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Equilibrium and X-Ray Structural Studies on Dimeric and Trimeric Species Formed in the Extraction of Nickel(II) with 2-Methyl-8-quinolinol

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Nickel(II) has been extracted with 2-methyl-8-quinolinol (Hmq) into chloroform under the following conditions: $C_{\mathrm{Ni}}=2\times10^{-5}$—$4\times10^{-3}$; $C_{\mathrm{Hmq}}=7.5\times10^{-3}$—$4.8\times10^{-1}$ mol dm^{-3}; supporting electrolyte: 0.1 mol dm^{-3} $NaClO_4$ or Na_2SO_4; $-\log\,[H^+]=4.5$—9. An equilibrium analysis has demonstrated that neutral species, $(Ni_2(mq)_4)_o$ and $(Ni_3(mq)_6)_o$, are responsible for extraction from sulfate solutions, whereas ion-pair species, $([Ni_3H(mq)_6]ClO_4)_o$ and $([Ni_2H_3(mq)_6]ClO_4)_o$, are predominant from perchlorate solutions. The dimeric structure of $(Ni_2(mq)_4)_o$ is cleaved stoichiometrically along with adduct formation upon adding 1,10-phenanthroline, while being converted to $(NiH(mq)_3)_o$ and/or $(Ni_2H_2(mq)_6)_o$ at high concentrations of Hmq. X-ray crystallographic studies show that the complexes, $[Ni_3(mq)_6]\cdot 2C_2H_5OH$ and $[Ni_3H(mq)_6]ClO_4\cdot C_2H_5OH$, have discrete bent-trimeric structures, and maintain all the nickel atoms octahedral by two μ- and two μ_3-bridgings at the phenolate oxygen atoms. In the $[Ni_2H_3(mq)_6]ClO_4$ complex, each nickel atom is surrounded by three ligands in a fac configuration and two octahedrons are connected by three hydrogen bondings. All the three structures in solids are discrete and possibly the same as those in organic solvents. Compared with 8-quinolinol, the methyl group of Hmq makes the coordination of the third ligand unfavorable for both neutral and ion-pair species. Bridging at the phenolate oxygen atoms yields extractable oligomeric species.

Solvent extraction is one of the most efficient methods for separating and concentrating metal ions, and is widely used both in industries and laboratories.[1,2] Comprehensive compilation of equilibrium data for each combination of a metal ion, an extractant, an organic solvent, and a supporting electrolyte is indispensable for determining the best extraction system for a certain purpose.[3] Along this line, much effort has been exerted to identify the composition of extracted species and to determine equilibrium data, such as the extraction constants or distribution constants of metal complexes. These data, however, appear to be much less reliable than the stability constants of metal complexes in aqueous solutions or non-aqueous solvents.[4] In some cases, even the stoichiometry proposed for extracted species is unlikely and cannot stand up against the criticism of coordination chemists.

Quite often, distribution measurements have been made with a fixed total metal concentration. In addition, only one monomeric neutral complex was assumed as an extracted species, and the conventional log D vs. pH (D: the distribution ratio of a metal ion between aqueous and organic phases) plot was used to determine the extraction constant. A possible erroneous conclusion derived by using this type of plot has been pointed out and fully discussed.[5] Another reason is the exclusive adoption of radiometry for determining the distribution ratio. On the one hand, since even a very large or small distribution ratio can easily be measured, the stability constants of metal complexes in aqueous solutions and their distribution constants can separately be obtained with this method. On the other hand, a change in the composition of an extracted species is hard to be recognized at a high distribution ratio. Moreover, equilibrium data derived for a relatively low metal concentration, which is commonly used in radiometry, do not always reflect the actual extraction behavior. Distribution data under various conditions should be analyzed by appropriate equilibrium treatment to obtain reliable parameters. Other properties, such as the visible absorption spectra, should also be used as supplementary data. For the extracted species of an unusual composition, structural characterization is also required.

With a potentially monoanionic bidentate extractant, HL,[6] a trivalent metal ion forms a neutral tris complex, $M^{III}L_3$. When the ionic radius of the metal ion is not very large, $M^{III}L_3$ would be coordination-saturated and easily extracted into organic solvents. In the case of a divalent metal ion favoring an octahedral configuration, coordination-saturation does not occur at the same time as charge neutralization, and the resulting bis complex, $(M^{II}L_2)_o$,[7] is less extractable. For example, when nickel(II) was extracted with a 0.1 mol dm^{-3} chloroform solution of acetylacetone or benzoylacetone, the maximum extraction reached only 20 or 80%, respectively.[9] On the other hand, anhydrous nickel(II) complexes with β-diketones are fairly soluble in a dehydrated noncoordinating solvent. The solution structures have extensively been studied in relation to their seemingly abnormal magnetic properties.[10] Nickel(II) acetylacetonate has the trimeric structure in a noncoordinating solvent.[11] The addition of neutral bases, such as pyridine (py), cleaves the trimeric structure to yield $[Ni_2(acac)_2py]$ and $[Ni(acac)_2py_2]$.[12] Even a small amount of water transforms the trimer to a hydrated bis complex of $[Ni(acac)_2(H_2O)_2]$,[11] which does not remain dissolved in organic solvents at high concentrations.

Hence, the extracted species, expressed as $(Ni(acac)_2)_o$, is considered to be hydrated; this is one of the reasons for the low extractability of this type of complex. All the relevant species were isolated and structurally characterized by X-ray crystallography.[13—16]

Monoanionic bidentate extractants having a quinoline ring show a much higher extractability than β-diketones. In order to reveal the difference, we have carried out systematic studies on the extraction of divalent transition metal ions with these reagents from both equilibrium and structural points of view.[17] In an aqueous solution, 8-quinolinol reacts with Ni^{2+} to form a sparingly soluble complex of $[Niq_2(H_2O)_2]$. When an organic solvent is added to such an aqueous solution, metal complexes such as $(NiHq_3)_o$, $(Ni_2H_2q_6)_o$, and $([Ni_2H_3q_6]X)_o$[18] are extracted, depending on the pH, total concentrations of the metal ion and the ligand, anions, and organic solvents. The former two complexes are electrically neutral, whereas the last one has +1 charge and is extracted as an ion-pair with hydrophobic anions. The structures of $[Ni_2H_2q_6]$ and $[Ni_2H_3q_6]X$ (X: I_3, SCN, ClO_4) have been determined by X-ray crystallography.[17,19] Each nickel atom is surrounded by three ligands, and two such octahedrons are connected by two or three strong hydrogen bonds.

2-Methyl-8-quinolinol shows, in some cases, different reactivities to metal ions from 8-quinolinol because of the substituent adjacent to the donor atom. For example, aluminum is not effectively precipitated or extracted with 2-methyl-8-quinolinol, as with 8-quinolinol,[20,21] or vanadium(V) forms a black μ-oxo dimeric complex with 8-quinolinol, and a yellow monomeric complex with 2-methyl-8-quinolinol.[22—27] It has been reported that nickel(II) forms a precipitate of a monohydrated complex, $Ni(mq)_2(H_2O)$,[28,29] in aqueous solutions and is extracted as $(Ni(mq)_2)_o$.[30—33] If this is the case, the extractability is unexpectedly high compared with $(Ni(acac)_2)_o$, even when the difference in the distribution of the reagents is taken into account ($10^{3.24}$ for Hmq and $10^{1.3}$ for Hacac). Here, we report on detailed studies concerning the extraction equilibrium and X-ray crystal structures of three complexes corresponding to the extracted species.

Experimental

Equilibrium Measurement. A nickel(II) sulfate solution was standardized against a Na_2H_2edta solution. Chloroform was shaken successively three times with concd sulfuric acid, 2 mol dm^{-3} sodium hydroxide solution, and distilled water. The other reagents were used as received.

All experiments were carried out in a room at 25±2 °C. The absorption spectra and $-\log[H^+]$ were measured by using a thermoelectric circulating bath at 25±0.5 °C. The ionic strength was maintained at 0.10 mol dm^{-3} for perchlorate and 0.30 mol dm^{-3} for sulfate medium. The hydrogen-ion concentration was measured with a Radiometer pH METER 26. As an internal solution for a calomel electrode, saturated sodium chloride was used instead of potassium chloride. Solutions containing 1.00×10^{-2} mol dm^{-3} perchloric acid and 9.00×10^{-2} or 2.90×10^{-1} mol dm^{-3} sodium perchlorate were used as $-\log[H^+]$ standards. Visible and infrared absorption spectra were recorded on a Shimadzu spectrophotometer (UV-250) and on a JASCO infrared spectrophotometer (A-100), respectively. Atomic absorption spectrometry was carried out with a Daini Seikosha SAS-727.

A portion of 2×10^{-5} to 4×10^{-3} mol dm^{-3} nickel(II) solution was shaken with an equal volume of 7.5×10^{-3} to 4.8×10^{-1} mol dm^{-3} chloroform solution of 2-methyl-8-quinolinol at 200 strokes min^{-1}. After centrifugation, $-\log[H^+]$ and the nickel(II) concentration were measured for the aqueous phases. Visible absorption spectra of the organic phases were measured with a quartz cell of 1 or 10 mm. The absorbances at 400 nm were used for numerical analyses. Perchlorate ion in the organic phase was stripped into an aqueous phase buffered at $-\log[H^+]$ of 7 and was determined by modifying a method from the literature.[34]

Preparation of Nickel Complexes. According to a method from the literature,[27] $Ni(mq)_2\cdot H_2O$ was prepared in an aqueous solution. By the addition of water to a saturated solution of $Ni(mq)_2\cdot H_2O$ in ethanol, brown crystals of $[Ni_3(mq)_6]\cdot 2C_2H_5OH$ (**1**) were obtained after 10 d.

