X-Ray Crystal Structures of Nickel Complexes with 2-Methyl-8-quinolinol, $Ni(mq)_2(H_2O)_2$ and $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$

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Two Ni(II) complexes with 2-methyl-8-quinolinol (Hmq) were prepared and their structures determined by single-crystal X-ray diffraction techniques. In $Ni(mq)_2(H_2O)_2$, which is orthorhombic, space group *Pccn*, $Z=8$, the geometry is trans(*O,O*), cis(*N,N*), and cis(H_2O,H_2O), and the octahedron is appreciably distorted. In $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$, which is monoclinic, space group $P2_1/c$, $Z=4$, three binuclear units Ni(1)–Na(1), Ni(2)–Na(2), and Ni(3)–Na(3), are involved. All the Ni atoms are surrounded by three ligands in a mer configuration. The Na(1) and Na(2) atoms are five-coordinated with two ligands and an O atom bridging Na and Ni atoms within a dimer. The Na(3) atom has, together with the ligands, a coordinated water which is hydrogen-bonded to the O atom coordinating to the Ni(3) atom. These dimeric units are infinitely linked by intermolecular hydrogen bonds. Compared to the corresponding complexes of 8-quinolinol derivatives without 2-methyl substituent, the Ni–N is elongated by 0.06—0.12 Å, whereas the Ni–O is shortened by 0.01—0.05 Å. An increase in the bond angle (7—11 deg) between a N atom of a ligand and the donor atom (Y) which occupies the trans position to the O atom of the same ligand, reduces the steric interaction between the methyl group and Y in Hmq complexes. Shorter contacts between ligands in Hmq complexes than those in Hq complexes lead to their lower stabilities and, thus, the lower extractabilities.

8-Quinolinol[1] reacts with divalent transition metal ions (M^{2+}: Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) to form sparingly soluble complexes of $Mq_2(H_2O)_2$ in aqueous solutions. The structure of $Znq_2(H_2O)_2$ has been determined by X-ray crystallography; O and N atoms of the ligands and two water molecules, respectively, occupy positions trans to each other in a distorted octahedral configuration.[2,3] Other metal complexes are expected to have the same structure. When an organic solvent is added to such an aqueous solution, on the other hand, $M_2H_3q_6X$, MHq_3, and $M_2H_2q_6$ are extracted depending on the pH, total concentrations of M^{2+} and Hq, anions present (X^-) and organic solvents.[4] The crystal structures of $Ni_2H_3q_6X$ and $Ni_2H_2q_6$ have recently been determined.[4–7] In $Ni_2H_3q_6X$, both two nickel atoms are surrounded by three ligands with a facial configuration about their oxygen atoms; these complexes are joined by three hydrogen bonds to form a dimeric structure. In $Ni_2H_2q_6$, on the other hand, two nickel complexes, respectively, adopt facial and meridional configurations, and two hydrogen bonds are involved for dimerization. Two water molecules of $Mq_2(H_2O)_2$ at positions trans to each other are replaced by the third ligand occupying cis positions in the extracted species.

2-Methyl-8-quinolinol is known to show in some cases different reactivities to metal ions from 8-quinolinol owing to the substituent adjacent to the donor atom; e.g., aluminum can not be effectively precipitated or extracted with 2-methyl-8-quinolinol as with 8-quinolinol,[8,9] or vanadium(V) forms a black μ-oxo dimeric complex with 8-quinolinol and a yellow monomeric complex with 2-methyl-8-quinolinol.[10–14] It has been believed that divalent transition metal ions form precipitates of monohydrated complexes $M(mq)_2(H_2O)$[15] and are extracted as $M(mq)_2$ with this reagent.[16–19]

Very recently, we have made a systematic study on these extraction systems and found that Zn^{2+} and Cu^{2+} are just extracted as $M(mq)_2$, whereas Ni^{2+} and Co^{2+} are extracted as $M_3H(mq)_6X$, $M_2H_3(mq)_6X$, $M_3(mq)_6$, $M_2(mq)_4$, and $MH(mq)_3$ and/or $M_2H_2(mq)_6$.[20] The structures of $Ni_3H(mq)_6ClO_4$, $Ni_2H_3(mq)_6ClO_4$ and $Ni_3(mq)_6$ have also been determined. In several attempts to isolate the other complexes, we have obtained unexpected compounds: a monomeric 1:2 complex, $Ni(mq)_2(H_2O)_2$ (**1**) by recrystallization from aqueous ethanol and a mixed metal complex with sodium, $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$ (**2**) by sodium silicate gel method.[21]

Table 1 summarizes the structures of the metal complexes with 2-methyl-8-quinolinol previously determined by X-ray crystallography. As expected from steric crowdedness, a coordination number of five is predominant for smaller metal ions. There have been no reports on a tris complex with this ligand. This paper describes the first X-ray crystallographic study of the tris complex to show how a substituent close to a donor atom is accomodated in an octahedral configuration.

Experimental

Preparation of the Complexes. A crude 1:2 complex was prepared as described previously.[29] The water content has been determined by Karl Fischer's method to be 4.72%, which is in good agreement with that (4.58%) calculated for $Ni(mq)_2(H_2O)$.

$Ni(mq)_2(H_2O)_2$ was obtained by recrystallizing the above compound from aqueous ethanol. Found: C, 58.44; H, 5.03; N, 6.68%. Cacld for $Ni(mq)_2(H_2O)_2$: C, 58.43; H, 4.91; N,

6.82%. IR spectrum of this compound was practically the same as that of $Ni(mq)_2(H_2O)$, except that the absorption centered at 3450 cm^{-1} is more intense.

