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Equilibrium Studies on the Species Formed in the Extraction of Divalent Transition Metal Ions with 8-Quinolinethiol and Its 2-Methyl Derivative

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The equilibria were studied in the extraction of divalent transition metal ions (M^{2+}: Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) with 8-quinolinethiol(Hqt) and its 2-methyl derivative (Hmqt). Precipitates form in the Cd–Hqt and Cu–Hmqt systems. In other systems except the Co–Hqt, ML_2(L^-: qt^- or mqt^-) is responsible for the extraction. Effects of anions and solvents were examined in the Zn–Hqt system. The $Ni(qt)_2$, $Ni(mqt)_2$, and $Co(mqt)_2$ complexes hold the capacity to form the adduct with 1,10-phenanthroline. A mixture of diamagnetic Co(III) complexes is extracted in the Co–Hqt system. The main species was assigned as *mer(S)*-$Co(qt)_3$ by the ^{13}C NMR spectrum. The structures of other complexes are also discussed.

8-Quinolinethiol(Hqt), the sulfur-containing analogue of 8-quinolinol(Hq), has been used as a reagent having a preference for soft metal ions.[1] Several equilibrium studies on this reagent have been published.[2–9] The bis chelate, $M(qt)_2$ was assigned to the extracted species for common divalent transition metal ions (M^{2+}: Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}), whereas $Co(qt)_2(Hqt)$ or $Co(qt)_2(Hqt)_2$ to that for Co^{2+}.[5,9] The cobalt complex prepared, on the other hand, was characterized as $Co(qt)_2$ by IR and mass spectrometry,[10,11] or as $Co(qt)_3$ by polarography.[12]

Recently, we have made a systematic study on the extraction of divalent transition metal ions with 8-quinolinol.[13] Remarkable effects of solvents and anions (X^-) on the extraction were found, and were reasonably ascribed to the change in the contribution of three extracted species, $M_2q_3(Hq)_3X$, $Mq_2(Hq)$, and $M_2q_4(Hq)_2$.

In this work, we likewise studied the extraction equilibria of divalent transition metal ions with 8-quinolinethiol and its 2-methyl derivative (Hmqt) in detail. Complexes corresponding to the extracted species were prepared and their physicochemical properties as well as their capacities to form the adduct with 1,10-phenanthroline (phen) were investigated. Their structures are discussed through comparisons with the 8-quinolinol complexes.

Experimental

Reagents. 8-Quinolinethiol and its 2-methyl derivative were prepared as described in the literature,[14] and were stored as their disulfides or sodium salts.[15] Solutions of the thiols in organic solvents were prepared by extraction after the reduction of disulfides with phosphinic acid and neutralization with ammonia under a nitrogen atmosphere.

Metal(II) solutions were prepared from the sulfates and standardized against a Na_2H_2edta solution. Sodium perchlorate was recrystallized twice. Organic solvents were shaken, successively, three times with concd sulfuric acid, 4 mol dm^{-3} potassium hydroxide solution and distilled water.

Preparation of the Metal Complexes. The complexes of transition metal ions (Co, Ni, Cu, Zn, Cd) with Hqt and Hmqt were prepared by the reaction of a metal ion with a sodium salt of the thiols at the molar ratio of 1:2 in an aqueous solution. After being collected and washed with ethanol, these complexes were recrystallized from chloroform or benzene. The Cd–Hqt complex was not recrystallized because it is insoluble in common organic solvents. The precipitates obtained in the Co–Hqt and Cu–Hmqt systems were mixtures of chloroform-soluble and -insoluble species.

