March, 1990] © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 929—931 (1990) 929

Coordination Selectivity in the Fe(II) Complex with 8-Hydroxy-7-[(2-hydroxy-5-carboxyphenyl)azo]-5-quinolinesulfonic Acid

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(Received August 21, 1989)

Synopsis. The coordination of the title ligand (hcqs) to Fe(II) has been studied on the basis of its electronic absorption spectral characteristics, equilibrium, and stopped-flow kinetics in comparison with those of the related ligands. The bifunctional hcqs coordinates to Fe(II) not with a quinolinol (*O-N*) moiety, but selectively with a dihydroxyazo (*O-N-O*) one. The reaction mechanism of hcqs with Fe(II) and the thermodynamic stability of the complex are also discussed.

We have previously reported[1] that 8-hydroxy-7-[(2-hydroxy-5-carboxyphenyl)azo]-5-quinolinesulfonic acid (hcqs) reacts with Al(III) to form, initially, a yellow complex with the quinolinol (*O-N*) coordination mode; finally, it changes to a red complex with the dihydroxyazo (*O-N-O*) mode (this complex shows a linkage isomerism). In contrast, the coordination reaction of hcqs with Fe(II), which has an octahedral coordination like Al(III), revealed that the ligand reacts selectively with the metal ion to form a complex with the dihydroxyazo (*O-N-O*) coordination mode; the complex shows no linkage isomerism.

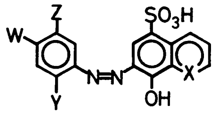


Chart 1. hcqs: X=N, Y=OH, Z=COOH, W=H; hcns: X=CH, Y=OH, Z=COOH, W=H; cqs: X=N, Y=H, Z=H, W=COOH.

The present paper will be concerned with the coordination selectivity[1,2] and reaction mechanism of hcqs to Fe(II) on the basis of the absorption spectral characteristics, the equilibrium, and the kinetics in comparison with those of the three related ligands.

Experimental

Materials. The syntheses of these ligands—hcqs, 4-hydroxy-3-[(2-hydroxy-5-carboxyphenyl)azo]-1-naphthalenesulfonic (hcns), and 7-[(4-carboxyphenyl)azo]-8-hydroxy-5-quinolinesulfonic (cqs) acids—have been described in a previous paper.[1] The 8-hydroxy-5-quinolinesulfonic acid (hqs) was supplied by the Aldrich Chemical Co. The Fe(II) solution was made according to the method in the literature[3] by dissolving $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ in dilute perchloric acid.[4]

Measurements. The apparatus and general procedures have been described elsewhere.[1] The equilibrium and kinetics were studied in a 0.10 mol dm^{-3} aqueous $NaClO_4$ solution at 22.0±0.1 °C. All the solutions were prepared anaerobically with N_2 gas. The reactions of Fe(II) with the ligands were monitored at 502 nm for hcqs, 500 nm for hcns, 497 nm for cqs, and 615 nm for hqs.

Results and Discussion

Coordination Mode of Fe(hcqs)$^{2-}$. Figure 1 shows the absorption spectra of the present complexes and ligands. In the region of 14—27×10^3 cm^{-1}, Fe(hcqs)$^{2-}$ exhibits spectral characteristics similar to those of Fe(hcns)$^{2-}$, where hcns functions as a dihydroxyazo (*O-N-O*) terdentate ligand as in the Al(III) complex.[1] On the other hand, these spectral characteristics differ from those of the Fe(cqs)$^{-}$, in which cqs functions as a quinolinol (*O-N*) bidentate ligand,[1] although cqs shows an absorption band due to the azo group quite similar to those shown by hcqs and hcns. These absorption spectral characteristics indicate that hcqs coordinates to Fe(II) with its dihydroxyazo (*O-N-O*) coordination mode, but not with its quinolinol (*O-N*) coordination mode.

Stability Constants. The compositions of the complexes were confirmed by the method of continuous variation;[5] a 1:2 (Fe(II):ligand) complex was formed for both hcqs and hcns, while a 1:3 complex was formed for cqs and hqs.[6] These results differ from

