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Synthesis and studies of spectroscopic and electrochemical properties of dinuclear ruthenium(II) and manganese(II) complexes

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New dinuclear ruthenium manganese complexes of general composition $(bpy)_2Ru(L)MnCl_x(H_2O)_2$ (L is 1,10-phenanthroline-5,6-dione, 3,3´-dicarboxy-2,2´-bipyridyl, or bis(pyrazolyl); $x = 2$ or 4) were synthesized by the reaction of $(bpy)_2Ru(L)$ with $MnCl_2 \cdot 4H_2O$. These compounds and the starting mononuclear ruthenium complexes were studied by spectrophotometric and electrochemical methods in MeCN. The position of the charge-transfer band $Ru^{II} \rightarrow L$ in the spectra depends on the donor-acceptor characteristics of the ligand L. For the dinuclear complex under study, the formal potentials of reversible one-electron oxidation of Ru^{II} are in the range of 0.9—1.2 V (*vs.* the standard hydrogen electrode), whereas oxidation of Mn^{II} occurs at more positive (by 0.1—0.2 V) potentials.

Key words: ruthenium(II) complexes, manganese(II) complexes, bipyridyl, electrochemistry.

Mixed-ligand Ru^{II} complexes of composition $(bpy)_2Ru(L)$ (L is a heterocyclic nitrogen-containing ligand, such as pyridine, pyrazole, bipyrimidine, *etc.*) are analogs of the well-known tris(bipyridyl) complex $[Ru(bpy)_3]^{2+}$ (**1**), which is used, in particular, for photocatalytic oxidation of water.[1] Mixed-ligand complexes are generally synthesized according to Scheme 1.

Scheme 1

$$Ru^{II}(bpy)_2Cl_2 + L \longrightarrow [Ru^{II}(bpy)_2L]Cl_2$$

Organic compounds containing functional groups capable of coordinating various metal cations are of particular interest as ligands L. These compounds serve as bridging ligands and, therefore, they can be used for the synthesis of dinuclear complexes (Scheme 2).

Scheme 2

$$Ru^{II}(bpy)_2L + M \longrightarrow Ru^{II}(bpy)_2LM$$

M is metal

In the present study, the properties of the mononuclear complexes $(bpy)_2Ru(L)$ (**2—4**), where L is 1,10-phenanthroline-5,6-dione, 3,3´-dicarboxy-2,2´-bipyridyl, or bis(pyrazolyl), respectively, were studied. Their dinuclear derivatives, *viz.*, Ru^{II} and Mn^{II} complexes **5—7** of the general formula $(bpy)_2Ru(L)MnCl_x(H_2O)_2$ (x = 2 or 4), were also synthesized and characterized.

These ruthenium manganese complexes have attracted attention as model catalytic systems for the biomimetic photochemical conversion of solar energy.[2] The aim of such studies is to develop devices, which can efficiently convert solar energy into electrical energy. Water is best to use for this purpose as the cheapest and ecologically pure "fuel" whose oxidation has been rather well studied[3] under conditions of natural photosynthesis. The key step of this process occurs with the involvement of several manganese ions present in a Mn cluster. Stepwise oxidation of manganese ions with the primary electron donor, *viz.*, chlorophyll P680 (through redox-active tyrosine), accumulates four oxidizing equivalents (Mn^{III} and Mn^{IV} ions), resulting in water decomposition (Scheme 3).

Scheme 3

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^-$$

The $(bpy)_2Ru^{II}LMn^{II}$ complexes can serve as artificial models of the P680—Mn-cluster interaction. Photooxi-

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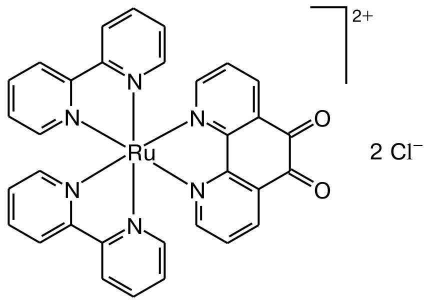

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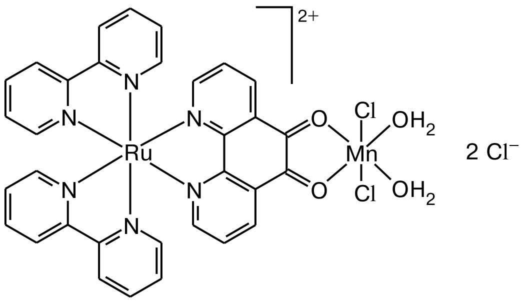

