3698 *Inorg. Chem.* **1981**, *20*, 3698-3703

Contribution from the Institute for Organic Chemistry TNO, 3502 JA Utrecht, The Netherlands,
and the Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Synthesis, Electrochemical Properties, and Charge-Transfer Band of Binuclear 1,10-Phenanthroline/Bis(2,2′-bipyridine) Complexes of Ruthenium

A. H. A. TINNEMANS,*[1a] K. TIMMER,[1a] M. REINTEN,[1a] J. G. KRAAIJKAMP,[1a] A. H. ALBERTS,[1a]
J. G. M VAN DER LINDEN,*[1b] J. E. J. SCHMITZ,[1b] and A. A. SAAMAN[1b]

Received February 26, 1981

The preparation of the mononuclear $[Ru(bpy)_2L]^{2+}$ (L = bpy, $phenOCH_3$, phenC(═O)NH-*n*-C_3H_7), the binuclear $[(bpy)_2RuLRu(bpy)_2]^{4+}$ (L = $phenO(CH_2CH_2O)_n$phen (n = 2–4), $phenC({=}O)NH(CH_2CH_2O)_nCH_2CH_2NH(O{=})Cphen$ (n = 1, 2), $phenC({=}O)NH(CH_2)_nNH(O{=})Cphen$ (n = 3, 6)), and the trinuclear $[N[CH_2CH_2OphenRu(bpy)_2]_3]^{6+}$ is described. Both the mononuclear and the binuclear complexes exhibit at a platinum electrode one oxidation wave and three reduction waves at potentials close to those observed for $Ru(bpy)_3{}^{2+}$. The oxidation and the reductions of the binuclear complexes are two-electron-transfer reactions. From the reduction of the peak width of the differential pulse polarograms it is concluded that $K_{con} \leq 1$ for the conproportionation equilibrium $[2,2] + [3,3] \leftrightarrow 2[2,3]$. The mixed-valence 5+ ion has an intervalence-transfer band in the solid state (KBr) in the near-infrared spectral region. Given the saturated character of the bridge, this represents a clear example of an intramolecular outer-sphere electron-transfer transition.

Introduction

A variety of aqueous systems have been described that generate hydrogen and/or oxygen under illumination.[2] Recently, the photocleavage of water with visible light in a combined device has been reported to occur in the presence of microheterogeneous (colloidal) catalysts.[3] The most crucial factor in the water-splitting reaction appears to be the oxidation of water into oxygen. In this process four electrons have to be transported by the catalyst. In the absence of a catalyst, dimeric intermediates have been postulated in the water-oxidation step with transition-metal complexes, and the production of oxygen in photosynthesis in vivo is thought to proceed via a binuclear complex of manganese.[4]

So far, ruthenium(II) tris(2,2′-bipyridine) complexes have been shown to be the most successful compounds capable of splitting water with visible light. These complexes are rather stable under the conditions of irradiation, have an absorption maximum at around 450 nm, and can undergo electron-transfer reactions with a quantum yield approaching unity.

There is by now a considerable knowledge of tris(bipyridyl)ruthenium(II) complexes, and electrochemical and spectral studies have given insight into the nature of the Ru(II)–ligand bond. In this report we describe the preparation of binuclear complexes derived from 1,10-phenanthroline bis(2,2′-bipyridine)ruthenium(II) with a saturated bridge between the two redox sites. Weak intervalence transfer (IT) absorption bands were expected to occur in these complexes, as they seem to fulfill the requirements formulated by Meyer,[5] i.e., there is a region of saturation so as to minimize electronic coupling through the bridge, and the redox sites are in close contact.

One of the goals of this work was to use the $(bpy)_2RuLRu(bpy)_2$ system and the results of electrochemical studies to develop a series of binuclear compounds that would provide the basis for a much more effective water-splitting reaction. A second was to obtain information about the role of bridging ligand on the extent of metal–metal interaction, supposed to have an influence in the water oxidation.

Experimental Section

Measurements. Absorption spectra were recorded with a Cary Model 14 or 15 spectrophotometer. Proton NMR spectra were recorded by using either a Varian T-60 or a Bruker WH-90 spectrometer with Me_4Si as an internal standard. Electrochemical measurements were made with a three-electrode Bruker E-310 instrument with platinum working (geometric area 0.071 cm^2) and auxiliary electrodes. Measurements were made on ca. (2–7) × 10^{-4} mol dm^{-3} complex solutions in acetone (0.1 mol dm^{-3} Bu_4NPF_6) with potentials referred to an Ag/AgCl (0.1 mol dm^{-3} LiCl) reference electrode. Normal- and differential-pulse polarograms were obtained at a scan rate of 5 mV s^{-1} with a pulse frequency of 2.0 pulses s^{-1}; differential-pulse amplitude was 25 mV. Cyclic voltammograms at scan speeds larger than 200 mV s^{-1} were displayed on a Textronix 564B storage oscilloscope. Controlled-potential electrolyses were carried out with a Wenking LB 75M potentiostat and a Birtley electronic integrator. Elemental analyses were performed by the TNO analytical department under supervision of Mr. W. J. Buis.

Materials. All synthetic reactions were performed under a nitrogen atmosphere unless stated otherwise. All solvents used for preparations were reagent grade and used without further purification. Glycols, diamines, and other starting organic chemicals were obtained commercially and were of reagent grade. Silver trifluoromethanesulfonate was used as received from Strem Chemicals. *cis*-$(bpy)_2RuCl_2 \cdot 2H_2O$ was prepared from commercial $RuCl_3 \cdot 3H_2O$ (Drijfhout Chemicals) as reported previously.[6] $[Ru(bpy)_3](PF_6)_2$ was obtained by passing an acetonitrile solution of $Ru(bpy)_3Cl_2$ (Strem Chemicals) over an anionic exchange column (PF_6^- form). Anal. Calcd for $RuC_{30}H_{24}N_6P_2F_{12}$: C, 41.92; H, 2.81; N, 9.78. Found: C, 41.71; H, 2.78; N, 9.72.

2-Chloro-1,10-phenanthroline was prepared from 1-methyl-1,10-phenanthrolin-2-one (mp 123.5–125 °C) according to Halcrow and Kermack.[7] The crude product (88%) was purified by column chromatography on alumina (Whoelm, neutral, activity I) with a chloroform/benzene mixture of increasing ratio (2:3 → 3:2) as eluant; mp 129–130 °C (colorless needles from benzene).

