Kinetics and Equilibrium Studies of the Formation of a Cobalt(II) Complex with *N*-(8-Quinolyl)aminoacetic Acid

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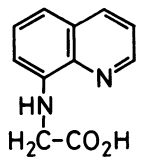
Stopped-flow kinetic and equilibrium studies have been made of the formation of a cobalt(II) complex with *N*-(8-quinolyl)aminoacetic acid in 0.10 mol dm^{-3} aqueous sodium chloride containing 12 vol% ethanol at 25 °C. Octahedral mono- and bis-ligand complexes were formed *via* the two pathways of the reactions of deprotonated and monoprotonated ligand species with the aquacobalt(II) ion. The coordination mechanism is discussed.

It is interesting to study spectrochemically the coordination characteristics of aromatic multidentate ligands to matal ions, which take several kinds of coordination geometry depending on the ligand employed, because the ligating groups are incorporated into the rigid frame of the aromatic ligand and because the electronic absorption spectrum of the ligand reflects its coordination mode. Furthermore, the nature of the ligating groups and the steric restriction due to the planarity of the ligand qualify the coordination behavior and mechanism of the metal ion.



Hqaa

The present study relates to the formation of a cobalt(II) complex with *N*-(8-quinolyl)aminoacetic acid (Hqaa).[1] In order to obtain detailed information on the coordination reaction characteristics, the coordination state of cobalt(II) and the coordination behavior of the ligand were spectrochemically and kinetically investigated. There has been only one paper concerning the ligand based on potentiometry.[2]

Experimental

Reagents. The ligand, QAA,[1] was synthesized by the condensation of chloro- or bromoacetic acid with 8-aminoquinoline in an alkaline medium, with some modifications of the literature procedure.[2] It was obtained as a monohydrochloride salt and was purified by repeated crystallizations from an aqueous solution. Calcd for $C_{11}H_{10}N_2O_2 \cdot HCl$: C, 55.35; H, 4.64; N, 11.73%. Found: C, 55.63; H, 4.59; N, 12.02%.

An aqueous cobalt(II) solution was prepared from analytical grade chloride salt from the Wako Pure Chemicals Ind. Co., Ltd., Osaka, and was acidified slightly with HCl to prevent its hydrolysis. It was then standardized by titration with EDTA. All the other chemicals were of an analytical or equivalent grade and were used without further purification.

Measurements. Electronic absorption spectral measurements were made with JASCO spectrophotometers, models UVIDEC-1 and SS-25, to the latter of which were attached a stopped-flow apparatus, Model SFC-5; a data processor, Model DP-500; and a RIKADENKI X-Y recorder, Model RW-11. The protonation and stability constants were determined spectrophotometrically at 340 nm in the former and at 303.5 nm in the latter in a 0.10 mol dm^{-3} aqueous sodium-chloride solution containing 12 vol% ethanol at 25.0±0.1 °C. Nitrogen gas was passed through the solution before the absorption spectral measurements to avoid any possible oxidation of cobalt(II). Kinetic runs were made at 303.5 nm under a pseudo-first-order kinetic condition with respect to the metal-ion or ligand concentration. The rate constant, k_{obsd}, was calculated from this relation:

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

where A_t and A_{eq} stand for the absorbances at 303.5 nm at time t and at equilibrium respectively. The hydrogen-ion concentration was calculated from the measured pH value, pH_{meas}, with a HORIBA pH meter, Model F7-SS, with glass and 3.33 mol dm^{-3} potassium chloride calomel electrodes, according to this relation:

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

The activity coefficient of the hydrogen ion, f_{H^+}, was estimated by defining a 12 vol% ethanol aqueous solution containing 0.0100 mol dm^{-3} HCl and 0.0900 mol dm^{-3} NaCl as $-\log [H^+] \equiv 2.00$. The f_{H^+} value estimated under these conditions agreed well, within the limits of experimental error, with the literature data of 0.83.[3] The hydrogen-ion concentration was adjusted mainly with an acetic acid-sodium acetate buffer solution, whose concentration was maintained as low as possible (usually less than 0.5×10^{-2} mol dm^{-3}) in order to confirm that there was no meaningful influence on the complex formation of cobalt(II) with QAA under the equilibrium and kinetic conditions adopted.

