ngs^{3-}, Hhqs$^-$, and hqs^{2-} were used to indicate individual chemical species of the ligands concerned.
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7. Aluminium(III) forms in slightly acidic to neutral aqueous solution the mononuclear hydroxo-species $[Al(OH)(H_2O)_5]^{2+}$, which reacts with a decrease of acidity to yield such polynuclear hydroxo species as $Al_2(OH)_2{}^{4+}$, $Al_3(OH)_5{}^{4+}$, etc.[24] (co-ordinated water molecules are omitted for simplicity). Our tentative calculation of fractions of dimers and trimers using reported hydrolysis constant data[24] in the pH range of 3.5 – 4.5 with a total aluminium(III) concentration of about 10^{-5} mol dm^{-3} showed their presence to be negligible compared with $[Al(H_2O)_6]^{3+}$ and $[Al(OH)(H_2O)_5]^{2+}$. Hence polynuclear hydroxo-species were not taken into consideration.
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12. Based on the fact that stepwise formation constants decrease with increasing numbers of co-ordinated ligands, some peculiarities may be noticed when $\beta_{11,1}$ and $\beta_{11,2}$ are compared with β_{101} and β_{102}. The former two are related to co-ordination of hqs to $[Al(hqs)(H_2O)_4]$, and the latter two to $[Al(H_2O)_6]^{3+}$, respectively. By taking donor abilities of the *N* and *O* atoms towards aluminium(III) into consideration, these apparent peculiarities may be explained in terms of electron densities on the central metal atom with different numbers of *N* and *O* donor atoms.
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APPENDIX

Like to the mixed-ligand complex case, the following relations can be derived for the formation of the *tris*-hqs complex with respect to total aluminium(III) and hqs concentrations, C''_{a1} and C''_{hqs}, and absorbance of a solution containing both aluminium (III) and hqs and of one containing hqs alone at the same $[H^+]$, A'' and A''_{min}, respectively.

$$\begin{aligned} C''_{a1} = {} & [[Al(H_2O)_6]^{3+}] + [[Al(OH)(H_2O)_5]^{2+}] + [[Al(hqs)(H_2O)_4]^+] \\ & + [[Al(hqs)_2(H_2O)_2]^-] + [[Al(hqs)_3]^{3-}] \end{aligned} \tag{A1}$$

$$\begin{aligned} C''_{hqs} = {} & [H_2hqs] + [Hhqs^-] + [hqs^{2-}] + [[Al(hqs)(H_2O)_4]^+] \\ & + 2[[Al(hqs)_2(H_2O)_2]^-] + 3\,[[Al(hqs)_3]^{3-}] \end{aligned} \tag{A2}$$

$$\begin{aligned} A'' = {} & \epsilon_{2Hhqs}[H_2hqs] + \epsilon_{Hhqs}[Hhqs^-] + \epsilon_{101}\,[[Al(hqs)(H_2O)_4]^+] \\ & + \epsilon_{102}\,[[Al(hqs)_2(H_2O)_2]^-] + \epsilon_{103}\,[[Al(hqs)_3]^{3-}] \end{aligned} \tag{A3}$$

$$A''_{min} = \{(\epsilon_{Hhqs} + \epsilon_{2Hhqs}k_{a2(hqs)}[H^+])/(1 + k_{a2(hqs)}[H^+])\}\,C''_{hqs} \tag{A4}$$

where ϵ_{101} and ϵ_{102} stand for the molar absorption coefficients of the *mono*- and *bis*-hqs complexes, respectively.

It would be appropriate to assume for such non-transition metal complexes of aluminium(III), where chromophoric characteristics concern solely the co-ordinated ligand side, that the molar absorption coefficient of the *bis*-hqs complex is approximately twice as large as that of the *mono*-hqs complex, $\epsilon_{102} \cong 2\epsilon(\epsilon \equiv \epsilon_{101})$, and that that of the *tris*-hqs complex is three times as large as that of the *mono*-hqs complex, $\epsilon_{103} \cong 3\epsilon$. Hence the following relation can be derived from (*A1*) - (*A4*).

$$\begin{aligned} F = {} & 3 - \{[3(1 + K_{OH}/[H^+]) + 2\beta_{101}[hqs^{2-}] + \beta_{102}[hqs^{2-}]^2\}/\{(1 + K_{OH}/[H^+]) \\ & + \beta_{101}[hqs^{2-}] + \beta_{102}[hqs^{2-}]^2 + \beta_{103}[hqs^{2-}]^3\} \\ F \equiv {} & (A'' - A''_{min})/[(\epsilon - A''_{min}/C''_{hqs})\,C''_{a1}] \end{aligned} \tag{A5, 25}$$

In (*A5*), ϵ can be calculated from the ϵ_{103} determined experimentally for the *tris*-hqs complex and $[\mathrm{hqs}^{2-}]$ from eq. (*A6*) which was in turn derived from (*A2*) - (*A4*).

$$
\begin{aligned}
[\mathrm{hqs}^{2-}] &= (C''_{\mathrm{hqs}}(A'' - \epsilon C''_{\mathrm{hqs}}))/(k_{a1(\mathrm{hqs})}[H^+]\,(1 + k_{a2(\mathrm{hqs})}[H^+])\\
&\quad \times (A''_{\mathrm{min}} - \epsilon C''_{\mathrm{hqs}}))
\end{aligned}
\tag{A6}
$$