Nickel(II) perchlorate hexahydrate (10 mmol in 20 cm^3 ethanol) was added dropwise into 2-methyl-8-quinolinol (20 mmol in 100 cm^3 ethanol). The mixture was filtered and concentrated. After several days, light-green crystals of $[Ni_3H(mq)_6]ClO_4\cdot C_2H_5OH$ (**2**) were obtained. The same procedure for a nickel:ligand ratio of 1:5 gave deep-green crystals of $[Ni_2H_3(mq)_6]ClO_4$ (**3**).

Structure Determination. Crystal data, intensity-data collection and least-squares processing are summarized in Table 1. The crystals, **1** and **2**, sealed in capillary tubes were subjected to measurement, whereas that of **3** was mounted as usual. Three-dimensional intensity data were collected on a Rigaku AFC-5 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ=1.54178 Å). The ω-2θ scan technique was employed; an ω-scan width of $(1.2+0.2\tan\theta)$ deg, a scan rate of 6 deg min^{-1}, and background counts of 5 s at both edges. No significant variations were observed for intensities of 3 standard reflections monitored every 100 measurements during data collection. Data were corrected for Lorentz and polarization effects. The structures were solved by the conventional heavy-atom method and refined by a block-diagonal approximation to minimize $\Sigma(w|\Delta F|^2)$. Variables were the positional and anisotropic thermal parameters of non-H atoms and the positional parameters of H atoms. The temperature factors of H atoms were set equal to the B_{eq}'s of bonded atoms. Absorption corrections were applied after an isotropic least-squares refinement by an empirical method based on the differences between the observed and calculated structure factors.[35]

It has been revealed by elemental analysis and density measurement that the asymmetric units of **1** and **2** contain two and one molecules of C_2H_5OH, respectively. The atoms of C_2H_5OH, excluding H atoms, could be located for **1**, but not for **2**. In a difference electron density map of **2**, eight peaks (0.3—0.6 e Å^{-3} in peak height) 1—2 Å apart from each other are distributed within a considerably narrow space. Although we assumed that the C_2H_5OH molecule is disordered in this space, we could not interpret the arrangement of the peaks with any disordered model. The comparatively high R value of **2** is probably due to our neglecting the contribution of

Table 1. Crystallographic Experiments and Computations

	1	2	3
Formula (mq=$C_{10}H_8NO$)	$[Ni_3(mq)_6]\cdot 2C_2H_5OH$	$[Ni_3H(mq)_6]ClO_4\cdot C_2H_5OH$	$[Ni_2H_3(mq)_6]ClO_4$
Formula weight	1217.32	1271.71	1168.95
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	13.241(4)	13.680(2)	14.514(1)
b/Å	20.935(6)	18.283(5)	12.347(1)
c/Å	11.361(5)	13.085(3)	33.044(3)
α/deg	97.45(4)	107.57(2)	90.0
β/deg	113.68(2)	99.37(2)	103.16(1)
γ/deg	92.33(4)	93.72(2)	90.0
Z	2	2	4
V/Å^3	2845(1)	3056(1)	5766(1)
ρ_c/g cm^{-3}	1.421	1.382	1.347
Crystal size/mm	0.2×0.15×0.1	0.4×0.2×0.1	0.8×0.1×0.1
μ/cm^{-1}	16.0	19.5	17.2
$2\theta_{max}$/deg	120.0	120.0	120.0
No. of unique reflections	8439	9078	8564
No. of observed reflections with $F_o > 3\sigma(F_o)$	5862	6003	6662
R	0.070	0.089	0.064
R_w	0.098	0.119	0.091
S (goodness of fit)	1.182	1.116	1.103
No. of reflections used at the last stage of least-squares	5744	5899	6504
No. of very strong reflections	13	17	9
No. of reflections with $w^{1/2}\lvert\Delta F\rvert\geq 4$	105	87	149
c^2 in weighting expression of $w=[\sigma^2(F_o)+c^2\lvert F_o\rvert^2]^{-1}$	0.004470	0.00660	0.00510

C_2H_5OH to the F_c calculation. Computations using the MULTAN87, PLUTO and XPACK86 SHIONOGI programs were performed on a FACOM M-730/10 computer at Shionogi Research Laboratories.[36]

Results

Protonation and Distribution of 2-Methyl-8-quinolinol. The second protonation constant was spectrophotometrically determined to be $K_2=[H_2mq^+]/[Hmq]/[H^+]=10^{5.67}$, which agrees with the value obtained by Dyrssen ($10^{5.7}$).[37] The distribution constant of Hmq between water and chloroform determined by the conventional method, $K_D=[Hmq]_o/[Hmq]=10^{3.24}$, is in good agreement with the value obtained by Fresco and Freiser ($10^{3.22}$).[38]

Extraction Behavior. The extraction of nickel(II) with 2-methyl-8-quinolinol was examined under various conditions ($C_{Ni}=2\times10^{-5}$—4×10^{-3} mol dm^{-3}, $C_{Hmq}=$

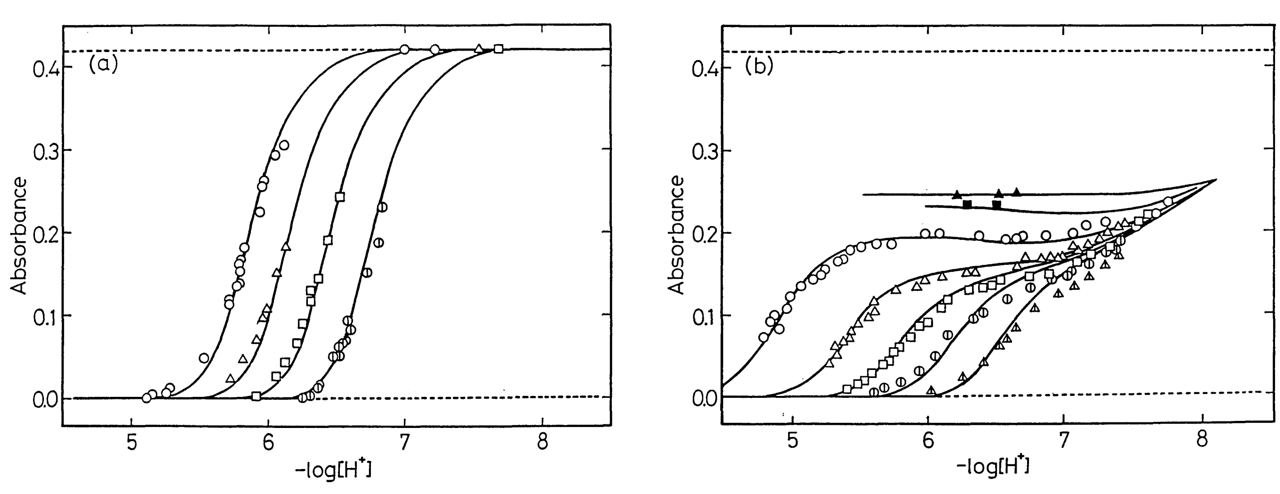

Fig. 1. Relationship between the absorbance of the organic phase at 400 nm and $-\log[H^+]$ in the aqueous phase in the extraction of nickel(II) with 2-methyl-8-quinolinol from 0.1 mol dm^{-3} Na_2SO_4 (a) and 0.1 mol dm^{-3} $NaClO_4$ (b). $C_{Ni}=0.99\times10^{-4}$ mol dm^{-3}. C_{Hmq}/mol dm^{-3}: ◬, 0.0075; ⦶, 0.015; □, 0.03; △, 0.06; ○, 0.12; ■, 0.24; ▲, 0.48. Solid lines are calculated using the constants obtained.

7.5×10^{-3}—4.8×10^{-1} mol dm^{-3}, supporting electrolyte: 0.1 mol dm^{-3} $NaClO_4$ or Na_2SO_4, $-\log[H^+]=4.5$—9). It took approximately 15 h for equilibration. The absorption spectra of the extracts from sulfate solutions were similar to each other, irrespective of $-\log[H^+]$ and C_{Hmq}. "Neutral" extracted species are expected from a sulfate medium. The extracts from perchlorate solutions, on the other hand, showed absorption spectra varying with $-\log[H^+]$ and C_{Hmq}. Ion-pair species as well as neutral complexes are responsible for extraction from a perchlorate medium. Figure 1 shows the absorbance of the organic phase at 400 nm plotted against $-\log[H^+]$ for these systems at the $C_{Ni}=10^{-4}$ mol dm^{-3} level.

