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SELECTIVITY IN COORDINATION OF 7-SUBSTITUTED-8-HYDROXY-5-QUINOLINESULPHONATES TO ALUMINIUM(III)

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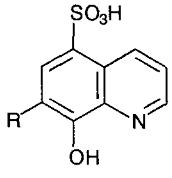
Abstract—Coordination reaction kinetics and mechanisms of 7-substituted-8-hydroxy-5-quinolinesulphonic acid ligands that have ligating substituents of nitrogen whose nature is different from that at the 1-position, i.e. 7-amino-8-hydroxy-5-quinolinesulphonic acid (**1**, H_2ahqs) and 7-phenylazo-8-hydroxy-5-quinolinesulphonic acid (**2**, H_2phqs), have been investigated spectrophotometrically in an aqueous sodium nitrate solution of constant ionic strength (0.10 mol dm^{-3}) at 25.0°C. These ligands selectively coordinate to aluminium(III) with its 8-quinolinolato moiety through pyridyl nitrogen and phenolato oxygen to form yellow and red complexes, indicating that the donor ability is higher for the aromatic than for the amino and azo nitrogens towards aluminium(III). The complex formation reaction proceeds through two parallel pathways of Al^{3+} with $Hahqs^-$ and $Hphqs^-$ and of $Al(OH)^{2+}$ with H_2ahqs and H_2phqs, the coordination of the phenolato oxygen to the central metal atom being the mechanistic rate-determining step. The role of substituent groups at the 7-position of the 8-quinolinolate framework on its coordinating nature as a bidentate ligand towards the central metal atom is emphasized.

Much attention has been paid to the selectivity in coordination of 7-substituted-8-hydroxy-5-quinolinesulphonic acids, a type of multidentate ligand having donor groups as a substituent.[1] As for their coordination behaviour to aluminium(III), it was found that the nature of the donor atoms adjacent to the phenolato oxygen, together with the size and number of chelate rings, play an important role in this selectivity. In order to obtain more generalized information on the selectivity related to aluminium(III), two ligands with amino and phenylazo groups at the 7-position of the 8-quinolinolato framework, i.e. 7-amino-8-hydroxy-5-quinolinesulphonic acid (**1**, H_2ahqs) and 7-phenylazo-8-hydroxy-5-quinolinesulphonic acid (**2**, H_2phqs), were synthesized with a view to changing the basicity of phenolate oxygen and to introducing nitrogen donor atoms of different nature at the 7-position that are in competition with the pyridyl nitrogen at the 1-position.



1 (H_2ahqs), R = NH_2
2 (H_2phqs), R = $N{=}N{-}C_6H_5$
3 (H_2hqs), R = H

Scheme 1.

The present paper is concerned with the selectivity in coordination and reaction kinetics and mechanisms of these multidentate ligands to aluminium(III).

EXPERIMENTAL

Materials

The ligand **2** was synthesized by the diazotization of aniline ($C_6H_5NH_2$) with sodium nitrite in an

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aqueous hydrochloric acid solution, followed by the coupling of the diazonium salt to 8-hydroxy-5-quinolinesulphonic acid [$C_9H_5N(OH)(SO_3H)$, **3**, H_2hqs] in an aqueous sodium hydroxide solution at pH 10–12. The crude ligand was purified by recrystallization from aqueous solution at pH 2–3. Found: C, 51.0; H, 3.0; N, 11.7. Calc. for $C_{15}H_{10}N_3O_4SNa$: C, 51.3; H, 2.9; N, 12.0%.

The ligand **1** was prepared by the reduction of **2** with sodium hydrosulphite at pH 9–10 under N_2 to produce aniline and **1**, the latter being precipitated as a hydrochloride salt at pH 1–2. The crude product was purified in the form of the same salt from an acidified aqueous solution. Found: C, 36.2; H, 3.1; N, 9.3. Calc. for $C_9H_7N_2O_4SNa \cdot HCl$: C, 36.2; H, 2.7; N, 9.4%.

