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Several Novel Ru(II) and Ru(III) Complexes Formed by Reduction of $[RuO_4bipy]$ and $[RuO_3phen]_2O$ with Hydroquinone and Methanol

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The geometrical isomers, *cis*-dichloro-*trans*-(methanol)(hydroquinone)(2,2′-bipyridine)ruthenium(II) and *cis*-dichloro-*cis*-(methanol)(hydroquinone)(2,2′-bipyridine)ruthenium(II), $[RuCl_2(MeOH)(QH_2)bipy]$ (complex I and II), were synthesized by reduction and substitution reactions of $[RuO_4bipy]$ and $[RuO_2(OH)_2bipy]$ with hydroquinone in hydrochloric acid solution, and methanol. *cis*-Chloro(hydroquinonato)bis(2,2′-bipyridine)ruthenium(II), *cis*-$[RuCl(QH)(bipy)_2]$, was obtained from the substitution reaction of complex I or II with 2,2′-bipyridine in methanol, and *cis*-chloro(hydroquinone)bis(2,2′-bipyridine)ruthenium(II) chloride, *cis*-$[RuCl(QH_2)(bipy)_2]Cl$, was also obtained from the substitution of *cis-trans*-$[RuCl_2(MeOH)(QH_2)bipy]$ in methanol containing hydrochloric acid. *cis*-Dihydroxobis(2,2′-bipyridine)ruthenium(II), *cis*-$[Ru(OH)_2(bipy)_2]$, was obtained by heating an aqueous solution of *cis*-$[RuCl(QH)(bipy)_2]$. Trihydroxoaquo(1,10-phenanthroline)ruthenium(III), $[Ru(OH)_3(H_2O)phen]$ was also synthesized from $[RuO_3phen]_2O$ and $[Ru(OH)_3phen]_2O$ by reduction reactions similar to those used for $[RuCl_2(MeOH)(QH_2)bipy]$. These complexes were characterized by the infrared, visible and ultraviolet absorption spectra, and also by polarographic and magnetic measurements. The structures are discussed.

The isolation and identification of metal complexes of hydroquinone has not yet been carried out. Wells and Kuritsyn[1)] investigated the kinetics of the reduction of aquomanganase(III) ions with hydroquinone in aqueous perchlorate media using the stopped-flow technique. They suggested the presence of an intermediate Mn^{III}–hydroquinone complex, $Mn \cdot QH_2{}^{3+}{}_{aq}$, on the basis of the oscilloscope trace, and the higher value of the extinction coefficient of the intermediate complex than the extinction coefficients of Mn^{3+} and $MnOH^{2+}{}_{aq}$ at 470 nm.

In previous work,[2–5)] $[RuO_4bipy]$ and $[RuO_3phen]_2O$ were obtained by the reactions of ruthenium tetraoxide with 2,2′-bipyridine and 1,10-phenanthroline in carbon tetrachloride, and $[RuO_2(bipy)_2]$, $[RuO_2(bipy)(phen)]$, $[RuO_2(phen)_2]$, $[Ru(OH)_2(py)_2bipy]$ and $[Ru(OH)_2(py)_2phen]$ were obtained by the reduction and substitution reactions of $[RuO_4bipy]$, $[RuO_3phen]_2O$ and $[RuO_4(py)_2]$ with 2,2′-bipyridine and 1,10-phenanthroline in methanol. In the present paper, six new complexes, *cis*-dichloro-*trans*-(methanol)(hydroquinone)(2,2′-bipyridine)ruthenium(II), *cis*-dichloro-*cis*-(methanol)(hydroquinone)(2,2′-bipyridine)ruthenium(II), $[RuCl_2(MeOH)(QH_2)bipy]$ (complex I and II), $[RuCl(QH)(bipy)_2]$, $[Ru(OH)_2(bipy)_2]$, $[RuCl(QH_2)(bipy)_2]Cl$ and $[Ru(OH)_3(H_2O)phen]$, are reported, and their structures are discussed.

Experimental

Materials. Ruthenium(III) chloride monohydrate (extra pure grade) supplied by Mitsuwa Chemicals was used without further purification. Oxalic acid (extra pure grade), hydroquinone, 2,2′-bipyridine and 1,10-phenanthroline were supplied by Wako Pure Chemicals. The first three were purified by recrystallization from water, and phenanthroline by recrystallization from ethanol after drying at 110 °C for 3 hr. Commercial methanol was dried by treatment with magnesium ribbon and iodine and distilled. Lithium perchlorate (Mitsuwa chemicals extra pure grade) was purified by recrystallization from methanol after heating at 110 °C for 3 hr. Wako Pure Chemicals dimethyl sulfoxide was used without further treatment. Monodeuteriomethanol made by E. Merck, Germany, was used for deuteration without further purification.

