Several Novel Ru(VI) and Ru(IV) Complexes Derived from [RuO_4bipy] and [RuO_3phen]$_2$O

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(Received August 31, 1970)

Five novel neutral complexes of ruthenium(VI) and ruthenium(IV) with 2,2′-bipyridine and 1,10-phenanthroline, [$RuO_2(OH)_2$bipy]·$3H_2O$, [$Ru(OH)_3$phen]$_2$O, [RuO_2bipy$_2$]·$3H_2O$, [RuO_2bipy·phen]·$3H_2O$ and [RuO_2phen$_2$], were prepared and characterized by a study of their infrared, visible and ultraviolet absorption spectra, and by polarographic measurements. [$RuO_2(OH)_2$bipy] and [$Ru(OH)_3$phen]$_2$O were obtained by the reduction of previously-reported complexes, [RuO_4bipy] and [RuO_3phen]$_2$O respectively, with methanol, and [RuO_2bipy$_2$], [RuO_2bipy·phen] and [RuO_2phen$_2$], by the reactions of [RuO_4bipy] and [RuO_3phen]$_2$O in methanol with 2,2′-bipyridine and 1,10-phenanthroline respectively. [RuO_2bipy·phen] and [RuO_2phen$_2$] were also obtained in methanol by the substitution reactions of [RuO_2bipy$_2$] and [RuO_2bipy·phen] with 1,10-phenanthroline respectively. The five complexes were all diamagnetic. [$RuO_2(OH)_2$bipy] was assumed to be a "ruthenyl" complex with two oxide ions coordinated at the *trans* positions, like such well-known *trans*-dioxoruthenyl analogues as $Cs_2[RuO_2Cl_4]$ and $[RuO_2(OH)_2(NH_3)_2]$, and [$Ru(OH)_3$phen]$_2$O was assumed to be a binuclear complex with an oxygen-bridge between ruthenium atoms. [RuO_2bipy$_2$], [RuO_2bipy·phen], and [RuO_2phen$_2$] were assumed to be mononuclear complexes with two oxide ions coordinated at the *trans* positions, and their oxidation numbers were found polarographically, to be 4.

Organic chelate compounds of "ruthenyl" and oxo-bridged binuclear ruthenium(IV) species with coordinated hydroxy groups have not been reported, since most "ruthenyl" and hydroxoruthenium species are very unstable and are easily hydrolyzed. Wagnerova[1] attempted to prepare a "ruthenyl" oxalate, [RuO_2ox$_2$]$^{2-}$, by the reduction of ruthenium tetroxide with oxalate ions. He reported that there was no evidence of a "ruthenyl" oxalate, [RuO_2ox$_2$]$^{2-}$, although the corresponding osmium(VI) species was very stable, and that [Ruox$_3$]$^{2-}$ might be obtained. Lott and Symons[2] and Woodhead and Fletcher[3] obtained several ruthenyl complexes formulated as $[Ru^{VI}O_2X_4]^{2-}$. They suggested that the two oxygen atoms of "ruthenyl" complexes, like their osmium analogues, could all be presumed to be *trans*, and reported that the complexes were all diamagnetic, probably because of the low symmetry of the ligand field.

Bis(2,2′-bipyridine)- and bis(1,10-phenanthroline)-ruthenium(IV) chelates, with two oxide ions coordinated at the *trans* positions in either case, have not been reported. Dwyer and his co-workers[4] prepared dichlorobis(2,2′-bipyridine)- and dichlorobis(1,10-phenanthroline)-ruthenium(II) complexes, and they denoted them as $[Ru^{II}B_2Cl_2]^0$. They reported that these neutral complexes were spin-paired and showed no tendency of disproportionation to the tris complexes under normal experimental conditions, although the bis-iron(II) chelates rapidly disproportionate in aqueous solutions, and suggested that the Ru(II) complexes isolated had *cis*-configurations.

In the present paper five new complexes, [$RuO_2(OH)_2$bipy]·$3H_2O$, [$Ru(OH)_3$phen]$_2$O, [RuO_2bipy$_2$]·$3H_2O$, [RuO_2bipy·phen]·$3H_2O$, and [RuO_2phen$_2$], are reported, they were obtained by the reduction and substitution reactions of two previously-reported complexes,[5),6)] [RuO_4bipy]·$3H_2O$ and [RuO_3phen]$_2$O, with 2,2′-bipyridine and 1,10-phenanthroline in methanol.

1) Wagnerova, D. M., *Collection Czech. Commun.*, **27**, 1130 (1962).
2) K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.*, **1960**, 973.
3) J. L. Woodhead and J. M. Fletcher, UKAEA, AERE, **R-4123**.
4) Late F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Aust. J. Chem.*, **16**, 544 (1963).