Results and Discussion

Electronic Absorption Spectra. Figures 1 and 2 show the electronic absorption spectra of QAA and its cobalt(II) complexes respectively. The qaa$^-$ species gives two distinct absorption maxima, at 29.20×10^3 and 39.40×10^3 cm^{-1}, due to the $\pi\rightarrow\pi^*$ transitions, which shift bathochromically on protonation at the heterocyclic nitrogen atom (Fig. 1). The coordination of the terdentate ligand qaa$^-$ to cobalt(II) brings about remarkable spectral features; several absorption maxima in the $(31.70—33.70)\times10^3$ cm^{-1} region and a maximum at 43.20×10^3 cm^{-1} are characteristic of the mono-QAA complex, and there are in addition a maximum at 39.53×10^3 cm^{-1} and a shoulder around

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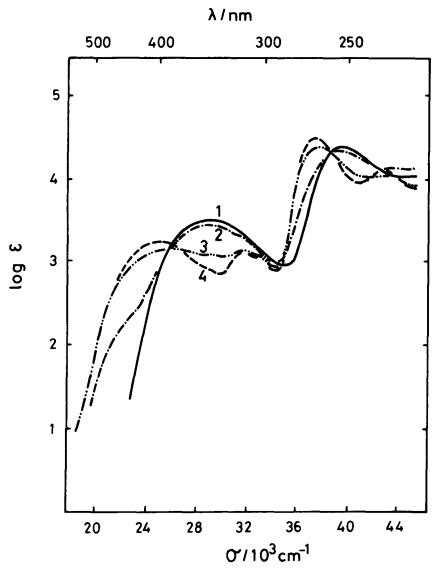

Fig. 1. Absorption spectra of QAA. 1: pH 9.70 (qaa^-); 2: pH 4.50; 3: pH 2.86; and 4: pH 0.38 (H_3 qaa^{2+}).

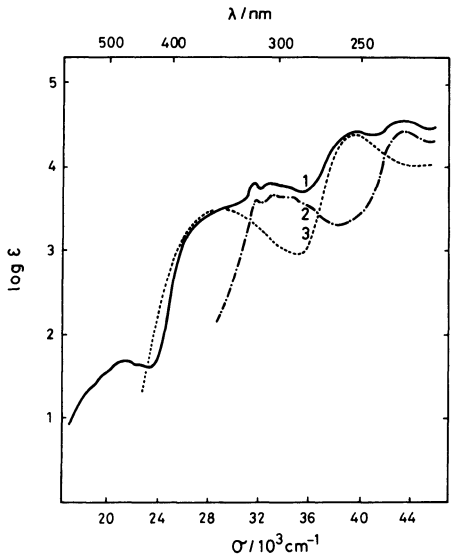

Fig. 2. Absorption spectra of the QAA complex. 1: $[Co(qaa)_2]$; 2: $[Co(qaa)(H_2O)_3]^+$; and 3: qaa^-.

$29.07\times10^3\,cm^{-1}$ of the bis-QAA complex. This shows that the transitions of π electrons related to the coordinated ligand are influenced by the numbers and arrangement of its chromophores.

The electronic absorption spectra in the d-d transition region of the bis-QAA complex and a typical cobalt(II) complex with octahedral coordination are given in Fig. 3. The absorption spectrum of the bis-QAA complex can be well correlated to that of a Schiff-base complex of the $[Co(N)_4(O)_2]$ type,[4] and the absorption maxima at 10.20×10^3 and 21.19×10^3 cm^{-1} of the bis-QAA complex can be assigned to the $^4T_{1g}(F)$-$^4T_{2g}(F)(O_h)$ and $^4T_{1g}(F)$-$^4T_{1g}(P)(O_h)$ transitions respectively.

Hence, it can be concluded that the QAA complex has an octahedral coordination and that the mono-

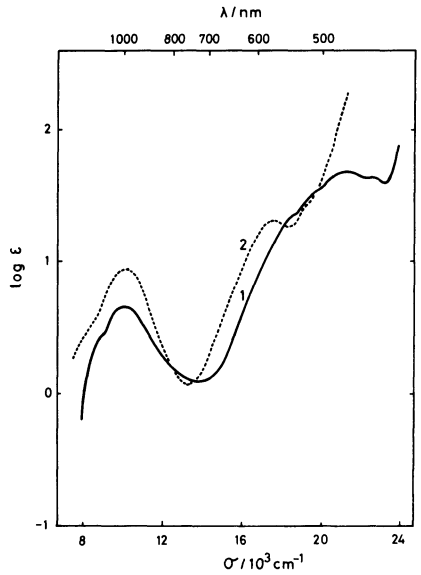

Fig. 3. Absorption spectra in the d-d transition region of $[Co(qaa)_2]$ and a Schiff base complex, $[Co(L)_2(py)_2]^+$, with octahedral coordination.[4] 1: $[Co(qaa)_2]$ and 2: $[Co(L)_2(py)_2]^+$, L: *ortho*-$OC_6H_4CHN(CH_2)_3CH_3$.