Syntheses. Tetraoxo(2,2′-bipyridine)ruthenium(VIII), $[RuO_4bipy] \cdot 3H_2O$, dioxodihydroxo(2,2′-bipyridine)ruthenium(VI), $[RuO_2(OH)_2bipy] \cdot 3H_2O$, μ-oxobis[trioxo(1,10-phenanthroline)ruthenium(VII)], $[RuO_3phen]_2O$ and μ-oxobis[trihydroxo(1,10-phenanthroline)ruthenium(IV)], $[Ru(OH)_3phen]_2O$: These complexes were synthesized as before,[2–4)] and gave satisfactory elemental analyses.

(1) Dichloro(methanol)(hydroquinone)(2,2′-bipyridine)ruthenium(II), $[RuCl_2(MeOH)(QH_2)bipy]$: To a solution of 1 g of $[RuO_4bipy] \cdot 3H_2O$ or $[RuO_2(OH)_2bipy] \cdot 3H_2O$ in 150 ml of 0.1 M hydrochloric acid, 2 g of hydroquinone was added. The mixture was refluxed with occasional shaking on a water bath for about 2 hr until the solution turned orange-brown. The solution was then evaporated to dryness, and the residue was washed repeatedly with diethyl ether and then dissolved in methanol. An insoluble material was filtered off. The solution was concentrated, and the crystals which formed were recrystallized from methanol and dried *in vacuo*. Complex I which was derived from $[RuO_4bipy]$ was stable in air, but complex II which was derived from $[RuO_2(OH)_2bipy]$ was slightly hygroscopic.

Found for complex I: Ru, 20.85; C, 43.55; H, 3.89; N, 5.36; Cl, 16.48; CH_3OH, 7.24%; mol wt, 510; yield 72.5%.

Found for complex II: Ru, 20.63; C, 43.00; H, 4.02; N, 5.22; Cl, 15.58; CH_3OH 7.49%; mol wt, 520; yield 90.1%. Calcd for $[RuCl_2(CH_3OH)(C_6H_6O_2)(C_{10}H_8N_2)]$: Ru, 21.49; C, 43.40; H, 3.83; N, 5.96; Cl, 15.10; CH_3OH, 6.80%; mol wt, 470.

Both complexes were insoluble in carbon tetrachloride, benzene, diethyl ether, ethyl acetate, chloroform and dioxane, but were slightly soluble in methanol, acetone, DMSO and DMF, and very slightly soluble in water. These complexes were green in methanol, but dark-brown in acetone, black in DMSO or DMF and pink in water, probably due to the replacement of coordinated methanol by the solvent molecules.

(2) Chloro(hydroquinonato)bis(2,2′-bipyridine)ruthenium(II), $[RuCl(QH)(bipy)_2]$: To a solution of 0.5 g of $[RuCl_2(MeOH)(QH_2)bipy]$ (complex I or II) in 250 ml methanol, 2 g of 2,2′-bipyridine was added. The mixture was refluxed with occasional shaking on a water bath for about 3 hr until the solution turned reddish-brown. The solution was then evaporated to dryness, and the residue was repeatedly washed with diethyl ether. The product was dissolved in methanol.

An insoluble material was filtered off. The solution was concentrated, and the crystals which formed were recrystallized from methanol and dried *in vacuo*. Yield: 89.5%. The complex was insoluble in carbon tetrachloride, benzene, diethyl ether, ethyl acetate, dioxane and chloroform, but soluble in water, methanol, ethanol, acetic acid, DMSO and DMF, and slightly soluble in acetone.

Found: Ru, 17.35; C, 57.89; H, 4.11; N, 10.39; Cl, 5.85%; mol wt, 585. Calcd for $[RuCl(C_6H_5O_2)(C_{10}H_8N_2)_2]$: Ru, 18.11; C, 55.96; H, 3.79; N, 10.04; Cl, 6.36%; mol wt, 558.