Experimental

Materials. Ruthenium(III) chloride monohydrate (extra pure grade) supplied by Mitsuwa Chemicals & Co. was used without further treatment. Both 2,2′-bipyridine and 1,10-phenanthroline were supplied by Yoneyama Chemicals. The former was purified by recrystallization from distilled water, and the latter, from ethanol after it had been dried by heating at 115°C for 3 hr. Commercial methanol was dried by treatment with magnesium ribbon and iodine. Lithium perchlorate (extra pure grade) supplied by Mitsuwa Chemicals & Co. was purified by recrystallization from methanol after drying.

Syntheses. *(1) Dioxodihydroxo(2,2′-bipyridine)-ruthenium(VI), [$RuO_2(OH)_2$bipy]·$3H_2O$, and μ-Oxo-bis[trihydroxo(1,10-phenanthroline)ruthenium(IV)], [$Ru(OH)_3$phen]$_2$O:* A solution of 1 g of [RuO_4bipy]·$3H_2O$ or [RuO_3phen]$_2$O in 150 m*l* of methanol was refluxed and shaken on a hot-water bath until the solution turned dark-brown. The solution was then evaporated to dryness, and the residue was recrystallized from methanol and dried *in vacuo*. Yields: dioxodihydroxo(2,2′-bipyridine)ruthenium(VI), 93.85%, and μ-oxo-bis[trihydroxo(1,10-phenanthroline)ruthenium(IV)], 95.15%, on the basis of the starting complexes. The product complexes are insoluble in carbon tetrachloride, benzene, ether, acetone, and dioxane, but are soluble in water, methanol, ethanol, acetic acid, and dimethyl formamide. Both complexes are stable in methanol, and [$RuO_2(OH)_2$bipy] is stable in water too. However, the aqueous solution of [$Ru(OH)_3$phen]$_2$O slowly changes from dark-brown to green, probably because of air oxidation in water. The ruthenium and water contents and the molecular weights of the complexes were measured by methods reported previously.[5)]

5) T. Ishiyama, *Ann. Rep. Rad. Ctr. Osaka*, **8**, 40 (1967).
6) T. Ishiyama, This Bulletin, **42**, 2071 (1969).

Found: Ru, 26.58; C, 32.24; H, 4.03; N, 7.47; H_2O, 14.05%; mol wt, 330. Calcd for $[RuO_2(OH)_2(C_{10}H_8N_2)]\cdot 3H_2O$: Ru, 26.79; C, 31.83; H, 4.24; N, 7.43; H_2O, 14.24%; mol wt, 325(anhydride).

Found: Ru, 31.36; C, 41.47; H, 3.28; N, 8.24%; mol wt, 650. Calcd for $[Ru(OH)_3(C_{12}H_8N_2)]_2O$: Ru, 29.95; C, 42.28; H, 3.23; N, 8.22%; mol wt, 681.

(2) Dioxobis(2,2′-bipyridine)ruthenium(IV), [RuO_2bipy_2]·$3H_2O$, and *Dioxobis(1,10-phenanthroline)ruthenium(IV), [RuO_2phen_2]*: To a solution of 1 g of $[RuO_4bipy]\cdot 3H_2O$ or $[RuO_3phen]_2O$ in 15 m*l* of methanol, 5 g of 2,2′-bipyridine or 1,10-phenanthroline was added. The reaction mixture was refluxed under shaking on a hot-water bath until the solution turned orange-brown. The solution was then evaporated to dryness, and the residue was repeatedly washed with benzene and then dissolved in pure water. An insoluble product was filtered off. The solution was concentrated, and the crystals formed were recrystallized from pure water and dried *in vacuo*. Yield: dioxobis(2,2′-bipyridine)ruthenium(IV), 96.15%, and dioxobis(1,10-phenanthroline)-ruthenium(IV), 98.35%, on the basis of the starting complexes. Both complexes are insoluble in carbon tetrachloride, benzene, ether, ester, and dioxane, but are soluble in water, methanol, acetic acid, acetone, and dimethyl formamide.

Found: Ru, 20.16; C, 47.29; H, 4.22; N, 10.19; H_2O, 11.00%; mol wt, 450. Calcd for $[RuO_2(C_{10}H_8N_2)_2]\cdot 3H_2O$: Ru, 20.40; C, 48.00; H, 4.40; N, 11.20; H_2O, 10.80%; mol wt, 446(anhydride).

Found: Ru, 20.35; C, 58.43; H, 3.41; N, 11.51%; mol wt, 510. Calcd for $[RuO_2(C_{12}H_8N_2)_2]$: Ru, 20.65; C, 58.30; H, 3.25; N, 11.33%; mol wt, 494.

(3) Dioxo(2,2′-bipyridine)(1,10-phenanthroline)ruthenium(IV), [$RuO_2bipy\cdot phen$]·$3H_2O$: To a solution of 1 g of $[RuO_4bipy]\cdot 3H_2O$ in 150 m*l* of methanol, 5 g of 1,10-phenanthroline were added. The reaction mixture was refluxed under shaking on a hot-water bath until the solution turned orange-brown. Then we followed the procedure described in the proceding section. Yield: 84.42%, on the basis of $[RuO_4bipy]\cdot 3H_2O$. The complex is insoluble in carbon tetrachloride, benzene, ether, ester, and dioxane, but is soluble in water, methanol, ethanol, acetic acid, acetone, and dimethyl formamide.