$Na_3Ni_3H_6(mq)_{15}\cdot H_2O$ was prepared by sodium silicate gel method;[21] 7 cm^3 of 2 mol dm^{-3} Na_2SiO_3 solution, 8 cm^3 of 1 mol dm^{-3} $NiSO_4$ solution and 15 cm^3 of water were mixed and left standing in a test tube to gel. After gelation, 0.7 mol dm^{-3} Hmq solution in ethanol was gently placed over it. After two months, greenish brown crystals suitable for X-ray structural determination were obtained. Since only small amounts of crystals were obtained, we could not perform sufficient chemical analyses about this compound. Sodium and nickel were determined by atomic emission and absorption spectrophotometry, respectively, after dissolving crystals in hydrochloric acid. Found: Na, 3.0; Ni, 7.4%. Calcd for $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$: Na, 2.6; Ni, 6.7%.

X-Ray Analysis. Crystallographic details for **1** and **2** are given in Table 2. X-Ray diffraction data were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ=1.54178 Å). The ω-2θ scan technique was employed with a ω-scan width of (1.2+0.2 tan θ) deg and a $2\theta_{max}$ of 100.0 deg at a scan rate of 6 deg min^{-1} with 5-second background counts. Only 69 and 67% of unique reflections measured for **1** and **2** were observed because of the smallness of the crystals used. No significant variations in intensities of 3 standard reflections monitored every 100 measurements were observed during data collection. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were not applied because of the constancy of the correction factors in the range of 2θ for crystals approximated as being spherical with a small μR value ($\mu R \approx 0.1$ for **1** and **2**). The structures were solved by the heavy-atom method and improved by a block-diagonal least-squares refinement of the positional and the thermal parameters of the non-H atoms and the positional ones of the H atoms except those of H_2O for **1** and except those of

Table 1. Coordination Numbers (n) and Structures of 2-Methyl-8-Quinolinol Complexes Determined by X-Ray Crystallography

Complex	n	Structure[a]	Ref.
$HVO_2(mq)_2$	5	Trigonal bipyramidal	14
$Al(mq)_2$–O–$Al(mq)_2$	5	μ-Oxo dimeric	22
$GaCl(mq)_2$	5	Trigonal bipyramidal	23,24
$VO(mq)_2$	5	Trigonal bipyramidal	23
$Fe(mq)_2$–O–$Fe(mq)_2$	5	μ-Oxo dimeric	25
$Ti(mq)_2(phenoxo)_2$	6	trans(O,O); cis(N,N); cis(A,A)	26
$TcOCl(mq)_2$	6	cis(O,O); cis(N,N); cis(A,B)	27
$RuCl(mq)_2(NO)$	6	cis(O,O); trans(N,N); cis(A,B)	28
$RuCl(mq)_2(NO)$	6	cis(O,O); cis(N,N); cis(A,B)	28
$Ni(mq)_2(H_2O)_2$	6	trans(O,O); cis(N,N); cis(A,A)	This work
$Na_3Ni_3H_6(mq)_{15}\cdot H_2O$	6	mer about Ni	This work
	5	Trigonal bipyramidal about Na	

a) A and B denote monodentate ligands.

Table 2. Crystallographic Details for **1** and **2**

	1	**2**
Formula (mq: $C_{10}H_8NO^-$)	$Ni(mq)_2(H_2O)_2$	$Na_3Ni_3H_6(mq)_{15}\cdot H_2O$
Formula weight	411.1	2641.8
Crystal system	Orthorhombic	Monoclinic
Space group	$Pccn$	$P2_1/c$
a/Å	22.018(9)	13.597(1)
b/Å	22.087(7)	26.146(4)
c/Å	7.816(2)	36.487(3)
β/deg	—	96.63(1)
V/Å^3	3801(2)	12885(2)
Z	8	4
D_c/g cm^{-3}	1.437	1.362
D_o/g cm^{-3}	1.438	1.38
μ(Cu $K\alpha$)/cm^{-1}	16.6	11.9
Crystal size/mm	0.15×0.1×0.1	0.2×0.2×0.15
Total no. of unique reflections	1948	13245
No. of observed reflections with $I>3\sigma(I)$	1344	8928
c^2 in weighting scheme	0.00603	0.00328
R, $\sum\|\Delta F\|/\sum\|F_o\|$	0.072	0.055
R_w, $(\sum w\|\Delta F\|^2/\sum w\|F_o\|^2)^{1/2}$	0.099	0.076
S, $[\sum w\|\Delta F\|^2/$(no. observations-no. variables)$]^{1/2}$	1.202	1.183
No. of reflections used at the last stage of refinement	1270	8224
Max. peak height in the last difference electron density map/e Å^{-3}	0.3	0.4
Max. ratio of shift to σ of refined parameters	0.1	0.5

H_2O, -OH, and $-CH_3$ for **2**. The temperature factor of each H atom was assumed to be isotropic and equal to the equivalent isotropic temperature factor of the attached atom. The weighting scheme was $w=[\sigma^2(F_o)+c^2|F_o|^2]^{-1}$ for the observed reflections with $w^{1/2}|\Delta F|<3$. Reflections with $w^{1/2}|\Delta F|\geq 3$ mostly found in those of weak intensities were excluded, because the $|F_c|$ values calculated during the last stage of refinement were thought to be good estimates of the corresponding $|F_o|$ values. A comparatively high R-value of **1** is probably due to the poor quality of crystals. Computations using the programs of MULTAN84, PLUTO and XPACK86 SHIONOGI were performed on a FACOM M-730 computer at Shionogi Research Laboratories.[30,31]