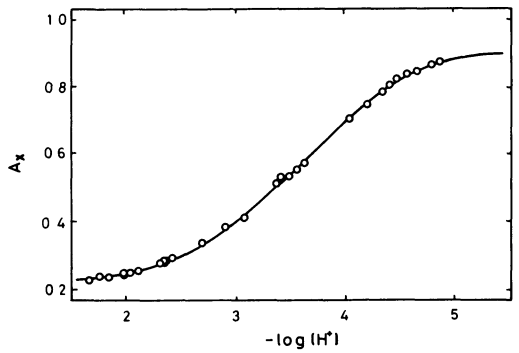

Fig. 4. Relation between A_x and $-\log[H^+]$ for QAA. Concentration of QAA, 1.41×10^{-4} mol dm^{-3}. Bald line is a theoretical curve drawn by using K_{a1} of $10^{4.04}$ and K_{a2} of $10^{2.99}$.

and bis-QAA complexes can be expressed as $[Co(qaa)(H_2O)_3]^+$ and $[Co(qaa)_2]$ respectively.

Stability. The protonation constants of QAA were determined by the use of the following relation (*cf.* Appendix I):

$$A_x = A_2 + \frac{(A_0-A_2)+(A_1-A_2)K_{a1}[H^+]}{1+K_{a1}[H^+]+K_{a1}K_{a2}[H^+]^2}. \quad (1)$$

Here, K_{a1} (=[Hqaa]/[H^+][qaa^-]) and K_{a2} (=[H_2qaa^+]/[H^+][Hqaa]) are the protonation constants related to the heterocyclic nitrogen base and the carboxylate group;[5] A_0 and A_2 are absorbances corresponding to the qaa^- and H_2 qaa^+ species; A_1 is an intrinsic absorbance of the Hqaa species, and A_x is an absorbance when these ligand species coexist. Equation (1) was solved by the curve-fitting method[6] with a normalized curve of:

$$Y = \{(A_0-A_2)+bt\}/(1+at+t^2) \text{ and } X = \log t, \quad (2)$$

with $\log K_{a1}K_{a2}=2(X-\log[H^+])$, $\log K_{a1}/K_{a2}=2\log a$,

Table 1. Protonation constants of QAA

log (K_{a1}/mol^{-1} dm^3)	log (K_{a2}/mol^{-1} dm^3)	Condition	Reference
4.26	2.98	0.1 mol dm^{-3} aqueous sodium perchlorate, 25 °C potentiometry[a]	2
4.04±0.05	2.99±0.05	0.10 mol dm^{-3} aqueous sodium chloride containing 12 vol% ethanol, 25 °C spectrophotometry	Present work

a) The log K_{a3} value related to protonation at the imino-nitrogen atom has been estimated to be 1.9.[2]

Table 2. Stability constants and related data

log (β_{11}/mol^{-1} dm^3)	log (β_{12}/mol^{-2} dm^6)	$-\Delta G^\circ_{11}$/kJ mol^{-1} [a]	$-\Delta G^\circ_{12}$/kJ mol^{-1} [a]	Condition	Reference
3.7	7.5	—	—	0.1 mol dm^{-3} aqueous sodium perchlorate,25 °C potentiometry	2
4.82±0.05	9.51±0.10	27.5±0.3	54.3±0.6	0.10 mol dm^{-3} aqueous sodium chloride containing 12 vol% ethanol, 25 °C spectrophotometry	Present work

a) Calculated by this relation: $-\Delta G^\circ_{1j}=RT\ln\beta_{1j}$ without the extrapolation of β_{1j} to the zero ionic strength ($j=1$ and 2).

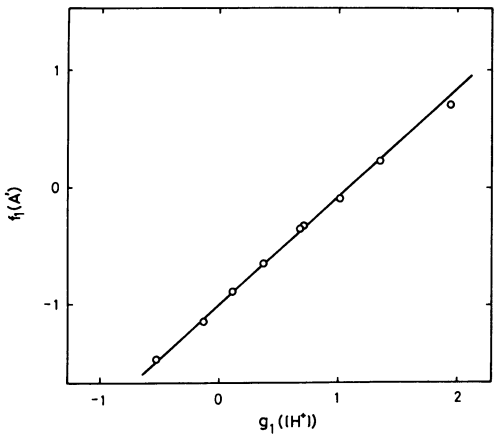

Fig. 5. Relation between $f_1(A')$ and $g_1([H^+])$. $f_1(A')\equiv \log\{(A'-A_{lig})/(A_{m.c}-A')\}$, $g_1([H^+])=-\log\{[H^+](K_{a2}[H^+]+1+1/K_{a1}[H^+])\}$. C_M, 1.60×10^{-2} mol dm^{-3} and C_L, 1.60×10^{-4} mol dm^{-3}.

