Chemically Significant Interactions between Ruthenium Ions in Oxo-Bridged Complexes of Ruthenium(III)[1]

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Abstract: A series of oxo-bridged complexes of ruthenium(III), $[(AA)_2XRuORuX(AA)_2]^{n+}$ (AA is 2,2′-bipyridine or 1,10-phenanthroline; X is Cl^-, NO_2^-, or H_2O), has been prepared. The formulation of the complexes as μ-oxo dimers of ruthenium(III) is based on the results of a variety of experiments, including elemental analyses, solution conductivity, and magnetism, and by their electron transfer properties. The chemical and electronic properties of the oxo-bridged dimers are unusual when compared to related bis(2,2′-bipyridine) complexes of ruthenium. From electrochemical studies in acetonitrile, the ion $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ can be oxidized to +4 and mixed-valence +3 (Ru(III)–Ru(IV)) ions and reduced to the mixed-valence (Ru(II)–Ru(III)) +1 ion. The +3 ion has been isolated as the salt $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$, and the results of an ESCA study indicate that the two ruthenium ions are equivalent. The chemical, spectral, and magnetic properties of the oxo-bridged ions can be interpreted by using a qualitative molecular orbital scheme, based on the assumption that strong, chemically significant interactions exist between the ruthenium ions through the bridging oxide ion ligand.

Transition metal systems in which metal ions or atoms are linked by a bridging ligand can differ significantly with regard to the nature and/or extent of metal–metal electronic interactions. Cases are known in which: (1) there is strong, direct metal–metal bonding; (2) strong metal–metal interactions exist, but through a bridging ligand; (3) weak metal–metal interactions exist, either through space or through a bridging ligand; (4) there is no evidence for metal–metal electronic interactions.

For nonorganometallic first-row transition metal ion systems, relatively weak metal–metal interactions are commonly found. The nature and extent of the interactions have been studied extensively using magnetic techniques. Although interactions do exist, the component ions usually have chemical and electronic properties similar to the properties expected for isolated monomeric complexes. In mixed-valence chemistry, systems which fall into class II in the Robin and Day classification scheme[2] also have relatively weak metal–metal interactions. For example, in mixed-valence ions like

and $[(C_5H_5)Fe(C_5H_4C_5H_4)Fe(C_5H_5)]^+$,[4] the available evidence indicates the presence of localized, integral oxidation states, and nonidentical metal centers.

In contrast to cases where there are weak metal–metal interactions, in compounds containing strong, direct metal–metal bonding, the constituent metal ions or atoms are significantly modified both chemically and electronically when compared to related monomeric complexes. The same strong modification in properties can also occur in ligand-bridged complexes if the metal–metal interaction across the bridging ligand is sufficiently strong. In principle, such systems constitute a new class of materials having distinct, and possibly synthetically controllable, chemical and electronic properties.

Well-characterized examples of compounds in which there are strong metal–metal interactions across a bridging ligand are uncommon. Oxo-bridged complexes, M–O–M, which have a short bridging distance with the possibility of strong π-overlap, would seem to be good candidates for this class. Griffith[5] has pointed out that oxo-bridged complexes of the first-row transition metal elements exhibit only weak metal–metal interactions, but that interactions seem to be much stronger for the second- and third-row metals.

We have prepared and characterized the oxo-bridged complexes of ruthenium(III), $[(AA)_2XRuORuX(AA)_2]^{n+}$ where AA is 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) and X is Cl^-, NO_2^-, or H_2O. The chemical and physical properties of the complexes are unusual when compared to related monomeric complexes and can be explained by invoking strong, chemically significant interactions between the ruthenium ions across the oxide ion bridge.

Experimental Section

Materials. All reagents and solvents used were reagent or spectral grade and were used without further purification. Reagent grade acetone was distilled from Drierite prior to use. The complexes $[Ru(bipy)_2Cl_2]$, $[Ru(phen)_2Cl_2]$, and $[Ru(bipy)_2(NO)Cl](PF_6)_2$ were prepared and purified by literature methods.[6]

Dichlorotetrakis(2,2′-bipyridine)-μ-oxo-diruthenium(III) Hexafluorophosphate, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$. The complex $[Ru(bipy)_2(NO)Cl](PF_6)_2$ (500 mg, 0.650 mmol) was dissolved in acetone (150 ml) in which potassium azide (53 mg, 0.650 mmol, 1.005 equiv) had been suspended. The mixture was stirred under a nitrogen atmosphere at 25° for 6 hr. The resulting solution of $[Ru(bipy)_2Cl(S)]^+$ (S = acetone)[7] was saturated with oxygen and stirred under 1 atm of oxygen, at room temperature, for 72 hr. After 72 hr the solution was filtered to remove KPF_6, and the product was precipitated by slow addition to rapidly stirred anhydrous diethyl ether (750 ml). The product was isolated by suction filtration and air dried. The resulting solid was purified by washing with small amounts of dichloromethane, until the wash was deep blue in color, followed by at least four reprecipitations from acetone (25 ml)–ether (250 ml). The blue-green powder which was obtained in 77% yield (300 mg), is soluble in acetone, acetonitrile, and dichloromethane, giving blue-green solutions. Elemental analyses and conductivity data for all complexes reported here are given in Table I.

The perchlorate and chloride salts of the complexes were prepared from the hexafluorophosphate salts. The additional salts were identified and analyzed by a quantitative comparison between their electronic spectra in acetonitrile solution and the spectrum of the corresponding hexafluorophosphate salt in solution. The chloride salt was prepared by dissolving the PF_6^- salt in a minimum amount of acetone followed by the addition of a saturated solution of tetra-n-butylammonium chloride in acetone. A precipitate formed immediately after the addition of Cl^- and was rapidly isolated by suction filtration, dried, and stored, in vacuo. The chloride salt was converted to the perchlorate salt by dissolving the Cl^- salt in a minimum amount of water, followed by the addition of a saturated aqueous solution of sodium perchlorate. The perchlorate salt, which precipitated rapidly, was isolated and air dried and then washed with several small portions of dichloromethane. The blue-green solid was then reprecipitated from acetone–ether, and dried, in vacuo.

Dichlorotetrakis(2,2′-bipyridine)-μ-oxo-diruthenium(III)(IV) Hexafluorophosphate, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$. The salt, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ (50 mg), prepared as above, was dissolved in dichloromethane (100 ml) at room temperature. Excess tetra-*n*-butylammonium hexafluorophosphate (2 g) was added, and the solution was filtered to remove any undissolved starting material. Chlorine gas, prepared and purified by the method described by Vogel,[8] was bubbled through the solution for ca. 5 min, during which time the solution changed from deep blue to brown, and a brown solid precipitated. The solid was collected by suction filtration, washed with dichloromethane and ether, and then dried, in vacuo.

Diaquotetrakis(1,10-phenanthroline)-μ-oxo-diruthenium(III) Perchlorate, $[(phen)_2(H_2O)RuORu(H_2O)(phen)_2](ClO_4)_4$. The salt was prepared in 86% yield by the method given by Dwyer, et al.[9] Dwyer and coworkers formulated the salt as containing a di-μ-hydroxy dimer, $[(phen)_2Ru(OH)_2Ru(phen)_2](ClO_4)_4{\cdot}3H_2O$. The procedure used was essentially identical with that given below for the preparation of the bipyridine analog, except that shorter reaction times were used. The dark microcrystalline product dissolves in water or acetonitrile giving intense green solutions.

Diaquotetrakis(2,2′-bipyridine)-μ-oxo-diruthenium(III) Perchlorate, $[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2](ClO_4)_4$. *cis*-Dichlorobis(2,2′-bipyridine)ruthenium(II) (2.00 g, 4.13 mmol) was suspended in water (80 ml) containing silver nitrate (1.76 g, 10.36 mmol, 2.51 equiv). The mixture was heated to reflux for 8 hr, then cooled to room temperature and centrifuged and the supernatant liquid filtered by suction onto a fine frit to remove silver chloride and silver metal. The filtrate was heated on a steam bath and treated with a saturated solution of sodium perchlorate until precipitation began to occur. Slow cooling to 0° produced the desired material, which was collected by suction filtration, washed with a small portion of cold water, and air dried. The salt could be recrystallized from hot water containing small amounts of $NaClO_4$, giving a dark microcrystalline solid and a deep green solution in water or acetronitrile. Yield was 1.51 g, or 56% of theoretical.

