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Structural Characterization of Several Metal(II) 2-Methyl-8-quinolinolato Complexes in Several Organic Solvents

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Bivalent metal complexes of cobalt(II), nickel(II), copper(II), and zinc(II) with 2-methyl-8-quinolinol (2MeHql) were prepared. Their properties, such as those shown by thermogravimetry (TG) and differential thermal analysis (DTA), X-ray diffraction, magnetic susceptibility, and the optical spectra, were measured and compared with those of 8-quinolinolato complexes. All the metal complexes prepared here are monohydrates, whereas their 8-quinolinolato complexes are dihydrates. The methyl group at the 2-position of the quinoline ring caused a shift of about 40—80 °C in the dehydration temperature, and, as a result of the dehydration, a dimer anhydrate was produced. The dimer-formation conditions were established in chloroform and dioxane solutions. However, the addition of such basic solvents as pyridine, water, and methanol cleaved the bridge linkages in complexes and produced a distorted octahedral configuration by solvent-binding in the axial position. The existence of a copper complex with a dimer structure such as has been shown in other metal complexes was not verified in any of the solvents used here.

8-Quinolinol (Hql) has been widely used as a useful analytical reagent to evoke insoluble stoichiometric precipitation with many bivalent metals.[1–5] Many studies have been done on the absorption spectra and the infrared (IR) analysis of their metal complexes.[6–10] However, from the standpoint of explaining the reaction mechanism involved in solvent extraction, the investigation of the solution state of their metal complexes in organic solvents has come to be especially important. However, there have been few reports on them.[11–13] In this work, 2-methyl-8-quinolinolato complexes of bivalent metals (Co, Ni, Cu, and Zn) have been prepared and studied in relation to their physical and chemical properties, their characterization in several organic solvents, and the mechanism of adduct formation. Furthermore, they have been compared with the metal 8-quinolinolato complexes.

Experimental

Reagents. The organic solvents, *e.g.*, chloroform, dioxane, and methanol, were of a reagent grade and were used after further purification, according to the handling methods of Sekido and Kunikida[13] or of Fieser.[14] The other reagents were of an analytical grade.

Preparation of Complexes. Preparation of several metal 2-methyl-8-quinolinolates: $M(2Meql)_2 \cdot H_2O$ (M=Co, Ni, Cu, and Zn). A definite quantity of each metal salt was placed in an acetic acid–acetate buffer solution at pH 5.0 (cobalt(II) and nickel(II)) or 6.2 (copper(II) and zinc(II)), and then the solution was added to an ethanolic 2-methyl-8-quinolinol solution to cause stoichiometric precipitation; the precipitate was filtered, washed several times with hot water to remove the excess 2-methyl-8-quinolinol, and dried in air. Their metal-complex anhydrates were prepared after heating their hydrates at a constant temperature (cobalt(II): 250 °C, nickel(II): 300 °C, copper(II): 150 °C, and zinc(II): 200 °C) for 3 h.

Apparatus and Procedures. A Rigaku Denki Differential Thermobalance TG-DSC was used for the measurement of the TG and DTA. A portion of about ten grams of each complex was heated in a small platinum dish in air and at the heating rate at 10 °C min^{-1}.

X-Ray analysis was carried out with a Rigaku Denki Geigerflex D-1 X-ray Diffractometer, using nickel-filtered Cu *Kα* radiation, except for the cobalt(II) complexes, for which iron-filtered Co *Kα* radiation was used.

The magnetic susceptibilities were measured by means of the Gouy method at room temperature.

The visible and ultraviolet spectra were measured with a Hitachi-124 Spectrophotometer, using the pure solvent as a blank, for cell path-lengths of 1, 10, 50, and 100-mm. A definite amount of a metal-complex anhydrate was dissolved in the appropriate solvent to give the desired concentration. The visible and ultraviolet spectra of the solution were measured within three hours after it had been prepared with the above method. Measurements with other solvents, *e.g.*, dioxane, pyridine, methanol, and their mixed solvents, were carried out with the same procedure.