(3) Dihydroxobis(2,2′-bipyridine)ruthenium(II), $[Ru(OH)_2(bipy)_2]\cdot 1.5H_2O$: A solution of 0.5 g of [RuCl(QH)(bipy)$_2$] in 150 ml of distilled water was refluxed with occasional shaking on a water bath for 3 hr. An insoluble material was filtered off. The solution was then evaporated to dryness, and the residue was repeatedly washed with diethyl ether. The product was recrystallized twice from water and dried *in vacuo*. Yield: 79.8%. The water content of the complex was determined by measuring the weight loss in the temperature range 100~130 °C with a thermobalance. The complex was insoluble in carbon tetrachloride, benzene, diethyl ether, ethyl acetate, dioxane and chloroform, but soluble in water, methanol, ethanol, acetic acid, acetone, DMSO and DMF.

Found: Ru, 20.15; C, 49.09; H, 4.39; N, 10.87; H_2O, 5.39%. Calcd for $[Ru(OH)_2(C_{10}H_8N_2)_2]\cdot 1.5H_2O$: Ru, 21.32; C, 50.62; H, 4.42; N, 11.81; H_2O, 5.69%.

(4) Chloro(hydroquinone)bis(2,2′-bipyridine)ruthenium(II) chloride, $[RuCl(QH_2)(bipy)_2]Cl$: To a solution of 0.2 g of [RuCl$_2$(MeOH)(QH$_2$)bipy] (complex I) in 100 ml methanol containing 0.05 ml of conc. hydrochloric acid, 0.8 g of 2,2′-bipyridine was added. The mixture was refluxed with occasional shaking on a water bath for about 3 hr until the solution turned reddish-brown. Then we followed the procedure described in section (2). Yield: 94.3%. The solubility of the complex in the several solvents was similar to [RuCl(QH)(bipy)$_2$], but the complex was slightly hygroscopic.

Found: Ru, 16.35; C, 53.78; H, 4.36; N, 10.41; Cl, 13.50%. Calcd for $[RuCl(C_6H_6O_2)(C_{10}H_8N_2)_2]Cl$: Ru, 17.00; C, 52.53; H, 3.73; N, 9.42; Cl, 11.93%.

(5) cis-Dichlorobis(2,2′-bipyridine)ruthenium(II), cis-$[RuCl_2(bipy)_2]\cdot 0.5H_2O$: To a solution of 0.2 g of [RuCl$_2$(MeOH)(QH$_2$)bipy] (complex II) in 100 ml methanol containing 0.05 ml of conc. hydrochloric acid, 0.8 g of 2,2′-bipyridine was added. The mixture was refluxed with occasional shaking on a water bath for 3 hr until the solution turned reddish-brown. The solution was slowly evaporated to dryness and the residue was repeatedly washed with diethyl ether. Then I followed the procedure in section (2). Yield: 75.6%. (Found: C, 50.49; H, 4.02; N, 11.11; Cl, 15.15%. Calcd for $[RuCl_2(C_{10}H_8N_2)_2]\cdot 0.5H_2O$: C, 48.72; H, 3.46; N, 11.36; Cl, 14.38%).

cis-[RuCl$_2$(bipy)$_2$] was also obtained by heating [RuCl(QH)(bipy)$_2$] and [RuCl(QH$_2$)(bipy)$_2$]Cl in methanol containing hydrochloric acid. Then we followed the procedure in section (2). The product which was synthesized from [RuCl(QH)(bipy)$_2$] was further recrystallized from chloroform according to the method reported by Liu *et al.*[6]

(6) Oxalatobis(2,2′-bipyridine)ruthenium(II), $[Ru(ox)(bipy)_2]\cdot 4H_2O$: To a solution of 0.5 g of $[Ru(OH)_2(bipy)_2]\cdot 1.5H_2O$ in 75 ml of methanol, 0.5 g of oxalic acid was added. The reaction mixture was refluxed with occasional shaking on a water bath for about 2 hr. The solution was then slowly evaporated to dryness and the residue was repeatedly washed with diethyl ether. The crystals were recrystallized from methanol and dried *in vacuo*. Yield: 86.7%. (Found: Ru, 18.26; C, 46.01; H, 3.89; N, 8.96%. Calcd for $[Ru(C_2O_4)(C_{10}H_8N_2)_2]\cdot 4H_2O$: Ru, 17.62; C, 46.07; H, 4.12; N, 9.76%).

(7) Trihydroxoaquo(1,10-phenanthroline)ruthenium(III), $[Ru(OH)_3(H_2O)phen]$: To a solution of 1 g of [RuO$_3$phen]$_2$O or [Ru(OH)$_3$phen]$_2$O in 150 ml of 0.1 M hydrochloric acid, 2 g of hydroquinone was added. Then we followed the procedure described in section (1). Yield: 79.3% and 83.5%, on the basis of [RuO$_3$phen]$_2$O and [Ru(OH)$_3$phen]$_2$O, respectively. The complex was insoluble in carbon tetrachloride, benzene, chloroform, diethyl ether, ethyl acetate and dioxane, but soluble in methanol, acetone, DMSO, and DMF, and slightly soluble in water.