Dinitrotetrakis(2,2′-bipyridine)-μ-oxo-diruthenium(III) Perchlorate, $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](ClO_4)_2$. The salt $[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2](ClO_4)_4$ (0.500 g, 0.382 mmol) was heated for 30 min on a steam bath in aqueous solution (100 ml) containing excess sodium nitrite (2 g). The solution was cooled to room temperature and filtered to remove the red solid, $Ru(bipy)_2(NO_2)_2$, which had precipitated. The filtrate was rewarmed on a steam bath and treated with a saturated aqueous solution of sodium perchlorate until the onset of precipitation. Upon cooling, a deep blue microcrystalline solid formed, which was isolated by suction filtration, washed with small volumes of cold water, and dried, in vacuo. The hexafluorophosphate salt was obtained by treating a warm aqueous solution of the complex with a filtered saturated solution of NH_4PF_6. Both salts gave deep blue solutions in water or acetonitrile.

Dinitrotetrakis(1,10-phenanthroline)-μ-oxo-diruthenium(III) Perchlorate, $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$. The salt was prepared in 68% yield by the same method used for the corresponding bipyridine complex.

Reduction of $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ by Chromium(II). The reduction of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ by aqueous Cr^{2+} solutions was studied by spectrophotometric titrations. An approximately millimolar solution of $CrCl_3$ in 0.1 *M* aqueous HCl was reduced over zinc-mercury amalgam. The solution was prepared and stored under an atmosphere of prepurified nitrogen. Aliquots of the solution were measured volumetrically and transferred under an atmosphere of N_2 using schlenk tube and syringe techniques.[10] The Cr^{2+} solution was standardized by spectrophotometric titrations in 0.1 *M* HCl using $[Ru(bipy)_2Cl_2]^+$ as the oxidant. The reduced ruthenium product under these conditions is $[Ru(bipy)_2(H_2O)Cl]^+$, and the extent of reaction was determined by the appearance of the visible spectrum of this ion.[11] The oxidizing power of solutions of the ion $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ was determined using the standardized Cr^{2+} solution. Varying aliquots of the Cr^{2+} solution were added to aqueous solutions of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ ($\sim 10^{-4}$ *M*) and the spectra of the solutions were recorded. The spectral results showed that a smooth conversion of the dimer to $[Ru(bipy)_2(H_2O)Cl]^+$ occurred and that the stoichiometry of the reaction is (to ±10%),

$$[(bipy)_2ClRuORuCl(bipy)_2]^{2+} + 2Cr^{2+} + H_2O + 2H^+ \longrightarrow 2[Ru(bipy)_2(H_2O)Cl]^+ + 2Cr(III) \quad (1)$$

Spectrophotometric titrations were also carried out by dissolving $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ ($\sim 10^{-4}$ *M*) in 0.1 *M* HCl. Under these conditions, the dimer decomposes, giving a spectrum characteristic of $[Ru(bipy)_2Cl_2]^+$. Spectrophotometric titrations of the 0.1 *M* HCl solutions also show that 2 equiv of $Cr^{2+}(\pm 10\%)$ were required for complete reduction, giving $[Ru(bipy)_2(H_2O)Cl]^{2+}$.

Measurements. Infrared spectra were recorded on a Digilab FTS-14 Interferometer as KBr pellets or Nujol mulls. Electronic spectra were recorded in 1-cm matched quartz cells on a Cary Model 17-1R spectrophotometer. Extinction coefficients were determined from measurements at three or more concentrations.

Conductivities were determined in acetone solution at 25° using an Industrial Instruments, Inc., Model RC-16B1 conductivity bridge. Cell constants were determined at 25° from measurements of the conductivity of 0.0100 *M* aqueous solutions of potassium chloride.[12]

All electrochemical measurements were made in MCB spectrograde acetonitrile, which had been dried over activated Davison 4 Å molecular sieves before use. The supporting electrolyte was 0.1 *M* tetra-*n*-butylammonium hexafluorophosphate (TBAH), which was prepared by standard techniques,[13] recrystallized three times from hot ethanol–water mixtures, and vacuum dried at 100° for 12 hr. All measurements were made at platinum electrodes vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2° and are uncorrected for junction potentials. Standard three-electrode methods were used, employing a PAR Model 173 potentiostat/galvanostat, Model 175 Universal potential programmer, and Model 176 current-to-voltage converter. Potentials given are half-wave potentials measured by cyclic voltammetry and stirred solution voltammetry. The total number of equivalents of electrons transferred per equivalent of complex (*n*) in an exhaustive electrolysis at a constant potential was determined by measuring the total area under a current vs. time curve with a planimeter. Integral valves of *n* are reported when the average of several coulometry experiments is within 5% of that integer.

Variable temperature magnetic susceptibility measurements on $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$ and $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$ were taken with a PAR Foner-type vibrating sample magnetometer[14] calibrated with mercury tetrathiocyanatocobaltate(II).[15,16] Measurements were recorded in the temperature range 77–275°K at a field strength of 15,000 G. Room temperature magnetic susceptibility measurements on $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ were obtained using a Faraday balance, also calibrated with $Hg[Co(CN)_4]$.[15,16] Susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constants.[17]

EPR spectra of powders and solutions of the dimers, where solvents utilized included dichloromethane, chloroform, acetone, and acetonitrile, were measured on a Varian Model E-3 spectrometer. We were unable to observe EPR resonances for any of the dimers, either at room temperature or at 77°K.

ESCA spectra were obtained on solid samples of $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$, and $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$ using a Du Pont 650 B electron spectrometer. Two methods of mounting the samples in the electron spectrometer were used. When possible a small amount of the sample compound was ground into a gold sample probe tip using a glass rod. When this was not possible the sample was held onto the probe with Permacel P02 double sided tape. All photoelectron peaks are referenced to the carbon C 1s peak at 284.4 eV.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Table I. Elemental Analyses, Magnetic, and Solution Conductivity Data For the Oxo-Bridged Ruthenium Dimers

	Elemental analyses												
	Calcd					Found							
Compound	C	H	N	Cl	F	C	H	N	Cl	F	μ_{eff}[a]	Λ_0[b]	M[c]
$[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$	39.91	2.68	9.31	5.89		39.18	2.67	9.27	5.73		1.87	347	1828
$[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$	35.62	2.39	8.31			35.58	2.47	8.27					
$[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]$-$(PF_6)_2$	39.23	2.63	11.44		18.61	38.77	2.81	11.31		18.78	1.8	324	1865
$[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]$-$(ClO_4)_2 \cdot 4H_2O$	39.84	3.34	11.62			39.03	3.00	11.53					
$[(phen)_2(NO_2)RuORu(NO_2)(phen)_2]$-$(ClO_4)_2 \cdot 4H_2O$	44.28	3.10	10.76			43.88	2.90	11.06			1.8		
$[(phen)_2(H_2O)RuORu(H_2O)(phen)_2]$-$(ClO_4)_4$	41.04	2.78	7.98			41.86	2.81	8.22			1.7[d]		
$[(bipy)_2(H_2O)RuORu(H_2O)(phen)_2]$-$(ClO_4)_4$	36.71	2.77	8.56			39.17	2.89	9.71				480	3400
$[Ru(phen)_3](PF_6)_2$[e]												395	1900
$[(n\text{-}Bu)_4N](PF_6)$[f]												181	710

[a] Magnetic moment in Bohr magnetons at 298°K. [b] Molar conductivity at 25°. [c] Slope of $(\Lambda_0 - \Lambda_e)$ vs. $C_e^{1/2}$ plot. [d] From ref 9. [e] Standard 2:1 electrolyte for conductivity measurements. [f] Standard 1:1 electrolyte.

