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A Complex Formed by the Reaction of Ruthenium Tetroxide with 1,10-Phenanthroline in Carbon Tetrachloride

Toshio Ishiyama

Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka

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The synthesis and identification of the organic chelate compound of ruthenium in its higher oxidation states, for instance, Ru(IV), Ru(VI), Ru(VII), and Ru(VIII), are quite difficult since most organic compounds are oxidized by ruthenium tetroxide in the reaction mixture. Martin[1] obtained an interesting complex as an orange-brown precipitate by the reaction of ruthenium tetroxide with nitric oxide in carbon tetrachloride according to the following equation:

$$2RuO_4 + 8NO = Ru_2N_6O_{15} + N_2O$$

He suggested that it might be a nitrato complex containing two bis(nitrosyl)ruthenium groups linked by an oxo-bridge $[RuO_2(NO)_2NO_3]_2O$. Koda[2] reported obtaining an addition compound of ruthenium tetroxide with pyridine, $RuO_4\cdot 2C_5H_5N$, as greenish-black crystals in carbon tetrachloride.

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[1] F. S. Martin, J. M. Fletcher, P. G. M. Brown and B. M. Gattehouse, *J. Chem. Soc.*, **1959**, 76.

[2] Y. Koda, *Inorg. Chem.*, **2**, 1306 (1963).

A previous paper[3] reported obtaining a ruthenium tetroxide complex with 2,2′-bipyridine by the reaction of ruthenium tetroxide with 2,2′-bipyridine in carbon tetrachloride. In the present paper a binuclear complex of ruthenium(VII) will be reported, together with the electronic spectra of the previous complex, [RuO_4 bipy].

Experimental

Materials. Ruthenium(III) chloride monohydrate (extra pure grade) supplied by Mitsuwa Chemicals & Co. was used without further treatment, while commercial 1,10-phenanthroline was dried by heating it at 115°C for 3 hr and was then recrystallized from ethanol. The carbon tetrachloride was washed with a 1.5 per cent alcoholic solution of potassium hydroxide more than three times and repeatedly with pure water, and then distilled.

Preparation. *Ruthenium(VII) Oxide Complex with 1,10-Phenanthroline,* [Ru_2O_7 $phen_2$]. Ruthenium tetroxide in a nitric acid solution was prepared according to the method reported in a previous paper.[3] Ruthenium tetroxide in a nitric acid solution was extracted with carbon tetrachloride. To the organic solution, cooled in an ice bath, there was added a carbon tetrachloride solution of 1,10-phenanthroline. A dark green precipitate of the ruthenium(VII) oxide complex with 1,10-phenanthroline was separated immediately. After 20 hr, the precipitate was filtered, washed with carbon tetrachloride, and dried *in vacuo.* The mole ratio of 1,10-phenanthroline to ruthenium tetroxide employed in the reaction varied from 1:1 to 1:4, but the product obtained was the same in any case. The dried precipitate was dissolved in pure water, and an insoluble product was filtered off. After concentration on a hot water bath, the crystals formed were separated, recrystallized once again from water, and dried *in vacuo.* Yield: 10.2% on the basis of the ruthenium tetroxide. The complex is insoluble in carbon tetrachloride, chloroform, benzene, acetone, ether, ethanol, and acetic acid, but soluble in water and methanol.

The ruthenium content and the molecular weight of the complex were measured by a method reported previously.[3]

Found: Ru, 29.36; C, 42.60; H, 2.69; N, 8.41%; mol wt, 680. Calcd for [$Ru_2O_7(C_{12}H_8N_2)_2$]: Ru, 30.12; C, 42.62; H, 2.41; N, 8.21%; mol wt, 675.

Ruthenium(VIII) Oxide Complex with 2,2′-Bipyridine, [RuO_4 bipy]·$3H_2O$. This was synthesized according to the method reported in a previous paper.[3]

Found: Ru, 26.33; C, 31.07; H, 3.79; N, 7.80; H_2O, 15.00%; mol wt, 330. Calcd, for [$RuO_4(C_{10}H_8N_2)$]·$3H_2O$; Ru, 27.06; C, 31.81; H, 3.70; N, 7.46; H_2O, 14.70%; mol wt, 321 (anhydride).