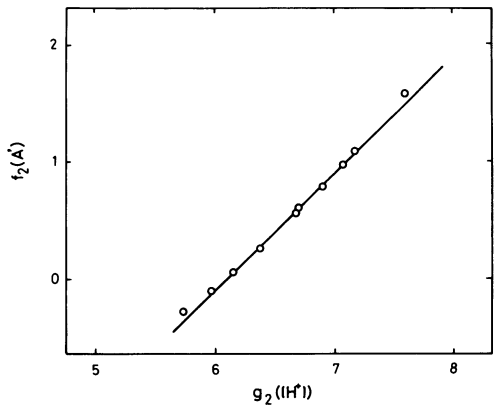

Fig. 6. Relation between $f_2(A')$ and $g_2([H^+])$. $f_2(A')\equiv \log\{(A'-A_{lig})/(A_{b.c}-A_{lig})\}-3\log\{(A_{b.c}-A')/((A_{b.c}-A_{lig})\}$, $g_2(H^+])\equiv-2\log\{[H^+](K_{a2}[H^+]+1+1/K_{a1}[H^+])\}$. C_M, 8.02×10^{-5} mol dm^{-3} and C_M, 1.60×10^{-4} mol dm^{-3}.

and $\log(A_1-A_2)=\log b+(1/2)(\log K_{a2}/K_{a1})$. Figure 4 shows the results, from which the K_{a1} and K_{a2} values were calculated; they are summarized in Table 1, together with those in the literature.[2]

The stability constants were determined by means of this relation:

$$\log\{(A'-A_{lig})/(A_{m.c}-A')\} = \log\beta_{11}C_M/K_{a1} - \log\{[H^+](K_{a2}[H^+]+1+1/K_{a1}[H^+])\}, \quad (3)$$

for the mono-QAA complex (β_{11}) under the condition of $C_M\gg C_L$, and by this relation:

$$\log\{(A'-A_{lig})/(A_{b.c}-A_{lig})\} - 3\log\{(A_{b.c}-A')/(A_{b.c}-A_{lig})\} = \log 4\beta_{12}C_M^2/K_{a1}^2 - 2\log\{[H^+](K_{a2}[H^+]+1+1/K_{a1}[H^+])\}, \quad (4)$$

for the bis-QAA complex (β_{12}) under the condition of $2C_M=C_L$ (*cf.* Appendix II). Here, C_M and C_L are the total concentrations of cobalt(II) and QAA respectively; A_{lig}, $A_{m\cdot c}$, and $A_{b\cdot c}$ denote absorbances corresponding to the ligand, the mono-QAA complex, and the bis-QAA complex respectively, and A' is the absorbance when the ligand and the complex coexist. Figures 5 and 6 show the findings on the relation between the absorbance term and the hydrogen-ion-concentration term in Eqs. (3) and (4), from which β_{11} and β_{12} were determined; they were summarized in Table 2, together with those in the literature.[2]

It is noteworthy that the stability constant of the mono-QAA complex is very close to the second step-by-step stability constant (β_{12}/β_{11}), as given in Table 2; this differs from general tendency for the step-by-step stability constants to decrease with increased

numbers of the coordinated ligands.[7] The molecular model reveals that there are no steric factors in QAA to bring about this particular aspect and that there are more possible geometrical isomers for the bis than for the mono-QAA complex, *i.e.*, six for the former and two for the latter. The relatively large values of the second step-by-step stability constant as compared with the first one may reflect either the bis-QAA complex being in equilibrium for some of its geometrical isomers or the mutual stabilizing interactions between the coordinated ligands in the bis-QAA complex.

Kinetics. By taking into consideration the protonation constants of QAA, the hydrolysis constant of cobalt(II) ($\log K_{OH}=-9.85$ (0 mol dm^{-3}, 25 °C) or -9.82 (1.0 mol dm^{-3}($NaClO_4$), 25 °C), $K_{OH}=[[Co(OH)(H_2O)_5]^+][H^+]/[[Co(H_2O)_6]^{2+}]$),[8] the stability constants of the mono- and bis-QAA complexes, and the rapid attainment of equilibria for the protolytic processes[9] as compared with the complex formation processes, which proceed at pH 2—5, the reaction pathways of the QAA complex can be given as follows (j=0—2);

$$[Co(H_2O)_6]^{2+} + H_jqaa^{(j-1)+} \xrightarrow{k_{0j}} [Co(qaa)(H_2O)_3]^+ + jH^+, \quad (\mathbf{I})$$

$$[Co(qaa)(H_2O)_3]^+ + H_jqaa^{(j-1)+} \xrightarrow{k_{1j}} [Co(qaa)_2] + jH^+. \quad (\mathbf{II})$$