Results and Discussion

Physical Properties of Several Metal 2-Methyl-8-quinolinolato Complexes. *TG and DTA*: Typical representative TG and DTA curves of the prepared complexes ($Co(2Meql)_2 \cdot H_2O$ and $Ni(2Meql)_2 \cdot H_2O$) are shown in Fig. 1. It can be seen that one molecule of hydration water is lost in the first step in the range of 170—210 °C for the cobalt(II) complex and in that of

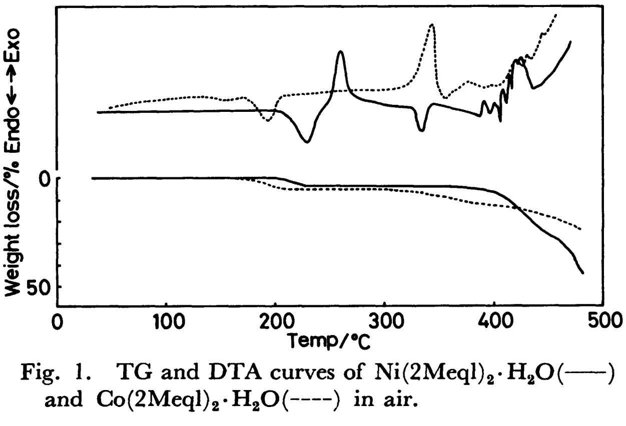


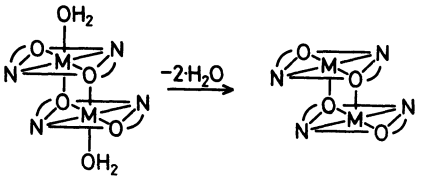
Fig. 1. TG and DTA curves of $Ni(2Meql)_2 \cdot H_2O$(——) and $Co(2Meql)_2 \cdot H_2O$(----) in air.

200—230 °C for the nickel(II) complex. The same patterns were also obtained for other metal (copper(II) and zink(II)) complexes. The composition and range of the dehydration temperatures of the hydrated complexes are shown in Table 1. As a reference, those of 8-quinolinolate hydrates are shown, too. From a comparison with hydrated 8-quinolinolato complexes, it can be seen, first, that hydrated 2-methyl-8-quinolinolato complexes have one molecule of hydration water and that the dehydration temperatures were 40—80 °C higher than those of the 8-quinolinolato complex dihydrates. This shows that the steric hindrance of the 2-methyl group prevents the complex formation;[15] consequently, the bond strength and length of M–N and M–O are rather weakened and lengthened in comparison with those of the 8-quinolinolato complex dihydrates, resulting in an increase in the bond strength from the axial directions; in other words, coordination becomes easier. The above discoveries enhanced the possibility of the formation of dimerization or polymer complexes and an adduct with a basic substance.

Second, the complexes which have one hydrated water molecule, $M(2Meql)_2\cdot H_2O$, probably prefer a dimer geometry coordinated with two molecules of hydrated water above and below the two molecules of metal as is shown in Scheme 1, to a five-coordinated geometry (square pyramidal). However, since the dehydration temperature was much higher (about 200—230 °C) than those of other metal complexes, since the exothermic peak appeared upon dehydration, and since no loss in gravimetric quantity involving the exothermic reaction was observed, the geometry of the nickel(II) complex may be different from the structure described above (Scheme 1). The X-ray diffraction pattern of the amorphous sample and exchange by means of dehydration with heating, were not observed; still, it seems that dimer anhydrates were formed as a result of the dehydration of water coordinated above and below the metals.