Found: Ru, 19.14; C, 50.53; H, 4.37; N, 11.17; H_2O, 11.00%; mol wt, 510. Calcd for $[RuO_2(C_{10}H_8N_2)(C_{12}H_8N_2)]\cdot 3H_2O$: Ru, 19.16; C, 50.57; H, 4.19; N, 10.68; H_2O, 10.30%; mol wt, 470(anhydride).

(4) Tetraoxo(2,2′-bipyridine)ruthenium(VIII), [RuO_4bipy]·$3H_2O$, and μ-Oxo-bis[trioxo(1,10-phenanthroline)ruthenium(VII)], [RuO_3phen]$_2O$. These substances were synthesized according to the methods reported in previous papers.[5,6] The results of the elemental analyses and the molecular weights coincided with those reported previously.

Absorption Spectra. The infrared absorption spectra were obtained on an infrared spectrophotometer, Model IR-S of the Japan Spectroscopic Co., by the KBr disk method. The crystalline water of the complexes was removed by heating for 15 hr at 115°C. It was ascertained from the elemental analysis that the structure of the complexes is not altered by this treatment. The visible and ultraviolet absorption spectra were measured with a Beckmann Model D.U. spectrophotometer.

Magnetic Measurements. The magnetic susceptibility was measured at 25°C with a Cahn R.G. Electrobalance by the Faraday method. The five new complexes were all found to be diamagnetic.

Polarographic Measurements. The polarographic measurements were carried out with a Yanagimoto Automatic Recording Polarograph (Type PA 101). The characteristics of the capillary used were m=0.648 mg/sec and t=4.63 sec/drop in a 0.5 mol/*l* $LiClO_4$ methanol solution when the height of the mercury reservoir was 70.0 cm and when the applied potential was 0 volt *vs.* a saturated mercurous sulfate reference electrode at 25°C. A conventional H-type electrolytic cell with a potassium sulfate-saturated agar bridge and a sintered glass disk was used as the reference electrode. The experimental procedure was as follows: In order to make the solutions to be measured, four standard solutions were first prepared by dissolving crystals of $[RuO_2bipy_2]$, $[RuO_2bipy\cdot phen]$, $[RuO_2phen_2]$, and $[Ru(OH)_3phen]_2O$ in methanol; the concentrations of the complexes were all adjusted to 10^{-3} mol/*l*. Lithium perchlorate was used as the supporting electrolyte, and its concentration was adjusted to 1 mol/*l*. A 10-m*l* portions of each standard solution was transferred into a 50-m*l* Erlenmeyer flask, to which was then added 10 m*l* of a mol/*l* solution of lithium perchlorate in methanol. A part of the mixture was transferred into an electrolytic cell. The dissolved oxygen was removed by bubbling nitrogen gas in for about half an hour, and the polarograms were recorded in a flow of nitrogen gas through the surface of the solution in an electrolytic cell.

Results and Discussion

Oxidation States of the Complexes. Polarograms of the four new complexes are shown in Fig. 1. All the complexes measured are reduced polarographically in two steps. The half-wave potentials of the first waves of $[RuO_2bipy_2]$, $[RuO_2bipy\cdot phen]$, $[RuO_2phen_2]$, and $[Ru(OH)_3phen]_2O$ are −0.18, −0.19, −0.22, and −0.21 V *vs.* Hg, Hg_2SO_4 (satd.) elec. respectively in 0.5 mol/*l* $LiClO_4$ methanol solutions,

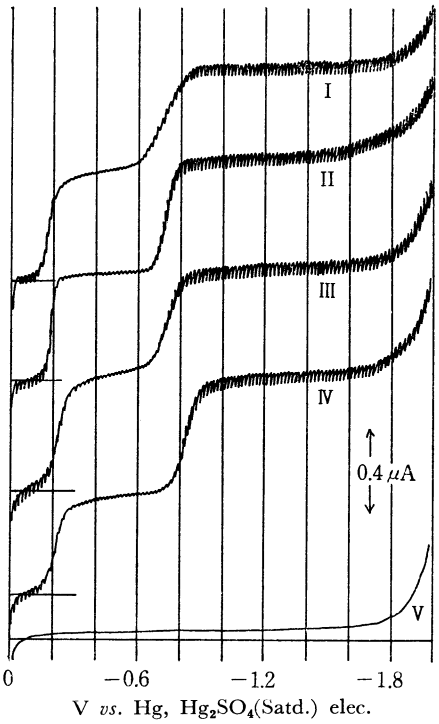

Fig. 1. Polarograms of the complexes.
I: 5×10^{-4} mol/*l* $[RuO_2bipy_2]$, II: 5×10^{-4} mol/*l* $[RuO_2bipy\cdot phen]$, III: 5×10^{-4} mol/*l* $[RuO_2phen_2]$, IV: 5×10^{-4} mol/*l* $[Ru(OH)_3phen]_2O$, V: 0.5 mol/*l* $LiClO_4$ in CH_3OH (the supporting electrolyte).