Results and Discussion

Atomic coordinates and equivalent isotropic thermal parameters for **1** and **2** are listed in Tables 3 and 4. Formula units of **1** and **2** found in respective asymmetric units are shown in Figs. 1 and 2. The atom-numbering system for the ligand is presented in Fig. 1. The crystal of **2** is composed of the three binuclear units Ni(1)–Na(1), Ni(2)–Na(2), and Ni(3)–Na(3), as shown in Fig. 3. The atoms of the two ligands coordinated to the Ni(1) atom are numbered similarly to those of **1**, and the third one and the two ligands around the Na(1) atom are represented by the numbers of the 200, 300, and 400 levels, respectively. The atoms in the Ni(2)–Na(2) unit are given by the corresponding primed numbers and those of the Ni(3)–Na(3) unit given by the double-primed numbers. The O atoms of water molecules are represented by O(201) and O(202) for **1**, and O(501) for **2**.

Structural Description. In **1**, the two ligands coordinate with the O atoms trans and the N atoms cis. The coordinated water molecules occupy positions cis to each other. The octahedron is appreciably distorted. The molecules related by a c-glide plane normal to the a-axis are linked by the intermolecular hydrogen bonds to form a molecular chain extended along the c-axis: O(12)···O(201) $(1/2-x, y, -1/2+z)$=2.587(8) Å, O(112)···O(201) $(1/2-x, y, 1/2+z)$=2.948(9) Å, and

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Temperature Factors (Å²×10) with e.s.d. Values in Parentheses for $Ni(mq)_2(H_2O)_2$

Atom	x	y	z	B_{eq}[a]
Ni	1720(1)	471(1)	1136(2)	31.9(5)
N(1)	1417(3)	−408(3)	2058(8)	35(3)
C(2)	1191(4)	−611(4)	3539(11)	36(3)
C(3)	1181(4)	−1230(4)	3923(11)	43(4)
C(4)	1371(4)	−1643(4)	2836(12)	44(4)
C(5)	1822(4)	−1860(4)	−66(13)	50(4)
C(6)	1989(4)	−1650(4)	−1608(13)	44(4)
C(7)	1974(4)	−1039(4)	−1957(12)	45(4)
C(8)	1786(4)	−601(4)	−766(12)	35(3)
C(9)	1606(4)	−843(4)	893(10)	33(3)
C(10)	1596(4)	−1465(4)	1202(11)	37(3)
C(11)	925(4)	−174(4)	4784(12)	43(4)
O(12)	1742(2)	−24(2)	−1037(6)	32(2)
N(101)	878(3)	921(3)	1257(8)	33(3)
C(102)	409(4)	907(4)	166(11)	36(3)
C(103)	−115(4)	1273(5)	554(14)	52(4)
C(104)	−128(4)	1617(4)	1939(14)	51(4)
C(105)	324(4)	1985(4)	4639(14)	50(4)
C(106)	836(5)	1962(5)	5707(14)	63(5)
C(107)	1363(5)	1598(5)	5311(12)	53(4)
C(108)	1367(4)	1262(4)	3791(10)	37(3)
C(109)	846(4)	1280(3)	2726(9)	29(3)
C(110)	337(4)	1623(4)	3140(12)	40(3)
C(111)	454(5)	567(5)	−1403(15)	64(5)
O(112)	1844(2)	931(2)	3371(7)	32(2)
O(201)	2638(3)	244(3)	1256(7)	38(2)
O(202)	2035(3)	1207(2)	−470(8)	39(2)

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

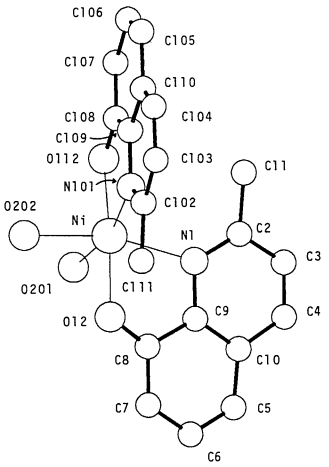

Fig. 1. Perspective drawing of $Ni(mq)_2(H_2O)_2$ with atomic numbering system of mq^-.

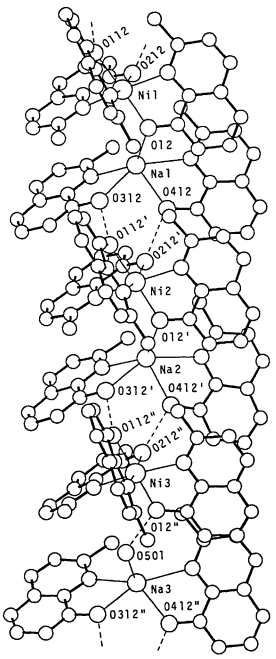

Fig. 2. Perspective drawing of $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$. Broken lines represent the intermolecular hydrogen bonds.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10$) with e.s.d. Values in Parentheses for $Na_3Ni_3H_6(mq)_{15} \cdot H_2O$