An aqueous solution of aluminium (III) was prepared as described elsewhere.[2] All other reagents were of analytical or equivalent grade.

Measurements

Electronic absorption spectra were recorded on the spectrophotometer specified in a previous paper.[1i] The apparatus used previously[1i] was also used for the stopped-flow kinetic spectrophotometric measurements.

Other instruments and the general procedures for the determination of protonation, stability and observed rate constants have been presented in a previous paper.[1i] Wavelengths used for the determination of protonation constants (see below) were 435 nm for $K_{a(phOH)}$, 420 nm for $K_{a(pyNH)}$ and 310 nm for $K_{a(amNH)}$ of **1**, and 510 nm for $K_{a(phOH)}$ and $K_{a(pyNH)}$ of **2** and those for the formation of the aluminium(III) complexes were 420 nm for **1** and 510 nm for **2**, respectively. These constants were determined at a temperature of 25.0±0.1°C and a constant ionic strength of 0.10 mol dm^{-3} sodium nitrate.

The hydrogen ion concentration, [H^+], was determined potentiometrically in the usual manner.[1g] The pH meter used for the potentiometric measurements, a Corning pH Meter, model 130, was calibrated by using the standard buffer solutions of pH 4.01 (phthalic acid–potassium hydrogen phthalate) and 6.86 (potassium dihydrogen phosphate–disodium hydrogen phosphate) at 25.0°C and was corrected for a solution containing 0.0100 mol dm^{-3} HNO_3 and 0.0900 mol dm^{-3} $NaNO_3$ to be $-\log [H^+] \equiv 2.00$.[1d]

Buffer solutions of acetic acid–sodium acetate, chloroacetic acid–sodium chloroacetate and sodium borate (or hydroxide)–disodium hydrogen phosphate (for the determination of $K_{a(phOH)}$) were used when necessary at a final concentration of less than 0.01 mol dm^{-3}.

RESULTS AND DISCUSSION

Selectivity in coordination

Preliminary study indicated that the aluminium (III)–**1** system showed a single sigmoidal curve on the absorbance vs. pH diagram from *ca* pH 2.6 upwards and ending at *ca* pH 4.0, and that no formation of the complex was noted around the pH corresponding to the protonation constants of the amino nitrogen donor atom ($K_{a(amNH)}$). A similar relationship was obtained in the aluminium(III)–**2** system. These results indicate that the aluminium(III) complexes of **1** and **2** have the same coordination mode. It has been found in studies on aluminium(III)–7-[(6-sulpho-2-naphthyl)azo]-8-hydroxy-5-quinolinesulphonic acid (H_3nqs)[1a] that the azo nitrogen has weaker donor ability to aluminium(III) than the pyridyl nitrogen. On this basis, the ligand **2** can be deduced to coordinate selectively to aluminium(III) with its 8-quinolinolato moiety, and this also holds for the ligand **1** by taking the similarity of the absorbance vs. pH relationship stated above of these two systems into consideration. This coordination–structural assignment is supported by the fact that the coordination of the ligand **3** to aluminium(III) proceeds in the pH region of 3.5–4.5, which is in close proximity to the coordination behaviour of **1** and **2**.

The absorption spectra of the aluminium(III) complexes of **1** and **2** that possess the 8-quinolinolato coordination mode are depicted in Fig. 1, together with those of the free ligand species.

The coordination of **1** to aluminium(III) causes a bathochromic shift of the $\pi^* \leftarrow \pi$ transition of the quinoline chromophore[2] from 24.0×10^3 cm^{-1} to 23.0×10^3 cm^{-1} as a most prominent spectral feature. On the contrary, the coordination of **2** to aluminium(III) causes a hypsochromic shift of the $\pi^* \leftarrow \pi$ transition of the azo group coupled to the quinoline and benzene rings from 20.0×10^3 cm^{-1}, with a shoulder around 19×10^3, to 25.0×10^3 cm^{-1}, with a shoulder around 19×10^3 cm^{-1}, which are the same spectral absorption characteristics of the aluminium(III) complex of H_3nqs.[1a] These spectral shifts of the intraligand charge-transfer transition caused by the substitution of aluminium(III) for proton(s) were applied to the investigation on formation equilibrium and kinetics of the aluminium(III)–**1** and aluminium(III)–**2** systems.