Extraction Equilibria for Neutral Species. The extraction curves shown in Fig. 2 depend upon the total concentration of nickel(II), suggesting the presence of polymeric species. The extraction equilibrium for a j-meric neutral extracted species, $Ni_jH_h(mq)_{2j+h}$, is written as[5]

$$j\,\mathrm{Ni}^{2+}+(2j+h)(\mathrm{Hmq})_o \rightleftarrows (\mathrm{Ni}_j\mathrm{H}_h(\mathrm{mq})_{2j+h})_o+2j\mathrm{H}^+ \qquad (1)$$

with the extraction constant

$$K_{ex}=[\mathrm{Ni}_j\mathrm{H}_h(\mathrm{mq})_{2j+h}]_o[\mathrm{H}^+]^{2j}/[\mathrm{Ni}^{2+}]^j[\mathrm{Hmq}]_o^{2j+h}. \qquad (2)$$

In highly extractable systems, the concentration of nickel(II) complexes in an aqueous phase is generally negligible compared with that of Ni^{2+}. The total concentration of nickel(II) in the organic phase, $C_{Ni,o}$, is written in a logarithmic form as

$$\log C_{Ni,o}=j(\log[\mathrm{Ni}^{2+}]-2\log[\mathrm{H}^+]) + \log jK_{ex}+(2j+h)\log[\mathrm{Hmq}]_o. \qquad (3)$$

Since Hmq was added in excess against nickel(II), the concentration of Hmq in the organic phase is practically equal to its total concentration and is constant over the relevant $-\log[H^+]$ range. The degree of oligomerization of the extracted species can be found from the slope of the plot of $\log C_{Ni,o}$ against $(\log[Ni^{2+}]-2\log[H^+])$.

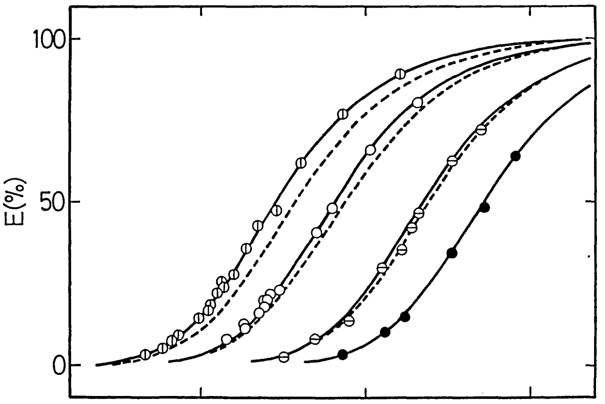

Fig. 2. Effect of the total nickel(II) concentration on the percent extraction (E). Supporting electrolyte: 0.1 mol dm^{-3} Na_2SO_4. $C_{Hmq}=0.06$ mol dm^{-3}. C_{Ni}/mol dm^{-3}: ●, 0.20×10^{-4}; ⊖, 0.99×10^{-4}; ○, 0.99×10^{-3}; ⦶, 0.40×10^{-2}. The solid lines were calculated by considering the presence of $(Ni_2(mq)_4)_o$ and $(Ni_3(mq)_6)_o$, whereas dotted lines were obtained by considering the unique presence of $(Ni_2(mq)_4)_o$.

As evident from Fig. 3, the slope, which is 2 at lower $C_{Ni,o}$, tends to be 3 at $C_{Ni,o}$ concentrations higher than $10^{-4.5}$. Both dimeric and trimeric species are responsible for extraction in this system. The number of protons involved in extracted species, h, was determined to be zero from a comparison of the data at different C_{Hmq} values. Consequently, the extraction equilibria are described as follows:

$$2\mathrm{Ni}^{2+}+4(\mathrm{Hmq})_o \rightleftarrows (\mathrm{Ni}_2(\mathrm{mq})_4)_o+4\mathrm{H}^+ \quad K_{ex}=10^{-15.86} \qquad (4)$$

and

$$3\mathrm{Ni}^{2+}+6(\mathrm{Hmq})_o \rightleftarrows (\mathrm{Ni}_3(\mathrm{mq})_6)_o+6\mathrm{H}^+ \quad K_{ex}=10^{-22.54} \qquad (5)$$

The solid curves in Figs. 1(a), 2, and 3 were calculated using the constants mentioned above, whereas the dotted lines in Figs. 2 and 3 were obtained by assuming the unique presence of $Ni_2(mq)_4$.

Reaction of $Ni_2(mq)_4$ with Neutral Ligands. The extracts from sulfate medium at the $C_{Ni}=10^{-4}$ mol dm^{-3} level were mixed with varying concentrations of neutral ligands such as 1,10-phenanthroline (phen) and Hmq; the reactions were spectrophotometrically studied. The complex $Ni_2(mq)_4$ almost stoichiometrically reacts with phen according to

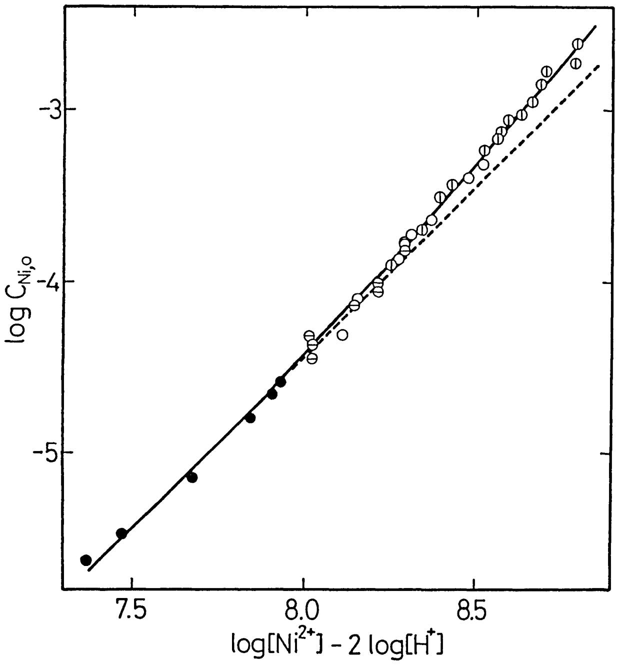

Fig. 3. Determination of the number of nickel(II) involved in the extracted species according to Eq. 3. The symbols for each total nickel(II) concentration are the same as those in Fig. 2. The solid curve is the normalized curve, $\log V(V+V^2)$ vs. $\log V$, where V is an arbitrary numeral. The dotted line has a slope of 2.

$$(Ni_2(mq)_4)_o + 2(phen)_o \rightleftarrows 2(Ni(mq)_2(phen))_o. \quad (6)$$

The dimeric structure is cleaved along with adduct formation.

Bhatki and others prepared anhydrous nickel(II) complexes of 2- and 4-methyl-8-quinolinol and examined their reactions with neutral bases in chloroform.[33] Although the same spectral change with our observation was obtained for the reaction of a nickel(II)–Hmq complex with phen, an unsound assumption was made that the adduct formed had no absorption at the wavelength of measurement, thus leading them to an incorrect equilibrium assignment. Since special care was not taken in their experiments to control the water concentration in chloroform, these anhydrous complexes are expected to have been hydrated to become $[Ni_2(mq)_4(H_2O)_2]$ and $[Ni(4\text{-}mq)_2(H_2O)_2]$, respectively. In the latter case, phen simply displaces water molecules,

$$(Ni(4\text{-}mq)_2)_o + (phen)_o \rightleftarrows (Ni(4\text{-}mq)_2(phen))_o. \quad (7)$$

Such difference in the reaction pattern was well reflected by the change in spectral characteristics. The parent $Ni_2(mq)_4$ had only one absorption maximum at 375 nm, whereas $[Ni(4\text{-}mq)_2(H_2O)_2]$ had two maxima at 340 and 450 nm. However, both of the adducts with phen showed similar absorption spectra, having maxima at 345 and 400 nm.[33]

Higher concentrations of Hmq (>0.3 mol dm^{-3}) change the absorption spectra of $Ni_2(mq)_4$. The formed species are expected to be $[NiH(mq)_3]$ and/or $[Ni_2H_2(mq)_6]$ in analogy with Hq complexes,[17] although this could not be confirmed by equilibrium analysis because of the minor contribution of these species.

Extraction Equilibria for Ion-Pair Species. The absorbance vs. $-\log[H^+]$ curves in Fig. 1(b) have plateaus at $-\log[H^+]=6$—7 and at $C_{Hmq}=0.06$—0.48