1,10-Phenanthroline-2-carboxylic acid was prepared according to Corey[8] from 1,10-phenanthroline monohydrate (Merck). The intermediate 2-cyano-1,10-phenanthroline was purified by column chromatography on alumina with chloroform/benzene (1:1) as eluant, mp 238–239 °C, from ethhanol (lit.[8a] mp 233–234 °C). NMR ($CDCl_3$): δ 9.27 (dd, H_9, $J \simeq 3$ Hz), 8.31 (dd, H_7, $J \simeq 13.7$ and 3.0 Hz), 8.39 and 7.94 (AB, $H_{3,4}$, $J_{AB} \simeq 13.6$ Hz), 7.94 and 7.83

---

(1) (a) Institute for Organic Chemistry TNO. (b) University of Nijmegen.

(2) (a) Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423; **1980**, *4*, 355 and references therein. (b) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377; *J. Mol. Catal.* **1980**, *7*, 539. (c) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214. Kiwi, J. *Isr. J. Chem.* **1979**, *18*, 369. (d) Kalyanasundaram, K.; Mimic, O.; Pramauro, E.; Grätzel, M. *Helv. Chim. Acta* **1979**, *62*, 2432.

(3) Kiwi, J.; Borgarello, E.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Angew. Chem.* **1980**, *92*, 663 and references therein.

(4) Calvin, M. *Science* **1974**, *184*, 375. Cooper, S. R.; Calvin, M. *Ibid.* **1974**, *185*, 376.

(5) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 752.

(6) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(7) Halcrow, B. E.; Kermack, W. O. *J. Chem. Soc.* **1946**, 155.

(8) (a) Corey, E. J.; Borror, A. L.; Foglia, T. *J. Org. Chem.* **1965**, *30*, 288. (b) Halbert, E. J.; Harris, C. M.; Sinn, E.; Sutton, G. J. *Aust. J. Chem.* **1973**, *26*, 951.

0020-1669/81/1320-3698$01.25/0

(AB, $H_{5,6}$, $J_{AB} \simeq 15$ Hz), 7.71 (dd, H_8, $J \simeq 7.4$ and 14 Hz).

Basic hydrolysis of the cyano derivative yielded 1,10-phenanthroline-2-carboxylic acid after acidification with concentrated hydrochloric acid to pH ~3.5. On acidification to pH ~1, an off-white precipitate was obtained, mp 262–265 °C, which was characterized as the hydrochloric acid salt of 1,10-phenanthroline-2-carboxylic acid. Anal. Calcd for $C_{13}H_9N_2O_2Cl{\cdot}0.69H_2O$: C, 57.17; H, 3.83; N, 10.26; Cl, 12.98. Found: C, 57.16; H, 3.41; N, 10.66; Cl, 13.01.

The carboxylic acid above was converted into 1,10-phenanthroline-2-carboxylic acid chloride as described by Creighton et al.[9] in almost quantitative yield.

2-Methoxy-1,10-phenanthroline (**1**) was prepared from the 2-chloro derivative as described by Claus and Rund.[10]

General Preparation of the Ligands phen-O-R-O-phen. 2,2′-(3-Oxopentamethylenedioxy)bis(1,10-phenanthroline) (**2**). In a typical preparation 5.5 g of sodium hydride (55% dispersion in mineral oil, 126 mmol) was added to a vigorously stirred solution of 2.2 g (21 mmol) of diethylene glycol in 100 mL of dried dimethylformamide, DMF. The mixture was stirred for 1 h at ambient temperature and subsequently for 1 h at 80 °C. To the suspension thus obtained was added 7.5 g (35 mmol) of 2-chloro-1,10-phenanthroline in 10 mL of DMF. The resulting mixture, stirred for 14 h at 100 °C, changed from colorless into brownish. Some solid remained undissolved. After evaporation of the solvent the residue was taken up in 100 mL of CH_2Cl_2 and 100 mL of water. The organic phase was washed with water and then dried on magnesium sulfate. The resulting solution was concentrated to a small volume and then poured into 125 mL of pentane. The crude product, precipitated as an oil, was purified by column chromatography on alumina eluting with ether/dichloromethane mixtures of increasing solvent ratio and finally with chloroform. A white crystalline material was obtained in 77% yield (5.0 g): mp 61–63 °C (after drying under vacuum at 80 °C (1 mmHg) for 8 h); NMR ($CDCl_3$): δ 9.14 (dd, H_9, $J \simeq 1.9$ and 4.3 Hz), 8.17 (dd, H_7, $J \simeq 1.8$ and 8.1 Hz), 8.02 and 7.14 (AB, $H_{3,4}$, $J_{AB} = 8.8$ Hz), 7.66 and 7.59 (AB, $H_{5,6}$, $J_{AB} \simeq 8.7$ Hz), 7.52 (dd, H_8, $J \simeq 4.4$ and 8.1 Hz), 5.07–4.97 (m, 4 H), 4.17–4.07 (m, 4 H). Anal. Calcd for $C_{28}H_{22}N_4O_3{\cdot}2H_2O$: C, 67.47; H, 5.22; N, 11.24. Found: C, 67.69; H, 4.83; N, 11.12.

2,2′-(3,6-Dioxooctamethylenedioxy)bis(1,10-phenanthroline) (**3**) was obtained in a way similar to that for the foregoing compound from 3.15 g (21 mmol) of triethylene glycol, 5.5 g of sodium hydride (55% dispersion, 126 mmol), and 7.5 g (35 mmol) of 2-chloro-1,10-phenanthroline: yield 64% (4.5 g); mp 116–118 °C (after drying under vacuum at 80 °C/1 mm Hg for 8 h); NMR ($CDCl_3$): δ 9.15 (dd, Hg, $J = 1.8$ and 4.4 Hz), 8.17 (dd, H_7, $J = 1.8$ and 8.1 Hz), 8.04 and 7.16 (AB, $H_{3,4}$, $J_{AB} = 8.8$ Hz), 7.72 and 7.57 (AB, $H_{5,6}$, $J_{AB} = 8.7$ Hz), 7.54 (dd, H_8, $J \simeq 4.3$ and 8.0 Hz), 5.01–4.91 (m, 4 H), 4.06–3.96 (m, 4 H), 3.83 (s, 4 H). Anal. Calcd for $C_{30}H_{26}N_4O_4$: C, 71.15; H, 5.14; N, 11.07; O, 12.65. Found: C, 69.57; H, 5.19; N, 10.93; O, 12.76.