Results

Preparation and Characterization of the Oxo-Bridged Complexes. We have often observed intense blue-green colors appearing in solutions of bis(bipyridine)ruthenium(II) complexes when exposed to the air for a period of days. In searching for a preparative route to pure samples of the blue-green materials, we have exploited the reaction between azide ion and nitrosyl bis(2,2′-bipyridine) complexes of ruthenium(II).[7] The products of the reaction are solvent complexes in which there is a single labile coordination site, e.g., eq 2.[7] When red-brown solutions of the acetone complex are exposed to oxygen for a period of 3 days at room temperature, an intense blue-green solution results (reaction 3) from which a dark green, powdery solid was isolated. The dark green solid has been characterized as the salt $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ by a variety of experimental techniques described below, including elemental analysis (Table I).

$$[Ru(bipy)_2(NO)Cl](PF_6)_2 + KN_3 + S \xrightarrow[(S = acetone)]{} [Ru(bipy)_2Cl(S)]^+ + N_2O + N_2 + KPF_6 + PF_6^- \quad (2)$$

$$2[Ru(bipy)_2Cl(S)]^+ + \tfrac{1}{2}O_2 \xrightarrow{acetone} [(bipy)_2ClRuORuCl(bipy)_2]^{2+} \quad (3)$$

The solid was shown to be a 2:1 electrolyte by conductivity measurements. Feltham and Hayter[18] have shown that plots of the equivalent conductivity vs. the square root of the equivalent concentration are linear with slopes which depend upon the electrolyte type. Equivalent conductivities (Λ_e) were determined by the formula

$$\Lambda_e = \left(\frac{1}{R} - \frac{1}{R_s}\right)\frac{1000k}{C_e} \quad (4)$$

where R is the solution resistance, R_s is the resistance of pure solvent, k is the cell constant, and C_e is the equivalent concentration. In this case the equivalent weight is the mass in grams per equivalent of mononegative anion. This last number can be determined experimentally from the elemental analysis results (Table I). Figure 1 shows plots of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ for three complexes in acetone at 25°: $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$; $[Ru(phen)_3](PF_6)_2$, a standard 2:1 electrolyte; and $[(n\text{-}C_4H_9)_4N](PF_6)$, a standard 1:1 electrolyte. Λ_0 is obtained by extrapolation of a plot of Λ_e vs. $C_e^{1/2}$ to infinite dilution. Plots of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ are useful since they have common intercepts. The slope of the $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ plot for $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ is nearly identical with that of the standard 2:1 electrolyte. Thus, the conductivity data clearly show that the dark green solid is a 2:1 electrolyte, and therefore it must be dimeric. Electrochemical results shown below are also consistent with the dimer formulation, since one electron is transferred per two ruthenium ions in both net oxidation and reduction processes.

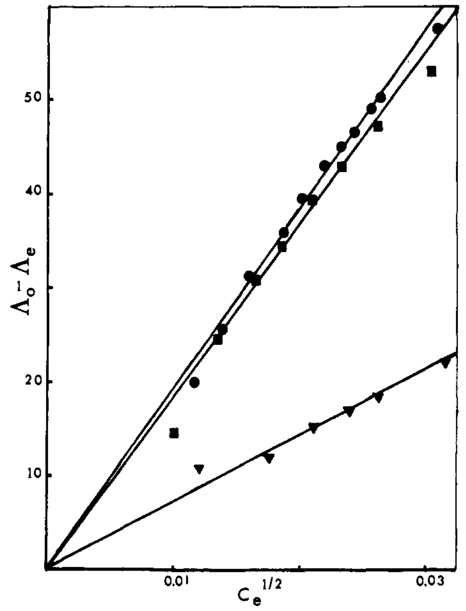


Figure 1. Plots of $(\Lambda_0 - \Lambda_e)$ vs. $C_e^{1/2}$ from conductivity data in acetone at 25° for $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ (■), $[Ru(phen)_3](PF_6)_2$ (●), and $[(n\text{-}Bu)_4N](PF_6)$ (▲).

The salt $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ is paramagnetic at room temperature, with a moment of 1.87 BM per ruthenium ion. The observed moment is consistent with each ruthenium being a ruthenium(III) ion in the low spin $4d^5$ configuration expected for complexes of ruthenium(III).[19]

The dark green solid, then, is a dimeric 2:1 hexafluorophosphate salt of ruthenium(III). Considering the elemental analyses, and for reasons of charge balance, the bridging ligand must be bidentate and must have a −2 charge. Because of the method of preparation (reaction 3), the bridging ligand must be a reduction product of O_2. The reaction between the dimeric complex and Cr^{2+} was studied by spectrophotometric titrations. Two moles of Cr^{2+} were consumed per mole of dimer, and the ruthenium product was shown to be $[Ru(bipy)_2(H_2O)Cl]^{2+}$. The net reaction is

$$[(bipy)_2ClRuORuCl(bipy)_2]^{2+} + H_2O + 2H^+ + 2Cr^{2+} \longrightarrow 2[Ru(bipy)_2(H_2O)Cl]^+ + 2Cr(III) \tag{1}$$

The 2:1 Cr^{2+}-dimer stoichiometry rules out a peroxide-bridged dimer, $[(bipy)_2ClRuO_2RuCl(bipy)_2]^{2+}$, since, in that case, 4 mol of Cr^{2+} should have been consumed per mole of dimer.

The salt $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ is fairly stable, but care must be taken when handling it in solution. Slow decomposition is observed in the presence of acid or halide ion, and the effect of having them both present is to enhance the rate of decomposition. Spectral evidence indicates that in dilute, aqueous hydrochloric acid, the oxo-bridged ion is rapidly converted into $[Ru(bipy)_2Cl_2]^+$ (reaction 5).

$$[(bipy)_2ClRuORuCl(bipy)_2]^{2+} + 2HCl \longrightarrow 2[Ru(bipy)_2Cl_2]^+ + H_2O \tag{5}$$

The isolation and characterization of $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ has led to the preparation of a series of oxo-bridged ruthenium dimers, as described in the Experimental Section and below. All of the complexes were obtained as PF_6^- or ClO_4^- salts, and analyzed and characterized in essentially the same manner as described above. Table I gives elemental analysis, magnetic susceptibility, and conductivity data for the salts prepared.

The oxidation of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ by Ce(IV) in acetonitrile was followed spectrophotometrically. The complex was oxidized smoothly and cleanly (isosbestic points at 364, 425, and 523 nm) by 1 equiv of cerium(IV) to the mixed-valence, μ-oxo-ruthenium(III)-ruthenium(IV) dimer,

$$[(bipy)_2ClRuORuCl(bipy)_2]^{2+} + Ce(IV) \longrightarrow [(bipy)_2ClRuORuCl(bipy)_2]^{3+} + Ce(III) \tag{6}$$

The PF_6^- salt of the mixed-valence ion, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$, was isolated by the oxidation of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ by chlorine in dichloromethane which contained excess tetra-*n*-butylammonium hexafluorophosphate. The oxidation is rapid and the PF_6^- salt precipitates from the solution after oxidation. We have obtained good elemental analysis results for the mixed-valence salt but it is not particularly stable, even in the solid state, and cannot be stored for long periods of time.

