Syntheses and Electronic Spectra of 2,2′-Isopropylidenedi-8-quinolinol, Its Nickel(II), and Copper(II) Chelates

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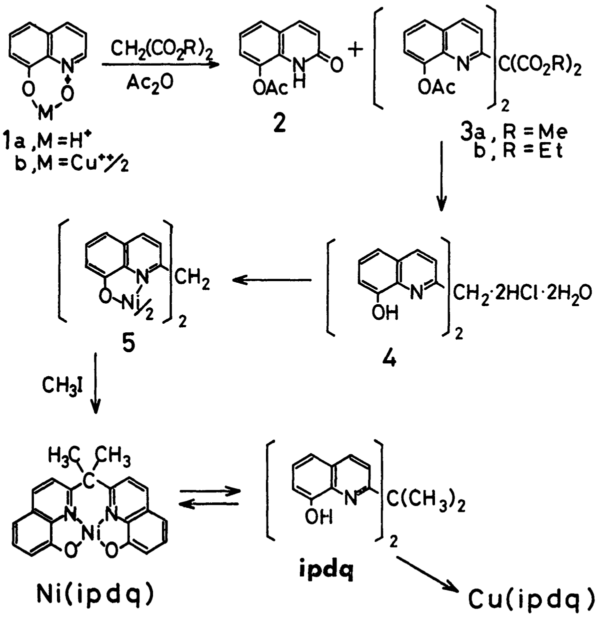
The title ligand, which contains two 8-quinolinol (oxine) functions in one molecule, and the Ni(II) and Cu(II) chelates have been synthesized and characterized. Visible and ultraviolet spectra of the chelates and the ligand in several solvents have been measured. Square-coordination of the ligand to the metal has been revealed by a comparison of the d-d bands between the chelates and quadridentate Schiff base chelates in the literature. Intra-ligand transition bands of the title chelates and the solvent effects on the frequency shifts have been compared with those of the ligand, 8-hydroxy-1-methylquinolinium hydroxide, bis(8-quinolinolato)palladium(II), -copper(II), and -nickel(II), and have been discussed.

The quadridentate ligand, 2,2′-isopropylidenedi-8-quinolinol, abbreviated as ipdq, has been prepared in our laboratory, in expectation of forming such type of stable metal chelates as *cis*-bis(8-quinolinolato)metal. The synthetic pathway is outlined in Scheme 1. It has been shown that ipdq readily reacts with both nickel(II) and copper(II) to give the crystalline compounds, Ni(ipdq) and Cu(ipdq), respectively. These chelates are sufficiently soluble in many organic solvents to examine the d-d absorption bands, which provide significant information regarding the coordinating structure. This paper presents the absorption data of Ni(ipdq) and Cu(ipdq) in eight solvents in the ultraviolet and visible regions, and the spectra have been compared with those of related compounds.



Scheme 1.

The chief purpose of this work was to determine the effect of the metal ion on the spectra of the 8-quinolinol-type ligand, of value from the viewpoint of the development of analytical colorimetric reagents, and in connection with the spectra of the corresponding 8-quinolinol chelates, NiQ_2 and CuQ_2.[1] It is known that the position of the lowest energy intra-ligand band of CuQ_2 is highly dependent upon the solvent[2] and the spectrum of NiQ_2 changes drastically with solvent.[3-7] The low solubility, however, restricts the elucidation of the relationship among the spectra, coordinating structure, and nature of solvent.

Results

Preparations. As shown in Scheme 1, Ni(ipdq) has been obtained from 8-quinolinol *N*-oxide (**1a**) or its copper(II) complex (**1b**) in a four-step process. The intermediate compounds (**3**—**5**) have also been isolated and characterized, the detailed procedures and results of which are given in the experimental section.

The malonates, **3a** and **3b**, have been prepared by a method similar to that reported by Hamana and Yamazaki[8] for the synthesis of diethyl di-2-quinolylmalonate by the treatment of quinoline *N*-oxide with diethyl malonate in the presence of acetic anhydride (Ac_2O). It is known that the treatment of **1a** with Ac_2O at room[9] or bath-temperature[10,11] affords 8-acetoxy-2-

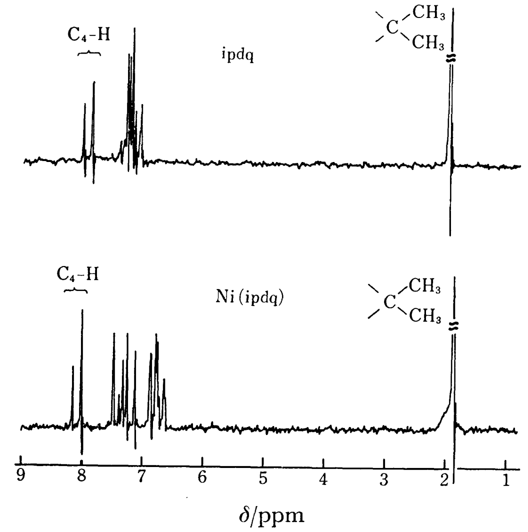


Fig. 1. The 60 MHz PMR spectra of ipdq and Ni(ipdq) in $CDCl_3$. For the spectrum of Ni(ipdq) (29 mg/0.6 cm^3), the relative intensity are 3 (siglet), 4 (multiplet), and 1 (doublet). For the spectrum of ipdq (40 mg/0.6 cm^3), those are 3, 4.4, and 1.2, respectively, and the latter two contain probably the phenolic proton.