2,2′-(3,6,9-Trioxoundecamethylenedioxy)bis(1,10-phenanthroline) (**4**) was obtained in a way similar to that given above from 1.16 g (6 mmol) of tetraethylene glycol, 1.57 g of sodium hydride (55% dispersion, 36 mmol), and 2.15 g (10 mmol) of 2-chloro-1,10-phenanthroline. After chromatography the fractions containing the almost pure product were dissolved in a little CH_2Cl_2 and then poured into pentane. A white precipitate was obtained (0.7 g, 32%): mp ~35 °C; NMR ($CDCl_3$) δ 9.18 (dd, H_9), 8.21 (dd, H_7), 8.16 and 7.10 (AB, $H_{3,4}$, $J_{AB} = 8.8$ Hz), 7.72 and 7.60 (AB, $H_{5,6}$, $J_{AB} = 8.7$ Hz), 7.57 (dd, H_8), 5.05–4.95 (m, 4 H), 4.06–3.96 (m, 4 H), 3.75 (br s, 8 H).

2,2′,2″-Tris((1,10-phenanthrolin-2-yloxy)ethyl)amine (**5**) was obtained in a way similar to that given above from 0.408 g (2.74 mmol) of triethanolamine in 20 mL of absolute DMF, 0.717 g of sodium hydride (55% dispersion, 16.4 mmol), and 1.85 g (8.6 mmol) of 2-chloro-1,10-phenanthroline in 5 mL of absolute DMF. The mixture was stirred for 12 h at 70 °C. The product could not be purified by chromatography but was obtained analytically pure by repeated precipitation of a solution of **5** in CH_2Cl_2 in pentane: yield 91% (1.71 g); mp 85–87 °C; NMR ($CDCl_3$) δ 9.09 (dd, H_9, $J \simeq 1.9$ and 4.3 Hz), 8.14 (dd, H_7, $J \simeq 1.8$ and 8.0 Hz), 7.93 and 7.10 (AB, $H_{3,4}$, $J_{AB} = 8.7$ Hz), 7.66 and 7.53 (AB, $H_{5,6}$, $J_{AB} = 8.7$ Hz), 7.48 (dd, H_8, $J \simeq 4.3$ and 8.1 Hz), 5.00 (t, 6 H), 3.44 (t, 6 H). Anal. Calcd for $C_{42}H_{33}N_7O_3{\cdot}H_2O$: C, 71.90; H, 5.00; N, 13.98. Found: C, 72.55; H, 5.06; N, 13.94.

***N*-*n*-Propyl-1,10-phenanthroline-2-carboxamide** (**6**). To a mixture of 5.16 g (18.5 mmol) of 1,10-phenanthroline-2-carboxylic acid chloride and 1.09 g (18.5 mmol) of freshly distilled *n*-propylamine in 80 mL of $CH_2Cl_2/CHCl_3$ (2:1) was added a solution of 4.0 g of NEt_3 in 20 mL of $CH_2Cl_2/CHCl_3$ (2:1). The mixture was refluxed for 1 h and cooled to room temperature. The solvent and excess amine was evaporated in vacuo, and 300 mL of water was added. After extraction with chloroform and drying over sodium sulfate, the solution was evaporated to give a pale yellow-brown residue. Chromatography on alumina with benzene/chloroform mixtures of increasing ratio (1:1 → 1:2) yielded 3.0 g (61%) of the product, which was crystallized from chloroform/pentane: mp 106–108 °C; NMR ($CDCl_3$) δ 9.62 (t, NH), 9.09 (dd, H_9), 8.56 and 8.35 (AB, $H_{3,4}$, $J_{AB} \simeq 13.3$ Hz), 8.28 (dd, H_7), 7.82 (s, $H_{5,6}$), 7.65 (dd, H_8), 3.55 (q, CH_2), 1.70 (m, CH_2), 1.00 (t, CH_3). Anal. Calcd for $C_{16}H_{15}N_3O{\cdot}1.2H_2O$: C, 66.98; H, 6.11; N, 14.64. Found: C, 66.94; H, 5.96; N, 14.58.

3-Oxopentamethylenebis(1,10-phenanthroline-2-carboxamide) (**7**) was prepared as described for **6** with 4.4 g (15.8 mmol) of the acid chloride, 1.4 g (7.9 mmol) of $H_2NCH_2CH_2OCH_2CH_2NH_2{\cdot}2HCl$, and 4.65 mL of NEt_3: yield 2.1 g (52%); mp 120–122 °C (after crystallization from acetone/chloroform (1:1)); NMR ($CDCl_3$) δ 10.07 (t, 2 NH), 8.84 (dd, H_9, $J \simeq 1.7$ and 4.4 Hz), 8.50 and 8.29 (AB, $H_{3,4}$, $J_{AB} = 8.2$ Hz), 8.21 (dd, H_7, $J \simeq 1.7$ and 8.1 Hz), 7.79 (s, $H_{5,6}$), 7.48 (dd, H_8, $J \simeq 4.5$ and 8.1 Hz), 3.88 (s, CH_2), 3.85 (s, CH_2). Anal. Calcd for $C_{30}H_{24}N_6O_3{\cdot}3H_2O$: C, 63.16; H, 5.30; N, 14.73. Found: C, 63.54; H, 5.28; N, 14.79.

3,6-Dioxooctamethylenebis(1,10-phenanthroline-2-carboxamide) (**8**) was prepared as described for **6** with 6.87 g (24.6 mmol) of the acid chloride, 1.82 g (12.3 mmol) of 1,8-diamino-3,6-dioxooctane, and 7.2 mL of NEt_3: yield 5.1 g (74%); mp 140–142.5 °C (after crystallization from acetone/chloroform (1:1)); NMR ($CDCl_3$) δ 9.68 (m, 2 NH), 9.07 (dd, H_9, $J \simeq 1.8$ and 4.4 Hz), 8.36 and 8.22 (AB, $H_{3,4}$, $J_{AB} = 8.4$ Hz), 8.23 (dd, H_7, $J \simeq 1.8$ and 8.1 Hz), 7.75 (s, $H_{5,6}$), 7.63 (dd, H_8, $J \simeq 4.4$ and 8.0 Hz), 3.83 and 3.77 (s, 2 CH_2), 3.51 and 3.57 (s, CH_2). Anal. Calcd for $C_{32}H_{28}N_6O_4{\cdot}2.6H_2O$: C, 63.28; H, 5.51; N, 13.87. Found: C, 63.29; H, 5.43; N, 13.63.