Atom	x	y	z	B_{eq}[a)]
Ni(1)	3033.4(7)	8262.5(4)	966.1(2)	46.0(3)
N(1)	1645(3)	8546(2)	1126(1)	47(2)
C(2)	1229(4)	9009(3)	1116(2)	56(2)
C(3)	312(5)	9090(3)	1257(2)	65(3)
C(4)	−174(5)	8700(3)	1401(2)	63(3)
C(5)	−224(4)	7786(3)	1560(2)	61(3)
C(6)	235(4)	7312(3)	1573(2)	58(2)
C(7)	1163(4)	7255(2)	1436(2)	49(2)
C(8)	1648(4)	7670(2)	1302(1)	45(2)
C(9)	1162(4)	8152(2)	1280(1)	45(2)
C(10)	231(4)	8210(3)	1419(1)	53(2)
C(11)	1738(5)	9450(3)	943(2)	68(3)
O(12)	2532(3)	7618(1)	1187(1)	47(1)
N(101)	2342(3)	8210(2)	388(1)	54(2)
C(102)	1725(4)	7868(3)	211(2)	60(3)
C(103)	1274(5)	7968(3)	−154(2)	77(3)
C(104)	1433(6)	8413(3)	−330(2)	81(3)
C(105)	2275(6)	9260(3)	−305(2)	75(3)
C(106)	2936(6)	9593(3)	−120(2)	78(3)
C(107)	3408(6)	9468(3)	235(2)	72(3)
C(108)	3205(5)	9013(2)	401(2)	55(2)
C(109)	2536(4)	8660(2)	210(2)	52(2)
C(110)	2081(5)	8788(3)	−145(2)	68(3)
C(111)	1524(5)	7373(3)	391(2)	66(3)
O(112)	3599(3)	8889(2)	740(1)	53(2)
N(201)	4527(3)	7951(2)	969(1)	45(2)
C(202)	4944(4)	7695(2)	719(2)	55(2)
C(203)	5992(5)	7621(3)	754(2)	63(3)
C(204)	6581(4)	7802(3)	1049(2)	66(3)
C(205)	6704(5)	8290(3)	1640(2)	76(3)
C(206)	6248(5)	8551(3)	1890(2)	76(3)
C(207)	5227(5)	8621(3)	1843(2)	63(3)
C(208)	4629(4)	8423(2)	1533(2)	50(2)
C(209)	5113(4)	8145(2)	1271(2)	49(2)
C(210)	6158(4)	8079(3)	1322(2)	57(2)
C(211)	4305(5)	7485(3)	388(2)	70(3)
O(212)	3660(3)	8490(2)	1477(1)	50(1)
Na(1)	3611.5(16)	6971.4(9)	1485.5(6)	54.1(8)
N(301)	5431(3)	6761(2)	1549(1)	51(2)
C(302)	6108(5)	6921(3)	1819(2)	61(3)
C(303)	7126(5)	6842(3)	1810(2)	71(3)
C(304)	7445(5)	6572(3)	1531(2)	73(3)
C(305)	7040(4)	6077(3)	950(2)	57(2)
C(306)	6344(5)	5893(3)	689(2)	61(3)
C(307)	5325(4)	6012(3)	706(2)	55(2)
C(308)	5037(4)	6293(2)	990(2)	45(2)
C(309)	5749(4)	6483(2)	1271(2)	48(2)
C(310)	6762(4)	6376(2)	1247(2)	55(2)
C(311)	5752(6)	7202(3)	2133(2)	75(3)
O(312)	4059(2)	6403(2)	1014(1)	51(1)
N(401)	2839(3)	7035(2)	2133(1)	50(2)
C(402)	2804(5)	7440(2)	2351(2)	55(2)
C(403)	2117(5)	7471(3)	2618(2)	64(3)
C(404)	1493(5)	7082(3)	2656(2)	62(3)
C(405)	895(5)	6212(3)	2460(2)	65(3)
C(406)	953(5)	5801(3)	2239(2)	64(3)
C(407)	1618(4)	5795(3)	1969(2)	54(2)
C(408)	2224(4)	6209(2)	1935(1)	46(2)
C(409)	2199(4)	6641(2)	2171(1)	43(2)
C(410)	1515(4)	6640(2)	2436(1)	52(2)
C(411)	3556(6)	7863(3)	2322(2)	70(3)
O(412)	2835(3)	6228(2)	1666(1)	53(2)
Ni(2)	2585.7(6)	5064.6(4)	916.7(2)	42.5(3)
N(1′)	1149(3)	5302(2)	1065(1)	42(2)

Table 4. (Continued)