Absorption Spectra. The infrared absorption spectra were obtained by the KBr disk method on a infrared spectrophotometer, Model IR-S, of the Japan Spectroscopic Co. The visible and ultraviolet absortion spectra were measured with a Beckmann Model DU spectrophotometer.

Magnetic Measurement. The mangetic susceptibility was measured at 27°C with a Gouy balance. The complex was found to be diamagnetic.

Results and Discussion

Composition of the Complex. From the results of the elemental analysis, the mole ratio of ruthenium to 1,10-phenanthroline was found to be 1:1. The observed molecular weight indicates that the complex is binuclear, [Ru_2O_7 $phen_2$].

Infrared Absorption Spectra. The main infrared absorption bands of the ruthenium(VII) oxide complex with 1,10-phenanthroline are shown in Table 1, together with those of the pure ligand. The C=N stretching peak is shifted to the higher frequency side by the ligation. This behavior is interpreted as an indication that the bond order of the carbon-nitrogen link is increased. The bands attributable to the C=C and C–H bonds are also shifted to the higher frequencies. Similar observations have also been reported for [Fe $phen_3$]Cl_2 and other phenanthroline complexes by Schilt and Taylor,[4] Inskeep,[5] and Busch and Bailor.[6]

TABLE 1. THE CHARACTERISTIC INFRARED ABSORPTION BANDS OF RUTHENIUM(VII) OXIDE COMPLEX WITH 1,10-PHENANTHROLINE (cm^{-1})

Assignment	phen	[Ru_2O_7 $phen_2$]
ν (C=N)	1621	1630
ν (C=C)	1585	1606
	1560	1575
ν (C–H)	762	775
	730	738

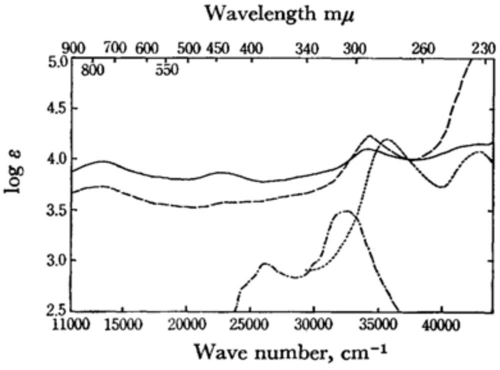

Fig. 1. Electronic absorption spectra of [RuO_4 bipy] and its components.

—— [RuO_4 bipy] in H_2O
—— [RuO_4 bipy] in CH_3OH
----- bipy in H_2O
-·-·- RuO_4 in H_2O

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[3] T. Ishiyama, Annual Report of the Radiation Center of Osaka Prefecture, **8**, 40 (1967).

[4] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

[5] R. G. Inskeep, *ibid.*, **24**, 763 (1962).

[6] D. H. Busch and J. C. Bailor, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).

Electronic Absorption Spectra. The visible and ultraviolet absorption spectra of ruthenium(VIII) and (VII) oxide complexes with 2,2′-bipyridine and 1,10-phenanthroline respectively were measured in water and methanol. They are shown in Figs. 1 and 2, together with those of pure ligands and ruthenium tetroxide in water.

The ruthenium(VIII) oxide complex with 2,2′-bipyridine has four absorption bands, at 740, 440, 292, and 245 mμ. A similar spectrum has also been reported by Koda[2] for bis(pyridine)ruthenium(VIII) oxide. The two peaks of a higher intensity observed in the visible region may both be assigned to the charge transfer from ligand to metal. The two absorption bands observed for ruthenium tetroxide have also been attributed to the charge transfer from oxygen to ruthenium.[7] The two peaks at 292 and 245 mμ can be assigned to the π_1 and π_2-bands respectively, corresponding to the 279 and 233 mμ bands in the 2,2′-bipyridine. The red-shifts of the π_1 and π_2-bands by ligation to ruthenium(VIII) can be explained as follows. The molecule of 2,2′-bipyridine has been proved by Fielding and LeFèvre,[8] and by Krumholz[9] to assume the *trans*-form in a neutral or basic aqueous solution and also in organic solutions. The facts that *trans*-bipyridine was changed to the *cis*-form, and that the π_1 and π_2-bands were shifted to a longer wavelength by coordination to a metal atom, were confirmed by Nakamoto[10] in the case of the tris-(2,2′-bipyridine)nickel(II) complex. The same effect must be felt in the present case of the ruthenium(VIII)-2,2′-bipyridine chelate.