Trimethylenebis(1,10-phenanthroline-2-carboxamide) (**9**) was prepared as described for **6** with 7.4 g (26.5 mmol) of the acid chloride, 0.98 g (13.3 mmol) of freshly distilled 1,3-propanediamine, and about 6 mL of NEt_3: yield 2.8 g (43%); mp 156–172 °C (after crystallization from acetone/chloroform); NMR ($CDCl_3$) δ 10.73 (t, 2 NH), 9.09 (dd, H_9, $J \simeq 1.7$ and 4.5 Hz), 8.36 (dd, H_7, J $\simeq$ 1.8 and 8.2 Hz), 8.62 and 8.40 (AB, $H_{3,4}$, $J_{AB} = 8.4$ Hz), 7.89 (s, $H_{5,6}$), 7.68 (dd, H_8, $J = 4.4$ and 8.1 Hz), 3.81 (q, 2 CH_2), 2.12 (m, CH_2). Anal. Calcd for $C_{29}H_{22}N_6O_2{\cdot}H_2O$: C, 69.04; H, 4.79; N, 16.66. Found: C, 68.82; H, 4.96; N, 16.42.

Hexamethylenebis(1,10-phenanthroline-2-carboxamide) (**10**) was prepared as described for **6** with 7.9 g (28.3 mmol) of the acid chloride, 1.64 g (14.2 mmol) of 1,6-hexanediamine, and about 5 mL of NEt_3. Crystallization from methanol/dichloromethane gave a sample which melted at 114 °C, solidified on further heating, and melted again at 201–203 °C: yield 60%; NMR ($CDCl_3$) δ 9.78 (t, 2 NH), 9.00 (dd, H_9, $J \simeq 1.8$ and 4.4 Hz), 8.27 (dd, H_7, $J \simeq 1.8$ and 8.1 Hz), 8.60 and 8.41 (AB, $H_{3,4}$, $J_{AB} = 8.4$ Hz), 7.86 (s, $H_{5,6}$), 7.58 (dd, H_8, $J \simeq 4.4$ and 8.2 Hz), 3.62 (q, 2 CH_2), 2.01–1.43 (m, 8 H). Anal. Calcd for $C_{32}H_{28}N_6O_2{\cdot}2H_2O$: C, 68.07; H, 5.71; N, 14.88. Found: C, 68.03; H, 5.75; N, 14.73.

General Preparation of $[(bpy)_2RuLRu(bpy)_2]X_4$ ($X = CF_3SO_3^-, PF_6^-, ClO_4^-$). Two methods were used for the synthesis of these complexes. In the first method a diacetone complex was used. For a typical preparation 3.12 g (12.1 mmol) of AgO_3SCF_3 was added to a solution of 3.12 g (6 mmol) of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in 600 mL of deaerated acetone. After the resulting mixture was stirred for 3.5 h under argon, the precipitated AgCl was cautiously filtered by gravity and washed three times with 10 mL of acetone. To the filtrate was added 1.42 g (2.8 mmol) of **3**, and the resulting mixture was heated at reflux temperature for 10 h. The reaction was followed by TLC. The reaction was stopped either when all starting ligand had disappeared or when the intermediate di- and/or monoacetone complexes did not longer react. The resulting dark orange to red solution was concentrated to a small volume (ca. 10 mL), and the residue was poured into 50 mL of water. Unreacted ligand, when present as solid, was

---

(9) Sigman, D. S.; Wahl, G. M.; Creighton, D. J. *Biochemistry* **1972**, *11*, 2236.

(10) Claus, K. G.; Rund, J. V. *Inorg. Chem.* **1969**, *8*, 59.

removed by suction filtration. This solution was kept at ~5 °C, and after a few days red crystals were obtained. After collection the product was washed copiously with water followed by ether.

The PF_6 or ClO_4 salt was obtained by adding an excess of NH_4PF_6 or $NaClO_4$ to the concentrated solution in acetone, after the reflux period.

Purification was achieved either by direct crystallization from EtOH/acetone or by dissolving the product formed in a minimum of hot acetone, followed by pouring it slowly into water. Crystallization at ~5 °C for a few days yielded 1.9 g of the red complex $[(bpy)_2RuLRu(bpy)_2](O_3SCF_3)_4$ (L = **3**). This process was repeated to obtain analytically pure salts.

A second method involving the ethanol/water technique was in some cases also applied. In a typical preparation a mixture of 0.62 g (1.2 mmol) of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and 0.3 g (0.6 mmol) of **3** in 100 mL of degassed EtOH was refluxed for 18.5 h. The mixture was kept at room temperature and then filtered. To the filtrate was added an excess of NH_4PF_6, which resulted in the formation of an orange precipitate. After the solution was kept at ~5 °C for 3 days, the product was purified as described above.

$[N\{CH_2CH_2OphenRu(bpy)_2\}_3](PF_6)_6$. A mixture of 0.42 g (0.8 mmol) of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and 0.18 g (0.26 mmol) of **5** in 50 mL of absolute EtOH was refluxed for 23 h. The unreacted $Ru(bpy)_2Cl_2$ was filtered off, and to the filtrate was added 0.32 g (2 mmol) of NH_4PF_6 in 2 mL of water. The orange precipitate was collected, washed with EtOH, and dried; total yield 0.35 g (47%). Anal. Calcd for $Ru_3C_{102}H_{81}N_{19}O_3P_6F_{36}{\cdot}2H_2O$: C, 43.28; H, 3.01; N, 9.40. Found: C, 43.42; H, 3.01; N, 9.42.

Preparation of the Mixed-Valence Complex. A solution of $(bpy)_2RuLRu(bpy)_2(PF_6)_4$ (0.052 g, 0.027 mmol) in acetonitrile was treated with a solution of cerium(IV) sulfate (1.4 equiv) in 0.1 M sulfuric acid. The immediately formed green product was quickly filtered, washed with diethyl ether, and dried. Thus obtained samples were gently pressed between two thin KBr pellets for the recording of the near-infrared spectrum on a Cary 14 spectrophotometer. This product is certainly a mixture of the three compounds [2,2], [2,3], and [3,3]. The [3,3] complex was obtained in the same way with use of excess cerium salt.

Results and Discussion

Syntheses. A series of simple open-chain ligands containing two phenanthroline moieties were prepared from 2-chloro-1,10-phenanthroline or 1,10-phenanthroline-2-carboxylic acid chloride (eq 1 and 2). Structures of different chain lengths were chosen to allow for variation of the distance of the ruthenium centers (Table I).

$$\text{phen-Cl} \xrightarrow[\text{NaH, DMF}]{\text{HOROH}} \text{phen-O-R-O-phen} \qquad (1)$$

$$\text{phen-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-Cl} \xrightarrow[\text{NEt}_3\text{, CH}_2\text{Cl}_2]{\text{H}_2\text{NRNH}_2} \text{phen-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH-R-NH-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-phen} \qquad (2)$$

The bis(disubstituted) complexes $[(bpy)_2RuLRu(bpy)_2]^{4+}$ could be prepared by reaction of the free ligand L with *cis*-$(bpy)_2RuCl_2$. Two different procedures,[6] known to be valuable synthetic pathways, were used: (i) a route involving aqueous solution (eq 3) or (ii) a route involving an intermediate diacetone complex produced when the chloride is precipitated as AgCl (eq 4). The latter appeared to be the most efficient synthetic method.