Formation and stability

The protonation constants of **1** and **2** were determined spectrophotometrically, according to a

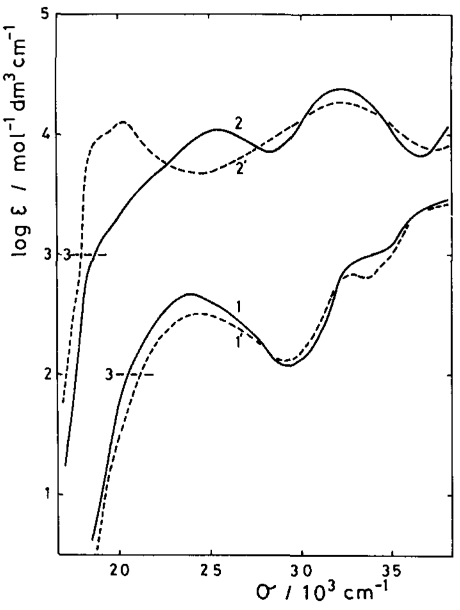

Fig. 1. Absorption spectra of the aluminium(III) complexes of **1** and **2**. (1) $Al(ahqs)^+$ (pH 4.15); (1′) H_2ahqs (pH 4.15); (2) $Al(phqs)^+$ (pH 3.50); (2′) $Hphqs^-$ (pH 3.50). Curves 1 and 1′ are shifted downward along the log ε axis by a unit merely for clarity.

literature procedure.[1g] The values of $K_{a(phOH)}$ and $K_{a(pyNH)}$, corresponding to the protonation constants of the phenolate oxygen and pyridyl nitrogen atoms of **1** and **2**, were determined from the experimental absorbance vs. hydrogen ion concentration plots by their assignment based on comparison with those of **3** and H_3nqs.[1a] A special precaution was taken for the determination of $K_{a(phOH)}$ of **1**, because it was easily oxidized in alkaline aqueous solution; this oxidation could be suppressed in aqueous ethanol (50 vol.%) solution to record reliable plots below pH 8.7, from which $K_{a(phOH)}$ was estimated by a best fit to the theoretical curve. The value of $K_{a(amNH)}$, corresponding to the protonation constant for the amino nitrogen of **1**, was determined in the same way as that of $K_{a(pyNH)}$ of **1**. The protonation constant of the azo nitrogen was estimated to be less than unity in terms of its logarithmic value, because no spectral change other than that due to $K_{a(pyNH)}$ with the hydrogen ion concentration was perceived down to pH 1. The estimated values of the protonation constants are compiled in Table 1.

The stability constants of the mono(ligand) aluminium(III) complexes of **1** and **2**, β_{11}, were determined spectrophotometrically under the conditions of $C_M \gg C_L$, where C_M and C_L represent the total concentrations of metal ion and ligand, respectively, according to a procedure described earlier:[1i]

$$\beta_{11} = [AlL^+]/[Al^{3+}][L^{2-}] \quad (L = \text{ahqs or phqs}) \qquad (1)$$

$$\begin{aligned} \log(A_{max} - A)/(A - A_{min}) &= \log[H^+]^2(K_{a(amNH)}[H^+] + 1 \\ &\quad + 1/K_{a(pyNH)}[H^+])(1 + K_{OH}/[H^+]) \\ &\quad - \log \beta_{11} C_M/K_{a(phOH)}K_{a(pyNH)} \quad (L = \text{ahqs}) \\ &= \log[H^+](K_{a(pyNH)}[H^+] + 1)(1 + K_{OH}/[H^+]) \\ &\quad - \log \beta_{11} C_M/K_{a(phOH)} \quad (L = \text{phqs}) \qquad (2) \end{aligned}$$