Found: Ru, 28.36; C, 40.47; H, 3.42; N, 8.07%; mol wt, 350. Calcd for $[Ru(OH)_3(H_2O)(C_{12}H_8N_2)]$: Ru, 28.94; C, 41.41; H, 3.71; N, 8.00%; mol wt, 350.

Measurements. Ruthenium in these complexes was determined spectrophotometrically by measuring the absorbance at 465 nm after thermal decomposition of the complexes at 350 °C followed by alkali fusion.[7] Chlorine was determined by use of micro-determing apparatus for halogens. The molecular weights of [RuCl$_2$(MeOH)(QH$_2$)bipy] (complex I and II) and [RuCl(QH)(bipy)$_2$], [RuCl(QH$_2$)(bipy)$_2$]Cl, [Ru(OH)$_3$(H$_2$O)phen] were measured in DMSO at 40 °C and in CH_3OH at 45 °C, respectively, with a Shibayama Model S-601 Vapor Pressure Osmometer. NMR spectra could not be measured owing to the poor solubilities of the complexes I and II in DMSO-d_6 and CD_3OD. Methanol in the complexes was determined by measuring the β-activity of [RuCl$_2$(^{14}CH$_3$OH)(QH$_2$)bipy] which was prepared using $^{14}CH_3OH$ (supplied by Daiichi Pure Chemical) with a liquid scintilator. Hydroquinone in the complexes was detected with a Shimadzu LKB-9000 GC-Mass spectrometor, but the amount could not be measured. The infrared absorption spectra were measured in KBr disks on a JASCO Model IR-S infrared spectrophotometer. In order to confirm the presence of coordinated water the complex was deuterated by standing at room temperature for two days in monodeuteriomethanol. Far infrared absorption spectra of the geometrical isomers (complex I and II) could not be obtained, because the two complexes did not mix well with Nujol. Visible and ultraviolet absorption spectra were measured with a Beckmann Model DU spectrophotometer. The magnetic susceptibility was measured by the Faraday method[8] at 25 °C with a Cahn R. G. electrobalance. Polarographic measurements were carried out at 25 °C with a Yanagimoto automatic recording polarograph (Type PA 101). A conventional H-type electrolytic cell was used with a saturated mercury(II) sulfate reference electrode, and an agar plug saturated with potassium sulfate was used for the junction. Lithium perchlorate was used as the supporting electrolyte. The measurements were performed in methanol as described previously.[4] The molar conductivity was measured at 25 °C with a Yanagimoto Model MY-7 conductivity outfit.

Results and Discussion

The ruthenium(II) and Ru(III) compounds obtained and the preparative pathways are summarized in Fig. 1. Two kinds of complex, I and II, of the same composition were formed by the reaction of [RuO$_4$bipy] and [RuO$_2$(OH)$_2$bipy], respectively, with hydroquinone in methanol. The compounds [RuCl(QH)(bipy)$_2$] and [RuCl(QH$_2$)(bipy)$_2$]Cl were derived

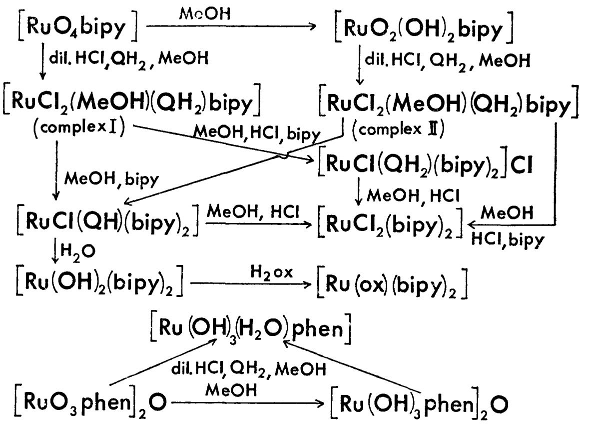


Fig. 1. Reduction and substitution reactions of $[RuO_4\text{-}bipy]$ and $[RuO_3phen]_2O$.