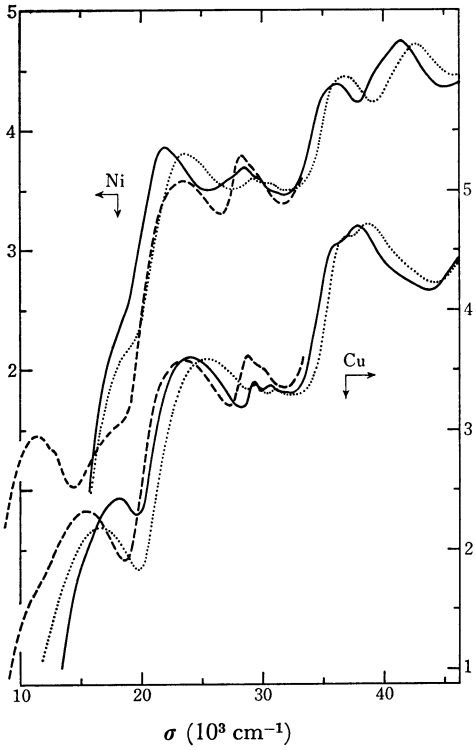


Fig. 2. The absorption spectra of Ni(ipdq) in MeOH (······), in THF (——), and in pyridine (------), and the spectra of Cu(ipdq) in MeOH (······), in 1,2-dichloroethane (——), and in pyridine (------).

quinolone (**2**) in high yield. It has been found, however, that the addition of dimethyl or diethyl malonate to the above system gives a mixture of **3** (**a** or **b**) and **2**, and that, on lowering the temperature, the yield of **3** increases at the expense of **2** as given in Table 4 in the experimental section.

The chelate, **5**, is not suitable for the present purpose, since in many common solvents it is not sufficiently soluble. However, **5** readily reacts with two moles of methyl iodide to yield a higher soluble chelate, Ni(ipdq). The PMR spectra of Ni(ipdq) and the metal-free ligand, ipdq, are shown in Fig. 1. The similarity of these spectra to those of 2-methyl-8-quinolinol and its Al(III) complex[12] supports the structure shown in Scheme 1.

Absorption Spectra. Absorption data obtained are set out in Tables 1—3. The spectra of some representative species are shown in Fig. 2. The intra-ligand transition bands have been divided into three parts, in an analogy with those of the 8-quinolinolate.[2,3,13] In this paper these bands have been denoted by A-, B-, and C- in the order of decreasing frequency.

The spectra of ipdq (Table 1) are comparable to those of 8-quinolinol[2,3,14] and its 2-methyl derivative.[3,15] A weak shoulder near 450 nm for ipdq in methanol (MeOH) is similar to a band for 8-quinolinol at 430 nm (ε: 51)[14c,f,h,i] in water or at 450 nm in MeOH (shoulder, log ε: −0.34),[14f] which is known to be due to the presence of the zwitter ionic form.[14c,h,i]

The spectrum of the 8-hydroxy-1-methylquinolinium salt in basic solvent is known to be a good model for the absorption characteristics of the zwitter ionic form of 8-quinolinol.[14c,g,i,j] The 8-hydroxy-1-methylquinolinium hydroxide (the isomer of 1-methylquinolinium-8-

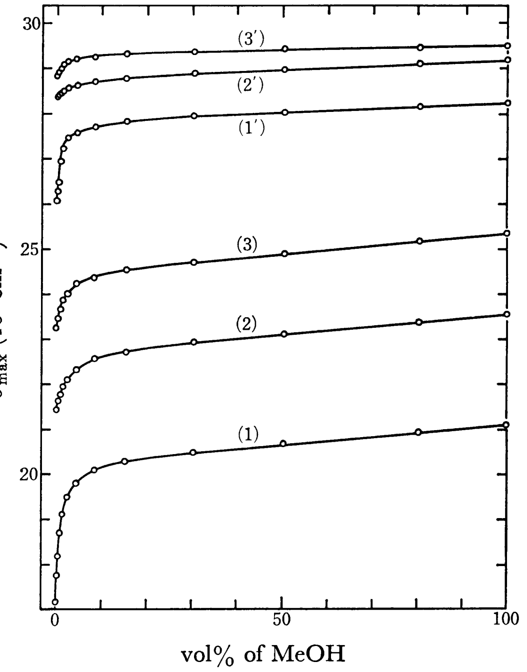


Fig. 3. Variation of the positions of the C- (1—3) and B-bands (1′—3′) of the compounds in benzene–MeOH mixtures as a function of the vol% of MeOH; (1) 8-hydroxy-1-methylquinolinium hydroxide, (2) Ni(ipdq), and (3) Cu(ipdq).