Atom	x	y	z	B_{eq}[a]
C(2′)	681(4)	5752(2)	1034(2)	47(2)
C(3′)	−219(4)	5818(3)	1188(2)	55(2)
C(4′)	−637(4)	5436(3)	1356(2)	57(2)
C(5′)	−584(4)	4513(3)	1537(2)	61(3)
C(6′)	−95(5)	4054(3)	1543(2)	60(3)
C(7′)	840(4)	4013(2)	1416(2)	52(2)
C(8′)	1284(4)	4434(2)	1274(1)	45(2)
C(9′)	744(4)	4906(2)	1242(1)	42(2)
C(10′)	−179(4)	4947(3)	1385(1)	49(2)
C(11′)	1090(5)	6176(2)	824(2)	57(2)
O(12′)	2181(2)	4412(1)	1161(1)	45(1)
N(101′)	1899(3)	4941(2)	344(1)	45(2)
C(102′)	1349(4)	4564(2)	184(2)	50(2)
C(103′)	949(5)	4595(3)	−189(2)	63(3)
C(104′)	1100(5)	5007(3)	−392(2)	64(3)
C(105′)	1881(5)	5861(3)	−431(2)	66(3)
C(106′)	2455(5)	6234(3)	−263(2)	67(3)
C(107′)	2876(4)	6178(2)	108(2)	54(2)
C(108′)	2695(4)	5752(2)	312(1)	46(2)
C(109′)	2076(4)	5357(2)	132(1)	45(2)
C(110′)	1676(4)	5420(3)	−236(2)	55(2)
C(111′)	1144(5)	4095(2)	403(2)	61(3)
O(112′)	3021(3)	5699(2)	665(1)	49(1)
N(201′)	4102(3)	4789(2)	930(1)	46(2)
C(202′)	4560(5)	4533(2)	684(2)	56(2)
C(203′)	5597(5)	4447(3)	741(2)	61(3)
C(204′)	6140(4)	4635(3)	1041(2)	62(3)
C(205′)	6226(4)	5122(3)	1633(2)	63(3)
C(206′)	5713(5)	5400(3)	1872(2)	65(3)
C(207′)	4686(4)	5471(3)	1803(2)	54(2)
C(208′)	4160(4)	5280(2)	1484(1)	46(2)
C(209′)	4661(4)	4987(2)	1240(1)	45(2)
C(210′)	5702(4)	4911(2)	1310(2)	52(2)
C(211′)	3955(5)	4326(3)	351(2)	70(3)
O(212′)	3185(2)	5364(1)	1409(1)	46(1)
Na(2)	3240.3(16)	3763.6(9)	1422.1(6)	54.3(8)
N(301′)	5038(4)	3590(2)	1493(1)	56(2)
C(302′)	5678(5)	3751(3)	1776(2)	63(3)
C(303′)	6706(5)	3655(3)	1792(2)	75(3)
C(304′)	7061(5)	3385(3)	1522(2)	77(3)
C(305′)	6749(5)	2869(3)	948(2)	67(3)
C(306′)	6093(5)	2710(3)	666(2)	71(3)
C(307′)	5072(5)	2841(3)	649(2)	62(3)
C(308′)	4749(4)	3135(2)	922(2)	51(2)
C(309′)	5404(4)	3314(2)	1220(2)	53(2)
C(310′)	6423(4)	3181(3)	1226(2)	60(3)
C(311′)	5212(6)	4030(3)	2080(2)	80(3)
O(312′)	3756(3)	3255(2)	911(1)	59(2)
N(401′)	2448(4)	3741(2)	2068(1)	54(2)
C(402′)	2284(5)	4130(3)	2276(2)	63(3)
C(403′)	1637(5)	4081(3)	2558(2)	71(3)
C(404′)	1236(5)	3635(3)	2626(2)	67(3)
C(405′)	1024(4)	2707(3)	2456(2)	66(3)
C(406′)	1204(5)	2311(3)	2233(2)	71(3)
C(407′)	1801(5)	2390(2)	1940(2)	57(2)
C(408′)	2178(4)	2873(2)	1892(2)	47(2)
C(409′)	2031(4)	3278(2)	2124(1)	46(2)
C(410′)	1405(4)	3194(3)	2409(2)	53(2)
C(411′)	2763(7)	4635(3)	2216(2)	87(4)
O(412′)	2695(3)	2973(2)	1599(1)	57(2)
Ni(3)	2484.8(7)	1901.2(4)	799.0(2)	49.3(3)
N(1″)	1047(3)	2071(2)	992(1)	49(2)
C(2″)	481(4)	2489(2)	969(2)	51(2)
C(3″)	−420(4)	2511(3)	1126(2)	63(3)
C(4″)	−708(5)	2100(3)	1313(2)	67(3)

Table 4. (Continued)