from the complex I and II, and the complex I, respectively. $[RuCl_2(bipy)_2]$ could not be directly derived from complex I without passing $[RuCl(QH)(bipy)_2]$ or $[RuCl(QH_2)(bipy)_2]Cl$. This indicates that the methanol and hydroquinone ligands of the complex I are coordinated at the *trans* positions, assuming that the positions of the other ligands were not changed by the ligand substitution reactions. On the other hand, $[RuCl_2(bipy)_2]$ was derived directly from complex II by a ligand substitution reaction. This indicates that the methanol and hydroquinone ligands of the complex II are coordinated at the *cis* positions. It was confirmed that three complexes with the same compostion, $[RuCl_2(bipy)_2]$, which were derived from $[RuCl_2(MeOH)(QH_2)bipy]$ (complex II), $[RuCl(QH)(bipy)_2]$ and $[RuCl(QH_2)(bipy)_2]Cl$, all had *cis* configurations by comparing their spectra with the spectrum of *cis*-$[RuCl_2(bipy)_2]$ which was reported by Bryant *et al.*[9] and Fergusson and Harris.[10] Since *cis*-$[RuCl_2(bipy)_2]$ could be directly derived from the monochlororuthenium(II) complexes, $[RuCl(QH)(bipy)_2]$ and $[RuCl(QH_2)(bipy)_2]Cl$, the two complexes were both *cis* configurations. This difference in reactivity of the geometrical isomers indicates that complex I was *cis-trans*- and complex II was *cis-cis*-$[RuCl_2(MeOH)(QH_2)bipy]$.

It was confirmed by elemental analyses by comparison of spectra that the same compound, $[Ru(OH)_3(H_2O)phen]$, was formed by the reaction of $[RuO_3phen]_2O$ and $[Ru(OH)_3phen]_2O$.

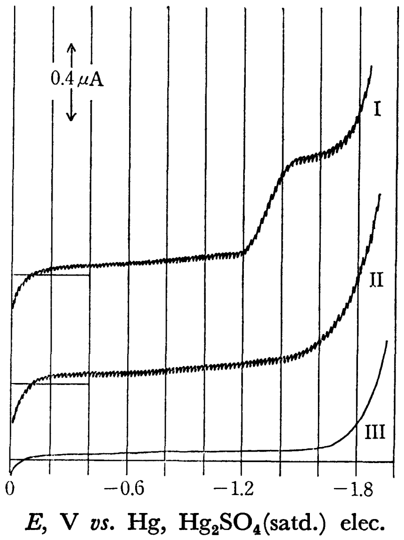


Fig. 2. Polarograms of the complexes.
I: 5×10^{-4} mol/l $[Ru(OH)_3(H_2O)phen]$, II: 5×10^{-4} mol/l $[RuCl_2(MeOH)(QH_2)bipy]$(complex I), III: 0.5 mol/l $LiClO_4$ in CH_3OH.

Polarograms of $[RuCl_2(MeOH)(QH_2)bipy]$ (complex I) and $[Ru(OH)_3(H_2O)phen]$ are shown in Fig. 2. In the case of $[RuCl_2(MeOH)(QH_2)bipy]$, no reduction wave was observed in 0.5 mol/l $LiClO_4$ methanol solution. The complex, $[Ru(OH)_3(H_2O)phen]$, was reduced polarographically in one step. The half-wave potential of the reduction wave of $[Ru(OH)_3(H_2O)phen]$ was −1.33 V *vs.* Hg, Hg_2SO_4 (satd.) elec. in 0.5 mol/l $LiClO_4$ methanol solution. The height of the reduction wave corresponded to a gain of one electron, indicating a reduction from Ru(III) to Ru(II). It has been reported by Niedrach and Tevebaugh[11] that ruthenium(IV) undergoes a stepwise reduction through Ru(III) to Ru(II) in perchloric acid solution. It was therefore concluded that the oxidation number of ruthenium in $[Ru(OH)_3(H_2O)phen]$ was 3. Since no reduction wave was obtained under the same experimental conditions as that of $[Ru(OH)_3(H_2O)phen]$, the oxidation number of ruthenium in $[RuCl_2(MeOH)(QH_2)bipy]$ must be 2, indicating that

Table 1. THE CHARACTERISTIC INFRARED ABSORPTION BANDS OF THE PRESENT Ru(II) COMPLEXES (cm^{-1})