Determination of the metal content after decomposition of the complex with hydrogen peroxide and sulfuric acid showed the metal : ligand ratio of 1 : 2 except for the Co–Hqt and Cu–Hmqt complexes.[16] Chloroform-insoluble species in the Cu–Hmqt system has the ratio close to 1 : 1 (results for the Co–Hqt complexes are described below). Infrared spectra of Hqt complexes were in good agreement with those reported previously.[10]

Procedure. All the solutions used for the extraction were purged for 30 min with nitrogen gas. Details of the distribution measurement were the same as described previously.[13,17] A 1×10^{-4} mol dm^{-3} metal solution of the ionic strength 0.1 was shaken with an equal volume of an organic solvent containing 7.5×10^{-4} to 6.0×10^{-3} mol dm^{-3} thiol at 250 strokes min^{-1}. After phase separation, $-\log[H^+]$ higher than 2 was measured with a Radiometer pH METER 26. A solution containing 1.00×10^{-2} mol dm^{-3} perchloric acid and 9.00×10^{-2} mol dm^{-3} sodium perchlorate was used as a $-\log[H^+]$ standard. Below $-\log[H^+]$ 2, the analytical concentration of hydrogen ion was used as $-\log[H^+]$. Change in the activity coefficient is not so serious in the $-\log[H^+]$ range used.[18] Visible absorption spectra of the organic phase were recorded on a Union spectrophotometer SM-401 with a quartz cell of 10 mm. All the measurements were carried out with a thermoelectric circulating bath at 25±0.5 °C.

The adduct-formation constants were spectrophotometrically determined by adding various amounts of 1,10-phenanthroline to the complex solution (1×10^{-4} mol dm^{-3}) in the presence of excess ligand.

^{13}C NMR spectra were recorded on a Varian XL-200 Fourier transform spectrophotometer at a frequency of 50.3 MHz. The magnetic moment was measured by Faraday method with a torsion balance. JASCO chromatographic system MULTI-320 with a silica-ODS column was used for the separation of cobalt complexes.

Results and Discussion

Protonation Equilibria of 8-Quinolinethiolates. Protonation equilibria given by Eqs. 1 and 2 were spectrophotometrically studied (L^-: qt^- or mqt^-).

$$\mathrm{L^- + H^+ \overset{\mathit{K}_1}{\rightleftharpoons} HL} \qquad (1)$$

$$\mathrm{HL + H^+ \overset{\mathit{K}_2}{\rightleftharpoons} H_2L^+} \qquad (2)$$

The protonation constants obtained and those in the literatures are as follows: log K_1=8.20 (8.38,[3] 8.36,[19] 8.39[20]) for Hqt and 9.03 (9.06[3]) for Hmqt, log K_2=2.08 (2.16,[3] 2.05[20]) for Hqt and 2.28 (2.28[3]) for Hmqt.

Partition of 8-Quinolinethiols. Distribution equilibria of 8-quinolinethiols between water and some organic solvents were studied at $-\log[H^+]$ around 5. The distribution constants obtained are as follows: K_D=325 (324[21]) for Hqt into chloroform, 166 (160[21]) for Hqt into benzene, 128 for Hqt into chlorobenzene, 353 for Hmqt into chloroform.

In neutral aqueous solutions, these thiols exist in both the molecular and the zwitter-ionic forms, which are related by

$$\text{(molecular)} \overset{K_t}{\rightleftharpoons} \text{(zwitter-ionic)}, \qquad (3)$$

where K_t is the tautomeric constant. The constants have been estimated for a series of substituted 8-quinolinethiols;[22] for example, $10^{1.43}$ for Hqt and $10^{1.79}$ for Hmqt. In nonpolar solvents, on the other hand, the equilibrium is shifted far to the left side, irrespective of the substituent. Thiols with tautomerism are expected to be distributed less into nonpolar solvents by a factor of $(1+K_t)$.

In a homologous series of organic extractants such as carboxylic acids and alkylamines, values of $\log K_D$ increase with increasing the carbon number. The increment of $\log K_D$ for an added methylene group, $\Delta\log K_D/CH_2$, ranges from 0.56 to 0.64.[23] The difference in $\log K_D$ between 8-quinolinol and its 2-methyl derivative is 0.64. The enhancement in partition must also operate on the molecular form of Hmqt, but may be compensated by the tautomeric effect. Thus, the K_D values for 8-quinolinethiol and its 2-methyl derivative do not differ so much (0.04 in logarithmic unit).