TABLE 1. THERMAL ANALYTICAL DATA

Molecular formula	Range of dehydration (°C)
$Cu(2Meql)_2\cdot H_2O$	100—120
$Zn(2Meql)_2\cdot H_2O$	130—160
$Co(2Meql)_2\cdot H_2O$	170—210
$Ni(2Meql)_2\cdot H_2O$	200—230
$Cuql_2\cdot 2H_2O$	50— 80
$Znql_2\cdot 2H_2O$	80—120
$Coql_2\cdot 2H_2O$	110—145
$Niql_2\cdot 2H_2O$	110—145



Scheme 1.

Susceptibility of Complexes: Table 2 shows the results of elemental analysis, the magnetic moments of metal 2Meql complex monohydrates, and their anhydrates compared with those of the 8-quinolinolato complexes. All the metal complexes have a high-spin magnetic moment;[16] these results suggest the possibility of dimer geometry.

X-Ray-diffraction-pattern Analysis: Figures 2 and 3 shows the X-ray diffraction patterns of metal 2Meql complex monohydrates and anhydrates. All the patterns of the cobalt(II), copper(II), and zinc(II) complex monohydrates, except for the nickel(II) complex, are similar, with some peaks of the same diffraction angles; the nickel(II) complex displayed different, rather complicated patterns. Metal-complex anhydrates of cobalt(II), copper(II), and zinc(II), except for nickel(II), also show very similar patterns; three peaks appeared at about $2\theta=10°$, and three or five peaks, at about $2\theta=30—40°$.

The Characterization of Several Metal 2Meql Complexes in Aqueous and Organic Solvents. Optical Spectra of 2MeHql in Aqueous Solutions: Figure 4 shows the optical spectra of 2MeHql in aqueous solutions. From the increase in the basicity of the oxygen and nitrogen atoms upon the substitution of the 2-position with the methyl group, the peaks showed a blue shift.[17] The substitution of the methyl group for hydrogen at the 2-position brought about an increase in the basicity of oxygen and nitrogen, resulting in a blue shift.

TABLE 2. ANALYTICAL DATA AND MAGNETIC SUSCEPTIBILITIES OF SEVERAL METAL 2-METHYL-8-QUINOLINOLATO COMPLEXES

Compound	Found (%)			Calcd (%)			μ_{eff} (BM)		Compound	μ_{eff} (BM)
	C	H	N	C	H	N	Found	Calcd		Found
$Co(2Meql)_2\cdot H_2O$	60.12	4.96	7.05	61.08	4.61	7.12	4.06	3.87	$Coql_2\cdot 2H_2O$	4.88
$Co(2Meql)_2$	63.20	4.59	7.39	64.01	4.30	7.46	4.72	3.87	$Coql_2$	4.64
$Ni(2Meql)_2\cdot H_2O$	60.61	4.85	7.35	61.12	4.62	7.13	3.19	2.83	$Niql_2\cdot 2H_2O$	3.18
$Ni(2Meql)_2$	62.84	4.69	7.56	64.05	4.30	7.47	3.19	2.83	$Niql_2$	3.25
$Cu(2Meql)_2\cdot H_2O$	60.78	5.25	7.00	60.37	4.56	7.04	2.00	1.73	$Cuql_2\cdot 2H_2O$	1.93
$Cu(2Meql)_2$	62.67	4.34	7.60	63.23	4.25	7.37	1.74	1.73	$Cuql_2$	1.84
$Zn(2Meql)_2\cdot H_2O$	60.00	4.93	6.99	60.10	4.54	7.01			$Znql_2\cdot 2H_2O$	
$Zn(2Meql)_2$	62.50	4.44	7.39	62.93	4.23	7.34			$Znql_2$	

μ: Bohr magneton at room temperature.

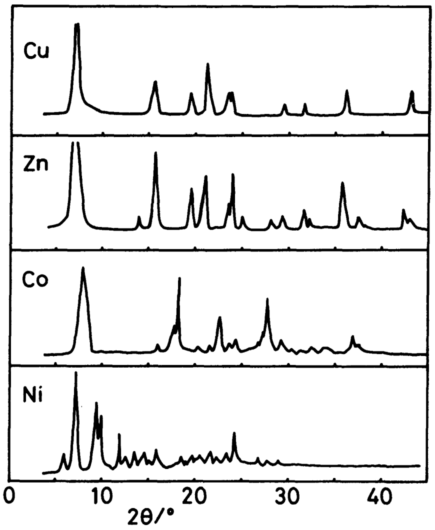


Fig. 2. X-Ray diffraction patterns of M(2Meql)$_2$·H$_2$O.