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2×10) for **1**

$$B_{eq}=4/3\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ni(1)	1730.5(8)	2119.2(5)	285.2(9)	48.2(3)	C(204′)	6862(6)	2792(4)	−838(8)	58(3)
N(101)	545(4)	1321(3)	−697(5)	43(2)	C(205′)	7950(6)	2386(5)	1223(8)	63(3)
C(102)	−548(6)	1270(4)	−1351(7)	55(3)	C(206′)	7932(6)	2067(5)	2143(8)	65(3)
C(103)	−1160(7)	655(5)	−1988(9)	80(4)	C(207′)	6975(6)	1787(4)	2162(7)	54(3)
C(104)	−657(9)	122(5)	−1947(10)	89(4)	C(208′)	5936(5)	1873(3)	1160(6)	43(2)
C(105)	1111(10)	−397(4)	−1130(9)	80(4)	C(209′)	5920(5)	2204(3)	179(6)	41(2)
C(106)	2214(9)	−327(4)	−432(10)	78(4)	C(210′)	6938(5)	2475(4)	172(7)	49(2)
C(107)	2813(7)	288(4)	180(9)	64(3)	C(211′)	3766(6)	2599(4)	−2851(7)	52(3)
C(108)	2241(6)	826(3)	46(7)	46(2)	O(212′)	4977(4)	1624(2)	1124(4)	49(2)
C(109)	1062(6)	769(3)	−638(6)	47(2)	Ni(3)	2319.5(8)	3359.3(5)	−321.1(9)	52.3(3)
C(110)	508(8)	130(4)	−1238(8)	66(3)	N(301)	2798(4)	4008(3)	1423(6)	46(2)
C(111)	−1131(6)	1860(5)	−1397(10)	77(4)	C(302)	2557(6)	4604(4)	1635(8)	55(3)
O(112)	2760(3)	1429(2)	558(4)	42(2)	C(303)	2939(8)	4963(4)	2917(10)	77(4)
N(101′)	1472(4)	2346(2)	1992(5)	37(2)	C(304)	3598(8)	4689(5)	3934(9)	80(4)
C(102′)	1759(5)	2080(3)	3041(6)	44(2)	C(305)	4550(8)	3716(5)	4777(7)	73(3)
C(103′)	1504(6)	2338(4)	4117(7)	54(3)	C(306)	4772(7)	3123(5)	4475(7)	70(3)
C(104′)	990(6)	2876(4)	4074(7)	59(3)	C(307)	4359(6)	2785(4)	3182(7)	53(2)
C(105′)	94(7)	3749(5)	2788(8)	69(3)	C(308)	3668(5)	3087(3)	2183(6)	40(2)
C(106′)	−210(7)	3990(4)	1673(9)	65(3)	C(309)	3429(5)	3720(3)	2448(6)	46(2)
C(107′)	38(6)	3696(4)	647(7)	54(3)	C(310)	3866(7)	4054(4)	3758(7)	61(3)
C(108′)	642(5)	3184(3)	786(6)	39(2)	C(311)	1859(8)	4934(4)	536(9)	69(4)
C(109′)	934(5)	2894(3)	1927(6)	44(2)	O(312)	3224(3)	2790(2)	943(4)	37(1)
C(110′)	668(6)	3187(4)	2955(7)	53(3)	N(301′)	3470(5)	3860(3)	−845(5)	45(2)
C(111′)	2379(7)	1492(4)	3160(8)	60(3)	C(302′)	4581(6)	3951(4)	−302(8)	53(3)
O(112′)	965(3)	2915(2)	−133(4)	38(1)	C(303′)	5148(7)	4323(4)	−874(10)	68(4)
Ni(2)	3659.8(8)	1845.5(5)	−321.8(9)	51.1(3)	C(304′)	4573(8)	4617(4)	−1912(9)	70(4)
N(201)	3028(4)	1171(3)	−2019(5)	43(2)	C(305′)	2745(10)	4888(5)	−3416(9)	79(4)
C(202)	3441(7)	652(4)	−2346(8)	59(3)	C(306′)	1640(11)	4823(5)	−3856(10)	89(5)
C(203)	2817(10)	224(4)	−3533(9)	81(4)	C(307′)	1102(8)	4412(4)	−3351(8)	68(3)
C(204)	1830(9)	335(4)	−4336(8)	72(3)	C(308′)	1705(6)	4077(4)	−2367(7)	52(3)
C(205)	285(7)	1060(5)	−4786(7)	68(3)	C(309′)	2895(7)	4166(3)	−1865(7)	53(3)
C(206)	−94(6)	1596(5)	−4422(7)	68(3)	C(310′)	3432(8)	4570(4)	−2411(7)	59(3)
C(207)	546(5)	2007(4)	−3262(7)	53(3)	C(311′)	5223(6)	3682(4)	911(8)	59(3)
C(208)	1580(5)	1863(3)	−2455(6)	38(2)	O(312′)	1256(4)	3692(2)	−1835(5)	52(2)
C(209)	1980(5)	1301(3)	−2838(6)	43(2)	C(401)	5567(19)	1123(15)	5653(16)	216(15)
C(210)	1336(7)	882(4)	−4023(7)	54(3)	C(402)	5741(19)	1342(9)	4595(19)	164(11)
C(211)	4575(9)	507(5)	−1469(10)	86(4)	O(403)	5148(8)	994(4)	3164(8)	113(4)
O(212)	2220(3)	2232(2)	−1309(4)	35(1)	C(404)	−2071(22)	3396(11)	−4967(18)	198(14)
N(201′)	4903(4)	2274(3)	−787(5)	42(2)	C(405)	−1754(18)	3236(10)	−3860(22)	189(12)
C(202′)	4870(5)	2562(4)	−1758(6)	46(2)	O(406)	−1066(8)	3717(6)	−2709(9)	142(5)
C(203′)	5840(6)	2844(4)	−1813(7)	54(3)					

Table 2. Determination of ClO_4^- Extracted with Nickel(II) Complexes in Chloroform[a]

$[Hmq]_o$ / $mol\,dm^{-3}$	$-\log[H^+]$	Abs.[b]	$C_{p,o}$[c] / $10^{-5}\,mol\,dm^{-3}$	R[d]
0.06	6.103	0.143	3.36	2.95
0.12	6.473	0.191	3.77	2.63
0.48	6.205	0.244	4.93	2.01

a) Under these conditions, Nickel(II) is completely extracted; $C_{Ni}=0.991\times10^{-4}$ mol dm^{-3}. b) Absorbance of organic phase at 400 nm. c) Total ClO_4^- concentration in chloroform. d) Ratio of total concentrations of Nickel(II) to ClO_4^- in chloroform.

mol dm^{-3}. The profile is the same as that in the extraction of nickel(II) with 8-quinolinol, except that the absorbances of the plateaus increase with C_{Hmq}.[17] This suggests that more than one ion-pair species with different metal-to-ligand ratios are extracted.

Perchlorate ions extracted together with nickel complexes were determined (Table 2). The ratio of nickel to perchlorate is 3 : 1 at lower C_{Hmq} and 2 : 1 at higher C_{Hmq}. By assuming various complexes as well as $(Ni_2(mq)_4)_o$, the extraction constants in each set were refined. The formation of $(Ni_3(mq)_6)_o$ is negligible at $C_{Ni}=10^{-4}$ mol dm^{-3} level. A combination of species giving satisfactory fits of absorbance vs. $-\log[H^+]$ curves is as follows:

$$2Ni^{2+}+4(Hmq)_o \rightleftarrows (Ni_2(mq)_4)_o+4H^+ \qquad K_{ex}=10^{-14.76}, \tag{8}$$

$$3Ni^{2+}+6(Hmq)_o+ClO_4^- \rightleftarrows ([Ni_3H(mq)_6]ClO_4)_o+5H^+ \qquad K_{ex}=10^{-10.92}, \tag{9}$$

and

$$2Ni^{2+}+6(Hmq)_o+ClO_4^- \rightleftarrows ([Ni_2H_3(mq)_6]ClO_4)_o+3H^+ \qquad K_{ex}=10^{-4.52}. \tag{10}$$

Table 4. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Temperature Factors ($Å^2\times10$) for **2**