In case the rate-determining step is in Stage **I**, Eqs. 6 and 7 can be deduced under the pseudo-first-order kinetic conditions with respect to the cobalt(II) and QAA concentrations (*cf.* Appendix III);

$$\begin{aligned} &d[[Co(qaa)(H_2O)_3]^+]/dt \\ &= k^M_{obsd}([[Co(qaa)(H_2O)_3]^+]_{eq} - [[Co(qaa)(H_2O)_3]^+]) \\ &= (k_{02}[H_2qaa^+] + k_{01}[Hqaa] + k_{00}[qaa^-])[[Co(H_2O)_6]^{2+}] \\ &\quad - (k_{-02}[H^+]^2 + k_{-01}[H^+] + k_{-00})[[Co(qaa)(H_2O)_3]^+], \end{aligned} \quad (5)$$

$$k^M_{obsd} = \{C'_M/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1) + 1/\beta_{11}\} \times (k_{02}K_{a1}K_{a2}[H^+]^2 + k_{01}K_{a1}[H^+] + k_{00}), \quad (6)$$

$$\begin{aligned} &d[[Co(qaa)_2]]/dt \\ &= k^L_{obsd}([[Co(qaa)_2]]_{eq} - [[Co(qaa)_2]]), \end{aligned}$$

$$k^L_{obsd} = \frac{\{C'_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1)\}^2 + 1/\beta_{12}}{C'_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1)} \times (k_{02}K_{a1}K_{a2}[H^+]^2 + k_{01}K_{a1}[H^+] + k_{00}), \quad (7)$$

where k^M_{obsd} and k^L_{obsd} are the observed rate constants under the condition of $C_M' \gg C_L'$ and $C_L' \gg C_M'$; k_{0j} is the forward rate constant for the pathway of $[Co(H_2O)_6]^{2+}$ and $H_j qaa^{(j-1)+}$; k_{-0j} is the backward rate constant for the same pathway; C_M' and C_L' are the total concentrations of cobalt II and QAA, and the suffix "eq" denotes the equilibrium state. Under the pseudo-first-order kinetic condition with respect to the ligand, Stage **II** may possibly be the rate-determining step and Eq. 8 can be deduced analogously:

$$k^L_{obsd} = \{C'_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1) + \beta_{11}/\beta_{12}\} \times (k_{12}K_{a1}K_{a2}[H^+]^2 + k_{11}K_{a1}[H^+] + k_{10}), \quad (8)$$

where k_{1j} is the forward rate constant for the pathway of $[Co(qaa)(H_2O)_3]^+$ and $H_j qaa^{(j-1)+}$. Hence, the reaction pathways can be deduced by plotting the $[H^+]$ dependence of $k^{M}_{obsd}{}'$ and $k^{L}_{obsf}{}'$, which are defined as follows;

$$k^M_{obsd}{}' \equiv k^M_{obsd}/\{C'_M/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1) + 1/\beta_{11}\}, \quad (6')$$

$$k^L_{obsd}{}' \equiv k^L_{obsd}\{C'_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1)\}/[\{C'_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1)\}^2 + 1/\beta_{12}], \quad (7')$$

or:

$$k^L_{obsd}{}' \equiv k^L_{obsd}/\{C'_L/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1) + \beta_{11}/\beta_{12}\}. \quad (8')$$

Figures 7 and 8 depict the $[H^+]$ dependences of $k^{M}_{obsd}{}'$ and $k^{L}_{obsd}{}'$ respectively, as defined by Eq. 7'. No meaningful result was obtained when $k^{L}_{obsd}{}'$ was defined by means of Eq. 8'. It can be concluded that the rate-determining step for both the mono- and bis-QAA complexes are in Stage **I** and that the reaction pathways of $[Co(H_2O)_6]^{2+}$ with Hqaa and with qaa^- really hold true. The rate constants and related data are summarized in Table 3.

The rate constants for the octahedral cobalt(II) complexes abstracted in Table 4 have been reported. All these ligands form cobalt(II) complexes by means of the preliminary formation of an outer-sphere complex, followed by transformation to the inner-sphere complex; then the chelate complexes are formed with a liberation of the coordinated water from the outer-sphere complex as the mechanistic rate-determining step.[10-19] The two exceptions are β-alaninate and 3-aminobutyrate, which show the chelate-ring closure as the rate-determining step.[16,17] In this reaction mechanism, the formation rate constant (k_f) can be equated with a product of the

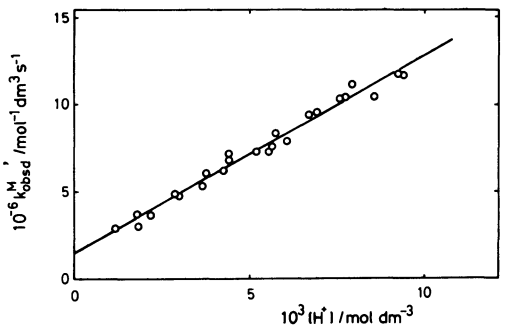

Fig. 7. Relation between $k^{M}_{obsd}{}'$ and $[H^+]$. C'_M, (2.01—7.99)$\times 10^{-3}$ mol dm^{-3} and C'_L, 8.02×10^{-5} mol dm^{-3}.

