The Syntheses and Spectroscopic Investigation of Copper(II), Nickel(II), and Cobalt(II) Complexes of 8-Quinolinecarboxamide

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The syntheses of the bivalent metal complexes of 8-quinolinecarboxamide (abbreviated as 8-QCA) were attempted; the complexes obtained have the compositions of $M(8\text{-QCA})_2X_2$ (M=Cu(II), Ni(II), and Co(II) ions; X=Cl^-, Br^-, I^-, and NO_3^-) and $Cu(8\text{-QCA})Cl_2$. The diffuse reflectance, the infrared and far-infrared spectra, and the magnetic moments of these metal complexes were measured. The coordination sites of 8-QCA have been suggested for the amide oxygen and the quinoline nitrogen from the diffuse reflectance spectra and the infrared spectra. The values of 3.13—3.21 B.M. and 4.81—5.03 B.M. were observed for $Ni(8\text{-QCA})_2X_2$ and $Co(8\text{-QCA})_2X_2$ respectively. From these magnetic moments, an octahedral structure has been proposed for the nickel and the cobalt complexes, whose far-infrared spectra (600—200 cm^{-1}) also supported this structure, with a *trans*-planar coordination of the 8-QCA molecules around the metal ions. Since the $Cu(8\text{-QCA})_2X_2$ complexes are of the mononuclear form, judging from the magnetic moments of 1.87—1.93 B.M., and since the far-infrared spectra suggested a structure belonging to the C_{2h} point group, a distorted octahedral configuration is conceivable.

Some quinoline derivatives, such as 8-hydroxyquinoline and 8-mercaptoquinoline, which are able to form a chelate ring with metal ions are well known to show a strengthened antibacterial action upon the addition of some kinds of metal ions. The present authors have long been interested in the metal chelates of the quinoline derivatives because of their biological significance, in this investigation the syntheses of the bivalent metal complexes of 8-quinolinecarboxamide (abbreviated as 8-QCA in this paper) were attempted.

It has previously been reported that, when a carboxamide group participates in metal-complex formation, it can coordinate on metal ions with or without the proton released from the carboxamide group. The former is called a cationic complex, and the latter, a neutral complex; both of them have been found in the metal complexes of 2-pyridinecarboxamide.[1] However, 8-QCA does not form neutral complexes in an aqueous solution because of the formation of metal hydroxides; only the cationic complexes were obtained. The complexes have the compositions of $Cu(8\text{-QCA})Cl_2$ and $M(8\text{-QCA})_2X_2$ (M=Cu(II), Ni(II), and Co(II) ions; X=Cl^-, Br^-, I^-, and NO_3^-). The coordination sites and the structures of the cationic chelates of 2-pyridinecarboxamide and its related derivatives with the bivalent metal ions have been studied by Sekizaki and Yamasaki;[2–7] it has also been concluded that the chelate-ring formation took place through the amide oxygen and the pyridine nitrogen, as confirmed by X-ray analyses.[8–10]

The magnetic moments, the diffuse reflectance spectra, and the infrared and far-infrared spectra of the bivalent metal complexes of 8-QCA were measured as part of the analyses. The data will be compared with those of the metal complexes of 2-pyridinecarboxamide, and the coordination sites and the structures of the metal complexes of 8-QCA will be discussed.

Experimental

Materials. The metal halides and metal nitrates were analytical-grade products of Wako Pure Chemical Industries, Ltd.

Synthesis of 8-Quinolinecarboxamide. To an excess of thionyl chloride (25 g) we added 5 g of 8-quinolinecarboxylic acid, which has been synthesized according to the method reported by Campbell *et al.*;[11] the resultant solution was refluxed for 4 hr at 80 °C on a water bath. When the excess of thionyl chloride was distilled away under reduced pressure, crude 8-quinolinecarbonyl chloride was obtained as a reddish brown residue, which was subsequently dissolved in 50 ml of methanol. The methanol solution was added gradually to a large excess of an ice-cold methanol solution of ammonia, from which crude 8-quinolinecarboxamide was then deposited as yellow crystals. It was recrystallized twice from water. Yield, 60%.