Dwyer and coworkers[9] have isolated a deep blue, dimeric salt of ruthenium(III), which they identified, solely on the basis of elemental analysis and conductivity data, as containing a di-μ-hydroxy complex, $[(phen)_2Ru(OH)_2Ru(phen)_2](ClO_4)_4 \cdot 3H_2O$. Using Dwyer's procedure, we have prepared both this and the analogous 2,2′-bipyridine salt. From elemental analysis, solution conductivity, and magnetic data, it is impossible to distinguish between the di-μ-hydroxy formulation, favored by Dwyer and coworkers, and a μ-oxo-bridged formulation, e.g., $[(phen)_2(H_2O)RuORu(H_2O)(phen)_2](ClO_4)_4 \cdot 2H_2O$. In aqueous solution, spectral and conductivity data indicate that the ion $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ is slowly (∼2 hr) converted into the 2,2′-bipyridine analog of Dwyer's complex (reaction 7). When heated in aqueous solution containing excess sodium nitrite, both the 1,10-phenanthroline and 2,2′-bipyridine complexes are converted into nitro complexes (reaction 8) which have been isolated and characterized as the perchlorate salts, $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](ClO_4)_2$ and $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$. The solution reactivity of the Dwyer complex and its 2,2′-bipyridine analog, and the similarity in their electronic spectra to the oxo-bridged dimers (see below), suggest that they can better be formulated as the diaquo-μ-oxo complexes, $[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+}$ and $[(phen)_2(H_2O)RuORu(H_2O)(phen)_2]^{2+}$.

$$[(bipy)_2ClRuORuCl(bipy)_2]^{2+} + 2H_2O \longrightarrow [(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+} + 2Cl^- \tag{7}$$

$$[(AA)_2(H_2O)RuORu(H_2O)(AA)_2]^{4+} + 2NO_2^- \longrightarrow [(AA)_2(NO_2)RuORu(NO_2)(AA)_2]^{2+} + 2H_2O \tag{8}$$

AA = 2,2′-bipyridine or 1,10-phenanthroline

The nitro complexes are stable in solution for long periods of time and can be recrystallized from hot water containing small amounts of nitrite ion and perchlorate ion.

Electrochemistry. The electrochemistry of the oxo-bridged ions, $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ and $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{2+}$, was studied by cyclic voltammetry, stirred solution voltammetry, and coulometry using platinum electrodes in acetonitrile containing 0.1 *M* TBAH as the supporting electrolyte. Potentials reported here are $E_{1/2}$ values vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2°. When possible, the electrochemical reversibility of the reactions was determined from stirred-solution voltammetry experiments by determining the slopes of plots of log $(i_l - i)/i$ vs. E for the electrode reactions. In cases where decomposition of the oxidized or reduced products was evident in stirred solution voltammograms, reversibility was determined by the peak separations (ΔE_p) and the ratio of the anodic to cathodic peak currents ($i_{p,a}/i_{p,c}$) of cyclic voltammograms. Under our experimental conditions, the reversible couple $[Ru(bipy)_2Cl_2]^+$-$[Ru(bipy)_2Cl_2]$ had $\Delta Ep \sim 65$ mV, which was used as the criterion for electrochemical reversibility. This value is slightly higher than the theoretical value of 59 mV, probably due to uncompensated solution resistance. Since the voltammetric or cyclic voltammetric waves are electrochemically reversible, the $E_{1/2}$ values are approximately the standard reduction potentials, neglecting a small correction term involving diffusion coefficient ratios.[20]

In Figure 2 cyclic voltammograms for $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ are shown. The oxidation-reduction properties of the ion and relevant $E_{1/2}$ data are summarized in Scheme I, where the notation $RuORu^{n+}$ is used for $[(bipy)_2ClRuORuCl(bipy)_2]^{n+}$ for simplicity. The letter designation A, B, and C in Scheme I refers to the various cyclic voltammetric waves in Figure 2. In addition to the waves shown in Figure 2 there is an additional one-electron oxidation wave at $E_{1/2} = 1.91$ V ($\Delta E_p = 80$ mV). At 0.68 V, the +2 ion undergoes a chemically and electrochemically reversible one-electron oxidation, giving the mixed-valence

Scheme I

$$\begin{array}{cccccccc} & & & \mathrm{A} & & \mathrm{B} & & \mathrm{C} \\ \mathrm{RuORu^{4+}} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{RuORu^{3+}} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{RuORu^{2+}} & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{RuORu^{+}} & \xrightarrow{+e^-} \\ & +1.91\ \mathrm{V} & & +0.68\ \mathrm{V} & & -0.32\ \mathrm{V} & & -1.0\ \mathrm{V} \\ & & & \multicolumn{5}{r}{\mathrm{RuORu} \longrightarrow \text{decomposition products}} \end{array}$$

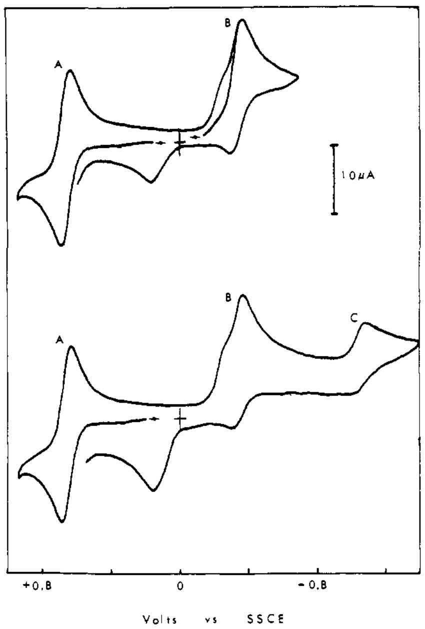


Figure 2. Cyclic voltammograms of $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ in 0.1 *M* TBAH-acetonitrile at Pt vs. the SSCE (25 ± 2°). Scan rate is 200 mV/sec.

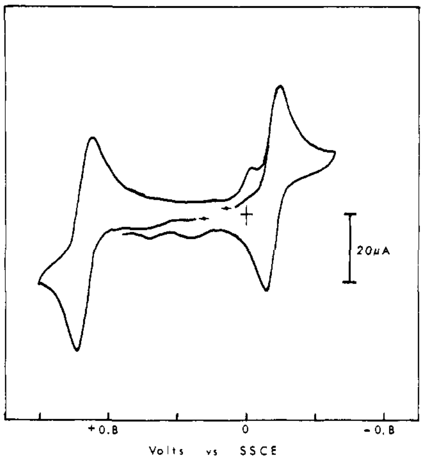


Figure 3. Cyclic voltammogram of $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$ in 0.1 *M* TBAH-acetonitrile at Pt vs. the SSCE (25 ± 2°). Scan rate is 200 mV/sec.

ion $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$. Coulometry measurements at 0.80 V gave $n = 1$ for the net electrochemical oxidation. The solution resulting from this oxidation has an electronic spectrum identical with that of acetonitrile solutions of the +3 ion prepared in situ by Ce(IV) oxidation (and was also identical with the spectrum of the PF_6^- salt of the ion isolated after chlorine oxidation). The oxidized solution can be quantitatively reduced electrochemically ($n = 1$) giving back $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$. Cyclic voltammograms of solutions of the mixed-valence salt, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$, were identical with the voltammogram shown in Figure 2, and exhaustive electrolysis at 0.55 V gave $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ quantitatively ($n = 1$). As shown by cyclic voltammetry, the +3 ion undergoes a further one-electron oxidation to give the +4 ion, $(bipy)_2ClRuORuCl(bipy)_2{}^{4+}$.

The cyclic voltammogram of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ also has two reduction waves. The one-electron reduction at −0.32 V is electrochemically reversible on the time scale of cyclic voltammetry; however, exhaustive electrolysis at slightly lower potentials gave complete conversion of ruthenium(III) to ruthenium(II), followed by decomposition of the Ru-O-Ru dimeric structure. A second reduction wave occurs near −1.0 V ($E_p = -1.0$ V). This wave is irreversible and also leads to decomposition of the dimeric structure yielding $[Ru(bipy)_2(CH_3CN)Cl]^{2+}$, $[Ru(bipy)_2(CH_3CN)_2]^{2+}$, and other unidentified products.

Figure 3 shows a cyclic voltammogram of an acetonitrile solution of $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{2+}$. The oxidation-reduction properties of the +2 nitro complex are similar to those of the +2 chloro complex, except that, for the nitro complex, the potentials of all three-electrode reactions are shifted anodically. There is also a further irreversible oxidation at ~2.2 V. The oxidation at +0.94 V is reversible on the time scale of voltammetry, but exhaustive electrolysis at 1.0 V gave n values greater than one. The mixed-valence ion, $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{3+}$, which is the initial one-electron oxidation product, undergoes a slower, subsequent reaction. This slow reaction is a common feature in the oxidation chemistry of ruthenium nitrite complexes and is currently under investigation. The ion $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{2+}$ also undergoes two electrochemical reductions. The first is a one-electron reduction at −0.15 V. It is electrochemically reversible on the voltammetry time scale, but exhaustive electrolysis at −0.2 V led to the decomposition of the dimer, as happened to the chloro complex. The second reduction occurs at about −0.75 V. This reduction is irreversible and gives a variety of products in acetonitrile solution.