TABLE 1. THE ABSORPTION DATA[a,b] OF ipdq AND 8-HYDROXY-1-METHYLQUINOLINIUM CHLORIDE (N–CH_3)

Compound	Solvent	A-band σ_{max} (log ε)	B-band σ_{max} (log ε)	C-band σ_{max} (log ε)
ipdq	Cyclohexane	39.18(4.94)	32.13(3.83)	31.1(sh 3.77)
	MeOH	39.64(4.91)	32.39(3.81)	31.3(sh 3.73) 22.5(sh −0.42)[c]
	0.1 M aq NaOH	37.91(4.79)	29.59(3.84)	28.3(sh 3.77)
	0.1 M KOH–MeOH	37.88(4.74)	29.41(3.80)	28.0(sh 3.72)
	1.0 M aq HCl	37.49(4.82)	30.53(3.92)	26.9(3.49)
N–CH_3	0.1 M aq NaOH	36.56(4.52)	28.9 (3.11)	22.4(3.21)
	0.05 M KOH–MeOH	35.91(4.52)	28.3 (3.30)	21.1(3.19)

a) The wave numbers are given in 10³ cm⁻¹ units, and sh means a shoulder band. b) Only the main peaks are tabulated. c) A 10 cm cell was used.

TABLE 2. THE ABSORPTION DATA[a,b] OF 8-HYDROXY-1-METHYLQUINOLINIUM HYDROXIDE (N–CH_3, OH) AND THE METAL CHELATES

Compound	Band		Solvent							
			MeOH	2-PrOH[c]	DMF	DCE[d]	Pyridine	$CHCl_3$[e]	THF	Benzene
N–CH_3, OH	A	σ_{max}	35.91	35.46		34.36		34.31	34.31	
	B	σ_{max}	28.3	27.9	26.3	26.5	26.0	26.7	26.3	26.1
		(log ε)	(3.31)	(3.39)	(3.66)	(3.66)	(3.71)	(3.53)	(3.64)	f)
	C	σ_{max}	21.1	20.2	18.2	18.0	17.7	18.3	17.5	17.2
		(log ε)	(3.16)	(3.16)	(3.12)	(3.16)	(3.12)	(3.09)	(3.09)	f)
CuQ_2[g]	A	σ_{max}[h]	38.83	38.61		37.95		38.02	37.95	
	B	σ_{max}	29.90	29.81	29.63	29.74	29.4	29.72	29.56	29.56
		(log ε)	(3.36)	f)	(3.49)	(3.38)	(3.51)	(3.34)	(3.50)	(3.42)
	C	σ_{max}	25.5	25.1	24.2	24.0	24.2	24.3	23.9	23.6
		(log ε)	(3.73)	f)	(3.76)	(3.77)	(3.77)	(3.78)	(3.77)	(3.77)
Cu(ipdq)	A	σ_{max}	38.69	38.31		37.88		37.74	37.66	
	B	σ_{max}	29.50	29.4	29.1	29.2	28.8	29.1	28.9	28.8
		(log ε)	(3.37)	(3.37)	(3.53)	(3.41)	(3.61)	(3.36)	(3.54)	(3.48)
	C	σ_{max}	25.4	24.6	24.2	24.0	23.5	23.7	23.5	23.3
		(log ε)	(3.59)	(3.60)	(3.61)	(3.61)	(3.58)	(3.60)	(3.58)	(3.56)
	d-d	σ_{max}	16.5	17.1	16.6	18.1	15.5	18.2	16.9	17.9
		(log ε)	(2.19)	(2.24)	(2.30)	(2.43)	(2.33)	(2.43)	(2.35)	(2.47)
PdQ_2	A	σ_{max}[i]	40.82	40.65		39.80		39.76	39.76	
		σ_{max}[j]	37.52	37.24		36.63		36.83	36.63	
	B	σ_{max}	29.63	29.67	29.46	29.46	29.3	29.4	29.4	29.2
		(log ε)	(3.31)	(3.31)	(3.44)	(3.42)	(3.51)	(3.38)	(3.48)	(3.52)
	C	σ_{max}	—	—	23(sh)	23(sh)	23(sh)	—	23(sh)	23(sh)
		σ_{max}	24.0	23.6	22.6	22.5	22.3	23.0[k]	22.1	22.0
		(log ε)	(3.84)	(3.83)	(3.83)	(3.82)	(3.84)	(3.82)	(3.85)	(3.88)
Ni(ipdq)	A	σ_{max}	42.68	42.28		41.67		41.67	41.41	
		σ_{max}	36.87	36.70		36.23		36.28	36.10	
	B	σ_{max}	29.2	28.9	28.7	28.7	28.3	28.6	28.5	28.4
		(log ε)	(3.60)	(3.59)	(3.68)	(3.66)	(3.79)	(3.67)	(3.69)	(3.72)
	l)	σ_{max}		28(sh)	28(sh)	28(sh)	—	28(sh)	27(sh)	27(sh)
	C	σ_{max}		24(sh)	24(sh)	24(sh)	—	23(sh)	23(sh)	23(sh)
		σ_{max}	23.6	22.9	22.5	22.3	23.4	22.1	21.8	21.4
		(log ε)	(3.81)	(3.81)	(3.88)	(3.85)	(3.57)	(3.85)	(3.86)	(3.83)
NiQ_2[m]	C[n]	σ_{max}	25.9[p]	25.8	24.6	26.1	24.4[q]	26.0	25.6	25.9
		(log ε)	(3.72)	f)	(3.67)	r)	(3.77)	r)	r)	r)
	C[o]	σ_{max}	—			23(sh)	—	23(sh)	22(sh)	22(sh)
		σ_{max}	—	23(sh)	22(sh)	21.6	—	21.7	21.4	21.2