Extraction Time and Absorption Spectra of Extracted Species. Preliminary experiments showed the precipitate formation in the extraction systems of Cd-Hqt and Cu-Hmqt. In the other systems, approximate time required for equilibration was studied by measuring the absorbance of the organic phase during the extraction (Table 1). In the Ni-Hmqt system, the spectral change was very complicated. At $-\log[H^+]$ 4, the species with an absorption maximum at 472 nm, which agreed with that of $Ni(mqt)_2$ prepared, was first extracted within a day. It changed to the other species with a maximum at 390 nm over several days. At lower $-\log[H^+]$, the latter species was directly extracted in a shorter period. These reactions could not be identified at this stage. The slow extraction in the Ni-Hqt system is just expected from inert character of Ni^{2+}. The Co-Hqt system took an abnormally long time for equilibration in spite of labile character of Co^{2+}, which was actually exemplified by the Co-Hmqt system. In the other systems, equilibria were reached relatively fast. Shaking longer than 5 days caused the decrease in the absorbance together with the formation of precipitates, which did not contain metal ions. Quinolinethiols are supposed to be slowly decomposed under these conditions.

Spectral characteristics of the extracted species are summarized in Table 1. Absorption maxima of any system lie at longer wavelengths than those of 1 : 1 complexes, which have been previously reported.[2,3] Molar absorption coefficients range from 6000 to 9000, whereas that of the species in the Co-Hqt system is definitely large.

Treatment of Extraction Equilibria. Distribution

Table 1. Extraction of Divalent Transition Metal Ions with Hqt and Hmqt at 25 °C

System	Condition[a)]	Shaking time	λ_{max}	ε	log K_{ex}	
			nm		Obtained	Reported[b)]
Co-Hqt	P-CF	48 h	467	12000	—	—
Ni-Hqt	P-CF	96 h	537	6200	4.52	3.4
Cu-Hqt[c)]	P-CF	5 m	430	9000	—	—
Zn-Hqt	P-CF	10 m	403	7800	3.83	3.8
Zn-Hqt	S-CF	20 m	403	7800	3.27	—
Zn-Hqt	P-B	20 m	414	8100	3.21	—
Zn-Hqt	P-CB	15 m	413	7800	3.42	—
Cd-Hqt[d)]	P-CF	—	—	—	—	—
Co-Hmqt	P-CF	100 m	454	7300	0.41	1.1
Ni-Hmqt[e)]	P-CF	—	472	6200	—	0.6
			390	9900		
Cu-Hmqt[d)]	P-CF	—	—	—	—	—
Zn-Hmqt	P-CF	10 m	403	7300	3.79	4.3
Cd-Hmqt	P-CF	5 h	390	9300	2.70	2.8

a) Anion: 0.1 mol dm^{-3} $NaClO_4$(P); 0.033 mol dm^{-3} Na_2SO_4(S). Solvent: chloroform (CF); benzene (B); chlorobenzene (CB). b) Ref. 5). c) 100% extraction. d) Precipitate formation. e) Two-step reaction.