while those of the second waves are −0.71, −0.73, −0.74, and −0.82 volt respectively. The ratios of the height of the first wave to that of the second are approximately 1 : 1 for all the complexes. Consequently, the first and second waves correspond to a gain of one electron each, indicating the reduction from Ru(IV) to Ru(III), and from Ru(III) to Ru(II) states, respectively. A similar polarogram has also been reported by Niedrach and Tevebaugh[7] for ruthenium(IV) in a perchloric acid solution. They interpreted this as meaning that ruthenium(IV) was step-by-step reduced to Ru(III) and to Ru(II) states. As a result, the oxidation numbers of ruthenium in [RuO_2bipy$_2$], [RuO_2bipy·phen], [RuO_2phen$_2$], and [$Ru(OH)_3$phen]$_2$O were all concluded to be 4.

Compositions of the Complexes. *(1) Dioxodihydroxo(2,2′-bipyridine)ruthenium(VI) and μ-Oxo-bis-[trihydroxo(1,10-phenanthroline)ruthenium(IV)]*: From the results of the elemental analysis, the mole ratios of ruthenium to 2,2′-bipyridine or 1,10-phenanthroline were both found to be 1 : 1. The data of the molecular weight indicate that the oxohydroxoruthenium(VI) complex with 2,2′-bipyridine is mononuclear, and that the hydroxoruthenium(IV) complex with 1,10-phenanthroline is an oxo-bridged binuclear species.

(2) Dioxobis(2,2′-bipyridine)ruthenium(IV) and dioxobis(1,10-phenanthroline)ruthenium(IV): From the results of the elemental analysis, the mole ratios of ruthenium to 2,2′-bipyridine or 1,10-phenanthroline were both found to be 1 : 2. The data of the molecular weight indicate that both of the complexes, [RuO_2bipy$_2$] and [RuO_2phen$_2$], are mononuclear.

(3) Dioxo(2,2′-bipyridine)(1,10-phenanthroline)-ruthenium(IV): From the results of the elemental analysis, the mole ratio of ruthenium, 2,2′-bipyridine, and 1,10-phenanthroline seems to be 1 : 1 : 1. The observed molecular weight indicates that the complex is mononuclear, [RuO_2bipy·phen].

Reduction and Substitution Reactions of [RuO_4bipy] and [RuO_3phen]$_2$O with 2,2′-bipyridine and 1,10-phenanthroline in Methanol. The reactions of [RuO_4bipy] and [RuO_3phen]$_2$O are shown schematically in Fig. 2.

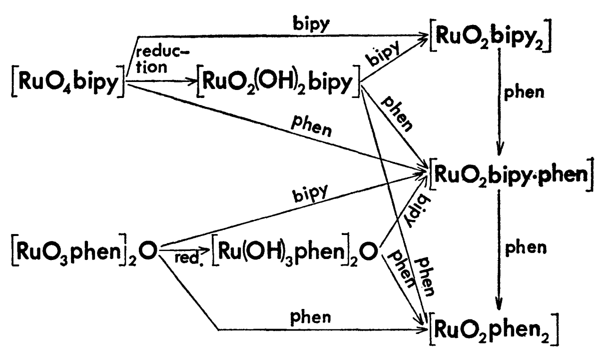

Fig. 2. Reduction and substitution reactions of [RuO_4bipy] and [RuO_3phen]$_2$O in methanol.

[$RuO_2(OH)_2$bipy] and [$Ru(OH)_3$phen]$_2$O are formed by the reduction of [RuO_4bipy] and [RuO_3phen]$_2$O respectively, with methanol. It was confirmed, by elemental analyses and by comparison of the spectra, that [RuO_2bipy$_2$] was formed by the reactions of [RuO_4bipy] or [$RuO_2(OH)_2$bipy] with 2,2′-bipyridine, and that [RuO_2phen$_2$] was produced by the reactions of [RuO_3phen]$_2$O or [$Ru(OH)_3$phen]$_2$O with 1,10-phenanthroline. It was also found that the mixed-ligand complex, [RuO_2bipy·phen], could be synthesized by the following reactions in mehtanol: (1) the reaction of [RuO_4bipy] with 1,10-phenanthroline, (2) the reactions of [RuO_3phen]$_2$O and [$Ru(OH)_3$phen]$_2$O with 2,2′-bipyridine, and (3) the stoichiometric reaction between equimolar 1,10-phenanthroline and [$RuO_2(OH)_2$bipy]. In the third reaction, [RuO_2phen$_2$] was formed if an excess of 1,10-phenanthroline was employed. [RuO_2bipy·phen] and [RuO_2phen$_2$] were also obtained in methanol by the substitution reactions of [RuO_2bipy$_2$] and [RuO_2bipy·phen] respectively with equimolar 1,10-phenanthroline. The structures of these bis-chelates of dioxoruthenium(IV) will be discussed later.

