Notes

Co-ordination Selectivity in the Reaction of Aluminium(III) with 8-Hydroxy-7-[(6′-sulpho-2′-naphthyl)azo]quinoline-5-sulphonic Acid

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Studies have been made on the co-ordination behaviour of aluminium(III) with 8-hydroxy-7-[(6′-sulpho-2′-naphthyl)azo]quinoline-5-sulphonic acid (H_3L), capable of two different co-ordination modes. The H_3L co-ordinates with aluminium(III) to form a chelate complex $[AlL(H_2O)_4]$ through the donation of its heterocyclic nitrogen and phenolic oxygen atoms with a five-membered chelate ring. The co-ordination mechanism is also presented.

ALUMINIUM(III) forms a wide variety of metal chelate complexes with ligands of oxygen and/or nitrogen donor atoms.[1] A close inspection of the available literature reveals that there have been few systematic studies on the co-ordination reaction of aluminium(III) with multidentate ligands which take more than two different modes of co-ordination, despite its interest in the co-ordination selectivity in metal chelate complex formation.

In the present study, 8-hydroxy-7-[(6′-sulpho-2′-naphthyl)azo]quinoline-5-sulphonic acid (H_3L) was chosen for such a ligand and electronic absorption spectral and spectrophotometric studies were carried out on the co-ordination behaviour of aluminium(III) with H_3L in 0.1 mol dm^{-3} aqueous sodium chloride solution at 25 °C.

EXPERIMENTAL

Reagents.—The ligand H_3L was synthesized according to the procedure by Fritz *et al.*[2] with some modifications and purified by repeated precipitation from dioxane. The ligand 2-[(6′-sulpho-2′-naphthyl)azo]-1-naphthol-4-sulphonic acid (H_3L^1) was newly synthesized for comparison according to the procedure for H_3L, except 1-naphthol-4-sulphonic acid was used instead of 8-hydroxyquinoline-5-sulphonic acid (H_2L^2) as a coupling component. Other chemicals used were of analytical or equivalent grade.

Apparatus.—Spectral and spectrophotometric measurements were carried out with the JASCO spectrophotometers, models UVIDEC-1 and SS-25, to which a stopped-flow attachment (SFC-5) and data processor (DP-500) were attached. Hydrogen ion concentration was measured with a Horiba pH meter, model F7-SS, and calculated according to the relation: $\log[H^+] = pH_{meas.} + \log f_{H^+}$, where f_{H^+} is the activity coefficient of the hydrogen ion in 0.1 mol dm^{-3} aqueous sodium chloride solution at 25 °C [the value of 0.83 (ref. 3) was used for the conversion]. All measurements were carried out in sodium chloride solution of constant ionic strength of 0.1 mol dm^{-3}.

RESULTS AND DISCUSSION

Figure 1 depicts the absorption spectra of H_3L and its aluminium(III) complex together with those of H_2L^2 and its aluminium(III) complex for comparison; from which it can be deduced that the hydroxyquinoline moiety in H_3L co-ordinates selectively to aluminium(III).

The protonation constants K_{a1} and K_{a2} of H_3L can be expressed by equations (1) and (2), where (1) corresponds to protonation at the phenolic oxygen site and (2) to that at the heterocyclic nitrogen site.

$$K_{a1} = [HL^{2-}]/[H^+][L^{3-}] \quad (1)$$

$$K_{a2} = [H_2L^-]/[H^+][HL^{2-}] \quad (2)$$

The values $\log K_{a1} = 7.62 \pm 0.05$ and $\log K_{a2} = 3.00 \pm 0.08$ were determined spectrophotometrically at 500 nm. The stability constant of the aluminium(III)–H_3L complex was determined again by a spectrophotometric method.[4]

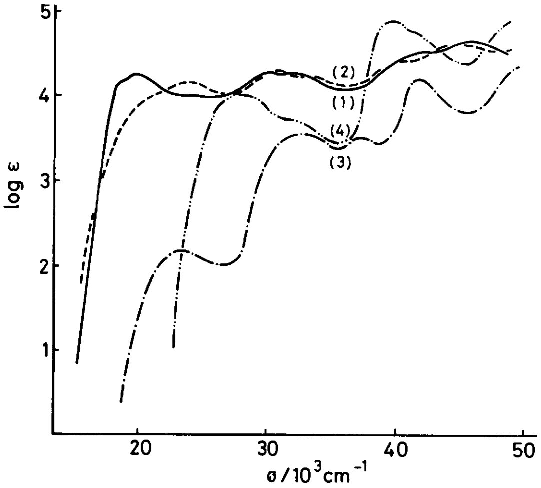

FIGURE 1 Electronic absorption spectra of the ligands and their aluminium(III) complexes: (1) H_3L (pH 4.33); (2) Al^{III}–H_3L complex (pH 4.41); (3) H_2L^2 (pH 7.44); (4) Al^{III}–H_2L^2 complex (pH 7.43). No spectral changes were observed for H_3L^1 with the aluminium(III) ion