The oxidation-reduction properties of the oxo-bridged dimers are quite different from the properties of related, monomeric bis(2,2′-bipyridine)ruthenium complexes.[21] As an example, $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ undergoes a reversible one-electron oxidation at 0.68 V, giving the mixed-valence ion $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$ which contains ruthenium in the formal +4 oxidation state. In acetonitrile, the Ru(III) ion $[Ru(bipy)_2Cl_2]^+$ is oxidized, but at a much higher potential, $E_{1/2} = 1.98$ V.[21] It is also interesting to note that $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ is a remarkably poor oxidant when compared to other bis(2,2′-bipyridine)ruthenium(III) complexes. Reduction of the +2 ion to the mixed-valence +1 ion, $[(bipy)_2ClRuORuCl(bipy)_2]^+$, containing ruthenium in the +2 formal oxidation state, is ~0.6 V more cathodic than the reduction of $[Ru(bipy)_2Cl_2]^+$ under identical conditions.[11,21]

$$[Ru(bipy)_2Cl_2]^+ + e \longrightarrow Ru(bipy)_2Cl_2 \qquad (9)$$

Ultraviolet-Visible Spectra. The electronic spectra of the oxo-bridged ruthenium(III) complexes show several interesting features. Table II lists absorbance maxima and extinction coefficients for each of the complexes. For comparison purposes, the spectra of some other bis(α,α′-diimine)ruthenium(II) and -ruthenium(III) complexes are also given in Table II. The high intensity, low energy band at about 650 nm is characteristic of the oxo-bridged dimers reported here, and gives them their intense blue or blue-green color. The 2,2′-bipyridine and 1,10-phenanthroline complexes of ruthenium(II) and ruthenium(III) have been widely studied, and their electronic spectra are well-characterized.[21-23] These high intensity, low energy bands are unique.

Ruthenium(II) complexes exhibit strong, metal-to-bipyridine, charge transfer bands in the visible region (e.g., the bands at 553 and 380 nm for $Ru(bipy)_2Cl_2$, see Table II). The analogous ruthenium(III) complexes exhibit weaker absorbances, generally only shoulders, in the visible region.

Table II. Electronic Spectral Data in Acetonitrile

Compound	λ_{max} (nm)[a]	ϵ[b]
$[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$	672	17,900
	289	39,000
	244	65,900
$[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$	470	19,700
	300	46,000
	246	42,000
$[(bipy)_2(H_2O)RuORu(H_2O)(bipy)_2]^{4+}$	660	25,000
	410	9,500
	284	53,000
	244	38,000
$[(phen)_2(H_2O)RuORu(H_2O)(phen)_2]^{4+}$	660	17,600
	264	87,000
$[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{2+}$	632	25,700
	284	48,900
	244	38,400
$[(phen)_2(NO_2)RuORu(NO_2)(phen)_2]^{2+}$	640	25,300
	264	88,000
$[Ru(bipy)_2Cl_2]$[c]	553	9,100
	380	8,850
	297	50,000
	243	21,000
$[Ru(bipy)_2Cl_2]^{+}$[c]	380	5,650
	310	22,400
	298	24,800
$[Ru(bipy)_2(CH_3CN)Cl]^{+}$[c]	480	6,740
	345	7,110
	292	50,700
	243	18,550
$[Ru(bipy)_2(CH_3CN)Cl]^{2+}$[d]	425	

[a] ±2 nm. [b] ±5%. [c] J. N. Braddock and T. J. Meyer, *Inorg. Chem.*, 12, 723 (1973). [d] R. W. Callahan unpublished results.

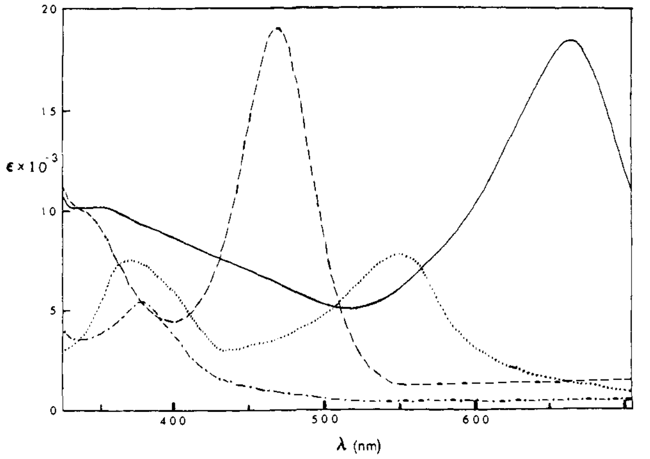


Figure 4. Visible spectra in acetonitrile: (——) $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$; (- - -) $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$; (· · ·) $Ru(bipy)_2Cl_2$; (–·–·–) $[Ru(bipy)_2Cl_2]^{+}$.

For comparison purposes, Figure 4 shows the visible spectra of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$, $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$, $[Ru(bipy)_2Cl_2]^{+}$, and $Ru(bipy)_2Cl_2$ in acetonitrile. The strong, low energy band (λ_{max} 668 nm, ϵ 17,000) for $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ is considerably blue shifted (λ_{max} 470 nm, ϵ 20,000) for the +3, one-electron oxidized, ion. It is interesting to note that the oxo-bridged complexes, while lacking the distinct charge transfer bands of the normal bis(bipyridine)ruthenium(II) complexes in the visible region, show considerably stronger absorbances in the 350–550-nm region than the bis(bipyridine) complexes of ruthenium(III) (see, for example, the spectrum of $[Ru(bipy)_2Cl_2]^{+}$ in Figure 4).

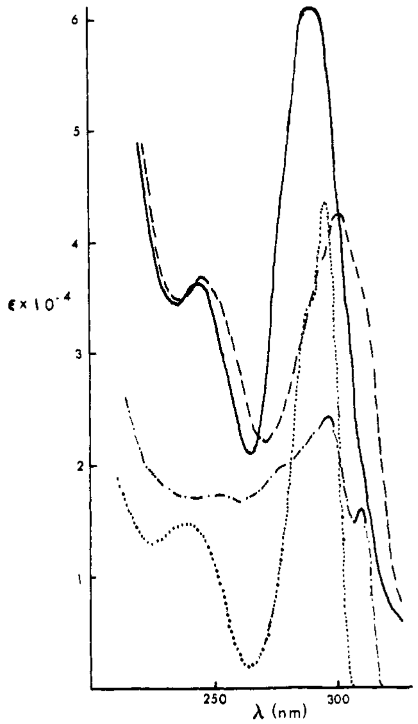


Figure 5. Ultraviolet spectra in acetonitrile: (——) $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$; (- - -) $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$; (· · ·) $Ru(bipy)_2Cl_2$; (–·–·–) $[Ru(bipy)_2Cl_2]^{+}$.

The ultraviolet spectra of the complexes are also informative. Figure 5 shows the electronic spectra, in the ultraviolet region, for the same four complexes in acetonitrile. A strong charge transfer band, assigned to a bipyridine $\pi \rightarrow \pi^*$ transition, occurs at about 300 nm in the ruthenium complexes. The position of this band depends upon the formal oxidation state of the ruthenium ion.[21] In ruthenium(II) complexes the band commonly occurs in the region 285–295 nm. Upon oxidation to ruthenium(III), the band is usually red-shifted to 300–310 nm, split into two bands, and considerably reduced in intensity. The ultraviolet spectrum of $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ is very similar to the spectra commonly observed for ruthenium(II) complexes (λ_{max} 289, ϵ 65,000), while the spectrum of $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$ is different from the spectra of both the ruthenium(II) and ruthenium(III) complexes (λ_{max} 300 nm, ϵ 46,000).