a) The wave numbers are given in 10^3 cm^{-1} units, and sh means shoulder band. b) Only the main bands are tabulated; see in Fig. 2. c) 2-Propanaol. d) 1,2-Dichloroethane. e) Containing 0.5 vol% EtOH. f) A saturated soln. g) *Cf.* Refs. 2 and 3. h) log ε is *ca.* 4.83. i) log ε is 4.6—4.7. j) log ε is *ca.* 4.5. k) *Cf.* K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953); E. Sekido, *Nippon Kagaku Zasshi*, **80**, 871 (1959). l) A new band. See text. m) *Cf.* Refs. 2—7. n) Of one form in an equilibrium mixture, presumed to be a polymeric species (ref. 22) or solvent-coordinated species. o) Of another form, presumed to be a planar species. p) The A-band: 38.54 (4.74), the B-band: 29.72 (3.59). q) The B-band: 28.9 (3.81). r) Immediately after suspension, filtration, and dilution. After one day standing considerable amounts of ppt were deposited.

olate monohydrate) is known as one of the solvatochromic compounds exhibiting large color changes with solvent polarity.[16,17] The band positions of this hydroxide in MeOH (Table 2) are seen to be almost the same as that of the corresponding chloride salt in MeOH–KOH (Table 1). From these results, the chloride in a basic solvent and the hydroxide in an organic solvent can best be utilized to establish the spectral behavior of the zwitter ionic form of ipdq.

The plots of the positions of the B- and C-bands of the hydroxide, Ni(ipdq), and Cu(ipdq) in benzene–MeOH mixtures *vs.* the vol% of MeOH are shown in Fig. 3.

Discussion

The coordinating structure of Cu(ipdq) in eight solvents can be classified into three groups according to the positions and the shapes of the d-d bands (Fig. 2 and Table 2). On the basis of the data of (*N,N'*-disalicylidene-1,2-propanediaminato)copper(II) which has been shown to be square-planar in chloroform

TABLE 3. THE d-d ABSORPTION DATA[a] OF THE NICKEL CHELATES[b,c]

Chelate	Solvent	Band I $\sigma_{\max}$ (log ε)	Singlet band $\sigma_{\max}$ (log ε)	Band II $\sigma_{\max}$ (log ε)
$NiQ_2 \cdot 2H_2O$	MeOH	9.71(1.12)	13.0(0.50)	16.3(0.97)
NiQ_2	MeOH[d]	9.8	13.0	16.3
	solid(mull)	9.76	13.0(sh)	16.0
	Pyridine[e]	10.70(1.03)	12.8(sh 0.72)	18.3(1.44)
Ni(ipdq)[c]	Pyridine	11.43(1.45)	12.8(sh 1.35)	18.5(sh 1.54)

a) The wave numbers are given in 10^3 cm^{-1} unit, and sh means a shoulder band. b) *Cf.* Ref. 21, the data of $KNiQ_3$. c) The d-d data of Ni(ipdq) in the other seven solvents are omitted. The spectra in MeOH and in THF shown in Fig. 2 are representative. d) A saturated soln, and a 10 cm cell was used. e) *Cf.* Refs. 3, 5, and 6.

(d-d$_{\max}$: 17760 cm^{-1}) and forming a five-coordinated monoadduct in pyridine (max: 16860),[18] it can be deduced that the benzene, chloroform, and 1,2-dichloroethane solutions of Cu(ipdq) involve a planar monomeric species; the tetrahydrofuran, *N*,*N*-dimethylformamide, and two alcoholic solutions involve a five-coordinated copper(II); and the pyridine solution involves a six-coordinated copper(II). The five-coordination in the solutions does not mean a dimeric structure since even in such an inert solvent as benzene the chelate is a monomer. Any relationship between the solvent-induced frequency shifts of the d-d band of Cu(ipdq) and those of the A-, B-, or C-band could not be found. The position of the C-band shifts linearly with the E_T value known as a solvent polarity parameter[19] with small deriation for the pyridine solution.

By comparing the d-d bands of Ni(ipdq) (Fig. 2 and Table 3) with those of the quadridentate Schiff base chelates of nickel(II),[20] it has been concluded that the pyridine solution involves a solvent-coordinated species and the other seven solutions involve a planar monomeric species. The difference in band position and intensity between the first d-d band of NiQ_2 in pyridine and that of Ni(ipdq) may be correlated with the difference in coordinated environment between *trans*-O_2N_4 and *cis*-O_2N_4 with a similar discussion of the d-d bands for *mer*- and *fac*-$KNiQ_3$.[21] From the band positions of the nickel chelates (Table 3), the form of NiQ_2 in MeOH and in the solid state have been assigned as solvent-coordinated O_4N_2 and oxygen-bridged polymeric O_4N_2, respectively. The latter is consistent with previous conclusions[22] of one form in an equilibrium mixture of NiQ_2 in inert solvent.