Air Oxidation of [$Ru(OH)_3$phen]$_2$O in an Aqueous Solution. An aqueous solution of [$Ru(OH)_3$phen]$_2$O changes slowly from dark-brown to green, probably because of air oxidation in water. It was confirmed from the spectral change that [$Ru(OH)_3$phen]$_2$O was transformed to [RuO_3phen]$_2$O in water.

Infrared Absorption Spectra. The main infrared absorption bands of the present complexes are shown in Table 1, together with those of free ligands. The C=N, C=C, and C–H stretching peaks are all shifted to the higher frequency side by ligation in a manner similar to the cases of [RuO_4bipy] and [RuO_3phen]$_2$O.[5,6] The absorption bands at 3380 and 3390 cm^{-1} of oxo-hydroxoruthenium(VI) and oxo-bridged hydroxoruthenium(IV) complexes with 2,2′-bipyridine and 1,10-phenanthroline respectively were assigned to the O–H stretching. Similar observations have been reported for hydroxo-complexes of osmium,[8] hydroxonitrosyl ruthenium complexes,[9] and [$Re(OH)Cl_2(O\cdot COC_3H_7)$]$_2$.[10] The infrared spectra of the ruthenium(IV) oxide complexes with 2,2′-bipyridine and 1,10-phenanthroline contain no peaks which can be attributed to the O–H stretching frequencies, indicating that the hydroxo groups are not present in the ruthenium(IV) oxide complexes.

Electronic Absorption Spectra. The visible and ultraviolet absorption spectra of oxo-hydroxoruthenium(VI), oxoruthenium(IV), and oxo-bridged hydroxoruthenium(IV) complexes with 2,2′-bipyridine and 1,10-phenanthroline were measured in water and methanol. They are shown in Figs. 3 to 7, together with those of pure ligands in water.

Dioxodihydroxo(2,2′-bipyridine)ruthenium(VI) has six absorption bands, at 670, 560, 450, 364, 290, and 244 mμ (Fig. 3). Four of those peaks, those at 670, 560, 450, and 364 mμ, may all be assigned to the charge transfer from ligand to metal. Considerable data on the spectra of tetrahedral oxyanions, which

7) L. W. Niedrach and A. D. Tevebaugh, *J. Amer. Chem. Soc.*, **73**, 2835 (1951).
8) W. P. Griffith, *J. Chem. Soc.*, **1964**, 245.
9) D. Scargill, *ibid.*, **1961**, 4444.
10) R. Cotton, "The Chemistry of Rhenium and Technetium," Interscience Publishers, New York (1965), p. 111.

Table 1. The characteristic infrared absorption bands of oxo-hydroxoruthenium(VI), oxo-bridged hydroxoruthenium(IV) and oxoruthenium(IV) complexes with 2,2′-bipyridine and 1,10-phenanthroline (cm^{-1})

Assignments	bipy	$[RuO_2(OH)_2bipy]$	$[RuO_2bipy_2]$	phen	$[Ru(OH)_3phen]_2O$	$[RuO_2phen_2]$
ν(O-H)		3380			3390	
ν(C=N)	1582	1605	1610	1621	1625 sh	1630
ν(C=C)	1560	1565	1580	1585 1560	1600 1580 sh	1595 1565
ν(C-H)	759	775	780	762 730	770 720	770 730

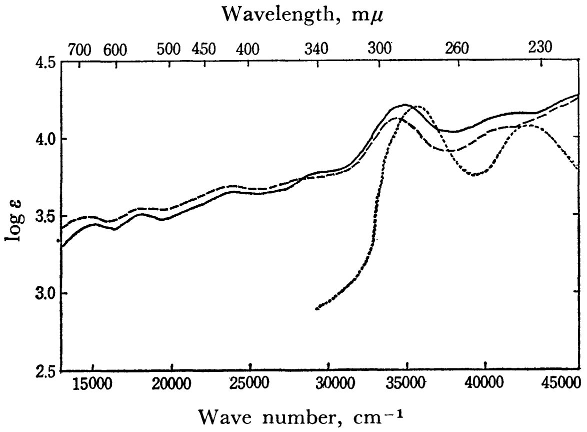

Fig. 3. Absorption spectra of $[RuO_2(OH)_2bipy]$ and 2,2′-bipyridine.
—— $[RuO_2(OH)_2bipy]$ in H_2O, ---- $[RuO_2(OH)_2bipy]$ in CH_3OH, ------ bipy in H_2O