Magnetic Data. The oxo-bridged complexes reported here are paramagnetic at room temperature, with moments of approximately 1.8 BM per ruthenium ion, the value expected for one unpaired electron per ruthenium. Variable temperature magnetic susceptibility measurements were made on the salts $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$ and $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$. The magnetic susceptibility of the 2,2′-bipyridine salt displays a maximum value at about 155°K, while the susceptibility of the 1,10-phenanthroline salt shows the same effect at about 110°K.

The systems were treated as consisting of a ground state singlet with a low-lying triplet state. The temperature dependence of the magnetic susceptibility for such a case is given by the Bleaney–Bowers equation[24] (10); where $2J$ is

$$X_M = \frac{Ng^2B^2}{3kT} 1 + \frac{1}{3} \exp(-2J/kT)^{-1} \qquad (10)$$

the energy separation between the singlet ground state and the triplet excited state, and where X_M is the molar susceptibility calculated per metal ion. The other constants have their usual meaning. A linear least-squares fitting routine

Table III. Ruthenium $3d_{5/2}$ Binding Energies

Compound	Ru $3d_{5/2}$, eV
$Ru(bipy)_2Cl_2$	279.9
$[Ru(bipy)_2Cl_2]Cl$	281.9
$[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$	280.5
$[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](ClO_4)_2$	280.5
$[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$	282.3

was utilized to determine the parameters g and $2J$ for each set of magnetic data. The experimental susceptibilities and theoretical curves generated by eq 10 with the best fit parameters for $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$ and $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$ are shown in Figures 6 and 7, respectively.

For the bipyridine complex, calculated parameters of $2J = -173\ cm^{-1}$ with $g = 2.48$ provided an excellent fit to the experimental results. Typically, g values for ruthenium(III) which have been reported are highly anisotropic, with average values varying widely from about 2.30 to well below 2.0.[25-28] The calculated g of 2.48 from the dimer susceptibility equation (10) is above the usual ruthenium(III) range, but the anisotropy associated with these systems suggests that a $\langle g \rangle = 2.48$ is not an unreasonable value. The Bleaney-Bowers fit of the experimental susceptibility data for $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$ gave as the best fit values, $g = 2.29$ and $2J = -119\ cm^{-1}$.

We have been unable to observe EPR signals for the dimers as powders at either room temperature or 77°K. Also no EPR signals have been observed in dichloromethane, chloroform, acetone, or acetonitrile solutions either at room temperature or in frozen solutions at 77°K. It has been pointed out[25] that the rapid lattice relaxation in low spin d^5 systems necessitates low temperatures to observe any EPR absorptions, which may explain our failure to obtain EPR results.

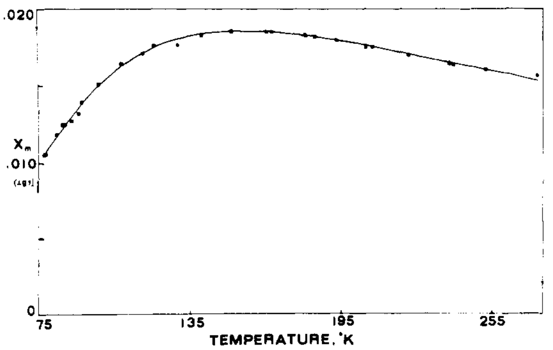


Figure 6. The temperature dependence of the magnetic susceptibility of $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$. The solid curve is the best fit of eq 10 to the experimental data which are depicted as solid squares.

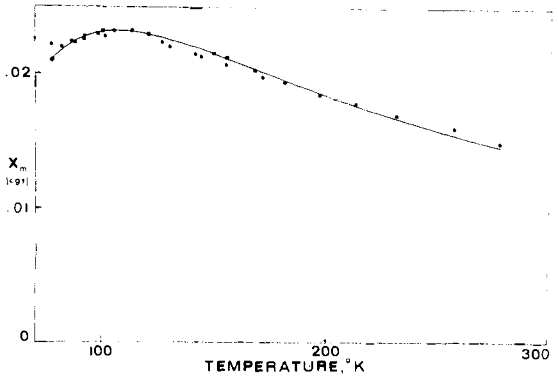


Figure 7. The temperature dependence of the magnetic susceptibility of $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2](ClO_4)_2$. The solid curve is the best fit of eq 10 to the experimental data which are depicted as solid squares.

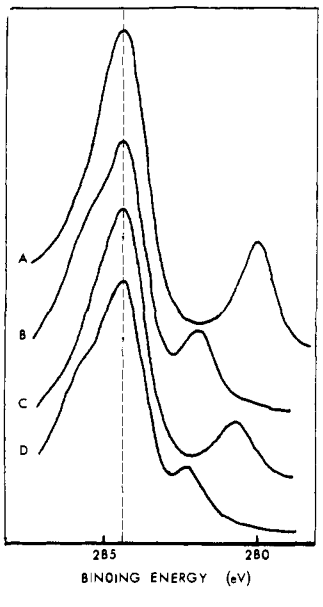


Figure 8. X-Ray photoelectron emission spectra. A, $Ru(bipy)_2Cl_2$; B, $[Ru(bipy)_2Cl_2]Cl$; C, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$; D, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$. The C 1s reference peak is defined as 284.4 eV in all cases.

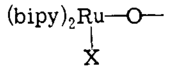
ESCA Spectra. X-Ray photoelectron data were taken in the range 272-292 eV with a DuPont 650 B electron spectrometer using Mg Kα X-radiation. Peaks occur in this region due to ruthenium (Ru $3d_{3/2}$ and Ru $3d_{5/2}$) and carbon (C 1s) electron transitions. All binding energies reported were measured relative to an arbitrarily assigned value of 284.4 eV for the C 1s peak due to the bipyridine carbons.[29] The absolute binding energies varied somewhat from sample to sample due to surface charging effects. In Figure 8, X-ray photoemission spectra are presented for $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ and $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$ and for the compounds $[Ru(bipy)_2Cl_2]Cl$ and $Ru(bipy)_2Cl_2$ which were chosen as standards. Binding energies for the Ru $3d_{5/2}$ peaks of these four compounds and for $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](ClO_4)_2$ are listed in Table III. The binding energies for the ruthenium(II) compound, $Ru(bipy)_2Cl_2$, and for the ruthenium(III) salt, $[Ru(bipy)_2Cl_2]Cl$, are in good agreement with the values for Ru(II) and Ru(III) found by other workers.[29,30] Two interesting observations can be made from the ESCA spectra of the oxo-bridged dimers. The first is that the Ru $3d_{5/2}$ binding energy for both $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ and $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](ClO_4)_2$ is 280.5 eV. Though both of the salts are formally ruthenium(III), the Ru $3d_{5/2}$ binding energies of the two salts are much closer to the value expected for ruthenium(II) (279.9 eV for $Ru(bipy)_2Cl_2$) than to the value expected for ruthenium(III) (281.9 eV for $[Ru(bipy)_2Cl_2]Cl$). Secondly, the X-ray photoemission spectrum for $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$ indicates that splitting or broadening of the ruthenium peaks is small or nonexistent. ESCA spectra, obtained by us and others,[29] for ruthenium(II) and ruthenium(III) ammines, where interference from C 1s peaks is not a problem, indicate that the Ru $3d_{3/2}$ and Ru $3d_{5/2}$ peaks are separated by 4.1 ± 0.1 eV. Assuming the same separation for the complexes reported here, splitting or broadening of the Ru $3d_{3/2}$ and Ru $3d_{5/2}$ peaks for $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$ due to the presence of two different ruthenium ions cannot be accommodated by the observed spectrum. Although the +3 dimer is a mixed-valence case, and in the formal sense contains ruthenium in both the +3 and +4 oxidation states, the ESCA data indicate that the two ruthenium centers are equivalent, or nearly equivalent.