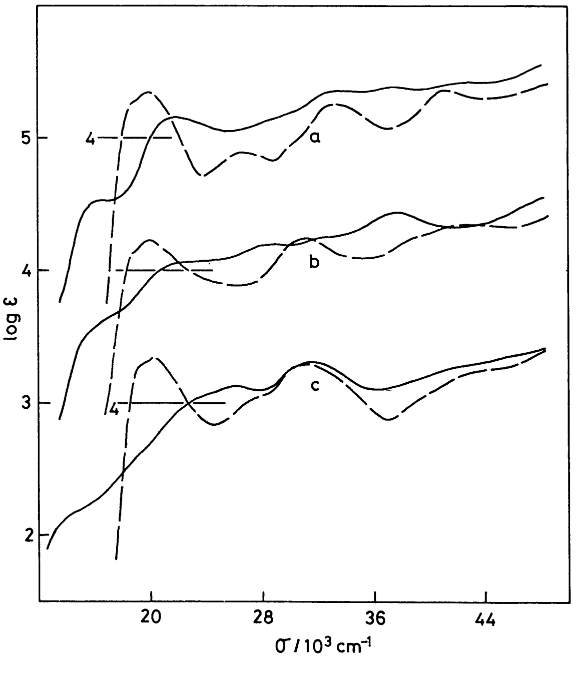


Fig. 1. Absorption spectra of ligands and their Fe(II) complexes: ——, complex; a, Fe(hcns)$^{2-}$; b, Fe(hcqs)$^{2-}$; and c, Fe(cqs)$^{-}$; ———, ligand; a, H_2hcns^{2-}; b, H_2hcqs^{2-}; and c, $Hcqs^{2-}$; 0.10 mol dm^{-3} $NaClO_4$, 22 °C, pH 3.8.

those of the Al(III) complexes, where only the 1:1 complexes were formed for hcqs, hcns, and cqs.[1]

The stability constant of $[Fe(hcqs)_2]^{6-}$ was determined on the basis of the following equilibrium with H_4edta at a constant pH:

$$[Fe(hcqs)_2]^{6-} + H_2edta^{2-} + 2H^+ \rightleftharpoons [Fe(edta)]^{2-} + 2H_2hcqs^{2-} \qquad (1)$$

Since both $[Fe(hcqs)_2]^{6-}$ and hcqs give an absorbance at 502 nm, but others do not, Eq. 2 can be derived thus under the experimental conditions of $C_{hcqs} > 3\, C_{Fe}$ and $C_{edta} > C_{Fe}$:

$$Y = \frac{\beta_2 \alpha_H^{edta}}{\beta_{Fe(edta)}(\alpha_H^{hcqs})^2} X \qquad (2)$$

$$\alpha_H^{hcqs} = 1 + K_{a1}[H^+](1 + K_{a2}[H^+](1 + K_{a3}[H^+](1 + K_{a4}[H^+]))) \qquad (3)$$

$$\alpha_H^{edta} = 1 + K'_{a1}[H^+](1 + K'_{a2}[H^+](1 + K'_{a3}[H^+](1 + K'_{a4}[H^+]))) \qquad (4)$$