Found: C, 69.69; H, 4.78; N, 16.30%. Calcd for $C_{10}H_8N_2O$: C, 69.76; H, 4.68; N, 16.26%.

Preparations of Metal Complexes. *1) Dichloro(8-quinolinecarboxamide)copper(II), Bis(8-quinolinecarboxamide)copper(II) Bromide, Bis(8-quinolinecarboxamide)copper(II) Nitrate, and Bis(8-quinolinecarboxamide)cobalt(II) Bromide*: To 15 ml of an ethanol solution containing 1 mmol of the corresponding metal salt, we added 344 mg (2 mmol) of the ligand dissolved in 20 ml of ethanol; the mixture was then kept standing at room temperature. The objective complexes were obtained as a crystalline powder. They were collected by filtration and washed with hot ethanol.

2) Bis(8-quinolinecarboxamide)nickel(II) Chloride, Bis(8-quinolinecarboxamide)nickel(II) Bromide, and Bis(8-quinolinecarboxamide)cobalt(II) Iodide: These complexes were obtained by treating ethanol solutions containing 1 mmol of the corresponding metal salt with 2 mmol of the ligand in 20 ml of ethanol. The resultant solution was evaporated to 2/3 volume on a water bath. After it had been kept standing overnight at room temperature, a crystalline powder was deposited.

3) Bis(8-quinolinecarboxamide)nickel(II) Iodide, Bis(8-quinolinecarboxamide)nickel(II) Nitrate, and Bis(8-quinolinecarboxamide) cobalt(II) Iodide: After mixing 1 mmol of the corresponding metal salt in 20 ml of an ethanol solution containing 2 mmol of the ligand, the solution was warmed on a water bath; a crystalline powder was then deposited out.

The results of elemental analyses of the obtained metal

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Table 1. Results of elemental analyses of bivalent metal complexes of 8-quinolinecarboxamide

Complexes	Found (%) C	Found (%) H	Found (%) N	Found (%) M	Calcd (%) C	Calcd (%) H	Calcd (%) N	Calcd (%) M	Yield (%)
$Cu(C_{10}H_8N_2O)Cl_2$	39.03	2.54	9.13	20.3	39.17	2.63	9.14	20.7	25
$Cu(C_{10}H_8N_2O)_2Br_2$	42.15	2.69	9.91	10.9	42.31	2.74	9.87	11.2	78
$Cu(C_{10}H_8N_2O)_2(NO_3)_2$	45.45	3.08	15.46	11.5	45.16	3.03	15.80	11.9	67
$Ni(C_{10}H_8N_2O)_2Cl_2\cdot 1/2H_2O$	48.70	3.68	11.22	12.3	48.94	3.70	11.42	12.2	32
$Ni(C_{10}H_8N_2O)_2Br_2$	42.61	2.87	9.95	10.0	42.67	2.87	9.96	10.4	50
$Ni(C_{10}H_8N_2O)_2I_2$	36.63	2.41	8.58	8.9	36.57	2.46	8.53	8.9	36
$Ni(C_{10}H_8N_2O)_2(NO_3)_2$	45.49	2.86	16.08	11.5	45.57	3.06	15.94	11.1	42
$Co(C_{10}H_8N_2O)_2Br_2\cdot 1/2H_2O$	41.67	2.94	9.60	10.4	41.98	2.99	9.79	10.3	70
$Co(C_{10}H_8N_2O)_2I_2$	36.64	2.33	8.52	9.3	36.56	2.45	8.53	9.0	43
$Co(C_{10}H_8N_2O)_2(NO_3)_2$	45.38	3.02	16.00	11.3	45.65	3.07	15.97	11.2	56

complexes are shown in Table 1.

Magnetic and Spectroscopic Measurements. The magnetic moments were measured with a Shimadzu MB-2-type magnetic balance. The diffuse reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer equipped with an integrating-sphere accessory by means of the method described in a previous paper.[12] A JASCO IRA-2 spectrophotometer and a JASCO DS-701 spectrophotometer were used to record the infrared spectra in the region of 400—4000 cm^{-1} and in the region of 200—600 cm^{-1} respectively by the Nujol and HCB mull methods.