Atom	x	y	z	B_{eq}[a)]
C(5″)	−354(5)	1220(3)	1552(2)	72(3)
C(6″)	281(5)	815(3)	1596(2)	75(3)
C(7″)	1177(5)	815(3)	1426(2)	65(3)
C(8″)	1430(5)	1232(2)	1231(1)	53(2)
C(9″)	788(4)	1659(2)	1191(2)	50(2)
C(10″)	−124(4)	1658(3)	1358(2)	56(2)
C(11″)	761(5)	2944(2)	754(2)	60(3)
O(12″)	2260(3)	1262(2)	1064(1)	57(2)
N(101″)	1727(3)	1719(2)	259(1)	52(2)
C(102″)	1216(5)	1304(3)	132(2)	70(3)
C(103″)	705(6)	1315(3)	−226(2)	82(3)
C(104″)	696(6)	1738(3)	−441(2)	82(3)
C(105″)	1259(6)	2620(3)	−531(2)	79(3)
C(106″)	1820(6)	3022(3)	−394(2)	82(3)
C(107″)	2358(5)	3008(3)	−33(2)	69(3)
C(108″)	2304(4)	2582(3)	184(2)	55(2)
C(109″)	1743(4)	2153(3)	41(2)	53(2)
C(110″)	1227(5)	2179(3)	−318(2)	63(3)
C(111″)	1206(7)	824(3)	354(2)	93(4)
O(112″)	2753(3)	2548(2)	526(1)	52(2)
N(201″)	4012(4)	1651(2)	779(1)	56(2)
C(202″)	4441(5)	1393(3)	525(2)	68(3)
C(203″)	5454(6)	1235(4)	595(2)	92(4)
C(204″)	5963(5)	1322(4)	922(2)	85(3)
C(205″)	6074(5)	1740(3)	1540(2)	76(3)
C(206″)	5610(5)	2022(3)	1783(2)	74(3)
C(207″)	4627(5)	2180(3)	1707(2)	59(3)
C(208″)	4101(4)	2049(2)	1369(2)	48(2)
C(209″)	4573(4)	1756(3)	1112(2)	53(2)
C(210″)	5558(5)	1591(3)	1193(2)	67(3)
C(211″)	3872(6)	1298(4)	156(2)	102(4)
O(212″)	3155(3)	2202(2)	1275(1)	52(1)
Na(3)	4110.5(18)	0.9(10)	1598.0(7)	61.9(9)
N(301″)	5915(4)	55(2)	1614(1)	58(2)
C(302″)	6560(6)	333(3)	1844(2)	74(3)
C(303″)	7575(5)	356(3)	1809(2)	83(3)
C(304″)	7929(6)	96(3)	1533(2)	92(4)
C(305″)	7661(5)	−509(3)	995(2)	79(3)
C(306″)	7011(5)	−780(3)	776(2)	71(3)
C(307″)	5999(5)	−788(3)	815(2)	60(3)
C(308″)	5653(4)	−506(2)	1090(2)	51(2)
C(309″)	6306(5)	−209(3)	1334(2)	57(2)
C(310″)	7321(4)	−206(3)	1281(2)	66(3)
C(311″)	6086(6)	615(3)	2140(2)	85(3)
O(312″)	4681(3)	−495(2)	1138(1)	54(2)
N(401″)	2948(4)	214(2)	2072(1)	62(2)
C(402″)	2787(5)	678(3)	2216(2)	77(3)
C(403″)	2085(6)	728(4)	2485(2)	98(4)
C(404″)	1570(6)	320(4)	2579(2)	94(4)
C(405″)	1174(5)	−609(4)	2499(2)	86(3)
C(406″)	1322(5)	−1059(4)	2334(2)	82(3)
C(407″)	2017(4)	−1098(3)	2073(2)	62(3)
C(408″)	2554(4)	−668(3)	1997(2)	55(2)
C(409″)	2397(4)	−189(3)	2163(2)	57(2)
C(410″)	1702(5)	−157(3)	2419(2)	74(3)
C(411″)	3356(7)	1116(3)	2098(3)	101(4)
O(412″)	3231(3)	−688(2)	1753(1)	59(2)
O(501)	3584(5)	540(2)	1141(2)	111(3)

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

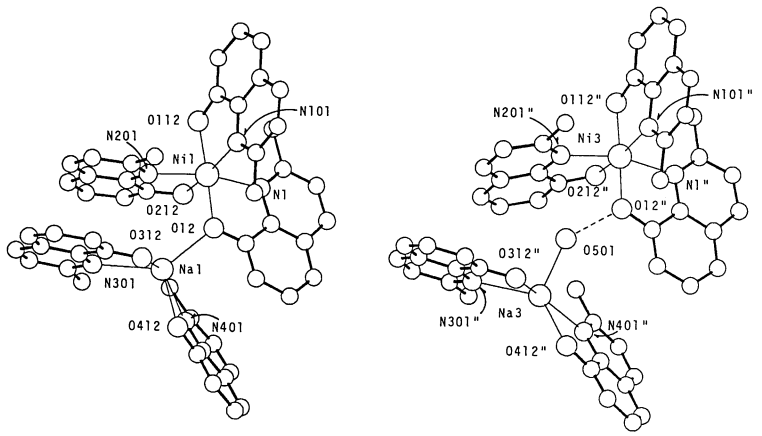

Fig. 3. Perspective drawing of Ni(1)–Na(1) (left) and Ni(3)–Na(3) (right) of **2**. A broken line represents the intermolecular hydrogen bond O(501)···O(12″).

Table 5. Metal–Ligand Distances (Å) and Angles (°) with e.s.d. Values in Parentheses for $Ni(mq)_2(H_2O)_2$

Ni–N(1)	2.176(7)	Ni–O(12)	2.020(5)
Ni–N(101)	2.106(7)	Ni–O(112)	2.039(6)
Ni–O(201)	2.085(7)	Ni–O(202)	2.168(7)
N(1)–Ni–O(12)	78.6(2)	N(1)–Ni–N(101)	97.8(3)
N(1)–Ni–O(112)	101.6(3)	N(1)–Ni–O(201)	93.9(3)
N(1)–Ni–O(202)	163.5(3)	O(12)–Ni–N(101)	108.3(2)
O(12)–Ni–O(112)	170.6(2)	O(12)–Ni–O(201)	83.4(2)
O(12)–Ni–O(202)	84.9(2)	N(101)–Ni–O(112)	81.0(2)
N(101)–Ni–O(201)	164.8(3)	N(101)–Ni–O(202)	87.3(3)
O(112)–Ni–O(201)	87.2(3)	O(112)–Ni–O(202)	94.6(2)
O(201)–Ni–O(202)	84.0(3)		

O(112)···O(202) (1/2−x, y, 1/2+z)=2.699(9) Å.