By taking the protonation constants, K_{a1} and K_{a2}, of H_3L and the hydrolysis constant, K_{OH}, of aluminium(III) expressed in equation (3) into consideration, the complex

$$K_{OH} = [Al(OH)(H_2O)_5{}^{2+}][H^+]/[Al(H_2O)_6{}^{3+}] = 3.25 \times 10^{-5} \text{ mol dm}^{-3} \text{ (ref. 5)} \quad (3)$$

formation equilibrium in slightly acidic media (pH 3—5) can be expressed by equation (4). If the total concentrations of aluminium(III) and H_3L are c_M and c_L respectively and if the equilibrium concentration of the

$$[Al(H_2O)_6]^{3+} + nHL^{2-} \overset{K_{1n}}{\rightleftharpoons} [AlL_n(H_2O)_{6-2n}]^{(3-3n)+} + nH^+ \quad (4)$$

complex is c, then K_{1n} can be approximated to be as in equation (5) under the condition of $c_L \gg c_M$.

$$K_{1n} = [AlL_n(H_2O)_{6-2n}{}^{(3-3n)+}][H^+]^n/[Al(H_2O)_6{}^{3+}][HL^{2-}]^n = c[H^+]^n/(c_M - c)c_L{}^n \quad (5)$$

$$\frac{1}{A_s - A_{lig.}} = \frac{1}{(\varepsilon_{com.} - n\varepsilon_{lig.})c_M} + \frac{[H^+]^n}{(\varepsilon_{com.} - n\varepsilon_{lig.})c_M c_L{}^n K_{1n}} \quad (6)$$

Equation (5) can be rewritten as equation (6), where A_s is the absorbance of the solution containing the complex, the metal ion, and the ligand at the hydrogen ion concentration of $[H^+]$, $\varepsilon_{com.}$ and $\varepsilon_{lig.}$ are the molar absorptivities of the complex and the ligand, and $\varepsilon_{lig.}c_L = A_{lig.}$.

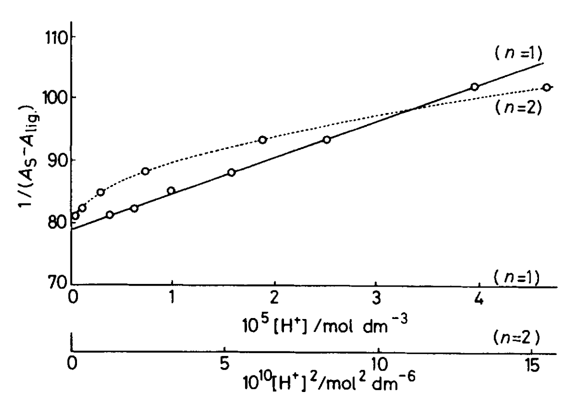

FIGURE 2 Relationship between $1/(A_s - A_{lig.})$ and $[H^+]^n$ for $n = 1$ and 2. Metal ion concentration = 4.00×10^{-6} mol dm^{-3}, ligand concentration = 4.00×10^{-5} mol dm^{-3}, absorbance measurement at 500 nm

Equation (6) indicates that the relation $1/(A_s - A_{lig.})$ *versus* $[H^+]^n$ should be linear for a specified integer value of n, which corresponds to the number of ligand molecules co-ordinated to the central metal ion (K_{1n} can be calculated from the slope and the intercept). Figure 2 shows the experimental results, from which n was determined to be unity, and thereby concluding that the complex $[AlL(H_2O)_4]$ is formed by the co-ordination reaction. This is consistent with a preliminary result by the method of continuous variations, which gave a maximum degree of complex formation at a molar fraction of aluminium(III) of 0.5. The equilibrium constant, K_{11}, was calculated to be 3.40 ± 0.05.

The stability constant of the complex $[AlL(H_2O)_4]$ was then calculated from K_{11} and K_{a1} [equation (7)] to be

$$\beta = [AlL(H_2O)_4]/[Al(H_2O)_6{}^{3+}][L^{3-}] = K_{11}K_{a1} \quad (7)$$

log $\beta = 7.88 \pm 0.18$. The Gibbs free energy change ($-\Delta G^\ominus$) at 25 °C in 0.1 mol dm^{-3} sodium chloride solution was calculated to be 45.0 ± 1.0 kJ mol^{-1}, which is about one third that of the aluminium(III)–H_2L^2 complex formation (141.0 ± 2.0 kJ mol^{-1}).[6] Since the latter has a composition of $[Al(L^2)_3]^{3-}$, it is reasonable to estimate that $-\Delta G^\ominus$ for co-ordination of the hydroxyquinoline moiety is *ca.* 47 kJ mol^{-1} and that the aluminium(III)–H_3L complex has the same co-ordination mode as aluminium(III)–H_2L^2.