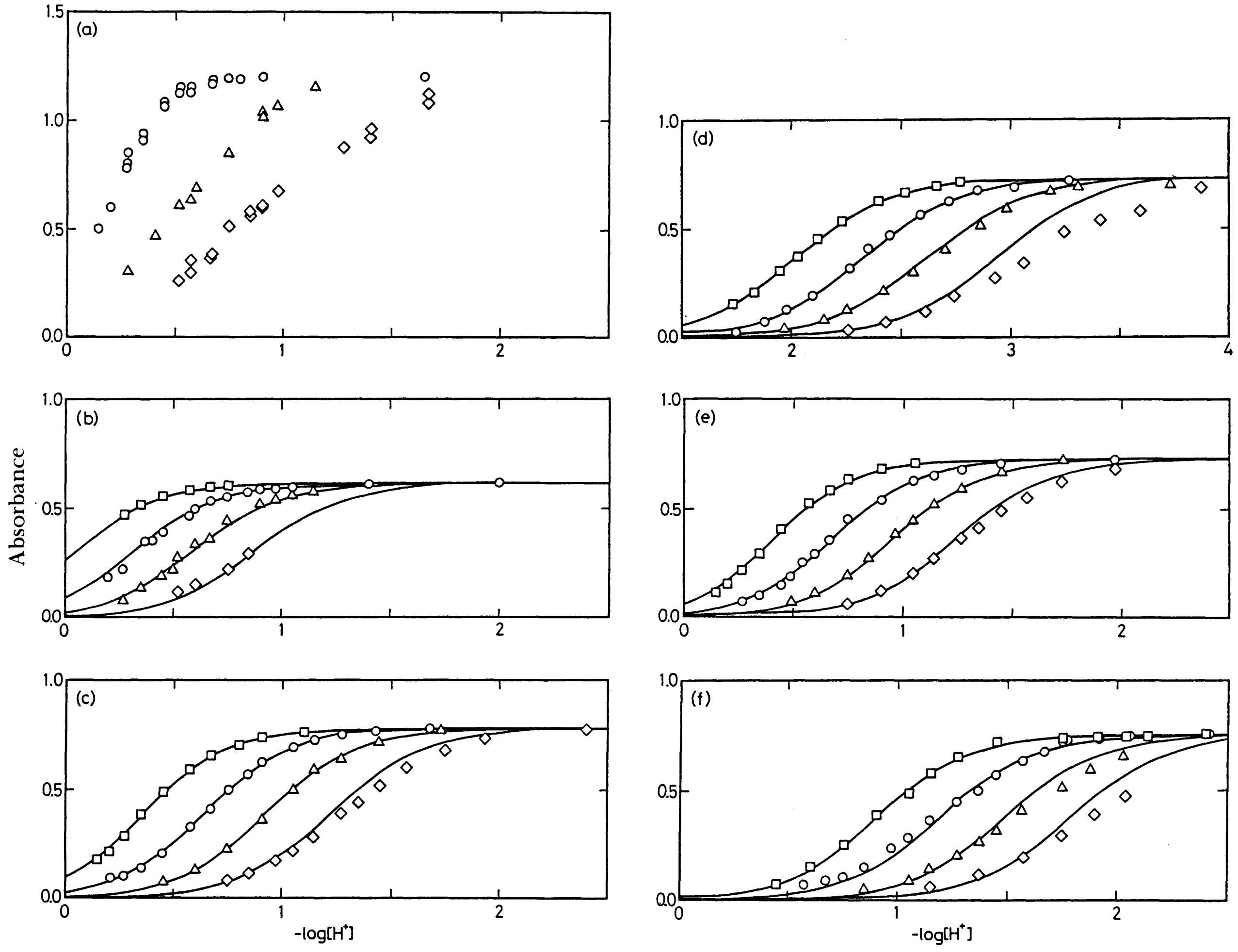

Fig. 1. Plot of absorbance vs. $-\log[H^+]$. Aqueous phase: $C_M=1\times10^{-4}\,\mathrm{mol\,dm^{-3}}$; $0.1\,\mathrm{mol\,dm^{-3}}$ $NaClO_4$. Organic phase: chloroform. C_{Hqt} or $C_{Hmqt}/10^{-3}\,\mathrm{mol\,dm^{-3}}$: (□) 6.0; (○) 3.0; (△) 1.5; (◇) 0.75. System, wavelength/nm: (a) Co^{2+}-Hqt, 467; (b) Ni^{2+}-Hqt, 537; (c) Zn^{2+}-Hqt, 403; (d) Co^{2+}-Hmqt, 454; (e) Zn^{2+}-Hmqt, 403; (f) Cd^{2+}-Hmqt, 410. Solid lines: calculated curves with constants in Table 1.

data were collected under various conditions in each system. Some of the results were shown as absorbance vs. $-\log[H^+]$ diagrams in Fig. 1.