Assignment	QH_2	bipy	$[RuCl_2(MeOH)\text{-}(QH_2)bipy]$ (complex I)	$[RuCl_2(MeOH)\text{-}(QH_2)bipy]$ (complex II)	$[RuCl(QH)\text{-}(bipy)_2]$	$[Ru(OH)_2\text{-}(bipy)_2]$	$[RuCl(QH_2)\text{-}(bipy)_2]Cl$
ν(O–H)	3300 s		3350 s , br	3340 s , br	3400 s	3400 s , br	3340 s
ν(C–H)	3080 s		3100 sh	3080 sh	3060 m	3060 w	3050 m
δ(C–H)	1845 s		1880 m	1875 m	1870 m		1868 m
ν(C=N)		1582 s	1605 s	1605 s	1603 s	1602 s	1602 s
ν(C=C)		1560 m	1580 sh	1585 sh	1590 m	1585 m	1586 s
ν(C–O)	1250 s 1235 w 1180 s		1260 sh 1235 m 1197 s	1260 sh 1235 m 1202 m	1265 w 1240 w 1210 m		1273 m 1240 m 1210 m
δ(C–H)	825 s		833 s	830 s	837 w		835 w
δ(C–H)		739 s	733 s	730 s	737 s	735 s	731 s

s = strong, m = medium, w = weak, br = broad, sh = shoulder tetraoxo(2,2′-bipyridine)ruthenium(VIII) was reduced to Ru(II) complex in hydroquinone in hydrochloric acid solution.

Infrared Spectra. The characteristic infrared absorption bands of the present Ru(II) complexes with hydroquinone and 2,2′-bipyridine are shown in Table 1 together with those of free QH_2 and bipy ligands. In the two geometrical isomers of $[RuCl_2(MeOH)(QH_2)bipy]$, ν(O–H), ν(C–H), ν(C–O) and δ(C–H) vibrations of coordinated hydroquinone closely resembled those of the free ligand, and the bands due to the benzoquinone were not observed. This shows that the hydroquinone which was added in excess to the hydrochloric acid solution of $[RuO_4bipy]$ or $[RuO_2(OH)_2bipy]$ as a reducing agent was coordinated to the metal atom, and that benzoquinone which was formed by oxidation of hydroquinone with $[RuO_4bipy]$ or $[RuO_2(OH)_2bipy]$ was not coordinated. In the present complexes, $[RuCl_2(MeOH)(QH_2)bipy]$ (complexes I and II), $[RuCl(QH)(bipy)_2]$ and $[RuCl(QH_2)(bipy)_2]Cl$, characteristic absorption bands of the coordinated hydroquinone were clearly observed in the regions from 837 to 830 and from 1880 to 1868 cm^{-1}, probably due to the C–H bending vibrations and their overtones. These were all shifted to higher frequency by coordination. The absorption bands observed in the regions from 3400 to 3340 and from 1273 to 1197 cm^{-1} were assigned to the phenolic O–H and C–O stretching vibrations, respectively.12,13)

In five present ruthenium-2,2′-bipyridine complexes, characteristic absorption bands of coordinated 2,2′-bipyridine were observed in the regions from 1605 to 1602, from 1590 to 1580 and from 737 to 730, probably due to the C=N, C=C stretching and C–H bending vibrations, respectively. The ν(C=N) and ν(C=C) vibrations were shifted to higher frequency on coordination, indicating that the bond orders of the carbon-nitrogen and carbon-carbon links were increased.14,15)

The absorption band at 3420 cm^{-1} of $[Ru(OH)_3(H_2O)phen]$ was assigned to the coordinated OH and H_2O stretching vibrations, and the absorption band at 1635 cm^{-1} was assigned to the H_2O bending vibration. These two bands were shifted to 2460 and 1200 cm^{-1} by deuteration.

Electronic Absorption Spectra. The visible and ultraviolet absorption spectra of $[RuCl_2(MeOH)(QH_2)bipy]$, $[RuCl(QH)(bipy)_2]$, $[Ru(OH)_2(bipy)_2]$, $[RuCl(QH_2)(bipy)_2]Cl$ and $[Ru(OH)_3(H_2O)phen]$ were measured in methanol, and are shown in Figs. 3, 4 and 5. The absorption spectra of the complexes are summarized in Table 2.

The spectrum of complex II (Fig. 3, curve II) resembles that of complex I, but the CT bands of complex II are stronger than those of the complex I, while the order of the π–π* bands is reversed. The spectrum of $[RuCl(QH_2)(bipy)_2]Cl$ resembles that of $[RuCl(QH)(bipy)_2]$ except in the vicinity of 520 nm.