$$B_{eq}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ni(1)	1784(1)	1909.3(8)	10020(1)	40.7(4)	C(203′)	1391(9)	3818(8)	14740(10)	63(5)
N(101)	2451(5)	915(4)	9586(6)	31(2)	C(204′)	1439(10)	4575(9)	14899(10)	68(5)
C(102)	2418(8)	372(5)	8625(9)	42(3)	C(205′)	2035(9)	5755(7)	14469(10)	57(4)
C(103)	3014(9)	−234(6)	8521(11)	52(4)	C(206′)	2528(9)	6022(7)	13857(9)	57(4)
C(104)	3605(9)	−294(7)	9412(11)	55(5)	C(207′)	3009(8)	5567(6)	13069(9)	45(3)
C(105)	4233(8)	196(7)	11399(12)	59(5)	C(208′)	2909(7)	4768(6)	12882(8)	39(3)
C(106)	4226(9)	730(8)	12364(12)	63(5)	C(209′)	2407(7)	4439(6)	13505(7)	37(3)
C(107)	3657(8)	1336(7)	12415(9)	47(4)	C(210′)	1942(8)	4937(7)	14317(9)	51(4)
C(108)	3041(7)	1410(5)	11509(8)	35(3)	C(211′)	1800(9)	2516(7)	13765(8)	52(4)
C(109)	3040(6)	856(5)	10502(9)	37(3)	O(212′)	3317(4)	4283(3)	12091(5)	33(2)
C(110)	3660(7)	225(5)	10433(10)	42(4)	Ni(3)	2040(1)	3292.6(8)	9421(1)	39.5(4)
C(111)	1688(10)	420(7)	7653(10)	54(4)	N(301)	698(5)	3769(4)	9276(6)	27(2)
O(112)	2467(4)	1966(3)	11526(5)	29(2)	C(302)	282(7)	4091(6)	8566(8)	39(3)
N(101′)	310(5)	1473(4)	9776(6)	32(2)	C(303)	−681(8)	4346(6)	8562(9)	43(3)
C(102′)	−172(7)	1139(5)	10351(8)	37(3)	C(304)	−1208(8)	4223(6)	9321(10)	47(4)
C(103′)	−1229(8)	951(6)	10050(10)	50(4)	C(305)	−1311(8)	3725(7)	10847(10)	49(4)
C(104′)	−1760(8)	1123(7)	9229(11)	54(4)	C(306)	−885(7)	3387(6)	11608(9)	44(3)
C(105′)	−1776(8)	1676(7)	7690(10)	51(4)	C(307)	108(7)	3182(6)	11573(7)	34(3)
C(106′)	−1229(8)	2015(7)	7125(10)	55(4)	C(308)	629(6)	3315(5)	10823(7)	29(3)
C(107′)	−179(8)	2168(6)	7429(8)	43(3)	C(309)	170(6)	3676(5)	10066(7)	30(3)
C(108′)	345(7)	2006(5)	8309(7)	32(3)	C(310)	−815(6)	3861(6)	10078(8)	37(3)
C(109′)	−225(6)	1651(5)	8913(8)	33(3)	C(311)	802(8)	4193(7)	7706(9)	49(4)
C(110′)	−1282(7)	1480(5)	8586(9)	41(3)	O(312)	1545(4)	3114(3)	10759(5)	28(2)
C(111′)	380(8)	948(7)	11273(9)	47(4)	N(301′)	2872(5)	3500(4)	8267(6)	31(2)
O(112′)	1326(4)	2182(3)	8664(4)	27(2)	C(302′)	2925(7)	3081(6)	7265(8)	38(3)
Ni(2)	2918(1)	3138.9(8)	11866(1)	41.2(4)	C(303′)	3505(9)	3360(7)	6622(9)	51(4)
N(201)	4426(5)	2989(4)	12156(6)	28(2)	C(304′)	3967(9)	4085(8)	6996(10)	57(4)
C(202)	5074(7)	3149(6)	13103(9)	43(3)	C(305′)	4360(8)	5350(7)	8532(10)	51(4)
C(203)	6071(8)	2947(7)	13104(9)	47(4)	C(306′)	4297(7)	5763(6)	9565(10)	47(4)
C(204)	6375(8)	2620(7)	12163(10)	52(4)	C(307′)	3791(7)	5419(5)	10168(9)	38(3)
C(205)	6008(8)	2173(6)	10139(10)	47(4)	C(308′)	3320(6)	4683(6)	9724(8)	36(3)
C(206)	5315(8)	2017(6)	9187(9)	46(4)	C(309′)	3358(6)	4239(5)	8672(8)	31(3)
C(207)	4337(7)	2196(5)	9211(8)	35(3)	C(310′)	3896(7)	4581(6)	8041(9)	42(3)
C(208)	4042(6)	2522(4)	10173(7)	25(2)	C(311′)	2396(9)	2289(7)	6769(9)	55(4)
C(209)	4737(6)	2667(5)	11199(8)	30(3)	O(312′)	2782(4)	4344(3)	10294(5)	31(2)
C(210)	5722(7)	2478(5)	11145(8)	36(3)	Cl(400)	8876(2)	2128(2)	4104(3)	57(1)
C(211)	4745(9)	3506(9)	14134(10)	64(5)	O(401)	7926(9)	2084(11)	4330(13)	135(8)
O(212)	3128(4)	2732(3)	10249(4)	26(2)	O(402)	9558(12)	2576(12)	5050(13)	161(9)
N(201′)	2340(6)	3654(5)	13319(6)	35(2)	O(403)	9345(21)	1501(12)	4062(23)	235(16)
C(202′)	1860(7)	3349(7)	13924(8)	44(3)	O(404)	8912(14)	2326(22)	3285(20)	296(23)

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2×10) for **3**

$B_{\mathrm{eq}}=4/3\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Ni(1)	4471.8(5)	−65.5(5)	1641.6(2)	41.6(2)	C(203)	4427(4)	3069(5)	−409(2)	53(2)
N(101)	3912(3)	28(3)	2187(1)	35(1)	C(204)	5118(4)	3596(5)	−141(2)	54(2)
C(102)	3826(4)	−729(5)	2465(1)	45(1)	C(205)	5896(4)	4050(4)	595(2)	56(2)
C(103)	3180(5)	−590(6)	2725(2)	57(2)	C(206)	5898(4)	3985(4)	998(2)	52(2)
C(104)	2660(5)	305(6)	2710(2)	59(2)	C(207)	5158(3)	3424(4)	1129(2)	46(2)
C(105)	2233(4)	2114(6)	2388(2)	58(2)	C(208)	4442(3)	2951(3)	845(1)	34(1)
C(106)	2374(4)	2886(5)	2118(2)	58(2)	C(209)	4432(3)	3020(3)	416(2)	36(1)
C(107)	3022(4)	2728(4)	1852(2)	45(1)	C(210)	5165(3)	3576(4)	289(2)	45(2)
C(108)	3518(3)	1761(4)	1879(1)	33(1)	C(211)	2986(5)	1869(5)	−564(2)	55(2)
C(109)	3401(3)	965(4)	2169(1)	36(1)	O(212)	3738(2)	2398(2)	951(1)	33(1)
C(110)	2753(4)	1146(5)	2426(2)	49(2)	N(201′)	1815(3)	3001(3)	569(1)	32(1)
C(111)	4382(5)	−1756(5)	2495(2)	58(2)	C(202′)	1648(4)	3994(4)	410(2)	41(1)
O(112)	4122(2)	1552(2)	1635(1)	32(1)	C(203′)	948(4)	4670(4)	514(2)	49(2)
N(101′)	4484(3)	−1781(3)	1542(1)	32(1)	C(204′)	438(4)	4342(4)	786(2)	53(2)
C(102′)	5202(4)	−2462(4)	1576(1)	41(1)	C(205′)	139(4)	2922(5)	1277(2)	50(2)
C(103′)	5028(4)	−3588(4)	1505(2)	49(2)	C(206′)	371(4)	1920(5)	1453(2)	49(2)
C(104′)	4156(5)	−3979(4)	1419(2)	52(2)	C(207′)	1056(3)	1275(4)	1333(1)	39(1)
C(105′)	2419(5)	−3638(4)	1280(2)	55(2)	C(208′)	1519(3)	1619(3)	1038(1)	30(1)
C(106′)	1709(4)	−2892(5)	1226(2)	58(2)	C(209′)	1312(3)	2666(4)	857(1)	31(1)
C(107′)	1907(4)	−1760(4)	1259(2)	45(1)	C(210′)	613(3)	3314(4)	974(2)	40(1)
C(108′)	2819(3)	−1408(3)	1348(1)	33(1)	C(211′)	2210(5)	4418(4)	117(2)	56(2)
C(109′)	3576(3)	−2156(3)	1429(1)	33(1)	O(212′)	2166(2)	1015(2)	907(1)	31(1)
C(110′)	3369(4)	−3291(4)	1374(2)	45(1)	N(201″)	1779(2)	780(3)	20(1)	31(1)
C(111′)	6191(4)	−2044(5)	1685(2)	51(2)	C(202″)	961(3)	980(4)	−241(1)	38(1)
O(112′)	3062(2)	−350(2)	1364(1)	30(1)	C(203″)	379(4)	136(5)	−451(2)	49(2)
N(101″)	5918(2)	472(3)	1820(1)	32(1)	C(204″)	653(4)	−911(4)	−385(2)	46(1)
C(102″)	6487(3)	664(4)	2189(1)	42(1)	C(205″)	1829(4)	−2241(4)	−13(2)	41(1)
C(103″)	7377(4)	1145(6)	2228(2)	61(2)	C(206″)	2688(4)	−2409(4)	245(2)	42(1)
C(104″)	7684(4)	1456(6)	1891(2)	61(2)	C(207″)	3284(3)	−1536(4)	411(1)	37(1)
C(105″)	7373(4)	1557(6)	1116(2)	62(2)	C(208″)	2987(3)	−487(3)	331(1)	29(1)
C(106″)	6778(4)	1347(5)	743(2)	51(2)	C(209″)	2071(3)	−286(4)	81(1)	31(1)
C(107″)	5896(3)	833(4)	719(1)	40(1)	C(210″)	1511(3)	−1162(4)	−108(1)	37(1)
C(108″)	5612(3)	557(3)	1078(1)	31(1)	C(211″)	613(4)	2115(5)	−318(2)	51(2)
C(109″)	6225(3)	776(4)	1471(1)	34(1)	O(212″)	3518(2)	377(2)	474(1)	29(1)
C(110″)	7112(3)	1276(5)	1489(2)	49(2)	Cl(300)	1575(1)	735(2)	3709(1)	80(1)
C(111″)	6172(4)	327(5)	2575(2)	52(2)	O(301)	2393(7)	1170(7)	3671(3)	155(4)
O(112″)	4792(2)	76(2)	1076(1)	31(1)	O(302)	1402(9)	−139(9)	3464(3)	179(5)
Ni(2)	2753.1(5)	1760.8(5)	463.6(2)	41.7(2)	O(303)	886(8)	1232(9)	3785(5)	215(8)
N(201)	3709(3)	2492(3)	140(1)	34(1)	O(304)	1756(9)	324(15)	4116(3)	226(7)
C(202)	3721(4)	2482(4)	−261(1)	39(1)					

Nickel ion has a stronger interaction with sulfate than with perchlorate in aqueous solutions,

$$\mathrm{Ni^{2+}+SO_4{}^{2-}\rightleftarrows NiSO_4}. \tag{11}$$

The equilibrium constant, K, at an ionic strength of 0.3 mol dm^{-3} is estimated to be $10^{1.2}$ based on the equilibrium constant at infinite dilution ($10^{2.3}$) and the activity coefficient for divalent ions ($10^{-0.55}$).[4] The side reaction coefficient of $\mathrm{Ni^{2+}}$ with sulfate, $\alpha=1+K[\mathrm{SO_4{}^{2-}}]$, is $10^{0.4}$. The difference between the extraction constants of $(\mathrm{Ni_2(mq)_4})_\mathrm{o}$ from perchlorate and sulfate media ($10^{1.1}$) is comparable to that estimated from the coefficient ($10^{0.8}$).