With these extracting reagents, metal ions start to be extracted at low $-\log[H^+]$. As the concentration of H_2qt^+ or H_2mqt^+ in the aqueous phase is not negligible in this $-\log[H^+]$ range, the prominent equilibrium treatment assuming a general species $(M_jL_{2j}(HL)_m)_o$ could not be applied.24) The composition of the solid complex prepared under the same conditions is taken into account, and the extracted species is assumed to be a neutral j-meric complex of the composition M_jL_{2j},13)

$$jM^{2+}+2j(HL)_o \overset{K_{ex}}{\rightleftharpoons} (M_jL_{2j})_o+2jH^+, \qquad (4)$$

where K_{ex} represents the extraction constant. The total concentration of metal(II) in the organic phase, $C_{M,o}$ is expressed as a logarithmic form by

$$\log C_{M,o}=j\,(\log C_{M,w}-2\log[H^+]+2\log[HL]_o)+\log jK_{ex}, \qquad (5)$$

where $[HL]_o$ is calculated from the total concentration of the extracting reagent, C_{HL}, as follows:

$$[HL]_o=K_D\cdot C_{HL}/(K_D+1+[H^+]/K_2). \qquad (6)$$

If the j-meric species is responsible for the extraction, the plot of $\log C_{M,o}$ vs. $(\log C_{M,w}-2\log[H^+]+2\log[HL]_o)$ would yield a straight line of slope j.

The results are shown in Fig. 2. Only a simple monomeric species, ML_2 is extracted except for the Co–Hqt system.

$$M^{2+}+2(HL)_o \rightleftharpoons (ML_2)_o+2H^+ \qquad (7)$$

The extraction constants obtained are summarized in Table 1 together with literature values, which have been recalculated with the K_1 and K_D values used in the paper.5)

Effects of Anions, Organic Solvents, and Central Metal Ions. In the extraction of divalent transition metal ions with 8-quinolinol, $M_2q_3(Hq)_3X$, $Mq_2(Hq)$, and $M_2q_4(Hq)_2$ are responsible for the extraction.13) In the systems containing a hydrophobic anion and a polar solvent, metal ions start to be extracted at lower $-\log[H^+]$ because of the larger contribution of

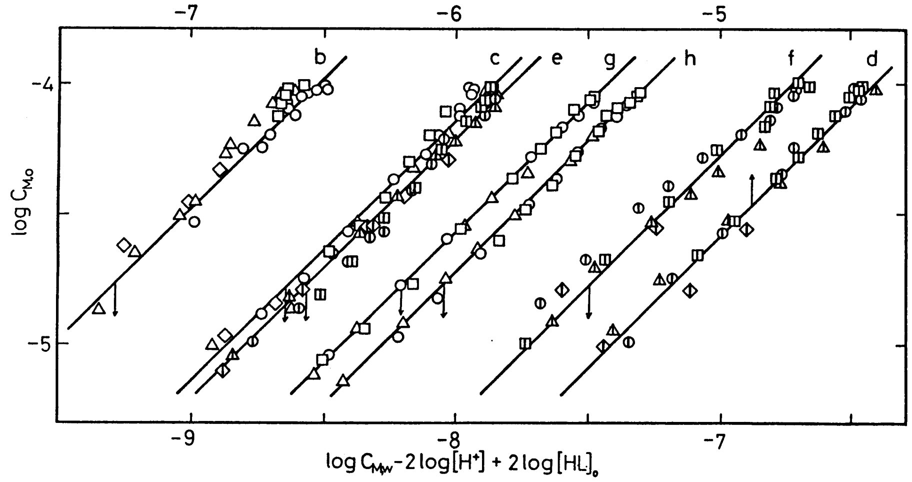

Fig. 2. Determination of the polymerization degree of metal(II) 8-quinolinethiolate according to Eq. 5. System: (b)—(f) same with Fig. 1; (g) Zn^{2+}-ClO_4^--Hqt-chlorobenzene; (h) Zn^{2+}-SO_4^{2-}-Hqt-chloroform. Solid lines: straight lines with a slope of unity.