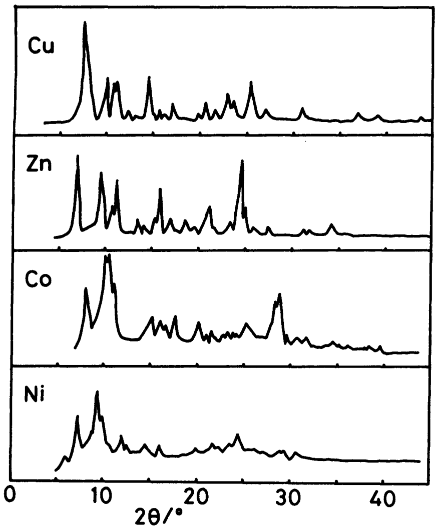


Fig. 3. X-Ray diffraction patterns of M(2Mqel)$_2$.

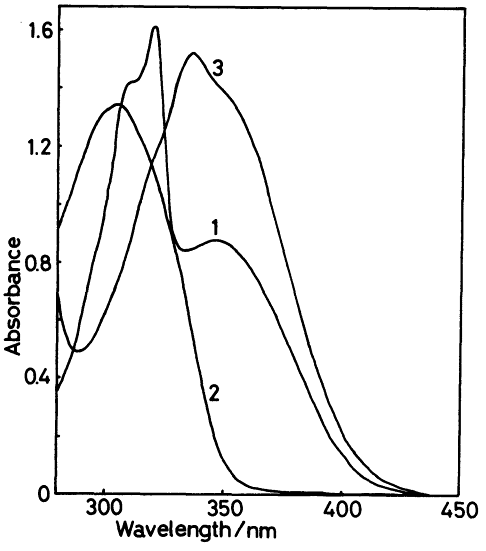


Fig. 4. Optical spectra of 2-methyl-8-quinolinol (2MeHql). 1: in 1M-HCl, 2: in CH$_3$OH, 3: in 1M-NaOH. [2MeHql]$=5.0\times10^{-4}$M.

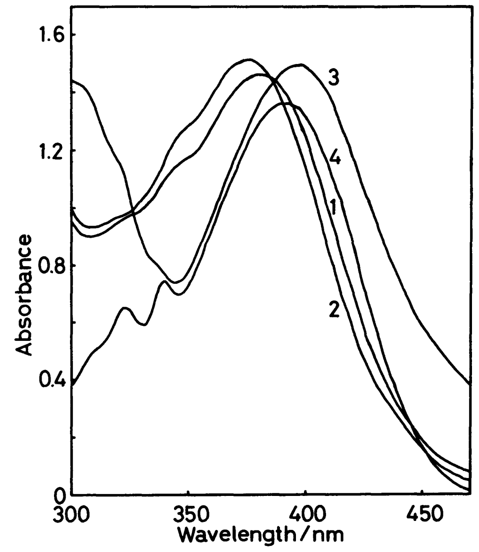


Fig. 5. Optical spectra of some metal(II) 2-methyl-8-quinolinolato complexes in chloroform. 1: Co(2.66×10^{-4} M), 2: Ni(3.04×10^{-4} M), 3: Cu(3.00×10^{-4} M), 4: Zn(3.04×10^{-4} M).