Results and Discussion

Magnetic Moments. The magnetic moments observed for the bivalent metal complexes of 8-QCA are shown in Table 2.

The copper complexes give normal magnetic moments in the region of 1.87—1.93 B.M., indicating no spin interaction among the adjacent copper ions. All the nickel complexes, $Ni(8\text{-}QCA)_2X_2$, give magnetic moments of 3.13—3.21 B.M., which fall within the region of 2.9—3.4 B.M. reported for octahedral complexes.[13] The magnetic moments observed for $Co(8\text{-}QCA)_2X_2$ are 4.81—5.03 B.M., corresponding to the reported values of 4.7—5.2 B.M. for octahedral cobalt complexes.[14]

Diffuse Reflectance Spectra. As is shown in Fig. 1, the absorption maxima (λ_{max}) in the diffuse reflectance spectra of $Cu(8\text{-}QCA)_2Br_2$ and $Cu(8\text{-}QCA)_2(NO_3)_2$ are observed at 700 and 675 nm.

Table 2. Magnetic moments of $M(8\text{-}QCA)_2X_2$ and $Cu(8\text{-}QCA)Cl_2$ (18—21 °C)

Complexes	Moments observed	Moments calcd for spin-only formula
$Cu(8\text{-}QCA)Cl_2$	1.90 B. M.	1.73 B. M.
$Cu(8\text{-}QCA)_2Br_2$	1.93	1.73
$Cu(8\text{-}QCA)_2(NO_3)_2$	1.87	1.73
$Ni(8\text{-}QCA)_2Cl_2$	3.13	2.82
$Ni(8\text{-}QCA)_2Br_2$	3.21	2.82
$Ni(8\text{-}QCA)_2I_2$	3.19	2.82
$Ni(8\text{-}QCA)_2(NO_3)_2$	3.19	2.82
$Co(8\text{-}QCA)_2Br_2$	4.98	3.88
$Co(8\text{-}QCA)_2I_2$	5.03	3.88
$Co(8\text{-}QCA)_2(NO_3)_2$	4.81	3.88

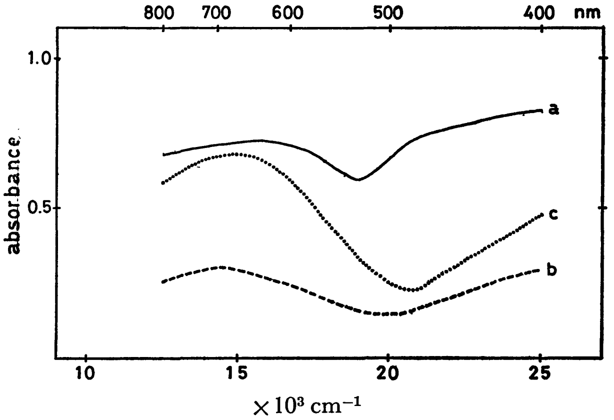

Fig. 1. Diffuse reflectance spectra of metal complexes.
a: $Cu(8\text{-}QCA)Cl_2$ b: $Cu(8\text{-}QCA)_2Br_2$,
c: $Cu(8\text{-}QCA)_2(NO_3)_2$

The λ_{max} values of these copper complexes are rather close to those of the metal chelates of 2-acetylpyridine[15] and 2-pyridinecarboxamide,[2] the N,O-coordination of the ligand having been determined. Therefore, the coordination sites of 8-QCA with a copper ion are considered to be the amide oxygen and the quinoline nitrogen.