For **2**, the molecular structure of the Ni(1)–Na(1) unit is shown in Fig. 3(left); the Ni(1) atom is surrounded by three ligands in a mer configuration about O atoms of ligands, and the Na(1) atom is five-coordinated with two bidentate ligands and O(12) which bridges the Ni(1) and Na(1) atoms. The structure of the Ni(2)–Na(2) unit is almost the same as that of Ni(1)–Na(1). In the Ni(3)–Na(3) unit [Fig. 3(right)], the Na(3) atom has, together with the ligands, a coordinated water which is connected to the O(12″) atom by the hydrogen bond O(501)···O(12″)= 2.601(9) Å. These dimeric units are linked by the intermolecular hydrogen bonds to form an infinite chain extended along the b-axis: O(312)···O(112′)= 2.566(7) Å, O(412)···O(212′)=2.512(6) Å, O(312′)··· O(112″)=2.609(7) Å, O(412′)···O(212″)=2.454(7) Å, O(112)···O(312″)=2.525(7) Å, and O(212)···O(412″)= 2.472(7) Å.

Metal–ligand distances and angles for **1** and **2** are summarized in Tables 5 and 6.

Coordination Geometry around Ni Atoms. Adducts of bis complexes of Ni(II) with two neutral monodentate ligands (C) usually show a configuration of trans(C,C), for example, Ni(5-Cl-q)$_2$Py$_2$,[32] $Ni(acac)_2(H_2O)_2$,[33] and $Ni(acac)_2Py_2$.[34] However, $Ni(mq)_2(H_2O)_2$ does not adopt this configuration because of the expected short contact between an O atom of one mq^- and a methyl group of the other. Even with the cis(C,C) configuration, there is an appreciable proximity, as shown in Table 7. In contrast to the Ni–8-quinolinol complexes described in introduction,[2-7] the Ni complex in **2** can simply be derived from **1** by replacing two water molecules with mq^-. This causes a new contact between a N atom and a methyl group to make other methyl-O contacts further short.

When 2-methyl-8-quinolinolate complexes are compared with the corresponding ones of 8-quinolinol derivatives without 2-methyl substituent (Table 8), the Ni–N bonds are elongated by 0.06—0.12 Å, $Ni(mq)_2(H_2O)_2$ compared to Ni(5,7-Cl$_2$-q)$_2$Py$_2$ or Ni(5,7-Br$_2$-q)$_2$Py$_2$, $Ni_2H_3(mq)_6^+$ compared to $Ni_2H_3q_6^+$, and $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$ compared to $Ni_2H_2q_6$. To compensate the weakening of Ni–N bonds, Ni–O bonds are slightly shortened (0.01—0.05 Å). The bite angles are practically the same for both Hq and Hmq complexes. An increase in the bond angle (7—11 deg) between a N atom of a ligand and the donor atom (Y) which occupies the trans position to the O atom of the same ligand, reduces the steric interaction between a

Table 6. Metal-Ligand Distances (Å) and Angles (°) with e.s.d. Values in Parentheses for $Na_3Ni_3H_6(mq)_{15}\cdot H_2O$

	Ni(1)-Na(1)	Ni(2)-Na(2)	Ni(3)-Na(3)
Ni-N(1)	2.169(5)	2.177(5)	2.199(5)
Ni-O(12)	2.020(4)	2.030(4)	1.972(5)
Ni-N(101)	2.212(5)	2.212(5)	2.168(5)
Ni-O(112)	2.025(5)	2.017(5)	2.017(5)
Ni-N(201)	2.187(5)	2.179(5)	2.186(6)
Ni-O(212)	2.047(5)	2.041(4)	2.025(5)
Na-O(12)	2.415(5)	2.352(5)	—
Na-N(301)	2.518(6)	2.471(7)	2.451(7)
Na-O(312)	2.402(6)	2.458(6)	2.324(6)
Na-N(401)	2.701(6)	2.703(7)	2.536(7)
Na-O(412)	2.342(6)	2.314(6)	2.270(6)
Na-O(501)	—	—	2.237(8)
N(1)-Ni-O(12)	80.4(2)	80.4(2)	79.6(2)
N(1)-Ni-N(101)	89.5(2)	89.0(2)	89.3(2)
N(1)-Ni-O(112)	102.5(2)	101.4(2)	101.9(2)
N(1)-Ni-N(201)	164.2(2)	164.3(2)	162.6(2)
N(1)-Ni-O(212)	86.5(2)	87.2(2)	88.6(2)
O(12)-Ni-N(101)	101.7(2)	100.7(2)	100.1(2)
O(12)-Ni-O(112)	177.1(2)	178.0(2)	178.4(2)
O(12)-Ni-N(201)	92.5(2)	90.9(2)	88.0(2)
O(12)-Ni-O(212)	90.2(2)	92.1(2)	89.3(2)
N(101)-Ni-O(112)	78.5(2)	78.7(2)	80.2(2)
N(101)-Ni-N(201)	105.9(2)	105.5(2)	104.9(2)
N(101)-Ni-O(212)	166.6(2)	165.8(2)	169.8(2)
O(112)-Ni-N(201)	84.7(2)	87.5(2)	90.5(2)
O(112)-Ni-O(212)	89.9(2)	88.7(2)	90.5(2)
N(201)-Ni-O(212)	79.3(2)	80.0(2)	79.0(2)
O(12)-Na-N(301)	137.2(2)	136.6(2)	—
O(12)-Na-O(312)	107.6(2)	107.3(2)	—
O(12)-Na-N(401)	94.2(2)	94.7(2)	—
O(12)-Na-O(412)	115.9(2)	123.8(2)	—
N(301)-Na-O(312)	66.7(2)	67.3(2)	68.5(2)
N(301)-Na-N(401)	114.2(2)	113.2(2)	132.2(2)
N(301)-Na-O(412)	105.3(2)	98.7(2)	126.5(2)
O(312)-Na-N(401)	145.2(2)	145.8(2)	154.3(2)
O(312)-Na-O(412)	81.3(2)	81.7(2)	88.1(2)
N(401)-Na-O(412)	64.6(2)	64.2(2)	67.4(2)
O(501)-Na-N(301)	—	—	102.4(3)
O(501)-Na-O(312)	—	—	85.3(3)
O(501)-Na-N(401)	—	—	101.5(3)
O(501)-Na-O(412)	—	—	123.6(3)