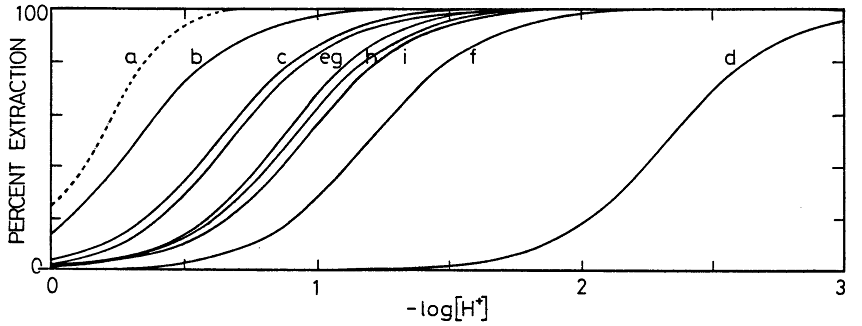

Fig. 3. Extraction curve for various systems. C_{Hqt} or C_{Hmqt}= 3.0×10^{-3} mol dm^{-3}. System: (a)—(h) same with Fig. 1 and 2; (i) Zn^{2+}-ClO_4^--Hqt-benzene. Curve (a) does not show the equilibrated state (see text for details).

$M_2q_3(Hq)_3X$. In the extraction with 8-quinolinethiol, on the other hand, the extraction curves do not change so much by solvents and anions (Fig. 3). This agrees with that only the neutral species $M(qt)_2$ is found as an extracted species.

Zinc ion has a stronger interaction with sulfate than with perchlorate in aqueous solutions.

$$Zn^{2+} + SO_4^{2-} \overset{K}{\rightleftharpoons} ZnSO_4 \qquad (8)$$

The constant, K at the ionic strength of 0.1 is estimated to be $10^{1.6}$ from the constant at infinite dilution ($10^{2.4}$) and the activity coefficient for divalent ions ($10^{-0.4}$). The side reaction coefficient of zinc with sulfate, $\alpha=1+K[SO_4^{2-}]$, is $10^{0.4}$, which is comparable to the difference in the extraction constant ($10^{0.56}$) between perchlorate and sulfate media.

The extraction constant for the Ni-Hqt system is larger than the literature value by 1.1 in logarithmic unit.[5] Care must be taken of slow equilibration in this system.

The data obtained in the Co-Hqt system (Fig. 1(a)) are not those expected for the equilibria expressed by Eq. 4. Moreover, species once extracted into chloroform could hardly be back-extracted. These, together with some findings mentioned above, indicate the formation of Co(III) complexes. This type of oxidation was suggested when abnormally large enthalpy change was found for the formation of the 1 : 1 complex with Hqt in 50v/v% aqueous dioxane.[4]

Adduct Formation. The complex solution (1×10^{-4} mol dm^{-3}) in chloroform was mixed with various amounts of 1,10-phenanthroline (4×10^{-5}—4×10^{-1} mol dm^{-3}) in the presence of excess thiol (3—6×10^{-3} mol dm^{-3}). Spectral change having isosbestic points was found with an absorption maximum shifted from 537 to 432 for $Ni(qt)_2$, and from 472 to 425 nm for $Ni(mqt)_2$. The $Co(mqt)_2$ complex also gave indication of the same reaction. This is ascribed to the formation of the 1 : 1 adduct,[25,26]

$$ML_2 + \text{phen} \overset{K_{add}}{\rightleftharpoons} ML_2(\text{phen}), \qquad (9)$$

where K_{add} denotes the adduct formation constant. From the absorbance change shown in Fig. 4, this constant was determined by the conventional method:

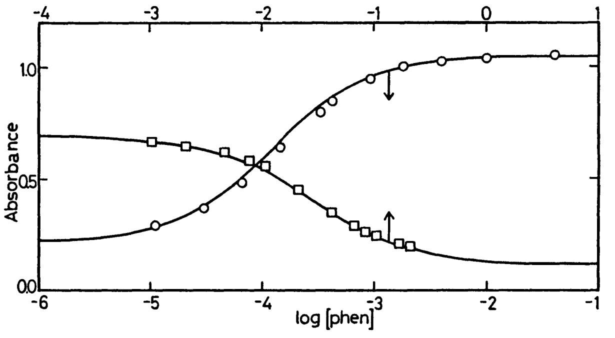

Fig. 4. Plot of absorbance vs. log[phen]. $C_{complex}$= 1×10^{-4} mol dm^{-3}; C_{Hqt} or C_{Hmqt}=$3-6\times10^{-3}$ mol dm^{-3}. Complex, wavelength/nm: (○) Ni(qt)$_2$, 432; (□) Ni(mqt)$_2$, 480. Solid lines: calculated curves with constants obtained.

Table 2. Analytical Data for the Co-Hqt Complexes Prepared under Various Conditions

Compound	Found (%)				
	Co	C	H	N	Cl
Prepared in aqueous ClO_4^- medium	9.47	53.5	3.0	6.7	6.0
Prepared in ethanol	10.66	55.0	3.1	7.8	
Extracted from SO_4^{2-} medium into benzene	10.70	60.3	3.2	7.6	
Calculated for Co(qt)$_2$	15.53	56.98	3.19	7.39	
Calculated for Co(qt)$_3$	10.92	60.10	3.37	7.79	

logK_{add}=3.92 (3.97)[25] for Ni(qt)$_2$, 1.55 for Ni(mqt)$_2$, and <0 for Co(mqt)$_2$. On the other hand, no change was observed for Cu(qt)$_2$, Zn(mqt)$_2$, and Cd(mqt)$_2$ as well as Zn(qt)$_2$.[6,27] Some effects of phen on the extraction of Co^{2+} with Hqt have been reported,[26] but the Co-Hqt complex prepared does not show any spectral change. The Cd-Hqt and Cu-Hmqt complexes prepared are insoluble in chloroform. In the presence of phen, however, the adducts of these complexes are extracted without precipitate formation (see below).

Structures of Co-Hqt and Co-Hmqt Complexes. Analytical data for the Co-Hqt complexes prepared in aqueous perchlorate and ethanolic media are shown in Table 2. Neither gave a definite composition. Especially, the complex obtained from perchlorate medium contained chlorine, and consisted of at least 4 species as shown by chromatogram in Fig. 5(a). Since this mixture is diamagnetic in contrast to the Co-Hmqt, the cobalt in these complexes is oxidized to Co(III).

The extracts from a sulfate medium into benzene, on the other hand, had a composition close to Co(qt)$_3$. Although two geometrical isomers are possible for Co(qt)$_3$, only one species was practically found in chromatogram of Fig. 5(b). The ^{13}C NMR spectrum of this species given by Fig. 6 showed very complicated resonances (more than 19). Thus the complex is assigned as the *mer*(*S*) isomer, because only nine signals are expected for the *fac*(*S*) geometry.[28]

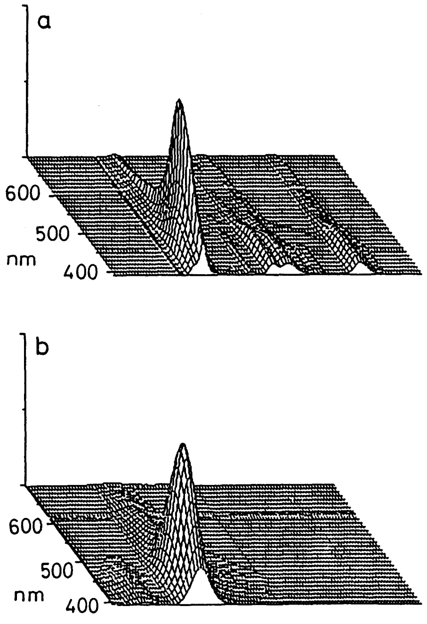

Fig. 5. Chromatograms of Co-Hqt complexes. (a) Complex prepared in perchlorate medium. (b) Complex extracted from sulfate medium into benzene. Column: CIG pre-packed column CPO-042-10 (200 mm×4-mm i.d.). Mobile phase: methanol-water (80:20 v/v).