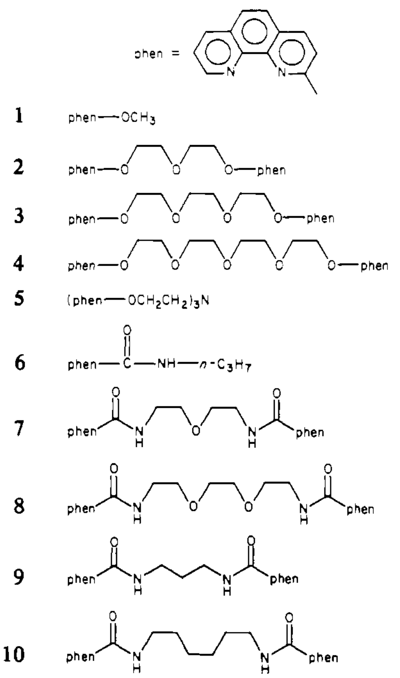
$$2\textit{cis}\text{-Ru(bpy)}_2\text{Cl}_2 \xrightarrow[\Delta]{\text{EtOH(H}_2\text{O), L}} [(\text{bpy})_2\text{RuLRu(bpy)}_2]^{4+} + 4\text{Cl}^- \qquad (3)$$

$$2\textit{cis}\text{-Ru(bpy)}_2\text{Cl}_2 + 4\text{AgO}_3\text{SCF}_3 \xrightarrow{\text{acetone}} 2\textit{cis}\text{-(bpy)}_2\text{Ru(CH}_3\text{COCH}_3)_2{}^{2+} + 4\text{AgCl} + 4\text{CF}_3\text{SO}_3{}^- \qquad (4a)$$

$$2\textit{cis}\text{-Ru(bpy)}_2\text{Ru(CH}_3\text{COCH}_3)_2{}^{2+} + \text{L} \rightarrow [(\text{bpy})_2\text{RuLRu(bpy)}_2]^{4+} + 4\text{CH}_3\text{COCH}_3 \qquad (4b)$$

Isolation of the substitution products was achieved by two methods: (i) addition of NH_4PF_6 or $NaClO_4$ to the ethanolic solution followed by filtration of the flocculent precipitate that appeared or (ii) evaporation of most of the acetone when the diacetone complex was used as the intermediate. The crude mixture was poured into water from which the product crystallized. Purification was accomplished either by reprecipitation of an acetone solution by adding water or by method i, followed by crystallization from acetone/ethanol or acetone/water mixtures. This procedure was continued until the product showed one spot on TLC.

Table I. Prepared Starting Materials



All compounds were obtained in good yields varying from ca. 40 to 60% as orange-red crystalline solids, stable to air for prolonged periods of time and highly fluorescent when irradiated in the visible (Table II).

Electrochemical Measurements. A representative cyclic voltammogram and differential pulse polarogram (DPP) showing the redox processes of the prepared complexes are presented in Figures 1 and 2.

The ruthenium complexes $[(bpy)_2RuLRu(bpy)_2]^{4+}$ (L = **2**, **4**, **7**, **8**) exhibit at a platinum electrode in acetone solution one oxidation wave at about 1.46 V and three reduction wave at about −1.09, −1.33, and −1.64 V (vs. an Ag/AgCl reference electrode). These potentials do not differ very much from those measured for the mononuclear complexes $[Ru(bpy)_2L]^{2+}$ (L = **1**, **6**).

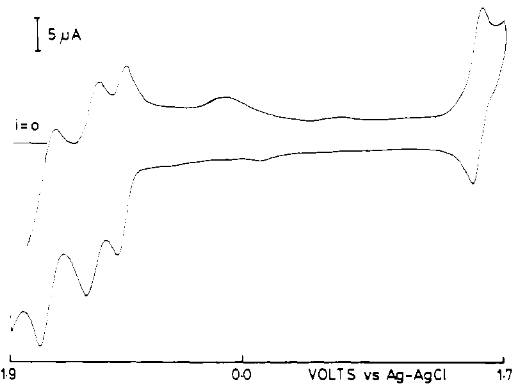


Figure 1. Cyclic voltammogram in 0.1 M TBAH/acetone of 2.5×10^{-4} M $[(bpy)_2RuLRu(bpy)_2]^{4+}$ (L = **2**) vs. Ag/AgCl electrode at a scan rate of 330 mV s^{-1}.

Table II. Elemental Analyses[a] and Absorption Spectra[b] (CTTL) for Salts of the Complexes $[(bpy)_2RuLRu(bpy)_2]X_4$ for L = **2**-**4** and L = **7**-**10** and $[(bpy)_2RuL]X_2$ for L = phen, **1**, and **6**

L	X	% C	% H	% N	% P	% S	% F	nH_2O^a	λ_{max}, nm (log ε)
phen	PF_6	43.31	2.63	9.43	6.81		26.02		448 (4.23)
		(43.50)	(2.74)	(9.51)	(7.01)		(25.80)		
1	CF_3SO_3	45.44	2.84	9.06		6.74	12.19		453 (4.19)
		(45.60)	(2.84)	(9.12)		(6.96)	(12.37)		
2	PF_6	42.69	2.95	8.80	6.43		23.69		453 (4.47)
		(42.86)	(3.07)	(8.82)	(6.50)		(23.93)	$2H_2O$	
3	PF_6	43.43	3.07	8.67	6.18		23.65		453 (4.52)
		(43.53)	(3.13)	(8.70)	(6.42)		(23.61)	$1H_2O$	
3	CF_3SO_3	45.99	3.18	8.68		6.31	11.63		453 (4.47)
		(45.63)	(3.11)	(8.63)		(6.59)	(11.71)	$1H_2O$	
4	PF_6	43.44	3.02	8.52	5.71		22.83		453 (4.47)
		(43.78)	(3.26)	(8.51)	(6.27)		(23.08)	$1H_2O$	
6	PF_6	43.89	3.25	9.94	5.71		22.62		446 (4.21)
		(43.82)	(3.37)	(9.94)	(6.28)		(23.11)	$1H_2O$	
7	CF_3SO_3	44.34	2.94	9.79		6.20	11.27		446 (4.50)
		(44.58)	(3.13)	(9.84)		(6.43)	(11.43)		
8	PF_6	42.45	3.13	9.53	5.90		22.01		446 (4.51)
		(42.78)	(3.29)	(9.70)	(6.13)		(22.56)	$3H_2O$	
10	PF_6	42.26	3.03	9.52	5.83		21.91		
		(43.46)	(3.34)	(9.86)	(6.23)		(22.92)	$3H_2O$	

[a] Calculated values in parentheses, based on the composition complex·nH_2O. [b] Measured in acetonitrile.