Optical Spectra of the Complexes in a Pure Organic-solvent Medium: It is important, from the standpoint of explaining the reaction mechanism involved in solvent extraction, to know whether or not the dimeric geometry of the cobalt(II), nickel(II), copper(II), and zinc(II) 2Meql complexes in organic solvents is kept. Figure 5 shows the optical spectra of the complexes in chloroform. In a previous paper,[13] Sekido and Kunikida have reported that a trace amount of water affects the optical spectra of nickel 8-quinolinolate anhydrate. We have been measured the optical spectra of metal complexes in chloroform treated with various desiccants; we have found that the red shifts of the optical maximum increase in this order: Ni(376 nm)<Co(381 nm)<Zn(391 nm)<Cu(397 nm), and that a variety of desiccants does not affect the optical spectra; that is, the dimer geometry of an anhydrate is maintained in a chloroform solution. Further, the behavior of the optical spectra in a dioxane solution is the same as in chloroform.

Optical Spectra of the Complexes in Mixed Solvents: From the viewpoint of adduct formation and configuration variation, the optical spectra of mixed solvents-in dioxane–pyridine, dioxane–methanol, and dioxane–water systems, were examined using the same preparing procedure in a chloroform solvent.[18] For example, the optical spectra of copper complexes are shown in Figs. 6, 7, and 8. In Fig. 6, with an increase in the amount of pyridine, the optical maximum at about 400 nm shifted toward 385 nm, involving only one isosbestic point at 394 nm. In Fig. 7, with an increase in the amount of methanol, the absorption maximum at about 400 nm shifted toward 385 nm, while the optical density decreased, and then the optical maximum at 339 nm turned into a shoulder. Isosbestic points were observed at 386 and 330 nm, so at least two species of metal complexes were present. In Fig. 8, a similar behavior of the optical spectra was observed in dioxane–water; however, the optical maximum at 339 nm completely disappeared. In this system, the precipitation of hydrate was observed at a water concentration of about 33.3 M (1M=1 mol dm^{-3}). From the results of the optical spectra of other mixed-solvent systems, it seems that the optical spectra of complex anhydrates depend upon their nature, the molar ratio, the concentration of the solvents, and the analytical concentration of the complexes. The results of the optical spectra of complex anhydrates in various organic solvents are shown in Table 3. The optical spectra in the dioxane solution of copper-

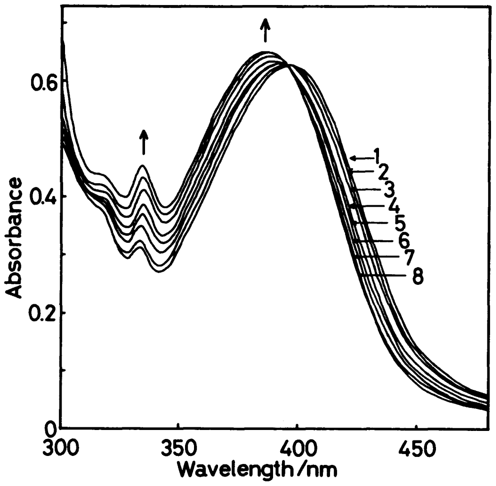


Fig. 6. Optical spectra of Cu(2Meql)$_2$ in dioxane containing various amounts of pyridine. 1: [py]= 0 M, 2: 6.19×10^{-2} M, 3: 1.86×10^{-1} M, 4: 3.72×10^{-1} M, 5: 6.19×10^{-1} M, 6: 1.24 M, 7: 2.48 M, 8: 4.96 M. [Cu(2Meql)$_2$]=1.15×10^{-4} M. Trends of spectral change with increase in base concentration are shown by arrows.