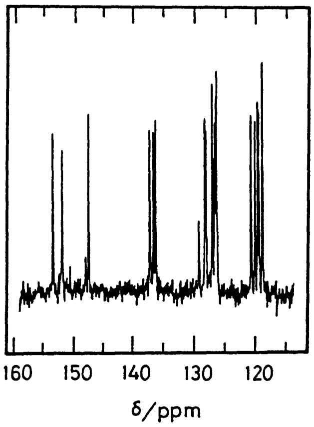

Fig. 6. ^{13}C NMR spectrum of Co(qt)$_3$ in CDCl$_3$ containing TMS as an internal standard.

The Co-Hmqt complex, on the other hand, is a simple 1 : 2 complex and is expected to have tetrahedral configuration judged from the magnetic moment (4.9 B.M.). The methyl group adjacent to the donor atom sometimes shows striking effect on the properties of the complex. In this case, steric hindrance in the formation of the tris chelate suppresses the oxidation of cobalt.

Structures of Other Complexes. The structure of Cu(qt)$_2$, which has the same composition with copper 8-quinolinolate, Cuq$_2$, was determined to be square-planar in solution by ESR spectra,[29,30] and in solid by X-ray crystallography.[31] This structure is stable and even phen cannot change the configuration to octahedron. On the other hand, the Cu–Hmqt prepared, which is insoluble in organic solvents, has a metal : ligand ratio close to 1 : 1 and is expected to be a copper(I) complex. Coordinated water molecules, which are identified by the IR spectrum, can be replaced by phen to make the complex soluble in organic solvents. The 2-methyl substituent makes the planar structure unfavorable and increases the reducibility of the copper complex.

With 8-quinolinol, zinc is precipitated as $Znq_2 \cdot 2H_2O$ and is extracted as $Znq_2(Hq)$ or $Znq_2(phen)$. With thiols, on the other hand, $Zn(qt)_2$ or $Zn(mqt)_2$ is precipitated or extracted, and neither thiol nor phen can change the configuration to octahedron. By the change of the donor atom from O to S, tetrahedral structure is relatively stabilized for zinc. Since the 2-methyl group does not hinder the coordination of the second mqt^- with this configuration, $Zn(qt)_2$ and $Zn(mqt)_2$ have similar characteristics.

The structure of $Cd(mqt)_2$ was determined to be tetrahedral by X-ray crystallography.[32] Although $Cd(qt)_2$ prepared also has a metal : ligand ratio of 1 : 2 without coordinated waters, the behavior is fairly different from those of $Zn(qt)_2$ and $Cd(mqt)_2$; for example, $Zn(qt)_2$ has a solubility of 4.8×10^{-2} mol dm^{-3} in chloroform, whereas $Cd(qt)_2$ is insoluble but is solubilized in the presence of phen. Since cadmium ion has a larger ionic radius than zinc ion, $Cd(qt)_2$ may change the configuration to octahedron.

From the magnetic susceptibility measurements, $Ni(qt)_2$ (3.32 B.M.) was estimated to have a polymeric square planar structure,[33] whereas $Ni(mqt)_2$ (3.14 B.M.) a distorted tetrahedron.[34] These structures were confirmed by X-ray crystallographic studies.[35,36] In solution, on the other hand, a monomeric planar structure was proposed for $Ni(qt)_2$ from a kinetic study on its reaction with alkyl halide,[37] and from the equilibrium study on the adduct formation reaction.[25] $Ni(mqt)_2$ differs from $Ni(qt)_2$ in the absorption spectra and in the solubilities in chloroform,[34] and is believed to have the same structure in solution with that in the solid.

The planar $Ni(qt)_2$ keeps some capacity to be coordinated. A configurational change does not occur with weak ligands such as water as found in the precipitation of $Niq_2 \cdot 2H_2O$, but it does occur with stronger ligands such as phen. The 2-methyl substituent hinders the structural change to octahedron to make K_{add} of $Ni(mqt)_2$ small.

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