The 1 : 1 complex, $Cu(8\text{-}QCA)Cl_2$, gives its absorption maximum at 650 nm, much like those of the 2 : 1 copper complexes; however, a new and characteristic shoulder is observed around 450—480 nm, as is shown in Fig. 1. The appearance of the shoulder may be due to the structural differences between the 1 : 1 complex and the 2 : 1 complexes. However, the λ_{max} value of the neutral copper chelate of 2-pyridinecarboxamide, $Cu(pia)_2$, the N,N-coordination of the ligand of which has been determined, was found at 530 nm in a chloroform solution.[1] The large difference in the λ_{max} values between $Cu(pia)_2$ and $Cu(8\text{-}QCA)Cl_2$ may indicate that the binding sites of 8-QCA are the amide oxygen and the quinoline nitrogen in the latter complex.

The nickel complexes, $Ni(8\text{-}QCA)_2X_2$, have the similar λ_{max} value of 680 nm, as is shown in Fig. 2.

Table 3. Main absorption peaks in infrared spectra

Complexes	ν_{NH_2}	$\nu_{asym(OCN)}$	δ_{NH_2}	$\nu_{sym(OCN)}$
8-QCA	3300, 3150	1665, 1648	1610	1370
$Cu(8\text{-}QCA)Cl_2$	3350, 3290, 3200	1643	1615	1380
$Cu(8\text{-}QCA)_2Br_2$	3200	1637	1615	1382
$Cu(8\text{-}QCA)_2(NO_3)_2$	3350, 3180	1656	1623	—
$Ni(8\text{-}QCA)_2Cl_2$	3300, 3130	1645	1615	1380
$Ni(8\text{-}QCA)_2Br_2$	3350, 3170	1643	1617	1380
$Ni(8\text{-}QCA)_2I_2$	3360, 3170	1642	1605	1380
$Ni(8\text{-}QCA)_2(NO_3)_2$	3350, 3180	1652	1620	—
$Co(8\text{-}QCA)_2Br_2$	3320, 3140	1637	1615	1380
$Co(8\text{-}QCA)_2I_2$	3350, 3300, 3170	1640	1603	1380
$Co(8\text{-}QCA)_2(NO_3)_2$	3350, 3180	1650	1620	—

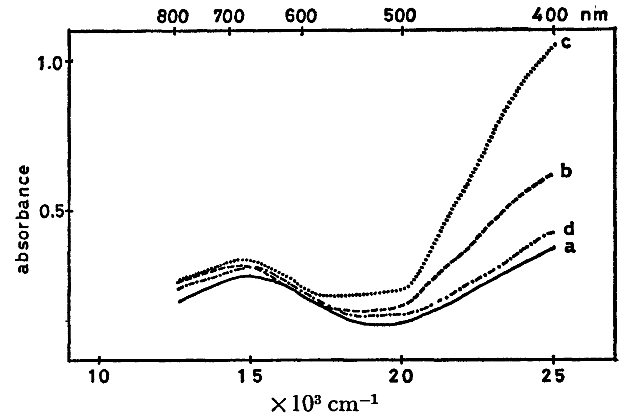

Fig. 2. Diffuse reflectance spectra of metal complexes.
a: $Ni(8\text{-}QCA)_2Cl_2$ b: $Ni(8\text{-}QCA)_2Br_2$
c: $Ni(8\text{-}QCA)_2I_2$ d: $Ni(8\text{-}QCA)_2(NO_3)_2$

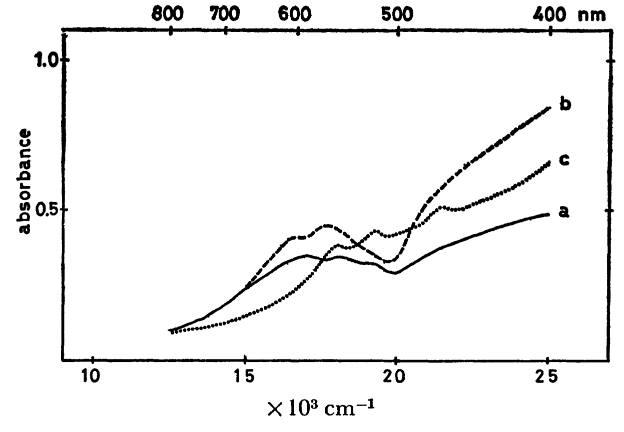

Fig. 3. Diffuse reflectance spectra of metal complexes.
a: $Co(8\text{-}QCA)_2Br_2$ b: $Co(8\text{-}QCA)_2I_2$
c: $Co(8\text{-}QCA)_2(NO_3)_2$