because the metal ion species of Al^{3+} and $Al(OH)^{2+}$ $\{K_{OH} = [Al(OH)^{2+}][H^+]/[Al^{3+}]$, $\log K_{OH} = -4.49$ (dilute $AlCl_3$ solution, 25°C)[3]$\}$ and the ligand species of H_3ahqs^+, H_2ahqs and $Hahqs^-$ for **1**, and those of H_2phqs and $Hphqs^-$ for **2**, are expected to participate in the complex formation equilibria in the acidity region of pH 2–5. Here, A_{max}, A and A_{min} represent the absorbances of solutions in which the aluminium(III) complex forms quantitatively, forms in fraction at $[H^+]$ and dissociates completely, respectively.

Experimental plots of the absorbance term against the hydrogen ion concentration term in eq. (1) are depicted in Fig. 2, which indicates that there exist linear relationships between these terms with a slope of unity. The values of β_{11} thus calculated from the intercept are summarized in Table 1 for the aluminium(III) complexes of **1** and **2**, together with those of concern to our further discussion.

It is evident from Table 1 that $\log \beta_{11}$ of the aluminium(III) complex with the 8-quinolinolato ligating mode is nearly proportional to $\log K_{a(phOH)}K_{a(pyNH)}$ of the coordinating ligands (*cf.* Fig. 3). This means that the effect of substituent groups at the 7-position of the quinolinolato framework on the Gibbs free energy of formation (ΔG°) of the aluminium(III) complex is ascribable to their effect on the basicity of the phenolate oxygen and pyridyl nitrogen donor atoms on the ligand. Hence, we can draw a general conclusion that the thermodynamic stability of the aluminium(III) complex with the 8-quinolinolate ligand can be modified by simply changing the basicity of the substituent group at the 7-position of the framework.

Kinetics and mechanism

The determination of k_{obs} of the aluminium(III)–**1** and aluminium(III)–**2** systems under the pseudo-first-order kinetic conditions as a function of C_L in the range of C_L/C_M molar ratio of 10–30 revealed a linear relationship between them with its extrapolation to the origin in a wide acidity region.

Table 1. Protonation and stability constants

Ligand	log $K_{a(phOH)}$ ($mol^{-1}\ dm^3$)	log $K_{a(pyNH)}$ ($mol^{-1}\ dm^3$)	log $K_{a(amNH)}$ ($mol^{-1}\ dm^3$)	Ref.
1 (H_2ahqs)	8.50 ± 0.50^a	4.85 ± 0.10	2.43 ± 0.10	This work
2 (H_2phqs)	7.36 ± 0.10	3.02 ± 0.10	—	This work
3 (H_2hqs)^b	8.97 ± 0.10	4.06 ± 0.11	—	2
H_3nqs^c	7.62 ± 0.05	3.00 ± 0.08	—	1a
H_3cqs^d	7.40 ± 0.08	2.43 ± 0.05	—	1d
H_3ceahqs^e	9.62 ± 0.10	6.23 ± 0.10	3.42 ± 0.10	1i
H_3cmahqs^e	9.45 ± 0.10	6.56 ± 0.10	3.48 ± 0.10	1i

Complex	log β_{11} ($mol^{-1}\ dm^3$)	Ref.
Al(ahqs)$^+$	8.52 ± 0.20	This work
Al(phqs)$^+$	7.53 ± 0.20	This work
Al(hqs)$^{+b}$	9.24 ± 0.14	2
Al(nqs)^c	7.88 ± 0.18	1a
Al(cqs)^d	7.49 ± 0.10	1d
Al(ceahqs-N,O)^e	11.88 ± 0.20	1i
Al(cmahqs-N,O)^e	11.23 ± 0.20	1i

0.10 mol dm^{-3} ($NaNO_3$); 25.0°C.