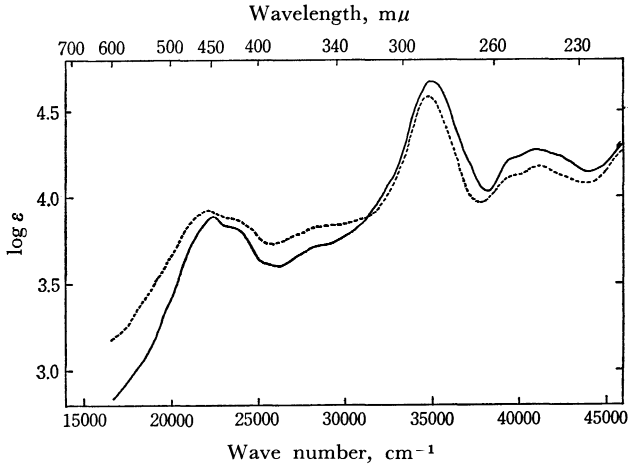

Fig. 4. Absorption spectra of $[RuO_2bipy_2]$ in water (——) and methanol (------).

have one or two d electrons in their ground states, were reported by Symons and his co-workers[11,12] and by Wolfsberg and Helmholz.[13] They suggested that the lowest transitions in such oxyanions as CrO_4^{3-}, MnO_4^{2-}, MnO_4^{3-}, and FeO_4^{2-} might also be interpreted as due to the charge transfer from oxygen to metal. The 290 and 244 mμ bands appear to be intraligand transitions corresponding to the two bands at 279 and 233 mμ in 2,2′-bipyridine.

Dioxobis(2,2′-bipyridine)ruthenium(IV) has five absorption bands and a shoulder at 450, 425, 350, 287, 244, and 255 mμ respectively (Fig. 4). A similar spectrum has also been reported by Fergusson and Harris[14] for tris(2,2′-bipyridine)ruthenium(II) chloride, which has six absorption bands at 452, 425, 348. 287, 250, and 245 mμ and which shows a close resemblance to those of the present complex, $[RuO_2bipy_2]$, in the intensity and the characteristic shape of each band. They suggested that the 452 and 425 mμ bands might be assigned to the charge transfer from metal to ligand ($t_{2g}\rightarrow\pi^*$ transitions), and the 348 mμ band, to the charge transfer from ligand to metal ($\pi\rightarrow e_g^*$ transition). The 450 and 425 mμ bands in the present complex, $[RuO_2bipy_2]$, may also be assigned to the charge transfer from metal to ligand, and the 350 mμ band, to the charge transfer from ligand to metal. The two peaks in the ultraviolet region appear to be intraligand transitions corresponding to the 279 and 233 mμ bands observed for free 2,2′-bipyridine.

Dioxobis(1,10-phenanthroline)ruthenium(IV) has four peaks and two shoulders at 450, 420, 265, 225, 310, and 290 mμ respectively (Fig. 5). A similar, spectrum has also been reported by Crosby, Perkins

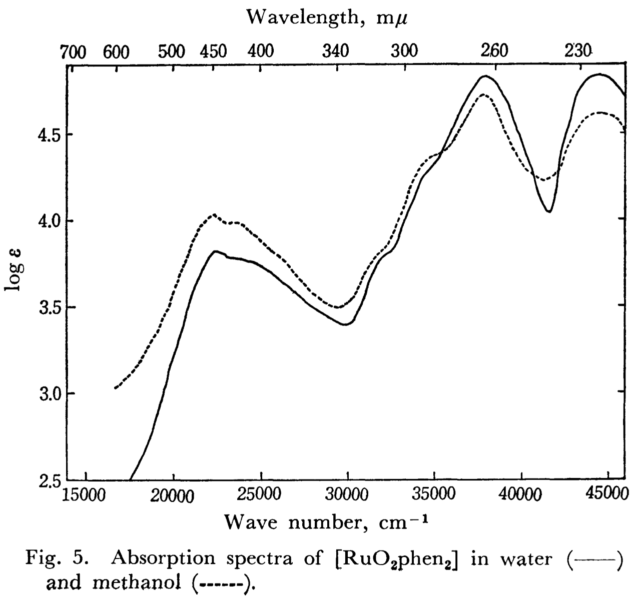

Fig. 5. Absorption spectra of $[RuO_2phen_2]$ in water (——) and methanol (------).

11) A. Carrington, D. S. Schouland, and M. C. R. Symons, *J. Chem. Soc.*, **1957**, 659.

12) A. Carrington, D. J. E. Ingram, D. S. Schouland, and M. C. R. Symons, *ibid.*, **1956**, 4710.

13) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

14) J. E. Fergusson and (Miss) G. M. Harris, *J. Chem. Soc., A*, **1966**, 1293.

and Klassen[15] for tris(1,10-phenanthroline)ruthenium(II) chloride, which has six absorption bands at 450, 420, 315, 288, 265, and 223 mμ; this spectrum bears a remarkable resemblance to those of the present complex, $[RuO_2phen_2]$, in the intensity and the characteristic shape of each band. They suggested that the 450 and 420 mμ bands might be assigned to the charge transfer from metal to ligand. The 450 and 420 mμ bands in the present complex, $[RuO_2phen_2]$, may also be assigned to the charge transfer from metal to ligand. The two shoulders and the two peaks observed in the ultraviolet region appear to be intraligand transitions corresponding to the 320, 290, 265, and 230 mμ bands in free 1,10-phenanthroline.

Dioxo(2,2′-bipyridine)(1,10-phenanthroline)ruthenium(IV) has six peaks at 450, 425, 370, 290, 265, and 225 mμ (Fig. 6). The 450 and 425 mμ bands may both be assigned to the charge transfer from metal to ligand, and the 370 mμ band, to the charge transfer from ligand to metal. The latter charge-transfer transition (ligand-to-metal) is probably due to the coordination of the 2,2′-bipyridine molecule. A similar absorption band has been reported by Fergusson and Harris[14] for $[Ru^{II}Cl_2bipy_2]$ and $[Ru^{III}Cl_2bipy_2]$-$Cl\cdot 3H_2O$. The three peaks observed in the ultraviolet region appear to be intraligand transitions corresponding to the 279 mμ band in 2,2′-bipyridine and to the 265 and 230 mμ bands in 1,10-phenanthroline respectively. The electronic absorption data show that this compound is a mixed-ligand complex of 2,2′-bipyridine and 1,10-phenanthroline.

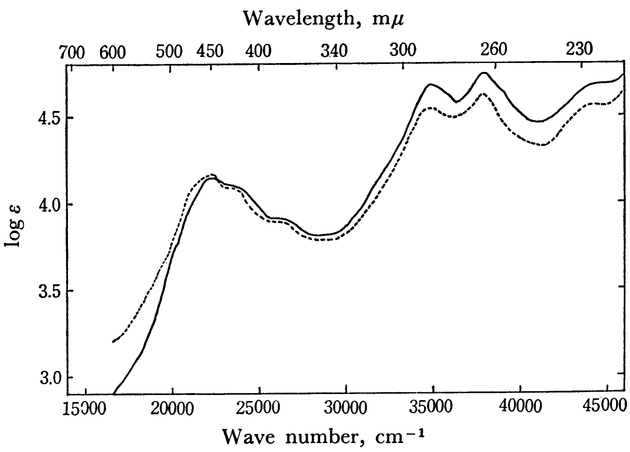

Fig. 6. Absorption spectra of $[RuO_2bipy\cdot phen]$ in water (——) and methanol (------).

μ-Oxo-bis[trihydroxo(1,10-phenanthroline)ruthenium(IV)] has four peaks and two shoulders at 450, 375, 265, 222, 315, and 290 mμ respectively (Fig. 7). The two peaks observed at 450 and 375 mμ may both be assigned to the charge transfer from metal to ligand, as in $[RuO_2phen_2]$. The charge-transfer bands for the present complex, $[Ru(OH)_3phen]_2O$, are observed in a shorter-wavelength region than those of the previous complex, $[RuO_3phen]_2O$. This fact shows that the charge-transfer transitions of $[Ru(OH)_3phen]_2O$ occur with a higher energy than those of $[RuO_3phen]_2O$. The two charge-transfer bands of $[Ru(OH)_3phen]_2O$ are diffusely observed in comparison with those of $[RuO_2phen_2]$, presumably due to an interaction between two ruthenium atoms or a low symmetry of the binuclear species. The two shoulders and two peaks observed in the ultraviolet region may all be assigned to the intraligand transitions of 1,10-phenanthroline. The spectrum of $[Ru(OH)_3phen]_2O$ which has been oxidized with air for a month in water coincides with that of the first complex, $[RuO_3phen]_2O$, showing that the present complex, $[Ru(OH)_3phen]_2O$, is transformed to $[RuO_3phen]_2O$ in water. This fact was also confirmed by the elemental analysis and by measurement of the molecular weight and the magnetic susceptibility.

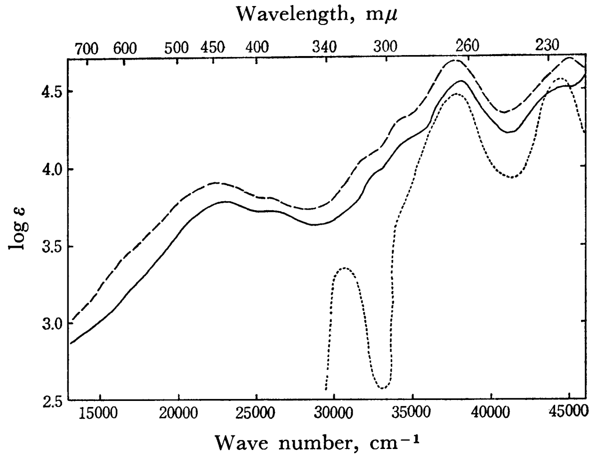

Fig. 7. Absorption spectra of $[Ru(OH)_3phen]_2O$ and 1,10-phenanthrolone.
—— $[Ru(OH)_3phen]_2O$ in H_2O, ---- $[Ru(OH)_3phen]_2O$ in CH_3OH, ------ phen in H_2O