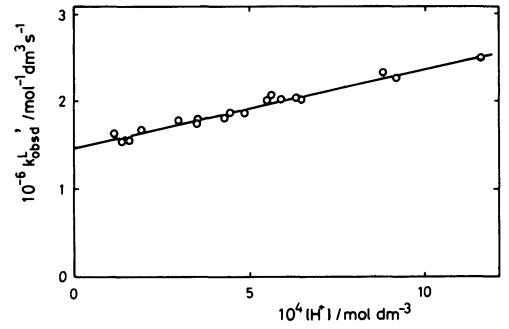

Fig. 8. Relation between $k^{L}_{obsd}{}'$ and $[H^+]$. C'_M, 8.02×10^{-6} mol dm^{-3} and C'_L, (2.01—4.02)$\times 10^{-4}$ mol dm^{-3}.

Table 3. Rate constants and related data

Pathway[a]	k_{0j}/mol^{-1} dm^3 s^{-1}	k_{-0j}/mol^{-j} dm^{3j} s^{-1} [b]	ΔG^{*}_{0j}/kJ mol^{-1} [c]	ΔG^{*}_{-0j}/kJ mol^{-1} [c]	Condition[d]
$Co^{2+}+Hqaa$	$(1.08\pm0.13)\times10^5$	—	—	—	$C_M' \gg C_L'$
($j=1$)	$(0.85\pm0.08)\times10^5$	—	—	—	$C_L' \gg C_M'$
	$(1.0\pm0.1)\times10^5$	$(1.7\pm0.6)\times10^4$	44.4±0.2	48.8±1.0	Average
$Co^{2+}+qaa^-$	$(1.50\pm0.23)\times10^6$	—	—	—	$C_M' \gg C_L'$
($j=0$)	$(1.47\pm0.10)\times10^6$	—	—	—	$C_L' \gg C_M'$
	$(1.5\pm0.2)\times10^6$	$(2.3\pm0.6)\times10$	37.7±0.3	65.2±0.7	Average

a) Abbreviation: Co^{2+}, $[Co(H_2O)_6]^{2+}$. b) k_{-0j} was calculated by means of this relation: $k_{-0j}=k_{0j}K_{a1}{}^j/\beta_{11}$. c) $\Delta G^{*}_{0j\,(or\,-0j)}$ was calculated by means of this relation: $\Delta G^{*}_{0j\,(or\,-0j)}=-RT(\ln k_{0j\,(or\,-0j)}-\ln kT/h)$, where R, T, k, and h have the usual meanings. d) 0.10 mol dm^{-3} aqueous sodium chloride containing 12 vol% ethanol, 25 °C.

Table 4. Formation-rate constants of cobalt(II) complexes concerned

Ligand[a]	k_f/mol^{-1} dm^3 s^{-1} [b]	Remarks[c]	Reference
Ammonia	9.5×10^4	0.1 mol dm^{-3} (NH_4NO_3), 20 °C, $k^{-H_2O}=8\times10^5$ s^{-1}	10
Imidazole	1.3×10^5	0.15 mol dm^{-3} (KNO_3), 25 °C, $k^{-H_2O}=4.4\times10^5$ s^{-1}	11
phen	3.2×10^5	No specification, 25 °C	12
5-NO_2-phen	1.6×10^5	No specification, 25 °C	12
bpy	6.3×10^4	No specification, 25 °C	12
tpy	2.5×10^4	No specification, 25 °C	13
Glycinate	1.5×10^6	0.10 mol dm^{-3} (—), 25 °C	14
Glycinate	4.6×10^5	0.15 mol dm^{-3} (KNO_3), 25 °C, $k^{-H_2O}=2.6\times10^5$ s^{-1}	11
Diglycinate	2.0×10^5	0.10 mol dm^{-3} (—), 25 °C	14
Diglycinate	4.6×10^5	0.15 mol dm^{-3} (KNO_3), 25 °C, $k^{-H_2O}=2.6\times10^5$ s^{-1}	11
Triglycinate	3.1×10^5	0.10 mol dm^{-3} (—), 25 °C	14
Tetraglycinate	2.6×10^5	0.10 mol dm^{-3} (—), 25 °C	14
pyc	1×10^7	0.10 mol dm^{-3} (—), 20 °C	15
α-Alaninate	6.0×10^5	0.10 mol dm^{-3} (KNO_3), 20 °C, $k^{-H_2O}=3\times10^5$ s^{-1}	16
β-Alaninate	7.5×10^4	0.10 mol dm^{-3} (KNO_3), 20 °C	16
2-Aminobutyrate	2.5×10^5	0.1 mol dm^{-3} (KNO_3), 20 °C	17
3-Aminobutyrate	2.0×10^4	0.1 mol dm^{-3} (KNO_3), 20 °C	17
pda	4.0×10^4	0.1 mol dm^{-3} (KNO_3), 15 °C	18
sal	1.3×10^5	0.10 mol dm^{-3} (KNO_3), 20 °C	19
5-ssal	2.7×10^5	0.10 mol dm^{-3} (KNO_3), 20 °C	19
qaa^-	1.5×10^6	0.10 mol dm^{-3} (NaCl), 25 °C	Present work