[a] 50 vol.% aqueous ethanol (*cf.* text).

[b] 0.1 mol dm^{-3} (NaCl); 25°C.

[c] 0.1 mol dm^{-3} (NaCl); 25°C. H_3nqs: 7-[6-sulpho-2-naphthyl)azo]-8-hydroxy-5-quinolinesulphonic acid.

[d] 0.10 mol dm^{-3} ($NaClO_4$); 22°C. H_3cqs: 7-[(4-carboxyphenyl)azo]-8-hydroxy-5-quinolinesulphonic acid.

[e] 0.10 mol dm^{-3}; 25.0°C. H_3ceahqs: 7-(2-carboxyethyl)amino-8-hydroxy-5-quinolinesulphonic acid. H_3cmahqs: 7-(c-carboxymethyl)amino-8-hydroxy-5-quinolinesulphonic acid.

Furthermore, a single exponential curve was obtained for both of the systems for more than 3.5 half-life periods. Accordingly, it can be concluded that the formation of the mono(ligand)aluminium (III) complex species determines the reaction rate for these two complex formation systems.

The rate equation for the formation of the aluminium(III) complexes of **1** and **2** were derived in the same way as has been described in a previous paper[1i] as follows:

$$k'_{obs} \equiv k_{obs}\{(K_{a(pyNH)}[H^+] + 1)[H^+]\}(1 + K_{OH}/[H^+])C_L^{-1}$$

$$k'_{obs} = k_{32}K_{a(pyNH)}[H^+]^2 + (k_{31} + k_{22}K_{a(pyNH)}K_{OH})[H^+] + k_{21}K_{OH}. \qquad (3)$$

Here, k_{ij} ($i = 2$ and 3; $j = 1$ and 2) is the rate constant for the formation of the complex through the pathway of $Al(OH)_{3-i}^{i+}$ and $H_jL^{(2-j)-}$ (L = ahqs and phqs). Equation (2) was derived under the conditions that in the acidity range of pH 3.5–4.9 the metal ion and ligand species are present in the forms of Al^{3+} and $Al(OH)^{2+}$ and of H_2L and HL^-, respectively, and that the protonation/deprotonation processes are much faster than the coordination reaction process.[1i]

Experimental data are plotted in Fig. 4, from which it is evident that a linear relation exists between k'_{obs} and $[H^+]$ for the complex with **2** as well as that with **1**. Hence, it is concluded that the reaction pathways of Al^{3+} with HL^- (k_{31}) and $Al(OH)^{2+}$ with H_2L (k_{22}), for which a proton ambiguity is noticed (see below), and of $Al(OH)^{2+}$ with HL^- (k_{21}) are actually for the formation of these complexes. The rate constants thus obtained are compiled in Table 2, together with others of relevance.

It has been accepted from the coordinated solvent molecule exchange kinetics[4] that aluminium(III) has a dissociative interchange (I_d) or dissociative (D) mechanism. However, we have already suggested[2] that an associative interchange (I_a) mech-