The spectrum of $[Ru(OH)_3(H_2O)phen]$ resembles that of $[Ru(phen)_3]^{3+}$16), but $[Ru(OH)_3(H_2O)phen]$ had the lower intensity in the vicinity of 450 nm than that $[Ru(phen)_3]^{3+}$. Fergusson and his co-workers10,17) of attributed the absorption bands observed in the visible region for tervalent ruthenium-2,2′-bipyridine complexes to the charge-transfer transitions from ligand to metal.

Conductivity. The molar conductivity of

Table 2. Electronic absorption data of the complexes

Complexes	Charge-transfer transitions				Intraligand transitions (π→π*)	
	Metal-to-ligand (t_{2g}→π*)		Ligand-to-metal			
	λ_{max}, nm	(log ε)	λ_{max}, nm	(log ε)	λ_{max}, nm	(log ε)
$[RuCl_2(MeOH)(QH_2)bipy]$ (complex I)	640	(2.66)			295	(4.22)
	440 sh	(3.18)			245 sh	(4.10)
	375	(3.50)			224	(4.46)
$[RuCl_2(MeOH)(QH_2)bipy]$ (complex II)	640	(3.14)			295	(4.04)
	460 sh	(3.36)			245 sh	(3.94)
	382	(3.56)			224	(4.26)
$[RuCl(QH)(bipy)_2]$	580 sh	(2.75)			287	(4.78)
	455	(3.93)			256 sh	(4.30)
	420 sh	(3.82)			244	(4.50)
	350 sh	(3.74)				
$[Ru(OH)_2(bipy)_2]$	640	(3.04)			290	(4.56)
	460	(3.84)			255 sh	(4.08)
	425 sh	(3.77)			244	(4.17)
	360 sh	(3.74)				
$[RuCl(QH_2)(bipy)_2]Cl$	600 sh	(2.65)			288	(4.68)
	520 sh	(3.30)			257	(4.26)
	460	(3.58)			237	(4.45)
	425 sh	(3.50)				
	350 sh	(3.50)				
$[Ru(OH)_3(H_2O)phen]$			450	(3.67)	290 sh	(3.87)
			383	(3.72)	265	(4.20)
					224 sh	(4.27)

sh = shoulder

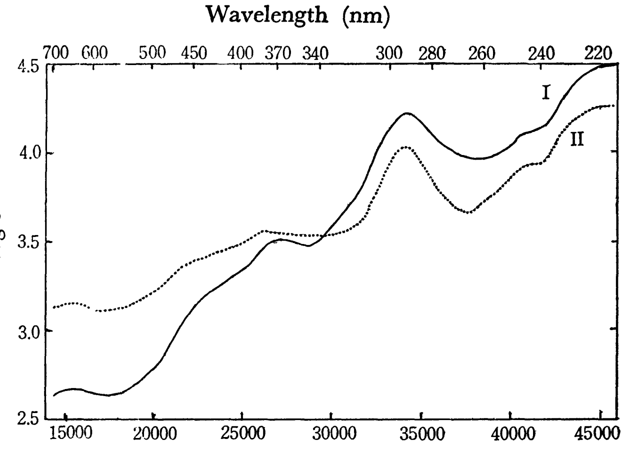


Fig. 3. Electronic spectra of the geometrical isomers of $[RuCl_2(MeOH)(QH_2)bipy]$.
I: complex I (*cis-trans* form), II: complex II (*cis-cis* form).

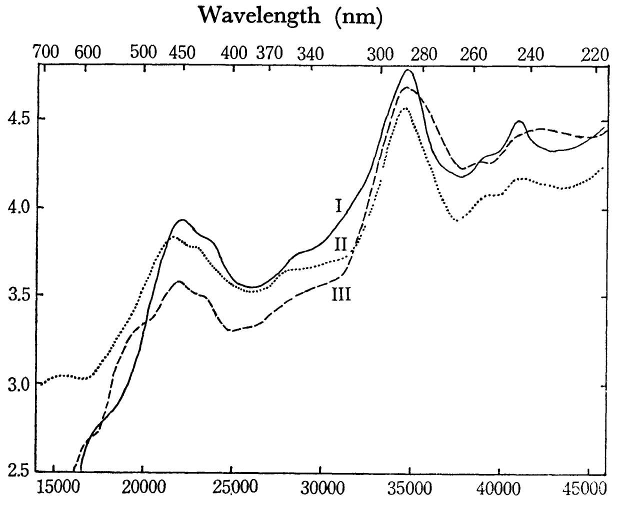


Fig. 4. Electronic spectra of the bis(2,2′-bipyridine)-ruthenium(II) complexes.
I: $[RuCl(QH)(bipy)_2]$, II: $[Ru(OH)_2(bipy)_2]$, III: $[RuCl(QH_2)(bipy)_2]Cl$.