The shapes of the A-, B-, and C-bands of planar Ni(ipdq), and possibly those of planar NiQ_2 also, differ markedly from those of the copper chelates and the six-coordinated nickel chelates, which are similar to those of the ligand cation[3,13,14a] and the zwitter ion (Fig. 2 and Table 2). The bands of the planar nickel chelates, however, may be correlated to those of the other chelates by an inspection of the spectra of PdQ_2 (Table 2), since PdQ_2 has intermediate spectral properties between the copper chelates and the planar nickel chelates. Thus, with change from the copper chelates to PdQ_2 or the planar nickel chelates, the A-band appears to be split into two strong bands and the C-band becomes sharper and more intense, shifting to the red. Planar Ni(ipdq) shows an additional band near 27—28 × 10^3 cm^{-1}, and there is no corresponding band in the spectra of PdQ_2. In this sence, the band is clearly a new one.

It has been noted that the frequency shifts of the C-band of planar Ni(ipdq) induced by the solvents are almost the same as those of Cu(ipdq). These shifts may be correlated to the solvatochromism of the *N*-methyl compound, in regard to the strong blue shift by the addition of a small amount of MeOH in the benzene solutions (Fig. 3) and to the approximately linear relationship with the E_T value[19] (Table 2). These facts suggest that the nature of the C-bands, *i.e.* the first π-π^* bands, of these species are similar to each other, and throw doubt upon the explanation[3] for the C-band of planar NiQ_2 in terms of a strong mixing of charge transfer from the metal to the ligand with the intra-ligand transition.

Burton and Davis have studied the spectrum of 8-quinolinol and explained that the lowest energy band of the neutral molecule involves a movement of the electronic charge from the phenol ring to the pyridine ring, and that an increase in the electron density in the phenol ring (*e.g.* by the formation of the dissociated anion) or a decrease in the electron density in the pyridine ring (*e.g.* by the formation of the protonated cation) will move the transition to lower energies.[23] Hence the strong red shift of the C-band of the zwitter ion is explained.

In CuQ_2 *etc.*, the considerable delocalization of the negative charge on the phenol ring has been suggested from the bond-length between the carbon at 8-position and the phenolic oxygen[24] and the electrophilic reaction.[25] The delocalization and good σ-bonding character[3,13] of the metal–nitrogen bond can bring the C-band positions of the chelates listed in Table 2 between those of the zwitter ion and protonated cation of the ligand. As suggested from the study of the hydroxide,[17] the sensitivity of the C-band to the protic solvent, shown in Fig. 3, may be ascribed in most part to a decrease in the degree of delocalization of the negative charge to the phenol ring, possibly due to the formation of the H-bond between the protic solvent and the anionic oxygen in the chelates.

While the position of the C-band of the copper chelates is near to that of the solvent-coordinated nickel chelates, a blue shift of the C-band of the polymeric NiQ_2 relative to CuQ_2 (*e.g.* *ca.* 2000 cm^{-1}, in benzene) has been observed. In analogy with the formation of the H-bond, the blue shift may be explained on the basis that the delocalization of the negative charge decreases due to the bonding of the phenolic oxygen to the two metal ions.

On changing from solvent-coordinated NiQ_2 to planar Ni(ipdq), the C-band is displaced to the red (*e.g. ca.* 2000 cm^{-1}, in MeOH). Although detailed analysis is not yet possible, the better σ-bonding character of the N–Ni (low spin) bond in the planar chelate may contribute much to this shift.

Experimental

Preparation of the Compounds. The spectral sample of NiQ_2 was obtained by heating $NiQ_2 \cdot 2H_2O$ at 140—150 °C for 10 h, which showed the bands (IR: KBr, in part) at 744, 737 (sh), and 731 cm^{-1}. A sample dehydrated by heating at lower temperature showed the single and somewhat broader peak at 730 cm^{-1} in this region.[26] The other MQ_2 were prepared by the usual method.[27]

8-Hydroxy-1-methylquinolinium chloride was prepared in a manner similar to the preparation of its perchlorate salt[14j] and recrystallized.[28] Mp 237—238 °C (lit,[28] 233 °C) (lit,[16] 197 °C). Found: C, 61.44; H, 5.27%. 8-Hydroxy-1-methylquinolinium hydroxide was prepared by the reported method.[17] Mp(dec) 117 °C (lit,[17] 115 °C) (lit,[16] 119 °C).

8-Quinolinol N-*Oxide (1a)*: The reported methods[29,30] were modified in the following way. To a hot solution of 8-quinolinol (73 g) dissolved in AcOH (200 cm^3), 30% aq H_2O_2 was added (50 cm^3). The mixture was heated at 75—80 °C, for 6 h. Additional peroxide (100 cm^3) was added in five equal portions, while heating, at hourly intervals. After cooling, the reaction mixture was concentrated with a rotary evaporator at 40—50 °C, and water (50 cm^3) added when the residue decreased. The resulting solution was concentrated again, and this procedure repeated three or four times until a solid separated. The resulting mixture was extracted with 150-, 100-, 100-, and 50 cm^3 of $CHCl_3$ and the combined extracts were washed with 2 M aq NH_3 (200- and 200 cm^3), water, 1 M aq HCl (200 cm^3), and finally water. The solvent of the organic layer, without drying, was distilled and the residual yellow solids were recrystallized from 50 vol% aq EtOH (210 cm^3) to give 47 g (58%) of **1a** as fine yellow needles; mp 138—139 °C (lit,[29] 138 °C) (lit,[30] 139 °C).