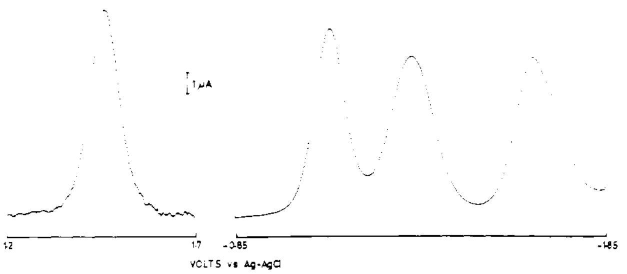


Figure 2. Differential-pulse voltammogram of 4.7 × 10^{-4} M $[(bpy)_2RuLRu(bpy)_2]^{4+}$ (L = **4**) in 0.1 M TBAH/acetone vs. Ag/AgCl electrode; scan rate 5 mV s^{-1}, pulse amplitude 25 mV, 2 pulses s^{-1}.

Compared with those of the well-studied[11] tris compound $[Ru(bpy)_3]^{2+}$, the data show (Table III) that by substitution of a bipyridyl ligand by a phenanthroline ligand (L = **2**, **4**, **7**, **8**) all redox potentials are shifted 20–60 mV to lower values. The length of the bridging ligand $phenO(CH_2CH_2O)_nphen$ (n = 2, 4) does not influence these potentials.

Cyclic voltammetry shows that the oxidations and reductions are not completely chemically reversible processes, for i_f/i_b ratios for the oxidation are in the range 0.8–1.0.

When an amide group (–C(=O)NH–) is incorporated into the bridge of the phenanthroline ligand (L = **6**, **7**, **8**), the dimeric compounds are less stable with respect to reduction. In the reversed scan of the cyclic voltammogram, only for the second and third reductions is an anodic peak observed; the first reduction is totally irreversible. Furthermore other anodic peaks at about −0.2 V are found, indicating that decomposition products are formed as well. Also the i_d/c and i_p/c values for the first reduction deviate from those expected (vide infra). The mononuclear complex with L = **6** suffers much less from this redox instability.

From controlled-potential oxidation of $[(bpy)_2RuLRu(bpy)_2]^{4+}$ (L = **2**, **4**) at 1.46 V in acetone it was concluded that two electrons per molecule are transferred. Reproducibility of these experiments is moderate because the potential is at the upper limit of the potential range of the solvent.

An examination of the measured current functions, i_d/c in normal-pulse polarography and i_p/c in differential-pulse polarography, also shows clearly that at all oxidations and reductions of the binuclear compounds two electrons per molecule are transferred (Table III).

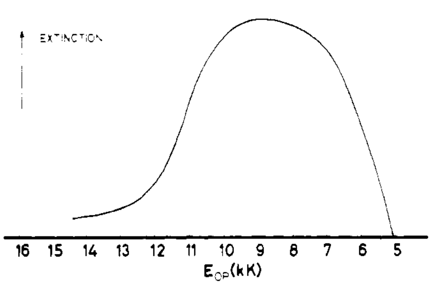


Figure 3. Intervalence-transfer band for the complex $[(bpy)_2RuLRu(bpy)_2]^{5+}$ (L = **3**) in the solid state (KBr).

In comparing the current functions of the mononuclear compounds $[Ru(bpy)_2L]^{2+}$ (L = bpy, **1**, **6**) with those of binuclear compounds $[(bpy)_2RuLRu(bpy)_2]^{4+}$ (L = **2**, **4**, **7**, **8**), one has to take into account the differences in their sizes. It is readily seen that a 1:2 ratio for their radii can be assumed. This leads to a $2^{1/2}$:1 ratio for their diffusion constants, according to the Stokes–Einstein relation,[12] and to a 1:$2^{1/2}$ ratio for the current functions. The experimentally obtained values agree very well with this ratio. Small deviations may be caused by changes in diffusion coefficients as charge is added or removed. Also the trinuclear complex $[N[CH_2CH_2OphenRu(bpy)_2]_3]^{6+}$ satisfies reasonably the required 1:$3^{1/2}$ ratio.

Thus, these results are consistent with a nearly reversible two-electron oxidation and three quasi-reversible two-electron reductions as described by eq 5.

$$\begin{aligned}&[(bpy)_2RuLRu(bpy)_2]^{2-} \underset{}{\overset{-1.6\text{ V}}{\rightleftharpoons}} \\ &\qquad [(bpy)_2RuLRu(bpy)_2]^{0} \overset{-1.3\text{ V}}{\rightleftharpoons} \\ &\qquad [(bpy)_2RuLRu(bpy)_2]^{2+} \overset{-1.1\text{ V}}{\rightleftharpoons} \\ &[(bpy)_2RuLRu(bpy)_2]^{4+} \overset{1.45}{\rightleftharpoons} [(bpy)_2RuLRu(bpy)_2]^{6+} \end{aligned} \tag{5}$$

In these binuclear compounds the ruthenium ions are coordinated in the same way, i.e., by two bipyridyl and one

---

(11) (a) Saji, T.; Aoyagui, S. *J. Electroanal. Chem.* **1975**, *58*, 401. (b) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.

(12) Bockris, J. O.; Reddy, A. K. N. "Modern Electrochemistry"; Plenum Publishing Co.: New York, 1970; p 380.

Table III. Electrochemical Data for Ruthenium Complexes[a]