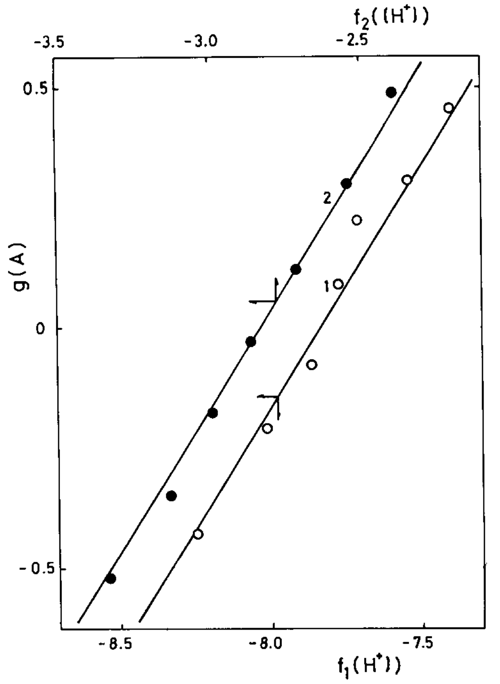

Fig. 2. Relation between the absorbance term and the hydrogen ion concentration term of the aluminium (III)–**1** and aluminium(III)–**2** systems. (1) Al(ahqs)$^+$, $C_{\rm M} = 1.00 \times 10^{-3}$ mol dm^{-3}, $C_{\rm L} = 1.00 \times 10^{-4}$ mol dm^{-3}; (2) Al(phqs)$^+$, $C_{\rm M} = 1.00 \times 10^{-3}$ mol dm^{-3}, $C_{\rm L} = 1.00 \times 10^{-4}$ mol dm^{-3}. $f_1([{\rm H}^+]) \equiv \log [{\rm H}^+]^2(K_{\rm a(amNH)}[{\rm H}^+] + 1 + 1/K_{\rm a(pyNH)}[{\rm H}^+])(1 + K_{\rm OH}/[{\rm H}^+])$. $f_2([{\rm H}^+]) \equiv \log [{\rm H}^+](K_{\rm a(pyNH)}[{\rm H}^+] + 1)(1 + K_{\rm OH}/[{\rm H}^+])$. $g(A) = \log (A_{\rm max} - A)/(A - A_{\rm min})$. Wavelengths: (1) 420 nm; (2) 510 nm. Ionic strength: 0.10 mol dm^{-1} (NaNO$_3$); 25.0°C.

anism may be valid in the case of coordination with multidentate ligands. Inspection of the kinetic parameters given in Table 2 implies that, as far as the pathways of Al(OH)$^{2+}$ with monoprotonated ligand species that can be directly compared with one another are concerned, there is a distinct dependence of the rate constant (k_{21}) on the nature of the entering multidentate ligands (*cf.* k_{21} of **1**, **2**, **3** and others in Table 2), supporting the validity of our previous findings.

Proton ambiguity is found for the reaction pathways of Al^{3+} and HL$^-$ (k_{31}) and of Al(OH)$^{2+}$ and H$_2$L (k_{22}). A tentative estimation of the maximum allowable magnitude of k_{22} with temporal neglect of k_{31} afforded us to estimate its magnitude: (0.34–5.0) × 10^3 mol^{-1} dm^3 s^{-1} for the aluminium(III) complexes of **1**, **2** and **3**, which is reasonable for an intrinsic kinetic characteristic of aluminium(III). Likewise, the same numerical treatment for k_{31} with temporal neglect of k_{22} allowed us to estimate a magnitude ranging from 10^1 to 10^3 mol^{-1} dm^3 s^{-1},

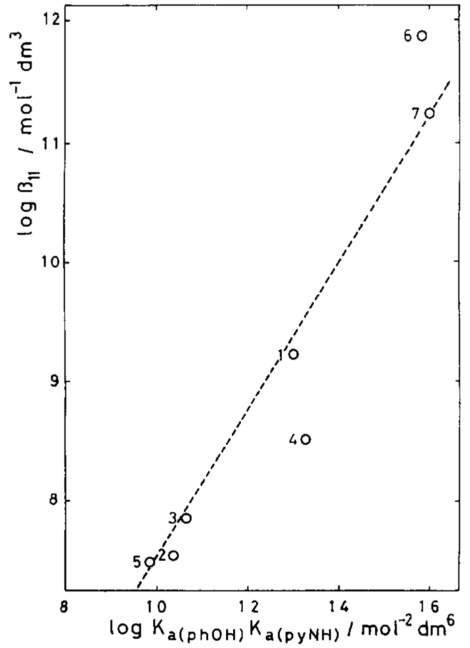

Fig. 3. Effect of ligand basicity ($\log K_{\rm a(phOH)}K_{\rm a(pyNH)}$) on the stability constant ($\log \beta_{11}$) of the mono (ligand)aluminium(III) complexes with N—O coordination mode. (1) Al(hqs)$^+$; (2) Al(phqs)$^+$; (3) Al(nqs); (4) Al(ahqs)$^+$; (5) Al(cqs); (6) Al(ceahqs-N,O); (7) Al(cmahqs-N,O).