Bis(8-quinolinol N-*oxidato)copper(II) (1b)*: The reported method[10] was modified for large scale preparation. To a hot solution of $Cu(NO_3)_2 \cdot 3H_2O$ (25 g) dissolved in water (500 cm^3), concd aq NH_3 (24 cm^3) was added, followed by **1a** (32 g) dissolved in 50 vol% aq EtOH (300 cm^3) with vigorous stirring. After continued heating and stirring at *ca.* 60 °C for 4 h, the resulting suspension was allowed to stand overnight at room-temperature. The light-green product was collected, washed with 1.5 M aq NH_3 (*ca.* 200 cm^3) and water, and dried at 110 °C until the color changed to a yellowish brown to give 37 g (97%) of **1b**; mp (dec) 257—262 °C. IR(KBr): 3100, 3060, 1584, 1567, 1510, 1453, 1388, 1350, 1313, 1301, 1052, 1034, 821, 789, 745, 715, and 512 cm^{-1}. Found: C, 55.77; H, 3.11; Cu, 16.56%. This complex was slightly soluble in aq NH_3.

Dimethyl and Diethyl Bis(8-acetoxy-2-quinolyl)malonate (3a and 3b): See text. The following procedure is representative. A suspended mixture of **1b** (19 g), $CH_2(COOMe)_2$ (12 g), and Ac_2O (40 cm^3) in a flask equipped with a $CaCl_2$ tube, was stirred for periods and bath-temperature's as given in Table 4. To the resulting deep-green suspension, MeOH (25 cm^3) was added, and after stirring for 2 h at room-temperature, water (50 cm^3) was added in limited amounts with continuous stirring for complete precipitation of the desired products. The collected precipitate was washed with 50 vol% aq AcOH (*ca.* 100 cm^3) and water to remove the AcOH and the copper salt, and dried at 110 °C. The solids were suspended in hot $CHCl_3$ (50 cm^3), and the crude quinolone (**2**) filtered off. The filtrate was distilled off and the pale brown residual solids were dissolved in boiling acetone (150 cm^3 per 10 g). After cooling a small amount of **2** separated. The new filtrate was warmed, and an equal volume of hot water added portionwise to separate the crystalline powder of **3a**. After cooling, the collected powder was washed with water and dried. Concentration and cooling of the mother liquor yielded a small amount of a mixture of **2** and **3a**, which were separated by acetone. The combined crude quinolone (**2**) was recrystallized from AcOH by adding water (30- and 30 cm^3 per 10 g) to give light-tan leaflets; mp 247—249 °C, the yield of which is given in Table 4. Recrystallization from EtOH gave pale yellow leaflects; mp 249—251 °C (lit,[11] 252—254 °C), whose IR spectrum was virtually identical with that given in the lit.[9] The combined crude malonate (**3a**) was recrystallized from $CHCl_3$ by adding MeOH (25- and 75 cm^3 per 10 g) to give colorless needles; mp 211.5—213 °C, the yield of which is given in Table 4. Recrystallization from MeOH (100 cm^3 per 0.8 g) gave an analytical sample of the colorless needles; mp 211.5—213 °C. IR(KBr): 1759 and 1741 cm^{-1} (C=O); PMR ($CDCl_3$): δ=2.49 (6H, s, $-OCOCH_3$), 3.91 (6H, s, $-COOCH_3$), 7.29—8.10 (10H, m). Found: C, 64.47; H, 4.43%. Calcd for $C_{27}H_{22}N_2O_8$: C, 64.54; H, 4.41%. The estimated solubility of **2** and **3a** in hot $CHCl_3$ were 0.7 g and 20 g per 50 cm^3, and in acetone at a room-temperature were 0.07 g and 3.5 g per 50 cm^3, respectively.

Table 4. The yields of **3** and **2**

Reactant		Conditions		Yield (%)	
N-oxide	Malonic ester	Temp[a)] (°C)	Time (days)	**3**	**2**
1a	Dimethyl malonate	15	21	40	31
		25	7	36	36
		35	5	29	45
		45	4	25	51
	Diethyl malonate	25	8	17	62
		35	5	15	66
		45	4	12	70
1b	Dimethyl malonate	15	33	55	10
		25	16	49	9
		35	10	43	14
		45	6	38	20
	Diethyl malonate	25	21	46	18
		35	13	40	25
		45	7	35	30

a) Bath temp, ±3 °C.

The treatment of **1a** (16 g) with the methyl ester and the treatment of **1a** or **1b** with $CH_2(COOEt)_2$ (14 g) in a similar manner gave the results given in Table 4. The two samples of **3a** obtained from **1a** and **1b** had identical IR spectra with each other and the mp of a mixture of the two samples was not depressed. The same was found with the two samples of **3b**.