$$X = (1 - x)[C_{hcqs} - 2\,x\,C_{Fe}]^2/x \qquad (5)$$

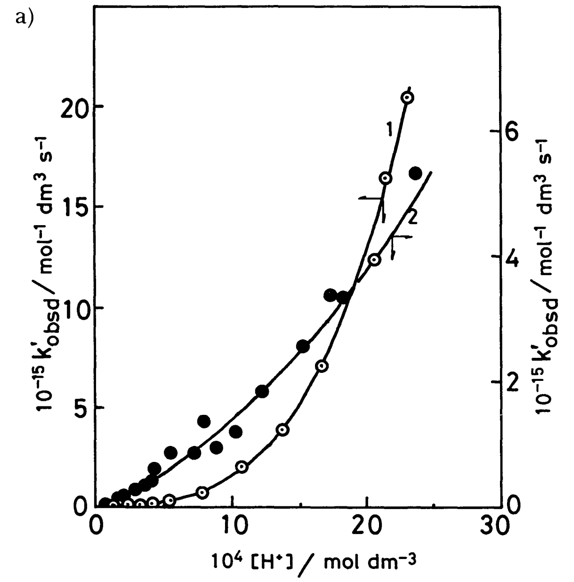
$$Y = C_{edta} - x\,C_{Fe} \qquad (6)$$

$$x = (A_{max} - A)/(A_{max} - A_{min}) \qquad (7)$$

C_{hcqs}, C_{Fe}, and C_{edta} are the total concentrations of hcqs, Fe(II), and edta respectively. β_2 and $\beta_{Fe(edta)}$ are the stability constants of the $[Fe(hcqs)_2]^{6-}$ and $[Fe(edta)]^{2-}$ complexes. K_{ai} and K'_{ai} are the protonation constants of hcqs (i=1—4)[7] and edta (i=1—4).[8] A_{max} and A_{min} are the absorbances of the hcqs and the $[Fe(hcqs)_2]^{6-}$ solutions, and A is the absorbance of a solution in which the $[Fe(hcqs)_2]^{6-}$ and the $[Fe(edta)]^{2-}$ complexes coexist. According to Eqs. 5—7, the experimental data plotted on Y against X may be expected to give a linear relation so long as Eq. 2 holds. A linear relation between X and Y was obtained for the Fe(II)-hcqs system, from the slope of which the stability constant of $[Fe(hcqs)_2]^{6-}$ was obtained as $\log \beta_2 = 25.79 \pm 0.10$ mol^{-2} dm^6. In the same way, the stability constants were determined to be $\log \beta_2 = 27.59 \pm 0.05$ mol^{-2} dm^6 for $[Fe(hcns)_2]^{6-}$ and $\log \beta_3 = 22.56 \pm 0.10$ mol^{-3} dm^9 for $[Fe(cqs)_3]^{7-}$. $[Fe(cqs)_3]^{7-}$ exhibits a quite similar magnitude of the stability constant to $[Fe(hqs)_3]^{4-}$ ($\log \beta_1 = 8.4$ mol^{-1} dm^3, $\log \beta_2 = 15.7$ mol^{-2} dm^6, $\log \beta_3 = 21.75$ mol^{-3} dm^9);[6] the quinolinol (*O-N*) coordination mode is possible for both cqs and hqs. These results are in line with the fact that the dihydroxyazo (*O-N-O*) coordination mode exhibited a larger stability than did the quinolinol (*O-N*) coordination mode in Al(III) complexes.[1,2]

Kinetics and Mechanism. The reaction rate of Fe(II) with hcqs was first-order in concentrations of both hcqs and Fe(II); a monophasic rate-determining step was observed for more than 3.5 half-life periods. In contrast to the case of the Al(III)-hcqs complex,[1] no evidence was observed for the linkage isomerism of the Fe(II)-hcqs complex. Similar kinetic results were obtained for the reactions of Fe(II) with hcns, cqs, and hqs. These results indicate that the coordination of the first ligand to the central metal is the rate-determining step,[3,9] which follows a rapid coordination[9] of the next ligand.

In order to deduce the reaction pathways, the dependence of the reaction rate on $-\log[H^+]$ was analysed under pseudo-first-order kinetic conditions, $C_{Fe} \gg C_{hcqs}$. In the same way as has been described previously,[1,10,11] three possible reaction pathways may



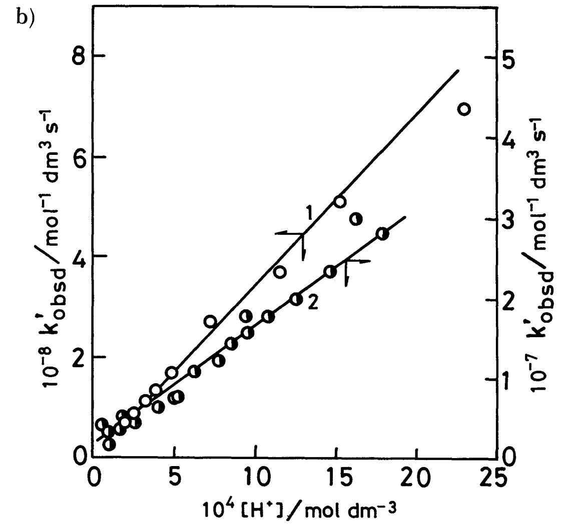


Fig. 2. a) Relation between k'_{obsd} and $[H^+]$ for Fe(II)-hcqs and Fe(II)-hcns complexes. (1): $C_{Fe(II)}$, 3.00×10^{-4} mol dm^{-3}; C_{hcqs}, 1.43×10^{-5} mol dm^{-3}, λ, 502 nm; (2): $C_{Fe(II)}$, 1.50×10^{-4} mol dm^{-3}; C_{hcns}, 8.59×10^{-6} mol dm^{-3}, λ, 500 nm; 0.10 mol dm^{-3} $NaClO_4$, 22 °C. b) Relation between k'_{obsd} and $[H^+]$ for Fe(II)-hqs and Fe(II)-cqs complexes. (1): $C_{Fe(II)}$, 1.00×10^{-3} mol dm^{-3}; C_{hqs}, 6.90×10^{-5} mol dm^{-3}, λ, 615 nm; (2): $C_{Fe(II)}$, 3.00×10^{-4} mol dm^{-3}; C_{cqs}, 1.39×10^{-5} mol dm^{-3}, λ, 497 nm; 0.10 mol dm^{-3} $NaClO_4$, 22 °C.

Table 1. Kinetic Parameters of Iron(II) Complexes

Pathway	Rate constant/mol^{-1} dm^3 s^{-1}			
	hcqs	hcns	cqs	hqs
Fe(II)+H$_2$L	k_{22}: (1.42±0.25)×10^5	k_{22}: (1.75±0.30)×10^3	—	—
Fe(II)+HL	—	k_{23}: (9.73±0.20)×10^6	k_{22}: (6.52±0.20)×10^2	k_{21}: (1.31±0.20)×10^3
Fe(II)+L	—	—	k_{23}: (1.37±0.22)×10^6	—

H$_2$L: H$_2$hcqs^{2-} and H$_2$hcns^{2-}, HL: Hhcns^{3-}, Hcqs^{2-}, and Hhqs$^-$, and L: cqs^{3-}. 0.10 mol dm^{-3} NaClO$_4$, 22 °C.