Structural Description. The atomic coordinates and equivalent isotropic temperature factors for **1**—**3** are listed in Tables 3—5, respectively. The atom-numbering system for Hmq is presented in Fig. 4(a). The ligands of Ni(1), Ni(2), and Ni(3) are distinguished, respectively, by the numbers of 100, 200, and 300 levels; those of each Ni are differently given by the corresponding normal, primed and double-primed numbers. Two $\mathrm{C_2H_5OH}$ molecules of **1** are represented by C(401)-O(403) and C(404)-O(406), and $\mathrm{ClO_4}^-$ anions of **2** and **3** by Cl(400)-O(404) and Cl(300)-O(304), respectively. Perspective drawings of $[\mathrm{Ni_3(mq)_6}]$, $[\mathrm{Ni_3H(mq)_6}^+]$ and $[\mathrm{Ni_2H_3(mq)_6}^+]$ are shown in Figs. 4(b)—(d), respectively. Selected bond lengths about the Ni atoms are given in Fig. 5 and the bond angles in Table 6.

Both **1** and **2** contain discrete trimeric complexes. Among the six O atoms of the ligands, two [O(212) and O(312)] coordinate to three Ni atoms, the other two [O(112) and O(112′)] to two Ni atoms, and the remainder two [O(212′) and O(312′)] to only one Ni. Complex **2** differs from **1** regarding the orientation of the two ligands not involved in bridging [O(212′) and

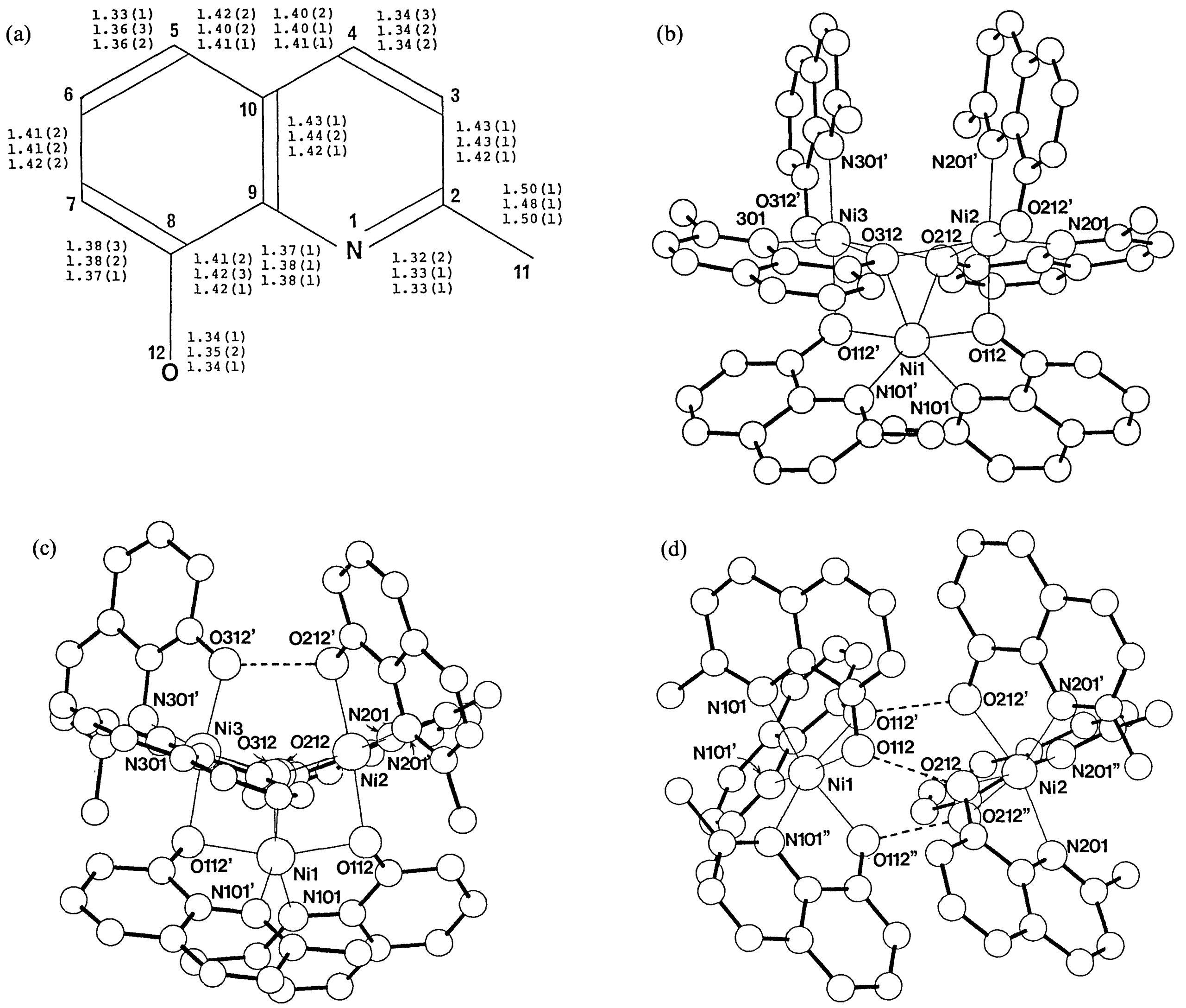

Fig. 4. (a) Atom-numbering for 2-methyl-8-quinolinol and the mean bond length in **1** (upper), **2** (middle), and **3** (lower). (b)—(d) Perspective drawings of **1**, **2**, and **3**.

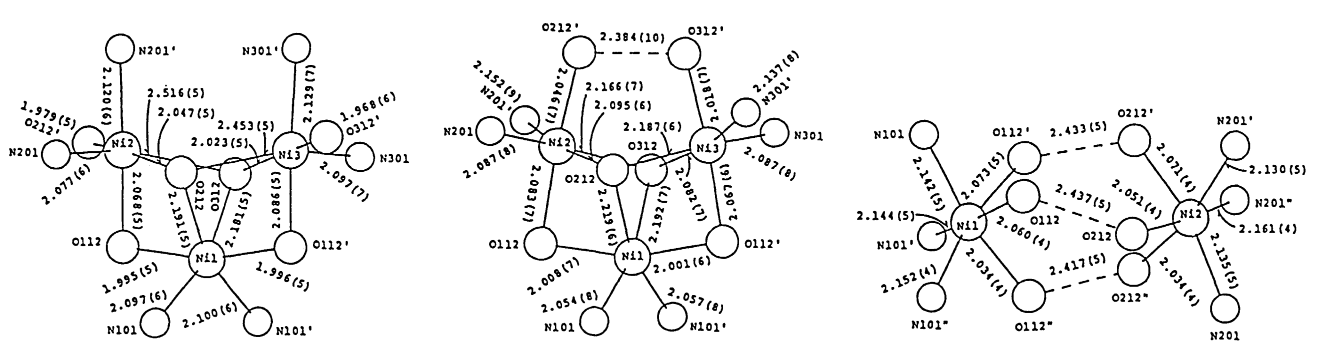

Fig. 5. Coordination geometry and bond distances around the Ni atoms in **1**, **2**, and **3**.

O(312′) trans to μ_3-O(phenolate) in **1** and trans to μ-O (phenolate) in **2**], and in existence of a strong intramolecular hydrogen bond between these O atoms [O(212′)···H···O(312′)=2.384 Å]. Upon protonation of **1** to form **2**, the distance between the bridging heads is kept constant [O(212)-O(312)=2.459 Å for **1**; 2.451 Å for **2**], whereas Ni(2)-O(312) and Ni(3)-O(212) are shortened by 0.3 Å. All of the Ni-Ni distances are decreased [Ni(1)-Ni(2), Ni(1)-Ni(3), and Ni(2)-Ni(3)=2.960, 2.925, and 3.695 Å for **1**; 2.889, 2.882, and 3.331 Å for **2**], but are still larger than twice the crystal radius of Ni [2.5 Å], indicating no metal-metal interac-