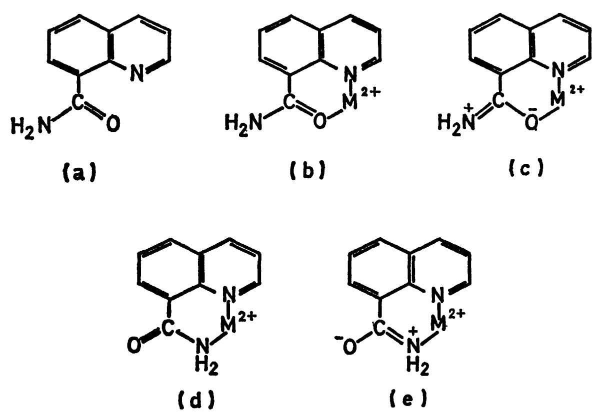

Fig. 4. Resonance forms for the ligand and the metal complexes.

Since the octahedral nickel complexes of the ligand with the N,N-coordination like ethylenediamine and bipyridyl are known to show their d-d bands in the region of 560—570 nm,[16,17] the large difference in the λ_{max} values between $Ni(8\text{-}QCA)_2X_2$ and both the $Ni(en)_2^{2+}$ and $Ni(bip)_2^{2+}$ systems may exclude the possibility of the N,N-coordination, that is, coordination through the amide nitrogen and the quinoline nitrogen. The other possibility is the coordination through the amide oxygen and the quinoline nitrogen, this possibility is supported by the resemblance of the diffuse reflectance spectra between $Ni(8\text{-}QCA)_2X_2$ and both $Ni(piaH)Cl_2$ and $Ni(2AP)_2X_2$ (piaH= 2-pyridinecarboxamide; 2AP=2-acetylpyridine).[2,15]

The $Co(8\text{-}QCA)_2X_2$ complexes give rather complicated diffuse reflectance spectra, shown in Fig. 3, with two or three absorption bands in the wavelength region of 550—600 nm which are characteristic of octahedral cobalt complexes. However, no tendency to the longer-wavelength shift has been reported for cobalt complexes with the variation in the N,N-, N,O-, and O,O-coordinations, and the bonding sites of 8-QCA can not be deduced from the diffuse reflectance spectra.

Infrared Spectra. The infrared data of the $M(8\text{-}QCA)_2X_2$ complexes are summarized in Table 3, together with those of the ligand and the 1 : 1 copper complex. The ligand gives two peaks, at 3300 and 3150 cm^{-1}, due to the stretching vibrations of the amino group. The asymmetric OCN stretching frequency of the amide group[2] is observed as two peaks at 1665 and 1648 cm^{-1}, with its symmetric stretching peak at 1370 cm^{-1}.

The deformation mode of the amino group is observed at 1610 cm^{-1} as a shoulder.

Upon complex formation, the asymmetric N–H stretching frequencies either shift toward frequencies higher by 50—60 cm^{-1} or remain at nearly the same frequency as that of the ligand. The asymmetric and symmetric OCN stretching vibrations shift toward lower and higher frequencies respectively. These

Table 4. Assignments in far-infrared spectra (in cm^{-1})

Complexes	Chelate ring def.	ν_{M-N}	ν_{M-O}	ν_{M-X}	Amide torsion	Unassigned
Cu(8-QCA)Cl_2	480	—	244	290	360	
$Cu(8\text{-}QCA)_2Br_2$	486	271	240	—	349	
$Cu(8\text{-}QCA)_2(NO_3)_2$	483	275	236	—	356	210
$Ni(8\text{-}QCA)_2Cl_2$	488	254	227	—	340	
$Ni(8\text{-}QCA)_2Br_2$	480	257	225	—	320	208
$Ni(8\text{-}QCA)_2I_2$	476	255	220	—	323	
$Ni(8\text{-}QCA)_2(NO_3)_2$	478	258	220	—	330	242
$Co(8\text{-}QCA)_2Br_2$	478	239	217	—	322	
$Co(8\text{-}QCA)_2I_2$	475	242	216	—	323	
$Co(8\text{-}QCA)_2(NO_3)_2$	475	233	223	—	317	

results show that the ligand may take the resonance form (a), while for the $M(8\text{-}QCA)_2X_2$ complexes various forms, (b)—(e) in Fig. 4, are conceivable.