a) Abbreviations: phen, 1,10-phenanthroline; 5-NO_2-phen, 5-nitro-1,10-phenanthroline; bpy, 2,2′-bipyridine; tpy, 2,2′ : 6′,2″-terpyridine; pyc, 2-pyridinecarboxylate; pda, 4-(2-pyridylazo)-*N*,*N*-dimethylaniline; sal, salicylate; and 5-ssal, 5-sulfosalicylate. b) k_f is the rate constant for the formation of the mono-ligand cobalt(II) complex. c) The value of k^{-H_2O} has been reported, for example, to be 1.35×10^6 s^{-1} (0.1 mol dm^{-3} ($HClO_4$), 25 °C)[20] and (2.15—2.35)$\times10^6$ s^{-1} (0.2—0.35 mol dm^{-3} ($HClO_4$) and 2 mol dm^{-3} (NH_4NO_3),[21] 25 °C) by ^{17}O-NMR line-broadening measurements related to coordinated water, 2×10^5 s^{-1} (20 °C)[22] by ultrasonic absorption measurement and $(3.18\pm0.17)\times10^6$ s^{-1} (25 °C)[23] by ^{17}O-NMR relaxation time and line-broadening measurements.

formation constant of the outer-sphere complex (K_{os}) and the rate constant for the liberation of the coordinated water from the cobalt(II) ion (k^{-H_2O}), which then should be independent of the entering ligands. Table 4 reveals that the formation-rate constant for the complex with qaa^- is in line with those for the complexes with glycinate, α-alaninate, *etc.*, even with no calculation of k^{-H_2O} from the estimated K_{os} and k_f values. Hence, it can be concluded that QAA forms a cobalt(II) complex in a "normal substitution" mode[16,17] through the preliminary formation of the outer-sphere complex, followed by the substitution of the coordinated water, with its liberation as the ultimate rate-determining step.

A comparison of k_{01} and k_{00} in Table 3 reveals that, as in the case of glycinate,[11] the carboxylato group of QAA coordinates more feasibly than does the heterocyclic nitrogen atom. The molecular model shows that the imino nitrogen atom may be less easily coordinated because its accessibility toward the metal atom is less than that of any other donor atoms in the ligand. Therefore, it can be stated that the carboxylato group of QAA coordinates first to the aquacobalt(II) ion as a unidentate ligand, followed by the donations of imino and heterocyclic nitrogen atoms to complete two five-membered chelate rings; this is followed by the coordination of the second QAA in a more rapid manner because of the labilization of the remaining coordinated water,[11] thus completing the bis-QAA complex.

Appendix

In this section, M, ML, ML_2, L, HL, and H_2L are used as simplified expressions of $[Co(H_2O)_6]^{2+}$, $[Co(qaa)(H_2O)_3]^+$, $[Co(qaa)_2]$, qaa^-, Hqaa, and H_2qaa^+; the molar absorption coefficients of the last five of those are ε_{11}, ε_{12}, ε_0, ε_1, and ε_2 respectively.

I. The following relations are given based on definitions in the text and the materials balance:

$$A_x = \varepsilon_0[L] + \varepsilon_1[HL] + \varepsilon_2[H_2L], \quad \text{(A-1)}$$

$$A_0 = \varepsilon_0[L]_m = \varepsilon_0 C_{lig}, \quad \text{(A-2)}$$

$$A_1 = \varepsilon_1[HL]_m = \varepsilon_1 C_{lig}, \quad \text{(A-3)}$$

$$A_2 = \varepsilon_2[H_2L]_m = \varepsilon_2 C_{lig}, \quad \text{(A-4)}$$

$$C_{lig} = [L] + [HL] + [H_2L] = [L]_m = [HL]_m = [H_2L]_m, \quad \text{(A-5)}$$

where C_{lig} is the total concentration of QAA. The suffix m specifies the portion of the concentration, in which only the unique ligand species is present. By taking K_{a1} and K_{a2} into consideration and by inserting Eqs. A-2—A-5 into Eq. A-1 with suitable rearrangements, Eq. 1 can be derived.