Table 6. Selected Bond Angles (°) for **1**, **2**, and **3**

	1	**2**		**1**	**2**
N(101)–Ni(1)–O(112)	81.8(2)	82.5(3)	N(201′)–Ni(2)–O(212′)	81.6(2)	80.1(3)
N(101)–Ni(1)–N(101′)	101.2(2)	101.6(3)	N(201′)–Ni(2)–O(312)	102.5(2)	94.5(3)
N(101)–Ni(1)–O(112′)	107.3(2)	107.8(3)	O(212′)–Ni(2)–O(312)	97.8(2)	92.0(3)
N(101)–Ni(1)–O(212)	96.8(2)	97.0(3)	O(112′)–Ni(3)–O(212)	77.0(2)	84.2(2)
N(101)–Ni(1)–O(312)	161.5(2)	162.2(3)	O(112′)–Ni(3)–N(301)	93.6(2)	92.1(3)
O(112)–Ni(1)–N(101′)	107.7(2)	109.1(3)	O(112′)–Ni(3)–O(312)	85.0(2)	81.6(2)
O(112)–Ni(1)–O(112′)	165.6(2)	162.3(3)	O(112′)–Ni(3)–N(301′)	169.0(2)	104.1(3)
O(112)–Ni(1)–O(212)	82.5(2)	79.4(2)	O(112′)–Ni(3)–O(312′)	87.7(2)	174.2(3)
O(112)–Ni(1)–O(312)	85.2(2)	85.9(3)	O(212)–Ni(3)–N(301)	145.7(2)	151.4(3)
N(101′)–Ni(1)–O(112′)	81.9(2)	83.4(3)	O(212)–Ni(3)–O(312)	65.8(2)	70.0(2)
N(101′)–Ni(1)–O(212)	160.4(2)	160.4(3)	O(212)–Ni(3)–N(301′)	103.6(2)	98.8(3)
N(101′)–Ni(1)–O(312)	95.2(2)	94.9(3)	O(212)–Ni(3)–O(312′)	99.7(2)	90.9(2)
O(112′)–Ni(1)–O(212)	85.3(2)	84.9(2)	N(301)–Ni(3)–O(312)	80.7(2)	81.4(3)
O(112′)–Ni(1)–O(312)	83.3(2)	80.5(2)	N(301)–Ni(3)–N(301′)	91.6(3)	109.5(3)
O(212)–Ni(1)–O(312)	68.4(2)	67.5(2)	N(301)–Ni(3)–O(312′)	113.0(3)	90.7(3)
O(112)–Ni(2)–N(201)	95.6(2)	92.4(3)	O(312)–Ni(3)–N(301′)	105.3(2)	167.1(3)
O(112)–Ni(2)–O(212)	84.4(2)	80.7(2)	O(312)–Ni(3)–O(312′)	164.9(2)	93.8(3)
O(112)–Ni(2)–N(201′)	166.3(2)	102.3(3)	N(301′)–Ni(3)–O(312′)	81.4(2)	79.7(3)
O(112)–Ni(2)–O(212′)	85.2(2)	176.0(3)	Ni(1)–O(112)–Ni(2)	93.5(2)	89.8(3)
O(112)–Ni(2)–O(312)	75.5(2)	84.8(3)	Ni(1)–O(112′)–Ni(3)	91.5(2)	90.2(2)
N(201)–Ni(2)–O(212)	80.8(2)	80.8(3)	Ni(1)–O(212)–Ni(2)	88.6(2)	84.0(2)
N(201)–Ni(2)–N(201′)	93.6(2)	114.3(3)	Ni(1)–O(212)–Ni(3)	77.9(1)	81.7(2)
N(201)–Ni(2)–O(212′)	116.0(2)	89.4(3)	Ni(2)–O(212)–Ni(3)	110.1(2)	102.1(2)
N(201)–Ni(2)–O(312)	144.5(2)	150.9(3)	Ni(1)–O(312)–Ni(2)	77.8(1)	83.0(2)
O(212)–Ni(2)–N(201′)	107.2(2)	164.3(3)	Ni(1)–O(312)–Ni(3)	88.1(2)	84.8(2)
O(212)–Ni(2)–O(212′)	161.0(2)	96.1(2)	Ni(2)–O(312)–Ni(3)	108.5(2)	103.3(3)
O(212)–Ni(2)–O(312)	64.2(2)	70.2(2)			

	3		**3**
N(101)–Ni(1)–O(112)	79.4(2)	N(101)–Ni(1)–N(101′)	101.6(2)
N(101)–Ni(1)–O(112′)	81.7(2)	N(101)–Ni(1)–N(101″)	106.6(2)
N(101)–Ni(1)–O(112″)	168.1(2)	O(112)–Ni(1)–N(101′)	165.2(2)
O(112)–Ni(1)–O(112′)	86.7(1)	O(112)–Ni(1)–N(101″)	85.8(1)
O(112)–Ni(1)–O(112″)	90.8(1)	N(101′)–Ni(1)–O(112′)	78.9(2)
N(101′)–Ni(1)–N(101″)	107.8(2)	N(101′)–Ni(1)–O(112″)	86.1(2)
O(112′)–Ni(1)–N(101″)	167.5(2)	O(112′)–Ni(1)–O(112″)	91.0(1)
N(101″)–Ni(1)–O(112″)	79.2(1)	N(201)–Ni(2)–O(212)	79.3(2)
N(201)–Ni(2)–N(201′)	106.9(2)	N(201)–Ni(2)–O(212′)	164.0(2)
N(201)–Ni(2)–N(201″)	107.3(2)	N(201)–Ni(2)–O(212″)	87.1(2)
O(212)–Ni(2)–N(201′)	87.3(2)	O(212)–Ni(2)–O(212′)	86.6(1)
O(212)–Ni(2)–N(201″)	168.2(2)	O(212)–Ni(2)–O(212″)	91.6(1)
N(201′)–Ni(2)–O(212′)	79.8(2)	N(201′)–Ni(2)–N(201″)	99.8(2)
N(201′)–Ni(2)–O(212″)	165.5(2)	O(212′)–Ni(2)–N(201″)	85.4(1)
O(212′)–Ni(2)–O(212″)	85.7(1)	N(201″)–Ni(2)–O(212″)	79.1(1)

tions. Protonation makes the trimeric structure more compact and symmetric.

The complex **3** has the same structure as $[Ni_2H_3q_6]X$ (**3′**).19) Each Ni atom is surrounded by three ligands in a facial configuration to form a distorted octahedron. Two such octahedra are connected by strong hydrogen bonds between three pairs of phenolate groups. Compared with **3′**, Ni–N is elongated by 0.08 Å, thus reducing the steric repulsion between a methyl group of one ligand and an N atom of another [C(111)–N(101′)=3.18, C(111′)–N(101″)=3.17, C(111″)–N(101)=3.26, C(211)–N(201′)=3.24, C(211′)–N(201″)=3.20, C(211″)–N(201)=3.18 Å]. This bond-weakening is partly compensated for by the shortening of Ni–O (0.02 Å). Hence, ∠N–Ni–N is increased by 7°, whereas ∠O–Ni–O is decreased by 2°. The distances between the methyl groups range from 3.62 to 4.17 Å [av 3.93 Å]. The average O···H···O distance of **3** (2.43 Å) is practically the same as **3′** [2.45 for **3′**(I_3), 2.43 and 2.46 for **3′** (ClO_4) and 2.43 Å for **3′** (SCN)]. The rotation angle of the two triangles consisting of three oxygen atoms around the pseudo three-fold axis is ca. 29°, in contrast with 25° for **3′** (I_3) and **3′** (SCN) and 30° for **3′** (ClO_4).

The average bond lengths of the ligands of the respective complexes (Fig. 4(a)) are all reasonable. The temperature factors of the atoms of ClO_4^- and C_2H_5OH are considerably larger than those of the complex parts, some of which exhibit a large anisotropy. The bond lengths and angles of ClO_4^- range broadly [1.24—1.41 Å for **2** and 1.25—1.41 Å for **3**], the respective mean values being 1.34 Å and 109° for both **2** and **3**. The bond lengths of C–C and C–O for C_2H_5OH average 1.35 and

1.52 Å, respectively. Although this seems to indicate a misplacement of the C and O atoms, O(403) and O(406) can be identified based on the formation of the respective intermolecular hydrogen bonds with O(212′) [2.75(1) Å] and O(312′) [2.83(1) Å]. The bond angles of ∠C–C–O average 121°.

The infrared spectra of **2** and **3** showed a broad band which was assigned to $\nu(\mathrm{O\cdots H\cdots O})$ ($\nu_{\max}$ at 955 cm^{-1} with half-width of 200 cm^{-1} for **2** and $\nu_{\max}$ at 925 cm^{-1} with half-width of 370 cm^{-1} for **3**). These are characteristic of strong hydrogen bonds.[39]

In a solid, all of these complexes have discrete oligomeric structures of the same composition as those identified by equilibrium studies on solvent extraction. Since Ni atoms are completely surrounded by hydrophobic ligands without any coordinated water molecules, the structures in solids are possibly the same as those in organic solvents.

Discussion

Suppression of Self-Adduct Formation. The extremely enhanced extractability from sulfate media found in the Ni–Hq system, compared with those in the Ni–Hmq and β-diketone systems is ascribed to the formation of a "self-adduct"; a neutral molecule of 8-quinolinol has some basicity ($K_2=10^{4.96}$) and can replace coordinated water molecules of $[\mathrm{Niq_2(H_2O)_2}]$ to yield a species that is extractable into organic solvents, $(\mathrm{NiHq_3})_\mathrm{o}$. Bidentate adduct-forming reagents are more effective than the corresponding unidentate ones,[40] just as the "chelating effect" found in usual complexation reactions. The resulting complex is involved in intermolecular hydrogen-bondings; the dimeric species, $(\mathrm{Ni_2H_2q_6})_\mathrm{o}$, becomes predominant at higher concentrations of nickel ion to further enhance the extractability.[17] Neither 1 : 2, 2 : 4 nor 3 : 6 extracted species have been found in the Ni–Hq system.