Since the asymmetric and symmetric OCN stretching vibrations arise mainly from the C=O and C–N stretching respectively, the N,N-coordination predicts that the contribution of the (d) resonance form would be larger that than of the (e) form because of the Coulombic repulsion in the latter form. In the (d) form the symmetric OCN stretchings are expected to shift toward the lower frequency side, while the asymmetric OCN stretchings remain at frequencies similar to that of the ligand. The observed frequency shifts of the amide group are opposite to the predicted shift for the N,N-coordination. However, when the $M(8\text{-}QCA)_2X_2$ complexes are in a resonance between the (b) and (c) forms, the *N,O*-coordination predicts the shifts of the asymmetric and symmetric OCN stretching to be to the lower- and higher-frequency side respectively. Therefore, the N,O-coordination seems reasonable for the $M(8\text{-}QCA)_2X_2$ complexes and Cu(8-QCA)Cl_2.

The same infrared spectral behavior of the amide group has been reported for $[M(H_2O)_2\ (piaH)_2]X_2$, where the N,O-coordination has been determined by *X*-ray analyses.[9—10]

Far-infrared Spectra. The ligand shows a peak at 233 cm^{-1} due to the amide torsion, a peak at 458 cm^{-1} assignable to the in-plane deformation of C=O, and other peaks due to quinoline-ring vibrations. Upon the complex formation, new peaks are observed in the region of 470—490 cm^{-1} and are assigned to the chelate-ring deformation. In the $M(8\text{-}QCA)_2X_2$ complexes, the peaks found around 320—360 cm^{-1} are assigned to the amide torsion.

Cu(8-QCA)$_2$X$_2$ and Cu(8-QCA)Cl$_2$: For Cu(8-QCA)Cl_2, a broad band due to the Cu–Cl stretching vibration is observed at 290 cm^{-1}, while the other peaks appear at 244 cm^{-1} below 300 cm^{-1}. The other 2 : 1 complexes give two common peaks in the regions of 271—275 cm^{-1} and 236—240 cm^{-1}, the peaks being assigned to the Cu–N (quinoline) and the Cu–O (amide) stretching respectively.

Ni(8-QCA)$_2$X$_2$: Since the $Ni(8\text{-}QCA)_2X_2$ complexes are supposed to be octahedral, the two nickel-ligand stretching vibrations can be expected to appear at relatively constant frequencies. In fact, the stretching vibrations assignable to the Ni–N (quinoline) and the Ni–O (amide) are found in the regions of 254—258 cm^{-1} and 220—227 cm^{-1} respectively.

Co(8-QCA)$_2$X$_2$: The peaks assignable to the Co–N (quinoline) and Co–O(amide) stretching vibrations are found in the regions of 239—242 cm^{-1} and 216—217 cm^{-1} for the bromide and iodide. For the nitrate, the peaks at 223 and 233 cm^{-1} are assigned to the Co–O (quinoline) and Co–O (amide) stretching vibrations.

Since the 2 : 1 complexes, $M(8\text{-}QCA)_2X_2$, do not give the peaks assignable to the metal-anion stretching vibrations above 200 cm^{-1}, the coordination of the anions on the metal ions can not be deduced. These assignments are summarized in Table 4.