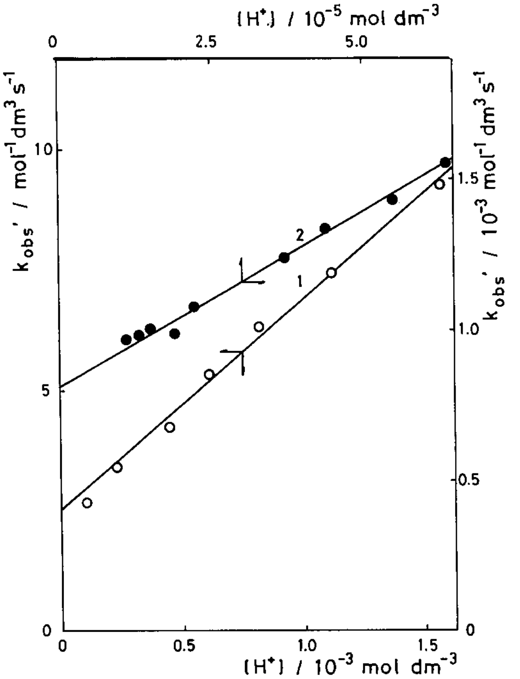

Fig. 4. Dependence of $k'_{\rm obs}$ on [H$^+$] for the aluminium(III)–**1** and aluminium(III)–**2** systems. (1) Al(ahqs)$^+$, $C_{\rm L} = 2.00 \times 10^{-4}$ mol dm^{-3}, $C_{\rm M} = 2.00 \times 10^{-5}$ mol dm^{-3}; (2) Al(phqs)$^+$, $C_{\rm L} = 2.00 \times 10^{-4}$ mol dm^{-3}, $C_{\rm M} = 2.00 \times 10^{-5}$ mol dm^{-3}. $k'_{\rm obs} \equiv k_{\rm obs} \{(K_{\rm a(pyNH)}[{\rm H}^+] + 1)[{\rm H}^+]\}(1 + K_{\rm OH}/[{\rm H}^+])\ C_L^{-1}$. Wavelengths: (1) 420 nm; (2) 510 nm. Ionic strength: 0.10 mol dm^{-3} (NaNO$_3$); 25.0°C.

Table 2. Reaction rate constants

Ligand	Pathway	k_{ij} (mol^{-1} dm^3 s^{-1})	Ref.
1 (H_2ahqs)	Al^{3+} + $Hahqs^-$ (k_{31})	$k_{31}+K_{22}k_{a(pyNH)}K_{OH}$:	This work
	and $Al(OH)^{2+}$ + H_2ahqs (k_{22})	$(4.31 \pm 0.20) \times 10^3$	
	$Al(OH)^{2+}$ + $Hahqs^-$ (k_{21})	k_{21}: $(7.81 \pm 0.22) \times 10^4$	
2 (H_2phqs)	Al^{3+} + $Hphqs^-$ (k_{31})	$k_{31}+k_{22}K_{a(pyNH)}K_{OH}$:	This work
	and $Al(OH)^{2+}$ + H_2phqs (k_{22})	$(1.16 \pm 0.20) \times 10$	
	$Al(OH)^{2+}$ + $Hphqs^-$ (k_{21})	k_{21}: $(2.51 \pm 0.20) \times 10$	
3 (H_2hqs)[a]	Al^{3+} + $Hhqs^-$ (k_{31})	$k_{31}+k_{22}K_{a(phNH)}K_{OH}$:	2
	and $Al(OH)^{2+}$ + H_2hqs (k_{22})	$(1.85 \pm 0.06) \times 10^3$	
	$Al(OH)^{2+}$ + $Hhqs^-$ (k_{21})	k_{21}: $(2.3 \pm 0.8) \times 10^2$[a]	
H_4hcqs[b]	$Al(OH)^{2+}$ + $Hhcqs^{3-}$ (k_{21})	k_{21}: $(1.37 \pm 0.35) \times 10^5$	1d
$H_3ceahqs$[c]	Al^{3+} + $Hceahqs^{2-}$ (k_{31})	$k_{31}+k_{22}K_{a(pyNH)}K_{OH}$:	1i
	and $Al(OH)^{2+}$ + $H_2ceahqs^-$ (k_{22})	$(8.92 \pm 0.20) \times 10^3$	
	$Al(OH)^{2+}$ + $Hceahqs^{2-}$ (k_{21})	k_{21}: $(1.26 \pm 0.20) \times 10^4$	
$H_3cmahqs$[c]	Al^{3+} + $Hcmahqs^{2-}$ (k_{31})	$k_{31}+k_{22}K_{a(pyNH)}K_{OH}$:	1i
	and $Al(OH)^{2+}$ + $H_2cmahqs^-$ (k_{22})	$(1.77 \pm 0.20) \times 10^4$	
	$Al(OH)^{2+}$ + $Hcmahqs^{2-}$ (k_{21})	k_{21}: $(9.10 \pm 0.20) \times 10^3$	