compd	pulse polarography			differential-pulse polarography			cyclic voltammetry
	$E_{1/2}$, V	$E_{3/4} - E_{1/4}$, mV	i_d/C, mA dm^3 mol^{-1}	E_p, V	$\Delta E_{1/2}$,[b] mV	i_p/C, mA dm^3 mol^{-1}	ΔE,[c] mV
Mononuclear Complexes							
$Ru(bpy)_3{}^{2+}$	1.50	58	50	1.49	96	13	68
	−1.08	61	41	−1.10	94	12	67
	−1.29	53	54	−1.29	97	13	63
	−1.58	53	52	−1.58	96	13	80
$[Ru(bpy)_2L]^{2+}$, L = 1	1.47	53	50	1.44	94	13	58
	−1.11	56	45	−1.13	95	11	61
	−1.33	49	52	−1.34	97	13	70
	−1.65	49	55	−1.65	95	13	75
L = 6	1.50	57	54	1.52	98	12	70
	−1.03	46	52	−1.03	89	13	66
	−1.33	57	51	−1.33	116	11	78
	−1.59	53	58	−1.59	103	11	74
Binuclear Complexes							
$[(bpy)_2RuLRu(bpy)_2]^{4+}$, L = 2	1.47	49	83	1.47	91	21	53
	−1.08	48	96	−1.09	98	18	60
	−1.30	51	86	−1.31	135	20	83
	−1.63	64	115	−1.63		17	95
L = 4	1.46	51	75	1.44	89	20	52
	−1.09	47	70	−1.10	87	20	60
	−1.33	55	77	−1.32	129	18	90
	−1.65	48	70	−1.66	110	17	100
L = 7	1.46	54	78	1.46	93	20	70
	−0.95	44	58	−1.00	89	13	78
	−1.36	57	81	−1.40	103	20	76
	−1.63	75	81	−1.66	132	16	73
L = 8	1.53	57	73	1.52	90	20	71
	−0.95	30	30	−0.96	90	9	d
	−1.36	97	94	−1.32	120	20	102
	−1.65	58	109	−1.64	103	26	94
Trinuclear Complex							
$[N[CH_2CH_2OphenRu(bpy)_3]_3]^{6+}$, L = 5	1.47	56	78	1.48	87	24	91
	−1.09	43	118	−1.11	103	26	74
	−1.32	48	138	−1.31	135	22	115
	−1.66	41	94	−1.64[e]	110	15	94

[a] In acetone vs. Ag-AgCl (0.1 M LiCl-acetone) electrode. [b] Width at half peak height. [c] Difference between the anodic and cathodic peak potentials at a scan rate of 100 mV s^{-1}. [d] No anodic wave observed. [e] Desorption spike at −1.68 V.

phenanthroline ligands, and they are well separated by a saturated bridge $(-OCH_2CH_2-)_n$ (n = 2–4).

Whether interaction exists between two redox sites in one molecule is commonly traced by considering K_{con} for the conproportionation equilibrium (eq 6) calculated with eq 9. Here ΔE is the observed difference in redox potentials for the redox processes (eq 7 and 8). The resulting possibilities, K_{con} <4, =4, and >4, have been discussed extensively.[13]

$$[2,2]^z + [3,3]^{z+2} \xleftrightarrow{K_{con},\ \Delta G_{con}} 2[2,3]^{z+1} \qquad (6)$$

$$[2,2]^z \xrightarrow{E_1,\ \Delta G_1} [2,3]^{z+1} + e^- \qquad (7)$$

$$[2,3]^{z+1} \xrightarrow{E_2,\ \Delta G_2} [3,3]^{z+2} + e^- \qquad (8)$$

$$RT \ln K_{con} = -\Delta G_{con} = \Delta G_2 - \Delta G_1 = F(E_2 - E_1) = F\Delta E \qquad (9)$$

By graphic superposition of two one-electron DPP's it is easily seen that for noninteracting redox sites, i.e., with K_{con} = 4 and thus $E_2 - E_1$ = 35.6 mV, these coalesce to a single polarogram with a peak width at half-height $\Delta E_{1/2}$ = 103 mV.

Table IV. $\Delta E_{1/2}$[a] Values for Ruthenium Complexes

process	complex	$\Delta E_{1/2}$, mV
oxidn	mononuclear, L = bpy, 1, 6	94–98
	dinuclear, L = 2, 3, 4, 7, 8	89–93
redn	mononuclear, L = bpy, 1	94–95
	dinuclear, L = 4	87

[a] Peak width at half-height in a differential-pulse polarogram, which for a reversible one-electron-transfer process is 92.5 mV with a pulse amplitude of 25 mV.[14]

For a reversible one-electron process $\Delta E_{1/2}$ = 92.5 mV for a DPP recorded with a pulse amplitude of 25 mV.[14]

The observed $\Delta E_{1/2}$ values (Table IV) for the studied binuclear complexes are all clearly smaller than 93 mV. So we conclude that for $[(bpy)_2RuLRu(bpy)_2]^{4+}$ $E_2 \leq E_1$ and thus $K_{con} \leq 1$. So far such a low value for K_{con} has been reported for one other binuclear ruthenium complex (Table V).

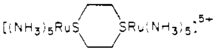
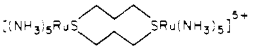
To the thermodynamic parameters as expressed in eq 6 and 7, which determine K_{con}, contribute terms like ΔG (solvation, ionization, Coulombic repulsion, coordination and configuration changes). In our case the larger attraction (upon oxidation) of the metal centers to the oxygen atoms in the bridge contributes to ΔG. This may account for a closer approach of both ruthenium centers in the [2,3] complex as compared

---

(13) (a) Gagné, R. R.; Coval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571. (b) Sokal, W. F.; Evans, D. H.; Niki, K.; Yogi, B. *J. Electroanal. Chem.* **1980**, *108*, 107 and references therein.

(14) Dillard, J. W.; Hanck, K. *Anal. Chem.* **1976**, *48*, 218.

Table V. Conproportionation Constants for the Equilibrium (Red–Red)$^{z-1}$ + (Ox–Ox)$^{z+1}$ $\rightleftarrows$ 2(Red–Ox)$^{z+}$ for Binuclear Ruthenium Complexes[a]

(Red–Ox)$^{z+}$	K_{con}	ref
$[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$	4×10^6	*b*
$[(NH_3)_5Ru(pyz)RuCl(bpy)_2]^{4+}$	1×10^7	*c*
$[(bpy)_2ClRu(dppm)RuCl(bpy)_2]^{3+}$	230	*d*
$[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$	100	*c, e*
	40	*f*
	10	*f*
$[(NH_3)_5RuNC_5H_4\text{–}C_5H_4NRu(NH_3)_5]^{5+}$	4–20	*g*
$[(NH_3)_5RuNCCNRu(NH_3)_5]^{5+}$	10^9	*h*
$[(NH_3)_5RuNCCH(t\text{-}Bu)CNRu(NH_3)_5]^{5\bullet}$	1^k	*i*
$[(NH_3)_5RuNCC(t\text{-}Bu)CNRu(NH_3)_5]^{4+}$	10	*i*
trans-$[SO_4(NH_3)_4Ru(His)Ru(NH_3)_4SO_4]^+$	160	*j*
$[(bpy)_2Ru(phenO)(CH_2CH_2O)_n phenRu(bpy)]^{5+}$	1	this work

[a] pyz = pyrazine; His = histidine; dppm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$. [b] Reference 16. [c] Powers, M. J.; Callahan, R. W.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* 1976, *15*, 1457. [d] Reference 5. [e] Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* 1977, *99*, 1064. [f] Stein, C. A.; Taube, H. J. *Ibid.* 1978, *100*, 1635. [g] Tom, G. M.; Creutz, C.; Taube, H. *Ibid.* 1974, *96*, 7827. [h] Tom, G. M.; Taube, H. *Ibid.* 1975, *97*, 5310. [i] Krentzien, H.; Taube, H. *Ibid.* 1976, *98*, 6379. [j] Gulka, R.; Isied, S. S. *Inorg. Chem.* 1980, *19*, 2842. [k] pH dependent.

with that in the [2,2] ion, resulting in E_2 being equal to or smaller than E_1.