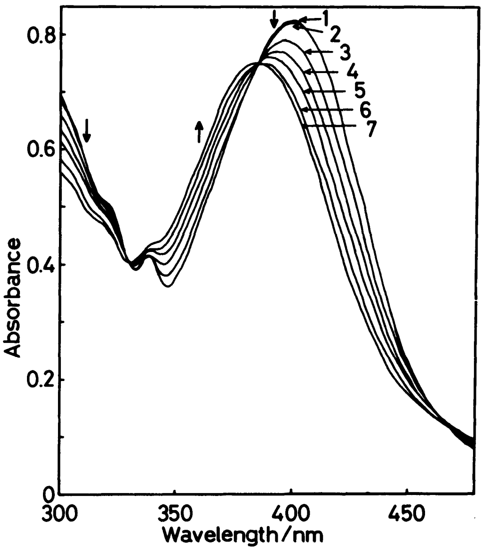


Fig. 7. Optical spectra of Cu(2Meql)$_2$ in dioxane containing various amounts of methanol. 1: [MeOH]= 0M, 2: 0.49M, 3: 2.47M, 4: 4.94M, 5: 7.41M, 6: 9.88M, 7: 12.35 M. [Cu(2Meql)$_2$]=1.47×10^{-4} M. Trends of spectral change with increase in base concentration are shown by arrows.

Table 3. Optical spectra data for several metal 2-methyl-8-quinolinolato complexes in various organic solvents

Solvent	Added reagent and its concn range (M)	λ at Absorption maxima (nm)			
		No reagent (Added reagent)		[Isosbestic points]	
		Co(2Meql)$_2$	Ni(2Meql)$_2$	Cu(2Meql)$_2$	Zn(2Meql)$_2$
Dioxane		392	388	400	388
		342	343	339	340
	Pyridine	387 (389)	390 (399)	396 (385)	385 (381)
	(0—7.4 M)	336 (338)	343 (345)	334	334 (336)
		[366, 423]	[387, 425]	[394]	[412]
	Methanol	389 (400)	390 (380)	400 (385)	390 (387)
	(0—12.4 M)	0—0.7 M			0—1.2 M
		400 (380)			387 (372)
		0.7—12.4 M			1.2—12.4 M
		342 (sh)	343 (341)	339 (sh)	
		[403, 348]	[394, 373, 339, 333, 320]	[386, 330]	[384, 330]
	Water	390 (405)	392 (384)	400 (378)	390 (381)
	(0—27.8 M)	0—0.5 M			0—4.7 M
		405 (391)			381 (370)
		0.5—2.5 M			4.7—16.7 M
		342	344 (341)	338 (sh)	339 (sh)
					324 (sh)
			[386, 353]	[328]	

(sh: shoulder).

(II) complex anhydrates were changed upon the addition of basic solvents, which resulted in a shifting of the isosbestic point. In other words, the configuration of the complex anhydrates in a dioxane solution turned into something else. However, in the case of other metal-complex anhydrates, upon the addition of basic solvents a new isosbestic point appears, so two equilibrium states at least are present. Depending on the amount of basic solvents added, the configuration of the complex anhydrate [1] in a dioxane solvent turns into a different structure [3a, 3b, or 3c] through a middle species [2a, 2b, or 2c] as is shown in Fig. 9. The amount of Lewis base added depended upon the strength of the basicity; it was preferred to the order of pyridine<water<methanol. For example, in nickel-complex anhydrate, the amounts of the basic solvents needed to change from one configuration to another were 2.5×10^{-3} M for pyridine, 1.1 M for water, and 4.9 M for methanol.

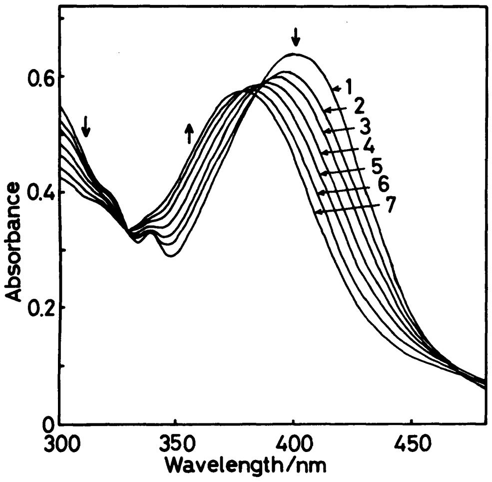


Fig. 8. Optical spectra of $Cu(2Meql)_2$ in dioxane containing various amounts of water. 1: $[H_2O]=0$ M, 2: 2.78 M, 3: 5.56 M, 4: 11.11 M, 5: 16.67 M, 6: 22.22M, 7: 27.78 M. $[Cu(2Meql)_2]=1.13\times10^{-4}$ M. Trends of spectral change with increase in base concentration are shown by arrows.