0.10 mol dm^{-3} ($NaNO_3$); 25.0°C.

[a] 0.1 mol dm^{-3} (NaCl); 25°C. The value of k_{21} is the probable largest one estimated from the composite rate constants of $k_{30}+k_{21}K_{a(phOH)}K_{OH}$ of $(6.9 \pm 0.6) \times 10^6$ mol^{-1} dm^3 s^{-1} for the reaction pathways of Al^{3+} + hqs^{2-} (k_{30}) and $AlOH^{2+}$ + $Hhqs^-$ (k_{21}) given in Ref. 2.

[b] 0.10 mol dm^{-3} ($NaClO_4$); 22°C. N—O chelation. H_4hcqs: 7-[(2-hydroxy-5-carboxyphenyl)azo]-8-hydroxy-5-quinolinesulphonic acid.

[c] 0.10 mol dm^{-3} ($NaNO_3$); 25.0°C. N—O chelation. $H_3ceahqs$ and $H_3cmahqs$: see Table 1.

which is also reasonable for aluminium(III). These results clearly demonstrate that both pathways make an important contribution to the formation of the aluminium(III) complexes of **1** and **2**.

The close resemblance of k_{31} and k_{22} thus estimated between the ligands **1** and **3** indicates that the reaction mechanism of **1** belongs to the same category as **3** that has been postulated to be a mechanistic rate-determining donation of phenolato oxygen to the central metal atom, followed by rapid chelate ring closure with the donation of pyridyl nitrogen. The small difference of k_{31} of **2** from **1** and **3** may reflect a steric influence of the bulky phenylazo group at the 7-position of the former on the approach of the entering ligand molecule to the central metal atom. Incidentally, the ligand **2** forms the aluminium(III) complex with only a mono (ligand)aluminium(III) type, just as in the case of H_3nqs,[1a] whereas the ligand **1** forms various complex species with the highest one of tris(ligand) aluminium(III) type, as in the case of **3**,[2] according to the study by the method of continuous variations.[5]

In conclusion, the coordination of **1** and **2** to aluminium(III) proceeds through two parallel pathways: Al^{3+} with $Hahqs^-$ and $Hphqs^-$ and $Al(OH)^{2+}$ with H_2ahqs and H_2phqs; both are in proton ambiguity, and a pathway of $Al(OH)^{2+}$ with $Hahqs^-$ and $Hphqs^-$ also exists, with the donation of phenolato oxygen to the central metal atom as a mechanistic rate-determining step. The role of substituent groups at the 7-position on the thermodynamic stability of the complex through their controlling effect of the basicities of donor atoms on the 8-quinolinolate framework is emphasized.

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