The colorless leaflets of **3b** recrystallized from MeOH; mp 237.5—239 °C. IR(KBr): 1763 and 1736 cm^{-1} (C=O); PMR ($CDCl_3$): δ=1.30 (6H, t, J=7 Hz, $-CH_3$ of the ethyl ester), 2.49 (6H, s, $-OCOCH_3$), 4.43 (4H, q, J=7 Hz, $-CH_2-$), 7.24—8.13 (10H, m). Found: C, 65.96; H, 4.73%. Calcd for $C_{29}H_{26}N_2O_8$: C, 65.65; H, 4.94%.

2,2′-Methylenedi-8-quinolinol Dihydrochloride Dihydrate (4): This was prepared in a similar way to the conversion of di-2-quinolylmalonate into 2,2′-methylenediquinoline.8) A suspension of **3a** (10.1 g) in 20% aq HCl (700 cm^3) was heated under reflux for 2 h producing a yellow solution. While hot, a small amount of reddish material was filtered off, and the filtrate allowed to stand overnight at room-temperature. The separated yellow solid was collected, washed with acetone, dried at room-temperature under reduced pressure, and recrystallized from MeOH (150 cm^3) containing concd HCl (1.5 cm^3) by adding concd HCl (15 cm^3) to give the yellow crystals of **4**, which were washed with 20% HCl and then with acetone. The yield was 7.8 g (95%). Further recrystallization from 20% HCl (100 cm^3 per 2.5 g) gave an analytical sample of the yellow plates, salmon-pink above 110 °C, dec at 255—270 °C. IR(KBr): 3360, 3180—2500, 1631, 1599, 1502, 1422, 1391, 1302, 1090, 863, 848, 837, 821, 748, 574, and 564 cm^{-1}. Found: C, 55.27; H. 4.80%. Calcd for $C_{19}H_{20}N_2O_4Cl_2$: C, 55.49; H, 4.90%. The weight loss after heating at 110 °C for 15 h was 17.64%, corresponding to the release of one molecule of HCl and two molecules of H_2O (Calcd: 17.63%). The treatment of **3b** was effected also with 20% HCl (10.6 g per 700 cm^3) under reflux for 3 h, resulting in a 95% yield of **4**. The IR spectrum was identical with that prepared from **3a**.

(2,2′-Methylenedi-8-quinolinolato)nickel(II) (5): To a hot solution of $Ni(OAc)_2 \cdot 4H_2O$ (4.7 g) dissolved in MeOH (100 cm^3), **4** (7.8 g) was added with stirring and heating at *ca.* 60 °C. When the reddish brown precipitate disappeared producing a sky-blue precipitate and deep-green mother liquor (after *ca.* 30 min), a hot solution of $NaOAc \cdot 3H_2O$ (7.8 g) dissolved in water (200 cm^3) was added portionwise. After heating and stirring for 2 h, the resulting yellowish brown solid was collected, washed with hot water, and dried at 110 °C to give 6.8 g (quantitative) of **5**; mp above 280 °C. IR(KBr): 3040, 2870, 1574, 1502, 1458, 1439, 1395, 1369, 1333, 1302, 1279, 1138, 1108 (C–O),31) 904, 828, 818, 768, 743, 729, 631, 536, and 525 cm^{-1}. Found: C, 63.84; H, 3.18; Ni, 16.37%. Calcd for $C_{19}H_{12}N_2O_2Ni$: C, 63.56; H, 3.27; Ni, 16.35%.

The structure of **5** was deduced from its characteristic visible spectra. This yellowish brown powder showed similar visible spectra (mull method, max: 445 nm, sh: 540 nm) to that of Ni(ipdq) discussed in the text. However, the solution spectra (*ca.* 4×10^{-4} M, a 0.1 cm cell) showed three sharp peaks near 500 nm (Scheibe's A-band).32) Thus in DMF at 452.5 nm (ε: 4700), 482 (9400), 515 (17600), and in 0.01 M methanolic NaOH at 447.5 (6400), 477 (15600), 511 (33200), these are similar to the metal chelates with 2,2′-methylenediquinoline.32) A spectral change with time was observed, probably due to air-oxidation.