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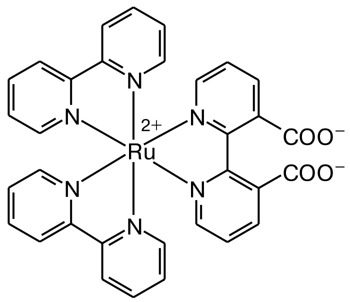

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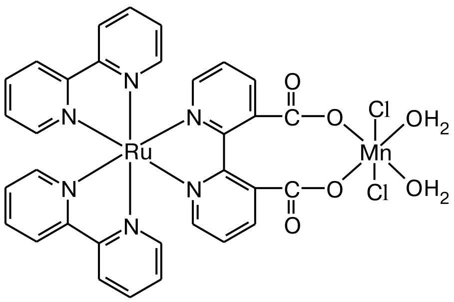

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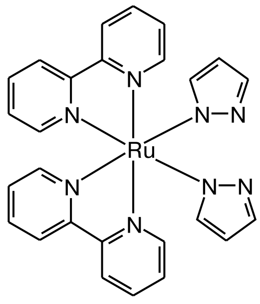

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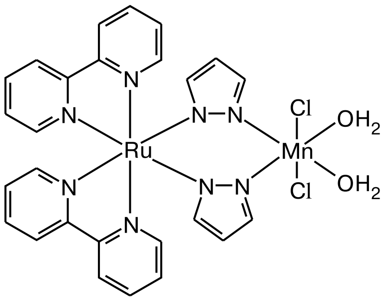

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dation of these complexes affords Ru^{III} complexes. The latter, like chlorophyll P680, have high oxidizing potential, which can lead to intramolecular electron transfer from Mn^{II} to Ru^{III}.[2] The construction of systems providing the most efficient photosensitized oxidation of Mn^{II} is a new line of research in the area of artificial photosynthesis.[4]

Results and Discussion

Starting mixed-ligand mononuclear ruthenium complexes **2—4** were synthesized according to known procedures[5] by the reaction of $(bpy)_2RuCl_2 \cdot 2H_2O$ with the corresponding ligands L in boiling ethanol (see Scheme 1). In the case of L = Pyr, an excess of KOH was added to the reaction mixture to bind HCl that was liberated.[6] The further reaction of complexes **2—4** with $MnCl_2 \cdot 4H_2O$ in ethanol at room temperature produced dinuclear complexes **5—7** in 70—80% yields.

The ^1H NMR spectra of complexes **5—7**, unlike the spectra of compounds **2—4**, show only strongly broadened signals due to the presence of paramagnetic manganese(II) ions. The mass spectra of compounds **5—7** have molecular ion peaks with low intensity, peaks of the mono- and dications $[(bpy)_2Ru(L)]^{z+}$ with high intensity, and peaks of ions that are formed by the loss of H_2O and HCl molecules from the molecular ion. Elemental analysis of complex **5** for C and H gave satisfactory results.

Solutions of the complexes in MeCN are bright yellow-orange ($[\mathbf{1}] \cdot Cl_2$, **2**, **3**, **5**, and **6**) or red-violet (**4** and **7**) in color. The absorption spectra of selected compounds are shown in Fig. 1. Data on the absorption maxima are given in Table 1. The absorption band at ~290 nm ($\varepsilon = 10^4—10^5$ L mol^{-1} cm^{-1}) is assigned to the π—π* transition