Other Measurements. Hewkin and Griffith[31] and Wing and Callahan[32] have commented on characteristic vibrational spectra of oxo-bridged metal complexes. For linear M-O-M species, an infrared active, asymmetric stretch is found in the range 800-900 cm^{-1}. Bending of the M-O-M linkage lowers the asymmetric stretching frequency, in some cases to as low as about 750 cm^{-1}. Bending can also make the symmetric stretch infrared active and raise the frequency from 200 to about 500 cm^{-1}. Attempts were made to identify characteristic M-O-M stretching frequencies for the oxo-bridged dimers reported here. Hexafluorophosphate anion absorbs strongly in the infrared in the region 800-900 cm^{-1}, and so perchlorate or chloride salts of all complexes reported here were prepared for infrared studies. Infrared spectra of Nujol mulls and KBr pellets showed no bands in any of the complexes that could be unequivocably assigned to an M-O-M stretch. The 800-900-cm^{-1} region is free of strong ligand vibrations for the bipyridine complexes.[33] No new bands with significant intensities were found in this region for the oxo-bridged complexes. Below 800 cm^{-1}, very strong ligand vibrations occur for 2,2′-bipyridine and 1,10-phenanthroline. In some of the oxo-bridged dimers, small bands or shoulders not present for monomeric Ru(II) and Ru(III) bipyridine or phenanthroline complexes appear in the spectra. However, definite band assignments could not be made.

Discussion

The results of a variety of experiments support the view that the compounds reported here are the dimeric, oxo-bridged complexes of ruthenium(III), $[(AA)_2XRuORuX(AA)_2]^{n+}$ (AA is bipy or phen; X is Cl^-, NO_2^-, or H_2O). The elemental analysis and solution conductivity data are consistent with the dimer formulation, as is the electrochemical data, since one electron is transferred per two ruthenium ions in each oxidation or reduction step. The magnetic data and the results of the spectrophotometric titration by Cr^{2+} are consistent with ruthenium(III). The latter experiment also rules out a peroxo bridge between the ruthenium ions. Infrared bands for the M-O-M asymmetric stretch are not found in the range 800-900 cm^{-1} but may be at lower energies. Unequivocal band assignments cannot be made because of strong ligand absorptions.

In the μ-oxo complexes, the X groups are almost certainly cis to the bridging oxide ion;[9,34]



$$\underset{\displaystyle X}{(bipy)_2\overset{}{Ru}}—O—$$

The absence of a band attributable to the asymmetric M-O-M stretch may indicate that the Ru-O-Ru linkage is significantly bent with the Ru-O-Ru angle less than 180°. However, molecular models show that the value of the Ru-O-Ru angle is somewhat restricted because of the bulkiness of the 2,2′-bipyridine and 1,10-phenanthroline ligands.

Properties of the Oxo-Bridged Complexes. The chemical and electronic properties of the oxo-bridged complexes are remarkable when compared to related complexes of bis(2,2′-bipyridine)ruthenium(II) and -(III).

(1) The mixed-valence ion $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$ and the +4 ion $[(bipy)_2ClRuORuCl(bipy)_2]^{4+}$ contain, in the formal sense, ruthenium in the +4 oxidation state. The +3 ion can be generated from $[(bipy)_2ClRuORuCl(bipy)_2]^{2+}$ at reasonable potentials in acetonitrile ($E_{1/2}$ = 0.68 V). In an electrochemical study of over 50 bis-2,2′-bipyridine complexes of ruthenium, only one other case[21] of Ru(IV) as an accessible oxidation state has been found up to the anodic limits of the medium (>2.0 V).[35]

(2) To our knowledge, the oxo-bridged nitrite complexes, $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2]^{2+}$ and $[(phen)_2(NO_2)RuORu(NO_2)(phen)_2]^{2+}$, are the first known examples of stable ruthenium(III) nitrite complexes.

(3) In other cases involving ligand-bridged dimers, e.g., $[(bipy)_2ClRu(pyrazine)RuCl(bipy)_2]^{2+}$ [36] and $[(bipy)_2Ru(NO_2)_2Ru(bipy)_2]^{2+}$,[37] the Ru(II)-Ru(II) dimers are reasonably stable in acetonitrile. Reduction of the oxo-bridged Ru(III)-Ru(III) dimers in acetonitrile results in the decomposition of the dimeric unit giving monomeric products, $Ru(bipy)_2(CH_3CN)Cl^+$ and $Ru(bipy)_2(CH_3CN)_2^{2+}$.

(4) In comparing $E_{1/2}$ values, it is apparent that the +2 dimeric ions are remarkably poor oxidants when compared to related bis(2,2′-bipyridine)ruthenium(III) ions, e.g.

$$[(bipy)_2ClRuORuCl(bipy)_2]^{2+} + e \longrightarrow [(bipy)_2ClRuORuCl(bipy)_2]^{+} \quad E_{1/2} = -0.32\ V$$

$$Ru(bipy)_2Cl_2^{+} + e \longrightarrow Ru(bipy)_2Cl_2{}^{11,21} \quad E_{1/2} = 0.30\ V$$

(5) The electronic spectra of the complexes are unusual because of the presence of high intensity, low energy bands (Figure 4). For the mixed-valence ion, $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$, the band is considerably blue shifted (from λ_{max} 668 nm for the +2 ion to 470 nm for the +3 ion), and the intensity remains high. Such highly intense, low energy bands are not observed for other bis(2,2′-bipyridine) complexes of either ruthenium(II) or ruthenium(III),[22,23] but are reminiscent of ruthenium red.[38]

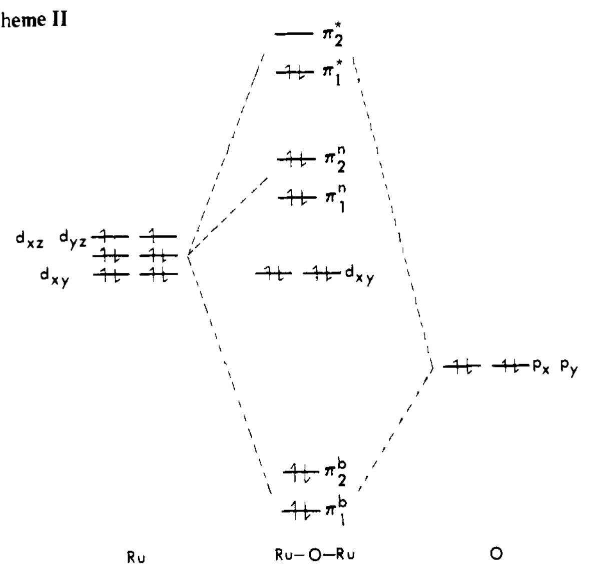
(6) From the X-ray photoelectron data, the Ru $3d_{5/2}$ binding energies for the salts $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_2$ and $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](ClO_4)_2$ are the same within experimental error and are much closer to the value expected for ruthenium(II) than for ruthenium(III).

(7) For the mixed-valence salt, $[(bipy)_2ClRuORuCl(bipy)_2](PF_6)_3$, the X-ray photoelectron data indicate that the two ruthenium centers are equivalent or nearly equivalent and that discrete Ru(III) and Ru(IV) oxidation states are not present. Since the two metal centers appear to be equivalent, the mixed-valence ion is an example of a class III case in the Robin and Day mixed-valence classification scheme.[2]

Electronic Structure and Magnetism. The magnetic data indicate that in the μ-oxo systems there is a singlet ground state with a relatively low lying triplet state. There is no evidence for interdimer coupling. X_M is not field dependent, and the fit of the data to the Bleaney-Bowers equation is good which would not be the case if interdimer interactions were significant.