II. In an acidic solution of pH 2—5, where the complex formation proceeds, the following relations hold for the equilibrium:

$$C_M = [M] + [ML] + [ML_2], \quad \text{(A-6)}$$

$$C_L = [L] + [HL] + [H_2L] + [ML] + 2[ML_2] = [L]_i + [HL]_i + [H_2L]_i, \quad \text{(A-7)}$$

$$A' = \varepsilon_0[L] + \varepsilon_1[HL] + \varepsilon_2[H_2L] + \varepsilon_{11}[ML] + \varepsilon_{12}[ML_2], \quad \text{(A-8)}$$

$$A_{b.c} = \varepsilon_{12} C_M, \quad \text{(A-9)}$$

$$A_{lig} = \varepsilon_0[L]_i + \varepsilon_1[HL]_i + \varepsilon_2[H_2L]_i. \quad \text{(A-10)}$$

Here, the suffix i specifies the initial concentration of the ligand. Under the condition of $2C_M = C_L$, the bis-QAA complex is assumed to be dominant over the mono-QAA complex. Hence, the following relations are derived from Eqs. A-6—A-10 by taking K_{a1} and K_{a2} into consideration:

$$[L] = (C_L - 2[ML_2])/(1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2), \quad \text{(A-11)}$$

$$[M] = \{(A_{b.c} - A')/(A_{b.c} - A_{lig})\} C_M, \quad \text{(A-12)}$$

$$[ML_2] = \{(A' - A_{lig})/(A_{b.c} - A_{lig})\} C_M, \quad \text{(A-13)}$$

The application of Eqs. A-11—A-13 into Eq. A-14:

$$\beta_{12} = [ML_2]/[M][L]^2, \quad \text{(A-14)}$$

and suitable rearrangements give us Eq. 4.

III. When Stage **I** is the rate-determining step, the following relations can be given under the condition of $C_M' \gg C_L'$:

$$C_M' = [M] + [ML] \approx [M] = [M]_{eq}, \quad \text{(A-15)}$$

$$C_L' = [L] + [HL] + [H_2L] + [ML] = [L]_{eq} + [HL]_{eq} + [H_2L]_{eq} + [ML]_{eq}. \quad \text{(A-16)}$$

By using Eqs. A-15 and A-16 together with Eq. A-17:

$$\beta_{11} = [ML]_{eq}/[M]_{eq}[L]_{eq}. \quad \text{(A-17)}$$

Equation 5 can be transformed into Eq. A-18:

$$\begin{aligned} d[ML]/dt &= (k_{02}K_{a1}K_{a2}[H^+]^2 + k_{01}K_{a1}[H^+] + k_{00}) \times ([M][L] - [ML]/\beta_{11}) \\ &= (k_{02}K_{a1}K_{a2}[H^+]^2 + k_{01}K_{a1}[H^+] + k_{00}) \times \{C_M'/(K_{a1}K_{a2}[H^+]^2 + K_{a1}[H^+] + 1) + 1/\beta_{11}\} \times ([ML]_{eq} - [ML]). \end{aligned} \quad \text{(A-18)}$$

A comparison of Eq. A-18 with Eq. 5 gives Eq. 6, which can be rewritten as:

$$k_{02}K_{a1}K_{a2}[H^+]^2 + k_{01}K_{a1}[H^+] + k_{00} = k^M_{obsd}', \quad \text{(A-19)}$$

by using the definition given in Eq. 6′. It was used for the data analysis.

Equations 7 and 8 can be derived from Eq. 5 in an analogous way.

References

1) Abbreviations: QAA, *N*-(8-quinolyl)aminoacetate ligand. H_3qaa^{2+}, H_2qaa^+, Hqaa, and qaa^- refer to various protonated and deprotonated species of QAA.

2) T. Tanabe, K. Kimura, and S. Takamoto, *Nippon Kagaku Zasshi*, **90**, 598 (1969).

3) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

4) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jpn.*, **37**, 1154 (1964).

5) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen, London (1962), Chaps. 7 and 8.

6) L. G. Sillen, *Acta Chem. Scand.*, **10**, 186 (1956).

7) For example, "Coordination Chemistry," ed by A. E. Martell, Van Nostrand-Reinhold, New York (1971), Vol.1, Chap. 8.

8) "Stability Constants of Metal-Ion Complexes," ed by L. G. Sillén and A. E. Martell, The Chemical Society, London (1971), Suppl. No. 1, Sp. Publ. No. 25, p. 23.

9) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

10) D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

11) G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

12) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

13) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

14) G. Davies, K. Kustin, and R. F. Pasternack, *Inorg. Chem.*, **8**, 1535 (1969).

15) A. Kowalak, K. Kustin, and R. F. Pasternack, *J. Phys. Chem.*, **73**, 281 (1969).

16) K. Kustin, R. F. Pasternack, and E. M. Weinstock, *J. Am. Chem. Soc.*, **88**, 4610 (1966).

17) K. Kowalak, K. Kustin, R. F. Pasternack, and S. Petrucci, *J. Am. Chem. Soc.*, **89**, 3126 (1967).

18) R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964).

19) J. C. Williams and S. Petrucci, *J. Am. Chem. Soc.*, **95**, 7619 (1973).

20) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); **41**, 2553 (1964).

21) P. E. Hoggard, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **10**, 959 (1971).

22) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).

23) Y. Ducommun, K. E. Newman, and A. E. Merbach, *Inorg. Chem.*, **19**, 3696 (1980).