Intervalence Absorption Band of the Mixed-Valence Ru(II)–Ru(III) Complex. The mixed-valence [2,3] species was prepared from the reaction of the [2,2] complex with a cerium(IV) salt. This is the only possible oxidation reagent because of the high oxidation potentials of these ruthenium complexes.

The [2,3] complex shows in the near-infrared spectrum in the solid state (potassium bromide pellet)[15,16] a broad band at 8800 cm^{-1} (1135 nm) (Figure 3). The bandwidth at half-height $\Delta\nu_{1/2} = 5.1 \times 10^3$ cm^{-1}, which compares reasonably well with the calculated value $\Delta\nu_{1/2} = (2310\nu_{max})^{1/2} = 4.5 \times 10^3$ cm^{-1}.[17]

The [2,2] compound is transparent in the solid state as well as in acetonitrile in the region measured, 650–2000 nm. Exhaustive oxidation of [2,2] with cerium(IV) delivered a product which was equally transparent in the solid state.

Such a low-energy absorption band is usually assigned to an intervalence-transfer transition by which a vibrationally excited isomer is formed (eq 10).

$$[Ru^{II}\text{–}Ru^{III}] \rightarrow [Ru^{III}\text{–}Ru^{II}]^* \qquad (10)$$

As the metal centers in these complexes are well separated by a large number of saturated units, i.e., $(\text{—}OCH_2CH_2\text{—})_n$ (n = 2–4), electron transfer through the bridge can be excluded and a through-space interaction seems likely. Molecular models (CPK models) of the binuclear compounds show that independent of the bridge length the two metal centers can approach each other as close as in the homogeneous case, $Ru(bpy)_3{}^{2+/3+}$.

The band is therefore assigned to the electron transfer between the two redox centers through outer-sphere orbital overlap. Other examples concerning binuclear ruthenium complexes containing bis(thioethers)[18] or diphosphines[5] as bridging ligands showing through-space interaction have been discussed recently, although these molecules suffer from much more strain when the redox sites are in close contact.

From the position of the near-infrared band an approximate rate of electron transfer can be calculated by using eq 11,

$$k_{et} = 10^{13} \exp[-(\Delta G^{*}/RT)] \qquad (11)$$

where $E_{op} = 4\Delta G^{*}$. The calculated value is 3×10^8 s^{-1}, which is in reasonable agreement with the values observed for other outer-sphere reactions in solution.[19]

The unavailability of the extinction coefficients hinders further calculations of the resonance energy.

Acknowledgment. We thank Professor Dr. J. J. Steggerda, Dr. J. G. Noltes, and Dr. A. Mackor for their interest in this work. These investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Pure scientific Research (ZWO), the VEG-Gasinstituut NV, and the European Commission.

Note Added in Proof. Recently Richardson and Taube[20] developed a method for the determination of potential separation for two-step electrochemical charge transfers from the measured peak widths in differential-pulse voltammograms. Following this procedure (Table IV) (with a small correction for the here applied E_{pulse} = 25 mV), we arrive at or slightly below the statistical value for the conproportionation constant, K_{con} = 3.2–4, for the reported complexes.

Registry No. **1**, 22426-16-0; **2**, 78609-89-9; **3**, 78609-90-2; **4**, 78609-91-3; **5**, 78609-92-4; **6**, 78609-93-5; **7**, 78609-94-6; **8**, 78609-95-7; **9**, 78609-96-8; **10**, 78609-97-9; $[(bpy)_2Ru(\mathbf{1})](CF_3SO_3)_2$, 78610-43-2; $[(bpy)_2Ru(\mathbf{2})Ru(bpy)_2](PF_6)_4$, 78610-45-4; $[(bpy)_2Ru(\mathbf{3})Ru(bpy)_2](PF_6)_4$, 78610-47-6; $[(bpy)_2Ru(\mathbf{3})Ru(bpy)_2](CF_3SO_3)_4$, 78610-48-7; $[(bpy)_2Ru(\mathbf{3})Ru(bpy)_2]^{5+}$, 78781-99-4; $[(bpy)_2Ru(\mathbf{4})Ru(bpy)_2](PF_6)_4$, 78610-50-1; $[(bpy)_2Ru(\mathbf{6})](PF_6)_2$, 78610-52-3; $[(bpy)_2Ru(\mathbf{7})Ru(bpy)_2](CF_3SO_3)_4$, 78610-54-5; $[(bpy)_2Ru(\mathbf{8})Ru(bpy)_2](PF_6)_4$, 78610-56-7; $[(bpy)_2Ru(\mathbf{10})Ru(bpy)_2](PF_6)_4$, 78610-58-9; $[N\{CH_2CH_2OphenRu(bpy)_2\}_3](PF_6)_6$, 78610-60-3; $[(bpy)_2Ru(phen)](PF_6)_2$, 60828-38-8; 2-cyano-1,10-phenanthroline, 1082-19-5; 1,10-phenanthroline-2-carboxylic acid, 1891-17-4; 2-chloro-1,10-phenanthroline, 7089-68-1; diethylene glycol, 111-46-6; triethylene glycol, 112-27-6; tetraethylene glycol, 112-60-7; triethanolamine, 102-71-6; 1,10-phenanthroline-2-carboxylic acid chloride, 57154-80-0; n-propylamine, 107-10-8; $H_2NCH_2CH_2OCH_2CH_2NH_2\cdot 2HCl$, 60792-79-2; 1,8-diamino-3,6-dioxooctane, 929-59-9; 1,3-propanediamine, 109-76-2; 1,6-hexanediamine, 124-09-4; $Ru(bpy)_2Cl_2$, 19542-80-4.

---

(15) No differences between solid state and solution spectra have been reported.[16] Also in the UV–vis region no differences between solid-state (KBr) and solution (CH_3CN) spectra were noted.

(16) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(17) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(18) Taube, H. In "Tunneling in Biological Systems"; Chance, B., Ed.; Academic Press: New York, 1979; p 173.

(19) Sutin, N. In "Tunneling in Biological Systems"; Chance, B., Ed.; Academic Press: New York, 1979, p 201.

(20) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.