The co-ordination mechanism of $[AlL(H_2O)_4]$ was followed by a stopped-flow spectrophotometric method under the pseudo-first-order kinetic condition for ligand concentration. It should be necessary for kinetic consideration to take into account such secondary constituent species as $[Al(OH)(H_2O)_5]^{2+}$ besides $[Al(H_2O)_6]^{3+}$ for the metal ion, and H_2L^- and L^{3-} besides HL^{2-} for the ligand. Consequently, six reaction pathways are anticipated in total for the complex formation reaction as given in equation (8), where k_{ij} is the forward rate constant for the pathway of $[Al(OH)_{3-i}(H_2O)_{3+i}]^{i+}$ (i = 2 and 3) and $H_{3-j}L^{j-}$ (j = 1—3) and k_{-ij} is the backward rate constant corresponding to the pathway of k_{ij}. In this case protolytic reactions for both metal and ligand species were assumed to be always at equilibrium since they are generally very fast compared with the complex formation process.[7] Equation (8) can further be correlated to equations (9)—(11), where c_L is the total ligand concentration maintained sufficiently in excess and constant over the metal ion concentration, and subscript eq. represents the equilibrium state. The forward rate constants k_{ij} can therefore be obtained from the experimental relation of $k_{obs.}'$ as a function of $[H^+]$. The data

$$d[AlL(H_2O)_4]/dt = (k_{31}[H_2L^-] + k_{32}[HL^{2-}] + k_{33}[L^{3-}])[Al(H_2O)_6{}^{3+}] + (k_{21}[H_2L^-] + k_{22}[HL^{2-}] + k_{23}[L^{3-}])[Al(OH)(H_2O)_5{}^{2+}] - \{k_{-31}[H^+]^2 + (k_{-32} + k_{-21})[H^+] + k_{-33} + k_{-22} + k_{-23}[OH^-]\}[AlL(H_2O)_4] \quad (8)$$

$$d[AlL(H_2O)_4]/dt = k_{obs.}\{[AlL(H_2O)_4]_{eq.} - [AlL(H_2O)_4]\} \quad (9)$$

$$k_{obs.} = k_{obs.}'[1/\beta + c_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1) \quad (10)$$

$$k_{obs.}' = k_{31}K_{a1}K_{a2}[H^+]^2 + (k_{32} + k_{21}K_{a2}K_{OH})K_{a1}[H^+] + (k_{33} + k_{22}K_{a1}K_{OH}) + k_{23}K_{OH}[H^+]^{-1} \quad (11)$$

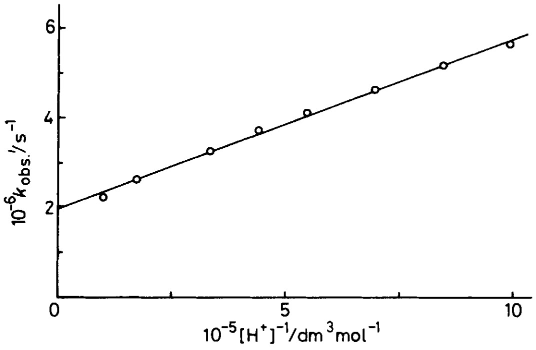

FIGURE 3 Relationship between $k_{obs.}'$ and $[H^+]^{-1}$. Metal ion concentration = 2.00×10^{-6} mol dm^{-3}, ligand concentration = $(4.00—10.00) \times 10^{-5}$ mol dm^{-3}, absorbance measurement at 500 nm, temperature = 25.0 ± 0.1 °C

of $k_{obs.}'$ were calculated from $k_{obs.}$ which had been obtained experimentally from the relation: $\ln A_{eq.}/(A_{eq.} - A) = k_{obs.}t$; where $A_{eq.}$ and A represent absorbances at equilibrium and at any time, t, respectively. Figure 3 shows that $k_{obs.}'$ is proportional only to the $[H^+]^{-1}$ term, from which it can be concluded that the complex formation reaction proceeds *via* reaction of $[Al(H_2O)_6]^{3+}$ with L^{3-} (k_{33}), $[Al(OH)(H_2O)_5]^{2+}$ with HL^{2-} (k_{22}) and with L^{3-} (k_{23}). $[(k_{33} + k_{22}K_{a1}K_{OH}) = (19.80 \pm 0.60) \times 10^{-5}$ dm^3 mol^{-1} s^{-1} and $k_{23} = (1.16 \pm 0.70) \times 10^{-5}$ dm^3 mol^{-1} s^{-1}].

In summary, $[Al(H_2O)_6]^{3+}$ and $[Al(OH)(H_2O)_5]^{2+}$ ions react with HL^{2-} and L^{3-} ligand species to form a complex $[AlL(H_2O)_4]$, with a structure of selective coordination of the hydroxyquinoline moiety and not the azophenol moiety of the ligand H_3L.

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