In the assignments of the metal-ligand stretching vibrations in the $M(8\text{-}QCA)_2X_2$ complexes, the far-infrared data of the bivalent metal complexes of quinoline and oxine are used as references. Ohkaku and Nakamoto[18] reported that the octahedral bivalent metal chelates of oxine, $[M(oxine)_2(H_2O)_2]$, have their M–O and M–N stretching vibrations at the frequencies shown in Table 5. Frank and Rogers[19] studied the far-infrared spectra of the bivalent metal complexes of quinoline, $M(Q)_2Cl_2$(Q=quinoline), and assigned the M–N stretching vibrations as is shown in Table 5. In general, it is recognized that metal complexes with larger stability constants give the metal-ligand stretching vibrations at higher frequencies so long as the structures of the objective complexes are similar to one another. Though here no study has been made of the stability constants of 8-QCA with bivalent metal ions, it can be assumed that the stability constants of 8-QCA fall in between those of oxine and quinoline as far as the same metal ions are concerned. In other words, the

Table 5. Far infrared data reported for $M(oxine)_2(H_2O)_2$ and $M(Q)_2Cl_2$ (in cm^{-1})

Complexes	ν_{M-O}	ν_{M-N}
$Cu(oxine)_2(H_2O)_2$	310.5	289
$Ni(oxine)_2(H_2O)_2$	301.2	264
$Co(oxine)_2(H_2O)_2$	295	240
$Zn(oxine)_2(H_2O)_2$	264	207
$Cu(Q)_2Cl_2$		259
$Ni(Q)_2Cl_2$		223
$Co(Q)_2Cl_2$		226
$Zn(Q)_2Cl_2$		205

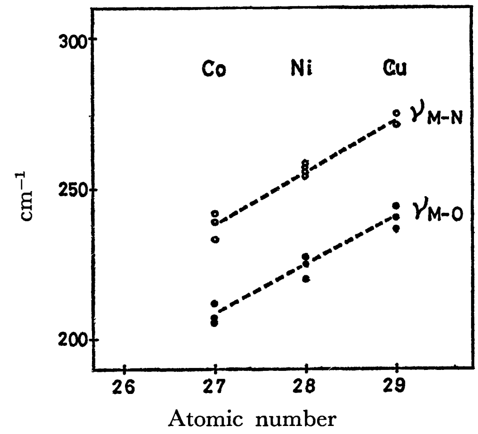

Fig. 5. A plot of M–N and M–O stretching frequencies *vs.* atomic number for $M(8\text{-QCA})_2X_2$.

copper 2 : 1 complexes should give the stretching vibration of the M–N (quinoline) in the frequency region of 259—289 cm^{-1}, and the nickel and the cobalt complexes, in the regions of 233—264 cm^{-1} and 226—240 cm^{-1} respectively. The M–O (amide) stretching frequencies are considered to be lower than the M–N (quinoline) stretching vibrations.

In order to ascertain the validity of the assignments, the stretching vibrations of the M–N (quinoline) and the M–O (amide) were plotted against the atomic number of the metal ions, as is shown in Fig. 5; linear relationships were found. The fact that the metal-ligand stretching vibrations number two throughout the metal complexes studied suggests a *trans*-planar coordination of the ligand molecules around the metal ions, since the octahedral structure with a *trans*-planar configuration of 8-QCA molecules on the metal ions belongs to the C_{2h} point group, which may be expected to produce two peaks due to the M–N (quinoline) and M–O (amide) stretching vibrations.

Conclusion

Through the analyses of the magnetic moments, the diffuse reflectance spectra, and the infrared and far-infrared spectra, the following conclusions have been deduced for the $M(8\text{-QCA})_2X_2$ complexes and $Cu(8\text{-QCA})Cl_2$:

1) The coordination sites seem to be the amide oxygen and the quinoline nitrogen.

2) For $Ni(8\text{-QCA})_2X_2$ and $Co(8\text{-QCA})_2X_2$, an octahedral structure with a *trans*-planar coordination of 8-QCA is suggested by the magnetic moments and the far-infrared spectra.

3) For $Cu(8\text{-QCA})_2X_2$, a distorted octahedral structure with a *trans*-planar coordination of 8-QCA is conceivable, judging from the magnetic moments and the far-infrared spectra. As for $Cu(8\text{-QCA})Cl_2$, no definite structure can be deduced from the present data.

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