The magnetic data can be interpreted in two reasonable ways, one assuming that coupling between the ruthenium ions is strong and the system delocalized. Molecular models indicate that a too pronounced bending of the Ru-O-Ru angle is not possible because of the bulkiness of the polypyridine ligands and so an appreciable, direct through-space Ru-Ru interaction is unlikely. Strong Ru-Ru interactions, if they are to occur, must occur via the bridging oxide ion. A qualitative molecular orbital scheme, based on the model given by Dunitz and Orgel for the linear ion, $[Cl_5RuORuCl_5]^{4-}$,[39] is given in Scheme II. In the scheme the direction for labeling the d orbitals of each of the ruthenium ions is taken along the Ru-O-Ru linkage. The scheme is slightly

Scheme II



modified from Orgel's. The degeneracy of the t_{2g} orbitals is lifted further than in $[Cl_5RuORuCl_5]^{4-}$ because of the lower symmetry of the bis(2,2′-bipyridine)ruthenium ions. A bent Ru-O-Ru linkage would also cause a loss in the d orbital degeneracy. If the system is delocalized and the molecular orbital treatment appropriate, the $|2J|$ values for the salts $[(bipy)_2(NO_2)RuORu(NO_2)(bipy)_2](PF_6)_2$ and $[(phen)_2(NO_2)RuORu(NO_2)(phen)](ClO_4)_2$ are a direct measure of the energy separation between the singlet state ${}^1(\pi_1{}^{*2})$ and the triplet state ${}^3(\pi_1{}^*\pi_2{}^*)$ with the singlet state lying lowest. As mentioned above, the $\pi_1{}^*$ and $\pi_2{}^*$ levels are expected to be nondegenerate because of the low symmetry at the ruthenium sites and possibly because the Ru-O-Ru linkage is bent. The remaining singlet state ${}^1(\pi_1{}^* \pi_2{}^*)$ is of higher energy than ${}^3(\pi_1{}^* \pi_2{}^*)$ from Hund's rules.

In the molecular orbital model the energy separation between the states ${}^1(\pi_1{}^{*2})$ and ${}^3(\pi_1{}^* \pi_2{}^*)$ $|2J|$ will depend upon the energy separating the $\pi_1{}^*$ and $\pi_2{}^*$ levels and upon the pairing energy in the $\pi_1{}^*$ level. Although it is difficult to estimate values for the two quantities, it is probably reasonable to assume that the pairing energy in an extensively delocalized orbital like $\pi_1{}^*$ is not large which would indicate a reasonable $\pi_1{}^*$-$\pi_2{}^*$ separation, especially if the Ru-O-Ru linkage is significantly bent.

The magnetic data can also be interpreted in terms of a moderate magnetic interaction between two spin-paired ruthenium(III) d^5 ions. In this interpretation a spin-spin interaction between the unpaired electron on each ruthenium site occurs. The spin-spin interaction gives rise to singlet and triplet states, and $|2J|$ is the energy separation between them. From electrostatic considerations, the unpaired electron on each ruthenium(III) ion would be predicted to be in the d orbital which lies in the plane of the slightly bent Ru-O-Ru unit. The spin-spin coupling mechanism by a superexchange process would involve, then, these two orbitals (d_{yz} in Scheme II) and the p orbital on the bridging oxygen atom which lies in the same plane. This is an example of the classical 180° cation-anion-cation interaction which has been discussed thoroughly by Goodenough.[40] This mechanism has been used to rationalize the near diamagnetism of $[(NH_3)_5CrOCr(NH_3)_5]Br_4$,[41] the magnetic properties of a large number of oxo-bridged iron(III) complexes,[42] as well as the magnetic interactions in extended arrays.[40] Sinn[43] has noted that the linear linkages result in strong interactions in some complexes. In view of the stability of these oxo-bridged ruthenium complexes and the presumed strong, short ruthenium-oxygen bonds, much stronger spin-spin coupling resulting in greater singlet-triplet splittings would have been expected.

The two models for explaining the magnetic data are fundamentally different. In the first case, strong, chemically significant Ru-Ru interactions are assumed, and, in the second, only a moderate spin-spin interaction between two paramagnetic sites is assumed. In the latter case the system can be considered as largely localized and the chemical and electronic properties of the Ru(III) centers should be similar to related monomeric complexes of ruthenium(III).

We clearly favor the delocalized description since it accounts for the properties of the oxo-bridged dimers in a reasonable and consistent way. The intense, low energy bands in the visible spectra can reasonably be assigned to $\pi^b \rightarrow \pi^*$ transitions involving delocalized Ru-O-Ru levels. The transitions would presumably be symmetry allowed, and the bands expected to have high molar extinction coefficients. In simple redox processes of the oxo-bridged ions, electrons are gained or lost from net antibonding molecular levels. The formation of $[(bipy)_2ClRuORuCl(bipy)_2]^{3+}$ at reasonable potentials and its relative stability are not surprising since the electron lost from the +2 ion comes from a π^* level. The equivalency of the ruthenium sites in the +3 ion is also consistent with the MO delocalized model. In this model the loss of an electron from the +2 ion giving the +3 ion occurs from a molecular level delocalized over both ruthenium ions (Scheme II) which would leave them equivalent. The equivalency of the ruthenium centers in the +3 ion suggests that the strong Ru-Ru interactions present in the +2 ions are maintained upon one-electron oxidation. Removal of a second electron from the +2 ion gives $(bipy)_2ClRuORuCl(bipy)_2{}^{4+}$ in which the π^* levels are completely depopulated.

The somewhat surprising instability of the reduced, mixed-valence ion, $[(bipy)_2ClRuORuCl(bipy)_2]^+$, is understandable since an electron added to the +2 ion would enter a valence π^* level. The added electron in the destabilized π^* levels apparently destabilizes the Ru-O-Ru linkages and leads to decomposition as expected.

The unusual chemical and physical properties of the oxo-bridged dimers are accounted for adequately using the MO scheme. Using this scheme the valence levels of the system are molecular levels delocalized over both ruthenium ions. The valence molecular orbitals have both ruthenium and bridging-oxide ion character. If the Ru-O-Ru interactions are strong, the valence levels ($\pi_1{}^*$ and $\pi_2{}^*$ in Scheme II) will be significantly destabilized compared to the nonbonding d levels ($\pi_1{}^n$, $\pi_2{}^n$, and d_{xy}). From the difference in $E_{1/2}$ values for the closely related couples $[(bipy)_2ClRuORuCl(bipy)_2]^{2+,+}$ ($E_{1/2} = -0.32$ V) and $Ru(bipy)_2Cl_2{}^{+,0}$ ($E_{1/2} = 0.30$ V), it can be estimated that the extent of destabilization may be several kilocalories per mole. If the extent of destabilization is large, it is expected that the identity of the ruthenium ions will be lost in determining the chemical and physical properties of the system. Such properties will be controlled largely by valence orbitals which are delocalized and include the properties of the two ruthenium ions and of the bridging oxide ligand.

Conclusions and Comparisons with Related Systems. The unusual chemical and physical properties of the oxo-bridged ruthenium complexes are consistent with the existence of strong, chemically significant interactions between the ruthenium ions through the bridging oxide ligand. Because of strong Ru-O-Ru interactions the identity of the separate ruthenium ions is lost in determining the chemical and physical properties of the systems. The valence levels which largely determine these properties are molecular orbitals delocalized over the Ru-O-Ru linkage. In order to understand the oxo-bridged dimers, it is necessary to treat them as molecular Ru–O–Ru systems with distinct chemical and physical properties of their own. From the reported spectral and chemical properties of the ion $[Os_2O(bipy)_2(terpy)_2]^{4+}$ (terpy is 2,2′,2″-terpyridine) it is probable that strong metal–metal interactions also exist in the osmium system.[44] On the other hand in related oxo-bridged complexes of iron(III), the properties of the ions are usually consistent with magnetically coupled systems in which the unpaired electrons are localized on the iron(III) ions.[5,45,46,47,48] In contrast to the ruthenium and osmium systems, the extent of metal–metal interactions between iron(III) ions is apparently insufficient to change appreciably the chemical and electronic properties of the dimeric ions, possibly because of a lesser d orbital radial extension for Fe(III) when compared to Ru(III) or Os(III).

Acknowledgments are made to the Materials Research Center of the University of North Carolina under Grant No. DAHC15 73 G9 with DARPA, to the Army Research Office-Durham under Grant No. DA-ARO-D-31-124-73-G104, and to the National Science Foundation under Grant No. GP-38633X for support of this research and to D. Salmon for assistance with the electrochemical measurements.

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(1) Presented in Part at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, as part of the Symposium on Extended Interactions between Metal Ions. Part of the work described here will appear in the ACS Symposium Series account of the Symposium on Extended Interactions.

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