(2,2′-Isopropylidenedi-8-quinolinolato)nickel(II), Ni(ipdq): To a warmed suspension of **5** (1.8 g) in MeOH (100 cm^3), CH_3I (5 cm^3) was added, followed by NaOH (0.5 g) dissolved in water (45 cm^3) with stirring and heating at 45—50 °C under reflux, to give a reddish black mixture. Soon a brown solid separated out. After continuous stirring and heating for 30 min, the reaction mixture was poured into hot water (200 cm^3) with stirring with caution against the remaining iodide. The precipitated reddish brown solids were collected, washed with hot water, dried at 110 °C (yield: 1.9—1.8 g), extracted with boiling MeOH (250 cm^3), and the residual solids (0.3—0.2 g) filtered off. After cooling the filtrate for some time, a small amount of the precipitated black material was filtered off, and the new filtrate allowed to stand at *ca.* 5 °C overnight. The crystals separated were collected, washed with MeOH, and dried to give 1.0 g (and 0.3 g from the mother liquor, total 67%) of Ni(ipdq). Repeated recrystallizations from MeOH (100 cm^3 per 0.8 g) gave an analytical and spectral sample as reddish brown leaflets (sometime gave needles having a virtually identical IR spectrum). PMR and UV: see in the text. TGA-DTA (5 °C/min, in air): a sharp endothermic peak at 336 °C, followed by a weight loss. IR(KBr): 3040, 2970, 1567, 1501, 1468, 1447, 1395, 1334, 1296, 1110 (C–O),31) 832, 772, 740, 638, and 551 cm^{-1}. Found: C, 65.21; H, 4.04; Ni, 15.16%. Calcd for $C_{21}H_{16}N_2O_2Ni$: C, 65.16; H, 4.17; Ni, 15.17%.

2,2′-Isopropylidenedi-8-quinolinol, ipdq: To a suspension of Ni(ipdq) (2.0 g) in EtOH (20 cm^3), concd HCl (4 cm^3) was added with swirling to give a clear deep-green solution, to which hot water (80 cm^3) was added in limited amounts, separating out the yellow leaflects (probably the hydrochloride of ipdq). The mixture was allowed to stand at *ca.* 5 °C overnight. The crystals were collected, washed with 1 M aq HCl, air-dried at room-temperature, and dissolved in hot EtOH (40 cm^3). To this solution a half portion of a hot solution of $NaOAc \cdot 3H_2O$ (2 g) in water (40 cm^3) was added to produce turbidity which was followed by crystallization. With continuous warming, the remaining portion of the acetate solution was added portionwise with swirling, followed by the addition of water (20 cm^3). After cooling, the crystals were collected, washed with water, air-dried, and recrystallized from hexane (40 cm^3) to give 1.4 g (and 0.1 g from the mother liquor, total 88%) of ipdq as colorless plates; mp 101.5—102.7 °C. Recrystallization from MeOH by adding water (40- and 100 cm^3 per 1.4 g) gave an analytical and spectral sample as colorless leaflects; mp 102.0—102.7 °C. IR(KBr): 3460, 3425, 3040, 2975, 2925, 1599, 1568, 1498, 1470, 1454, 1433, 1317, 1252, 1230, 1193, 1098, 1077, 838, 756, 719, 607, and 560 cm^{-1}. PMR and UV: see in the text. Found: C, 76.22; H, 5.33%. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.35; H, 5.49%.

(2,2′-Isopropylidenedi-8-quinolinolato)copper(II), Cu(ipdq): To a hot solution of ipdq (1.0 g) dissolved in EtOH (40 cm^3), a warmed solution of $Cu(OAc)_2 \cdot H_2O$ (0.6 g) in water (40 cm^3) was added to give a clear deep-green solution. Very soon green crystals separated out. After heating at *ca.* 60 °C for 30 min, the mixture was allowed to stand at *ca.* 5 °C overnight. The crystals were collected, washed with water, and dried at 110 °C to give 1.2 g (quantitative) of Cu(ipdq). Repeated recrystallizations from MeOH (100 cm^3 per 0.75 g) gave an analytical and spectral sample as deep-green needles. TGA-DTA (5 °C/min, in air): a sharp exothermic peak at 346 °C, accompanied by a weight loss. IR(KBr): 3040, 2980, 1601, 1552, 1494, 1432, 1383, 1343, 1333, 1309, 1272, 1107 (C–O),31) 826, 746, 605, 535, and 521 cm^{-1}. UV: see in the text. Found: C, 63.91; H, 4.18; Cu, 16.23%. Calcd for $C_{21}H_{16}N_2O_2Cu$: C, 64.36; H, 4.12; Cu, 16.21%.

Ni(ipdq) from ipdq: To a hot solution of ipdq (1.0 g) dissolved in MeOH (30 cm^3), a hot solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.75 g) in water (30 cm^3) was added to make the solution turbid. Soon the crystals separated out. After heating at *ca.* 60 °C for 1 h, the mixture was worked up in a manner similar to that of Cu(ipdq). The sample obtained had an identical IR spectrum with that prepared from **5**.

Measurements. All the melting points were uncorrected. The IR and PMR spectra were recorded with a JASCO IRA-2 and a Hitachi R-20 spectrometer respectively. The TGA-DTA measurements were carried out with a Rigaku-denki TG-DSC apparatus. The electronic spectra were measured with a Simadzu MPS-50L spectrometer at room-temperature, using a 0.1 cm cell for the ultraviolet region, a 1.0 cm cell for the near-ultraviolet and visible region, except PdQ_2 in MeOH (a 2.0 cm cell), and a 1.0 or 5.0 cm cell for the d-d region, unless otherwise stated. The solvents used were dried and distilled except DMF, THF, 1,2-dichloroethane, and cyclohexane which were of spectroscopic grade and used without further purification.

Analyses: A Shimadzu UM-3B apparatus was used for the elemental analyses. The metal contents in the complexes were determined gravimetrically, after the complete decomposition with H_2SO_4–HNO_3.

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