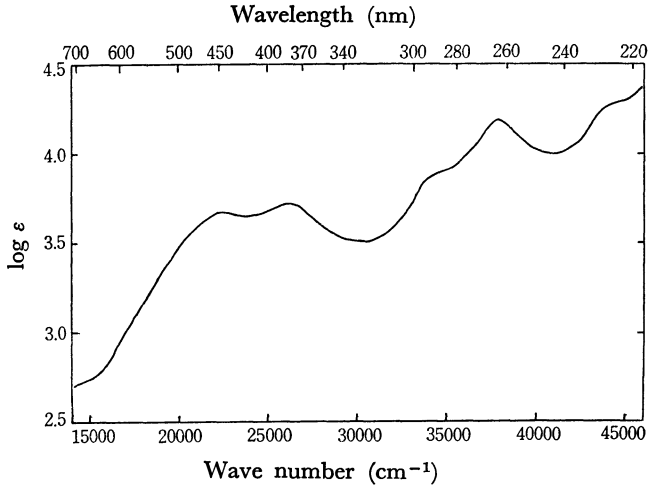


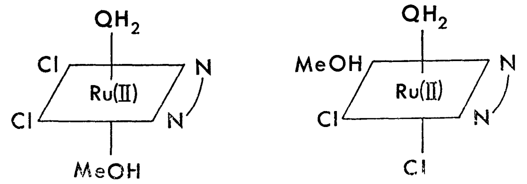
Fig. 5. Electronic spectrum of $[Ru(OH)_3(H_2O)phen]$.

chloro(hydroquinone)bis(2,2′-bipyridine)ruthenium(II) chloride in methanol solution was 111.4 ohm^{-1}·cm^2·mol^{-1} at 25 °C, showing that the complex was a 1 : 1 type electrolyte.

Magnetic Properties. The observed diamagnetism of the geometrical isomers of $[RuCl_2(MeOH)(QH_2)bipy]$ indicated that the ruthenium atom has a spin-paired d^6 configuration.

$[Ru(OH)_3(H_2O)phen]$ had a magnetic moment of 1.81 B.M., indicating that the ruthenium atom has a spin-paired d^5 configuration. The stereochemical configuration of $[Ru(OH)_3(H_2O)phen]$ is not clear.

The structures thus proposed for the geometrical isomers of $[RuCl_2(MeOH)(QH_2)bipy]$ are shown in Fig. 6.



cis-trans form
Complex I

cis-cis form
complex II

Fig. 6. The proposed structures of the geometrical isomers, $[RuCl_2(MeOH)(QH_2)bipy]$.

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References

1) C. F. Wells and L. V. Kuritsyn, *J. Chem. Soc.*, *A*, **1970**, 676.
2) T. Ishiyama, *Ann. Rep. Rad. Center Osaka*, **8**, 40 (1967).
3) T. Ishiyama, This Bulletin, **42**, 2071 (1969).
4) T. Ishiyama, *ibid.*, **44**, 1571 (1971).
5) T. Ishiyama and Y. Koda, *Inorg. Chem.*, **11**, 2837 (1972).
6) C. F. Liu, N. C. Liu, and J. C. Bailar, Jr., *ibid.*, **3**, 1197 (1964).
7) E. D. Marshall and R. R. Rickard, *Anal. Chem.*, **22**, 795 (1950).
8) L. N. Mulay, "Magnetic Susceptibility", Wiley, New York, London, Sydney (1963), p. 1836.
9) G. M. Bryant, J. E. Fergusson, and H. K. J. Powell, *Aust. J. Chem.*, **24**, 257 (1971).
10) J. E. Fergusson and G. M. Harris, *J. Chem. Soc.*, *A*, **1966**, 1293.
11) L. W. Niedrach and A. D. Tevebaugh, *J. Amer. Chem. Soc.*, **73**, 2835 (1951).
12) D. H. Anderson and N. B. Woodall, *Anal. Chem.*, **25**, 1906 (1953).
13) R. T. O'Connor, P. V. Haar, E. F. DuPre, L. E. Brown, and C. H. Pominski, *J. Amer. Chem. Soc.*, **76**, 2368 (1954).
14) D. H. Busch and J. C. Bailor, Jr., *ibid.*, **78**, 1147 (1956).
15) R. G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).
16) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, *A*, **1969**, 1428.
17) J. E. Fergusson, *Aust. J. Chem.*, **24**, 275 (1971).