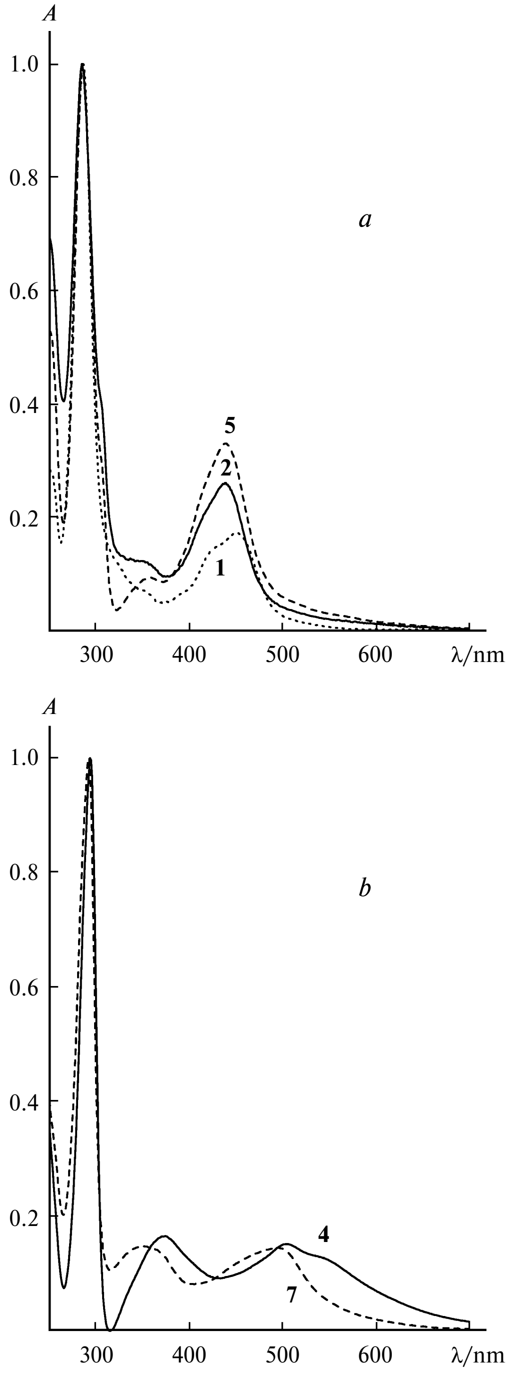

Fig. 1. Normalized absorption spectra of complexes **1**, **2**, **5** (*a*) and **4**, **7** (*b*) in MeCN.

of the ligand (bpy), and the absorption band at 440—500 nm corresponds to the metal—ligand charge transfer dπ(Ru) → π*(L).[6,7] In the spectra of complexes **2** and **3**, the latter band is slightly shifted to shorter wavelengths compared to the band in the spectrum of the tris(bipyridyl) complexes [**1**]·Cl_2, which is characteristic of ligands serving as better π-acceptors than bpy (for example, 1,10-phenanthroline). To the contrary, a substantial bathochromic shift of the charge-transfer band is observed in the spectrum of complex **4** containing Pyr as the bridging ligand, which is indicative of its strong π-donor character. Earlier,[5] it has been demonstrated that the bis(pyrazolyl) complex $Ru(bpy)_2(Pyr)_2$ can be protonated by even such weak proton donors as water. In this case, the charge-transfer band is shifted to shorter wavelengths from 581 nm ($Ru(bpy)_2(Pyr)_2$) to 510 ($[Ru(bpy)_2(Pyr)(PyrH)]^+$) and 470 nm ($[Ru(bpy)_2(PyrH)_2]^{2+}$). The observed long-wavelength absorption maximum of complex **4** in MeCN (at 503 nm) is indicative of the presence of the protonated form of this complex. The data for complexes **5** and **6** show that the energy of the charge-transfer band $Ru^{II} \rightarrow L$ remains unchanged upon the introduction of Mn^{II} ions into the Ru complex. However, coordination of Mn in complex **7** decreases the electron-donating properties of pyrazolyl, which causes a slight shift of this band to shorter wavelengths (from 503 to 494 nm) analogously to that observed upon protonation.

Table 1. Spectroscopic and electrochemical* properties of complexes **1—7** in MeCN

Complex	λ_{max}/nm	$E°'(Ru^{3+}/Ru^{2+})$	$E°'(Mn)$
		V	
1	289, 451	1.19	—
2	289, 439	1.17	—
3	289, 437	1.20	—
4	294, 374, 503	0.95	—
5	285, 439	1.25	1.46
6	288, 439	1.23	1.46
7	292, 352, 494	0.94	1.05

* The potentials are given relative to the standard hydrogen electrode, a 0.1 *M* Bu_4NPF_6 solution was used as the supporting electrolyte, the accuracy of measurements was ±0.01 V.