Effect of the Concentration of a Complex on Its Optical Spectra: The optical spectra of the nickel(II) 8-quinolinolato complex at various concentrations in dried chloroform were examined in a previous paper.[13] The monomer complex exists below 1×10^{-5} M, but the binuclear or trinuclear complex exists at concentrations above 1×10^{-5} M, and for the binuclear complex, the formation constant was calculated at K=2000:

$$2\cdot\mathrm{Niql_2} \overset{K}{\rightleftharpoons} (\mathrm{Niql_2})_2.$$

In the case of the metal 2Meql complexes, not enough change in the optical spectra upon the addition of basic solvents was obtained, so the equilibrium constant could not be calculated accurately. However, the dimeric complex of cobalt(II), nickel(II), or zinc(II) probably exists at concentrations above 2×10^{-5} M. The solvents added at lower concentrations coordinated at the axial positions of the dimer complex, and at higher concentrations the bridge linkages by 2Meql were broken by added solvents (refer to Fig. 9) and the axial positions were coordinated, resulting in a distorted octahedral geometry, as is shown in Fig. 9. The stability of dimer geometry increased in the order of: cobalt(II)≃nickel(II)>zinc(II); the dimer⇌monomer order

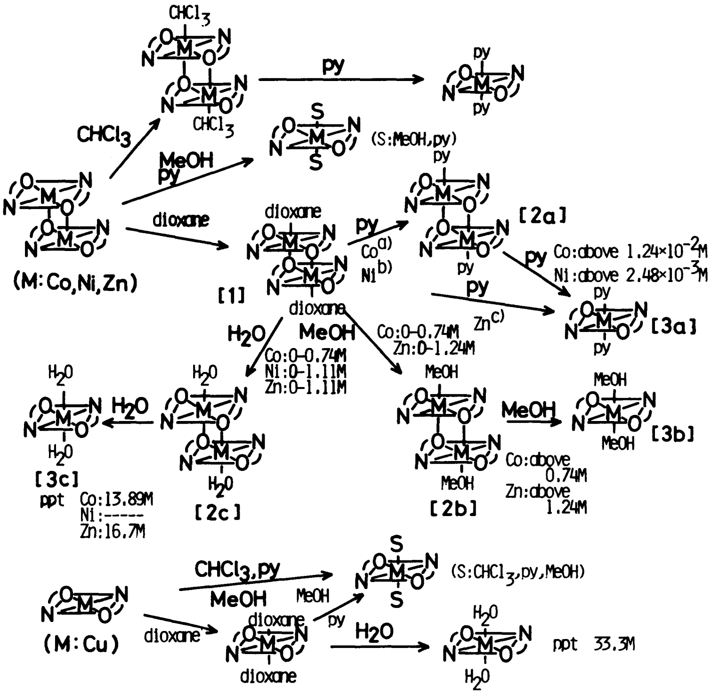


Fig. 9. Proposed structures of several metal(II) 2-methyl-8-quinolinolato complexes in various organic solvents. a) Co: 0—1.24×10^{-2} M, b) Ni: 0—2.48×10^{-3} M, c) Zn: above 0.743×10^{-3} M.

was affected by the nature of the basicity, and the dimer formed rapidly at low concentrations when a strong base such as in the pyridine solvent, was added. On the other hand, in the case of the copper(II) complex, from the optical spectra of all the organic solvents used here and the variation in the concentration of the copper(II) complex, it seems that the dimer structure did not exist; that is, an adduct complex with a planar geometry has formed.

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