In the case of β-diketones, no adducts have been found because of their negligibly small basicity as neutral molecules.[1,2,9,41] Although 2-methyl-8-quinolinol has a higher basicity than 8-quinolinol ($K_2=10^{5.36}$), self-adduct formation does not prevail in the Ni–Hmq system; the species $(\mathrm{NiH(mq)_3})_\mathrm{o}$ and/or $(\mathrm{Ni_2H_2(mq)_6})_\mathrm{o}$ are found only at very high extractant concentrations.

Using the sodium silicate-gel method, a mixed metal complex, $[\mathrm{Na_3Ni_3H_6(mq)_{15}\cdot H_2O}]$ (**4**) was obtained.[43] This compound comprises bis complexes of Na and tris complexes of Ni connected by hydrogen bondings. The Ni complex parts reflect the structure of the complex expressed as $[\mathrm{NiH(mq)_3}]$. Three ligands coordinate to Ni in a *mer* configuration. Compared with the *mer* complex part of $[\mathrm{Ni_2H_2q_6}]$,[17] Ni–N is elongated by 0.12 Å and Ni–O is shortened by 0.04 Å. Steric crowding around the Ni atoms is responsible for the lower stability and, thus, the lower extractability of $(\mathrm{NiH(mq)_3})_\mathrm{o}$ and/or $(\mathrm{Ni_2H_2(mq)_6})_\mathrm{o}$.

Ion-Pair Extracted Species Originated From Self-Adducts. The dimeric complex, $[\mathrm{Ni_2H_2q_6}]$, has some basicity to accommodate a proton and forms a cationic complex, $[\mathrm{Ni_2H_3q_6^+}]$, which is extracted as an ion-pair with perchlorate at lower pH. Preparative work also gave these complexes both in aqueous and ethanol solutions.[44] In extraction with Hmq, on the other hand, the corresponding species contributes only at a high Hmq concentration ($C_\mathrm{Hmq}>0.12$ mol dm^{-3}); the extraction constant of $([\mathrm{Ni_2H_3(mq)_6}]\mathrm{ClO_4})_\mathrm{o}$ is smaller than that of $([\mathrm{Ni_2H_3q_6}]\mathrm{ClO_4})_\mathrm{o}$ by $10^{12.5}$.[17]

As described in the structural description, octahedrons in **3** are distorted more than those in **3′**, and the coordination of quinoline N atoms is unfavorable because of the presence of a methyl group. These lead to the lower stability and lower contribution of **3** in the extraction process.

Oligomerization of Neutral Extracted Species. In the extraction of nickel(II) from sulfate media, adduct-formation does not contribute in either the Ni–Hmq or the Ni–Hacac system, though their extractabilities are appreciably different; the distribution ratio of Ni in the pH-independent region of the Ni–Hacac system is small and lower than unity,[9] whereas that of the Ni–Hmq system is too large to be determined without radiometry. In the case of Hacac, the hydrated complex, $[\mathrm{Ni(acac)_2(H_2O)_2}]$, is distributed into organic solvents. In the Ni–Hmq system, only oligomerized species, $(\mathrm{Ni_2(mq)_4})_\mathrm{o}$ and $(\mathrm{Ni_3(mq)_6})_\mathrm{o}$ are responsible for the extraction, and no monomeric species have been found, at least down to $10^{-5.5}$ mol dm^{-3} of the total nickel concentration in the organic phase (Fig. 3).

As shown in Fig. 4(b), $[\mathrm{Ni_3(mq)_6}]$ maintains an octahedral configuration around Ni by sharing triangular faces with other octahedrons at two adjacent faces of the central octahedron, and bears no water molecules. Although various trimeric structures have been reported for divalent metal complexes with acetylacetone,[45] these are all different from **1** or **2**. For example, $[\mathrm{Zn_3(acac)_6}]$ has a bent trimeric structure but lacks μ_3-bridging.[46] In the case of $[\mathrm{Ni_3(acac)_6}]$, sharing occurs at two coplanar faces of the central octahedron to give a linear array of nickel atoms, which can be accomplished by the ligand with potentially bridging atoms on both ends.[13] These acetylacetonate complexes are obtained only by vacuum sublimation of the dehydrated bis complexes and are easily converted to monomeric species, even with trace amounts of water both in solid and in solution.[11,13] On the other hand, $[\mathrm{Ni_3(mq)_6}]$ is stable, at least in aprotic solvents saturated with water.

On recrystallization of $\mathrm{Ni(mq)_2(H_2O)}$ from aqueous ethanol, we obtained $[\mathrm{Ni(mq)_2(H_2O)_2}]$ (**5**),[43] which was not found in the extraction process. Usually, nickel(II) complexes with two monoanionic bidentate and two neutral unidentate ligands (B) show a configuration of *trans*(B,B), for example, $[\mathrm{Ni(5\text{-}cq)_2py_2}]$, $[\mathrm{Ni(acac)_2(H_2O)_2}]$, and $[\mathrm{Ni(acac)_2py_2}]$.[14,15,47] In contrast, $[\mathrm{Ni(mq)_2(H_2O)_2}]$ has the geometry of *cis*($\mathrm{H_2O,H_2O}$). Among the three configurations possible for *cis*-

(H_2O,H_2O), [*trans*(O,O), *cis*(N,N)] is adopted in **5**. This is just a construction unit of **1**; three units of **5** are dehydrated and connected by bridging to become **1** without any rearrangement of the coordination sphere. The Ni–N and Ni–O distances in **1** are shorter than those in **5** by 0.04 and 0.03 Å, respectively. The coordination of mq^- is strengthened by oligomerization.

All attempt to isolate single crystals of the dimeric extracted species, $(Ni_2(mq)_4)_o$, have been unsuccessful. The precipitation reaction of Ni^{2+} with 2-methyl-8-quinolinol in an aqueous solution gives a complex having the composition of $Ni(mq)_2(H_2O)$.[28,29] In contrast to $[Niq_2(H_2O)_2]$,[48] this is easily dissolved in non-coordinating solvents to give a concentrated solution having the same absorption spectra as that of the extracted species. Hence, the species expressed as $Ni(mq)_2(H_2O)$ is the same as the extracted species, $(Ni_2(mq)_4)_o$, and is possibly $[Ni_2(mq)_4(H_2O)_2]$, which has one water molecule per one nickel atom and is expected to be more soluble in organic solvents than $[Ni(mq)_2(H_2O)_2]$. Several complexes with related ligands of the same composition have been isolated and structurally characterized, $[Ni_2(acac)_4(piperidine)_2]$ or $[Ni_2(tropolonate)_4(H_2O)_2]$.[16,49] In these complexes, the chelate rings containing μ-O atoms lie in the same plane as the $Ni_2(\mu\text{-}O)_2$ plane. The relevant complex, $(Ni_2(mq)_4)_o$, is expected to have the same structure, which is also obtained from two units of **5** without any rearrangement of the coordination sphere.

The following equilibria can be considered between these neutral complexes in solutions:

$$2(Ni_3(mq)_6)_o + 6H_2O \rightleftarrows 3(Ni_2(mq)_4(H_2O)_2)_o \qquad (12)$$

and

$$(Ni_2(mq)_4(H_2O)_2)_o + 2H_2O \rightleftarrows 2(Ni(mq)_2(H_2O)_2)_o. \qquad (13)$$

A higher concentration of water and a lower concentration of the complex promote cleavage of oligomeric structures. In chloroform, only trimeric and dimeric species are found because of the limited solubility of water. In ethanol, however, all the three species could exist, depending on the conditions.

Trimeric Ion-Pair Extracted Species. The complex $[Ni_3(mq)_6]$ is also protonated to form $[Ni_3H(mq)_6]^+$. One of three Ni complex units is the same as **5**, but the other two have the configuration of [*cis*(O,O),*cis*(N,N)]. The cation, $[Ni_3H(mq)_6]^+$ is a more bulky round ion than $[Ni_2H_3(mq)_6]^+$ and is easily extracted with hydrophobic anions.

Conclusion

In the extraction of nickel(II) with Hq, the third neutral ligand displaces the water molecules of 1:2 complexes to form neutral and ion-pair extracted species having a metal-to-ligand ratio of 1:3. In the case of Hmq, the coordination of the third ligand is sterically hindered for both neutral and ion-pair species. Bridging at the phenolate oxygen atoms plays a role to expel coordinated water molecules. Methyl groups have just the correct size to cause oligomerization of extracted species. Larger substituents would disturb the oligomerization as well as the formation of 1:3 species and would promote the formation of monomeric 1:2 complexes, as found for the Ni-dipivaloylmethane complex.[50]

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7) Equilibrium treatment never tells whether an extracted species is hydrated or not. Thus $(ML_2)_o$, where subscript $_o$ refers to the organic phase, could generally mean $(ML_2(H_2O)_n)_o$, n=0,1,2···. Although determination of water ocassionally presents important information about the composition of the extracted species,[5,8] it has rarely been adopted in this field.

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the species in brackets is a cationic complex and X a counter ion. Expression such as [$Mq_2(Hq)$], [$M_2q_4(Hq)_2$], and [$M_2q_3(Hq)_3$]X is not adopted here, since these hydrogen atoms are not attached to a single ligand as demonstrated below.

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