be proposed, with their rate equations (pH 2—4):

$$\mathrm{d[Fe(hcqs)^{2-}]}/\mathrm{d}t$$
$$= \{k_{23}[\mathrm{Hhcqs^{3-}}] + k_{22}[\mathrm{H_2hcqs^{2-}}] + k_{21}[\mathrm{H_3hcqs^{-}}]\}C_{\mathrm{Fe}^{2+}}$$
$$- (k_{-23}[\mathrm{H^+}] + (k_{-22}[\mathrm{H^+}]^2 + k_{-21}[\mathrm{H^+}]^3)[\mathrm{Fe(hcqs)^{2-}}] \qquad (8)$$

where k_{2j} refers to the rate constants for the forward reaction pathways of Fe^{2+} with H$_{4-j}$hcqs^{j-}, while k_{-2j} refers to the rate constants for the backward reaction pathways (j=1—3). By considering the protonation equilibria of hcqs, the dependence of the observed rate constant, k_{obsd}, on $-\log[\mathrm{H^+}]$ can be expressed as follows:

$$k'_{\mathrm{obsd}} \equiv k_{\mathrm{obsd}}/\{1/\beta_1 + C_{\mathrm{Fe}}/\alpha_{\mathrm{H}}^{\mathrm{hcqs}}\}$$
$$= k_{23}K_{\mathrm{a1}}[\mathrm{H^+}] + k_{22}K_{\mathrm{a1}}K_{\mathrm{a2}}[\mathrm{H^+}]^2 + k_{21}K_{\mathrm{a1}}K_{\mathrm{a2}}K_{\mathrm{a3}}[\mathrm{H^+}]^3 \qquad (9)$$

where k'_{obsd} and β_1 are the modified rate constant and the stability constant of Fe(hcqs)$^{2-}$ respectively. Since $1/\beta_1 \ll C_{\mathrm{Fe}}/\alpha_{\mathrm{H}}^{\mathrm{hcqs}}$ under the present experimental conditions, k'_{obsd} can be calculated as:

$$k'_{\mathrm{obsd}} = k_{\mathrm{obsd}}\alpha_{\mathrm{H}}^{\mathrm{hcqs}}/C_{\mathrm{Fe}} \qquad (10)$$

The k'_{obsd} is plotted versus [H$^+$] in Fig. 2(a). The best-fitting curve to Eq. 9 shows that k'_{obsd} is dependent on only [H$^+$]^2: Fe(hcqs-*O,N,O*)$^{2-}$ is formed mainly through the reaction pathway (k_{22}) of Fe^{2+} with H$_2$hcqs^{2-}. Similarly, the analyses of kinetic data (Fig. 2 (a) and (b)) revealed that the Fe(hcns-*O,N,O*)$^{2-}$ is formed mainly through the reaction pathways of Fe^{2+} with Hhcns^{3-} and H$_2$hcns^{2-}; Fe(cqs)$^-$, through those of Fe^{2+} with Hcqs^{2-} and cqs^{3-}, and Fe(hqs), through that of Fe^{2+} with Hhqs$^-$. These rate constants are summarized in Table 1.

The deprotonation at the phenolate oxygen causes an increase in the rate constant ($k_{22} \ll k_{23}$) in the Fe(II)-hcns and -cqs complexes (Table 1). The rate constants k_{22} of the Fe(II)-hcns and -cqs complexes and that k_{21} of the Fe(II)-hqs complex have the same magnitudes (Table 1). These data suggest that the mechanistic rate-determining steps in the formation of these complexes are controlled by the same factor: the donation of the phenolate oxygen on the naphthalene or the quinoline ring to Fe(II). Accordingly, the mechanistic rate-determining step of the Fe(II)-hcqs complex may also be the donation of the phenolate oxygen on the heterocyclic ring of hcqs, since it has a coordination mode analogous to that of the Fe(II)-hcns complex. The tendency of the k_{22} values in the Fe(II)-hcqs, -hcns, and -cqs complexes to decrease is in line with the tendency of the protonation constants1) of the phenolate oxygen on the naphthalene ($\log K_{\mathrm{a2}}$=6.74 for hcns) or quinoline rings ($\log K_{\mathrm{a2}}$= 6.36 for hcqs and $\log K_{\mathrm{a1}}$=7.40 for cqs) of the corresponding ligands to increase. This fact indicates that the basicities of the phenolate oxygen plays an important role in the donation process.

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8) The protonation constants of edta: $\log K'_{\mathrm{a1}}$=10.26, $\log K'_{\mathrm{a2}}$=6.16, $\log K'_{\mathrm{a3}}$=2.67, and $\log K'_{\mathrm{a4}}$=2.0; (G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947)).

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