Magnetic Properties. The observed diamagnetism of dioxodihydroxo(2,2′-bipyridine)ruthenium(VI) indicates the pairing of the two *d* electrons in Ru(VI). The complex contains the ruthenium atom octahedrally bonded one 2,2′-bipyridine, two oxide, and two hydroxide ligands. The molecular orbital treatments of $[RuO_2Cl_4]^{2-}$ and $[OsO_2(OH)_4]^{2-}$ which have been reported by Lott and Symons[2] may be applied to $[RuO_2(OH)_2bipy]$ just as to the asymmetrical "ruthenyl" complex, $[RuO_2(OH)_2(NH_3)_2]$.[16]

The diamagnetism of μ-oxo-bis[trihydroxo(1,10-phenanthroline)ruthenium(IV)] may be explained by applying the molecular orbital treatment of $K_4[Ru_2OCl_{10}]$ which has been reported by Dunitz and Orgel.[17]

The diamagnetism of dioxobis(2,2′-bipyridine)-, dioxobis(1,10-phenanthroline)-, and dioxo(2,2′-bipyridine)(1,10-phenanthroline)-ruthenium(IV) is especially interesting. Each of the present complexes, $[RuO_2bipy_2]$, $[RuO_2phen_2]$, and $[RuO_2bipy\cdot phen]$, contains the ruthenium atom octahedrally bonded to two oxide and two 2,2′-bipyridine or 1,10-phenanthroline ligands, and the four d electrons must exist as two pairs, assuming a *trans*-configuration with two

15) G. A. Crosby, W. G. Perkins, and D. M. Klassen, *J. Chem. Phys.*, **43**, 1498 (1965).

16) W. P. Griffith, "The Chemistry of the Rarer Platinum Metals," Interscience Publishers, New York (1967), p. 157.

17) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, **1953**, 2594.

oxide ligands. It was reported by Deguchi[18] and Nakai for $[Cu(bipy)_2(ClO_4)]ClO_4$ and $[Cu(phen)_2(H_2O)](NO_3)_2$ that the steric interference between H-

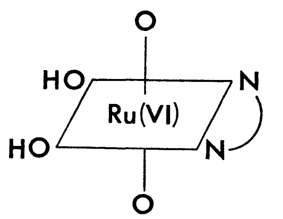

Fig. 8. The proposed structure of $[RuO_2(OH)_2bipy]$.

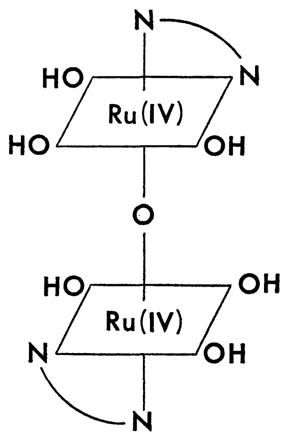

Fig. 9. The proposed structure of $[Ru(OH)_3phen]_2O$.

atoms linked to the 3- and 3′- or 2- and 9-carbon atoms might be removed by the tetrahedral distortion of the two 2,2′-bipyridine or 1,10-phenanthroline molecules respectively. This may be assumed to be a *trans*-configuration when the above consideration is applied to the present complexes, $[RuO_2bipy_2]$, $[RuO_2phen_2]$, and $[RuO_2bipy \cdot phen]$.

The structures shown in Figs. 8 and 9 seem clear possibilities for the two types of the present complexes. The oxidation number of $[RuO_2(OH)_2bipy]$ is assumed to be 6, and those of $[Ru(OH)_3phen]_2O$, $[RuO_2bipy_2]$, $[RuO_2phen_2]$ and $[RuO_2bipy \cdot phen]$, to be 4.

The author wishes to express his thanks to Professor Shinichi Kawaguchi of Osaka City University for his kind guidance and encouragement throughout this work, and to Professor Hideo Yamatera, the University of Nagoya, for his guidance in molecular orbital consideration. His thanks are also due to Dr. Tetsuo Mamuro, the chairman of the Department of Health Physics and Instrumentation of the Radiation Center of Osaka Prefecture, for his encouragement and support, to Dr. Toyokichi Kitagawa of Osaka City University for his guidance in the measurement of polarograph, and to Dr. Shichio Kawai, the University of Osaka, for his guidance in the measurement of the magnetic susceptibility.

18) Y. Deguchi and H. Nakai, Report of the 20th Symposium on the Chemistry of Metal Coordination Compd, p. 189 (1970).