Table 7. Short Contacts (Å) between Ligands within a Complex

(a) Around Ni of complex **1**					
C(11)-O(112)	3.36	C(111)-O(12)	3.14	C(11)-C(108)	3.41
(b) Around Ni of complex **2**					
C(11)-O(112)	3.09	C(11′)-O(112′)	3.02	C(11″)-O(112″)	3.10
C(111)-O(12)	3.13	C(111′)-O(12′)	3.07	C(111″)-O(12″)	3.04
C(11)-C(108)	3.18	C(11′)-C(108′)	3.23	C(11″)-C(108″)	3.26
C(111)-C(8)	3.40	C(111′)-C(8′)	3.28	C(111″)-C(8″)	3.35
C(211)-N(101)	3.27	C(211′)-N(101′)	3.22		
(c) Around Na of complex **2**					
C(311)-C(411)	3.59	C(311′)-C(411′)	3.77	C(311″)-C(411″)	3.92
O(312)-O(412)	3.09	O(312′)-O(412′)	3.12	O(312″)-O(412″)	3.19

methyl group and Y in Hmq complexes.

Coordination to Na Atoms. Three Na complexes, respectively, have rather short contacts between methyl groups and between phenolate oxygen atoms (Table 7). Only this configuration, however, allows the orientation of the O atoms favorable for two hydrogen

Tabe 8. Average Bond Lengths (Å) and Angles (°) Relevant to Metal Centers of Nickel(II) Complexes with 8-Quinolinol Derivatives

Complex	Ni–O	Ni–N	Ni–C[a]	∠N–Ni–O[b]	∠N–Ni–Y[a]	n[c]	Ref.
			Bis complexes				
$Ni(mq)_2(H_2O)_2$	2.03	2.14	2.13	79.8	105.0	2	This work
$Ni(5,7\text{-}Cl_2\text{-}q)_2Py_2$	2.05	2.08	2.09	80.2	94.4	2	35
$Ni(5,7\text{-}Br_2\text{-}q)_2Py_2$	2.04	2.07	2.11	80.5	93.4	8	36
			Tris complexes having three hydrogen bonds				
$Ni_2H_3(mq)_6ClO_4$	2.05	2.14		79.4	104.9	6	20
$Ni_2H_3q_6I_3$	2.07	2.06		79.3	98.2	6	5
$(H_2q)(Ni_2H_3q_6)_2(ClO_4)_3$	2.07	2.06		79.5	98.4	12	6
$Ni_2H_3q_6SCN$	2.08	2.06		79.7	97.5	3	7
			Tris complexes having two hydrogen bonds				
$Na_3Ni_3H_6(mq)_{15}\cdot H_2O$	2.02	2.19		79.6	102.7	9	This work
$Ni_2H_2q_6$	2.07	2.07		79.9	95.1	6	4

a) See text for details. b) Bite angle. c) Number of data averaged.

bonds to the Ni complexes. An unbalanced arrangement of five donor atoms around the Na(1) and Na(2) atoms is also ascribed to this, together with a stacking of quinoline rings between the Na and Ni complexes. The Na(3) complex, on the other hand, has an usual structure that is intermediate between a trigonal bipyramid and a square pyramid, due to the presence of a coordinated water.

Alkali metal and silver ions (M′) react with 8-quinolinol to give compounds of a general formula, $M'H_nq_{(n+1)}$, n=1 for Li^+, Na^+, K^+, and Ag^+; n=2 for K^+, Rb^+ and Cs^+.[37] The structures of KHq_2, KH_2q_3, and $AgHq_2Py$ have been determined.[38,39] In these complexes, as well as some nickel complexes in Table 8, hydrogen bonds are generally found to form polynuclear species or an extended network between complexes.

Implication for the Extraction Behavior. When Ni^{2+} in sulfate medium is extracted with 8-quinolinol into chloroform, the extracted species are $NiHq_3$ and $Ni_2H_2q_6$.[4] In the case of 2-methyl-8-quinolinol, on the other hand, $Ni_2(mq)_4$ is extracted under the corresponding conditions.[20] Only at a very high concentration of the extractant (>0.3 mol dm^{-3}), $NiH(mq)_3$ or $Ni_2H_2(mq)_6$ is extracted. The structures of these extracted species are reflected in the Ni complex part of **2**. Shorter contacts between ligands in **2** than in $Ni_2H_2q_6$ lead to a lower stability and, thus, a lower extractability of this complex.

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1) Ligand abbreviation: Hq, 8-quinolinol; Hmq, 2-methyl-8-quinolinol; H(5-Cl-q), 5-chloro-8-quinolinol; H(5,7-Cl_2-q), 5,7-dichloro-8-quinolinol; H(5,7-Br_2-q), 5,7-dibromo-8-quinolinol; Hacac, 2,4-pentanedione; Py, pyridine.

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