In an aqueous solution of the ruthenium(VII) oxide complex with 1,10-phenanthroline, three absorption bands and a shoulder are observed at 685, 450, 264, and 315 mμ respectively. The two peaks of a higher intensity observed in the visible region may both be assigned to the charge transfer from ligand to metal. The first charge-transfer bands of [RuO_4 bipy] and [Ru_2O_7 phen$_2$] are observed in a region of wavelength longer than those of [Ru bipy$_3$]Cl_2 and [Ru phen$_3$]Cl_2 which were reported by Crosby *et al.*[11] These facts show that the charge-transfer transitions in Ru(VIII)-2,2′-bipyridine and Ru(VII)-1,10-phenanthroline chelates occur with a lower energy because the t_{2g} orbitals are not filled. A shoulder and a peak, observed at 315 and 264 mμ respectively, nearly coincide with the two absorption bands, at 320 and 265 mμ, of 1,10-phenanthroline. It should be noticed that the influence of ruthenium bonding on the spectrum of 1,10-phenanthroline is much less than in the case of 2,2′-bipyridine. The same situation was also observed in the case of mono-2,2′-bipyridine and mono-1,10-phenanthroline complexes of cobalt(II) and nickel(II) by Sone *et al.*[12]

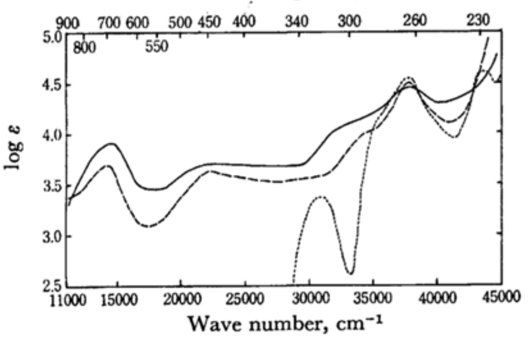

Fig. 2. Electronic absorption spectra of [Ru_2O_7-phen$_2$] and 1,10-phenanthroline.

—— [Ru_2O_7 phen$_2$] in H_2O
– – – [Ru_2O_7 phen$_2$] in CH_3OH
------ phen in H_2O

Magnetic Property. The measured molecular weight suggests that the ruthenium(VII) oxide complex with 1,10-phenanthroline is binuclear. The observed diamagnetism of the binuclear complex, [Ru_2O_7 phen$_2$], may be explained as follows. When the Ru(VII) ions, each containing one unpaired d electron, form the binuclear complex with an oxygen-bridge between ruthenium atoms (presumably linear), one electron from each Ru(VII) and two from the oxygen atom will be form two electron pairs occupying the lower two of the three center MO's. The molecular orbital treatments of $K_4Ru_2OCl_{10}$ and $[RuO_2(NO)_2NO_3]_2O$ which have been reported by Dunitz and Orgel[13] and by Martin *et al.*[1] can be applied to [Ru_2O_7-

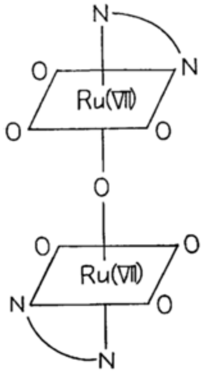

Fig. 3. The proposed structure of [Ru_2O_7 phen$_2$].

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7) D. S. McClure, *Solid State Phys.*, **9**, 507 (1959).

8) P. E. Fielding and R. J. W. LeFèvre, *J. Chem. Soc.*, **1951**, 1811.

9) P. Krumholz, *J. Am. Chem. Soc.*, **73**, 3487 (1951).

10) K. Nakamoto, *J. Phys. Chem.*, **64**, 1420 (1960).

11) G. A. Crosby, W. G. Parkins and P. M. Klasser, *J. Chem. Phys.*, **43**, 1498 (1965).

12) K. Sone, P. Krumholz and H. Stammreich, *J. Am. Chem. Soc.*, **77**, 777 (1955).

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

phen$_2$]. The structure thus proposed for the present complex is shown in Fig. 3; its oxidation number is assumed to be 7.

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