The redox properties of complexes **1—7** were studied by cyclic voltammetry. The direct-current cyclic voltammograms of the complexes in MeCN on a stationary platinum electrode are shown in Fig. 2. The complex [**1**]·Cl_2 exhibits two reversible oxidation—reduction waves, the potential difference between cathodic ($E_{p,c}$) and anodic ($E_{p,a}$) peaks being ~60 mV. This is evidence that two successive reversible one-electron steps occur. The first oxidation peak corresponds to the process

$$Ru^{II} - e^- \rightleftharpoons Ru^{III},$$

and the second peak is associated with oxidation of the chloride ions present in the complex. This assignment of the peaks is confirmed by the fact that an increase in the concentration of Cl^- ions (upon the addition of LiCl) leads to an increase in the height of the second wave. The oxidation wave of Cl^- ions at 1.4—1.5 V is observed also for the other complexes under study. The formal redox

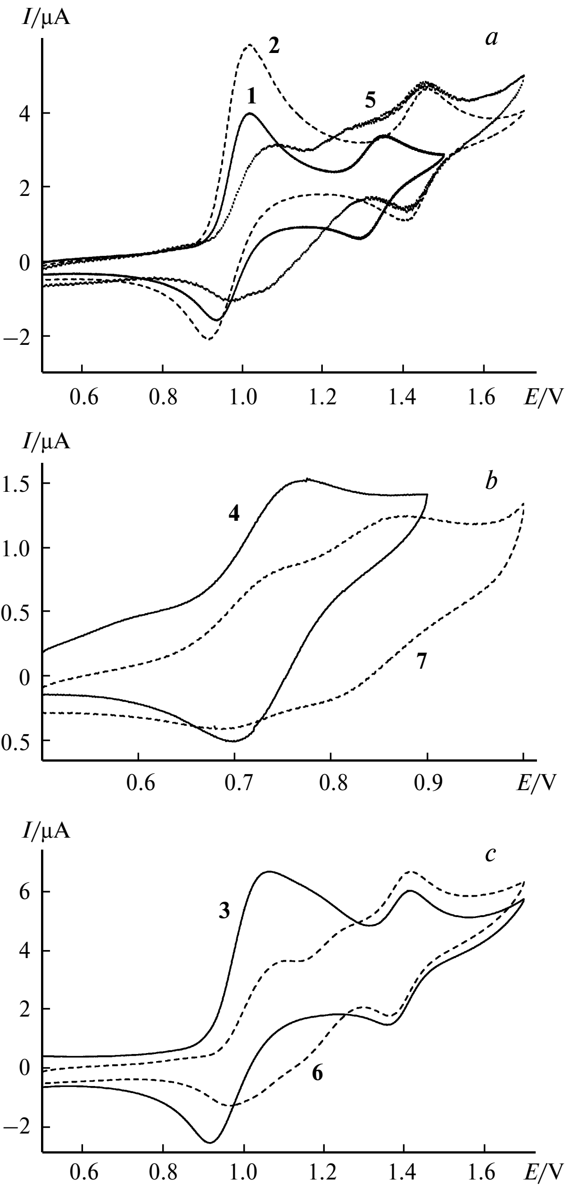

Fig. 2. Direct-current cyclic voltammograms of complexes **1**, **2** and **5** (*a*), **4** and **7** (*b*), **3** and **6** (*c*) in MeCN. The potentials are given relative to the potential of an Ag/AgCl/3 *M* KCl solution electrode (0.211 V *vs.* the standard hydrogen electrode); the potential scan rate was 20 mV s^{-1}.

potential of the Ru^{III}/Ru^{II} system for $[\mathbf{1}]\cdot Cl_2$ calculated by the equation

$$E^{\circ\prime} = (E_{p,c} + E_{p,a})/2$$

is 1.19 V *vs.* the standard hydrogen electrode, which can be compared with the known data for aqueous solutions ($E^{\circ\prime}$ = 1.27 V for a 0.01—0.1 *M* H_2SO_4 solution and $E^{\circ\prime}$ = 1.29 V for a 0.1 *M* HNO_3 solution)[8] and for a solution in MeCN ($E^{\circ\prime}$ = 1.38 V).[7] Analogous quasireversible oxidation of Ru^{II} was observed also for complexes **3—7**. The potential of the Ru^{III}/Ru^{II} system for complexes **2** and **3** is equal to that for the complex $[\mathbf{1}]\cdot Cl_2$ to within experimental error, which is indicative of an insignificant difference between bpy and the additional ligand L in the $Ru^{II}(bpy)_2L$ complex. A considerable (~0.25 V) decrease in $E^{\circ\prime}$ of the Ru^{III}/Ru^{II} system is observed for the complexes containing the pyrazolyl ligand, which is a strong π donor. An analogous behavior of ruthenium has been observed earlier in the $Ru(bpy)_2(Pyr)_2$, $[Ru(bpy)_2(Pyr)(PyrH)]^+$, and $[Ru(bpy)_2(PyrH)_2]^{2+}$ complexes.[5,9]

In the dinuclear Ru^{II} and Mn^{II} complexes, oxidation—reduction of ruthenium is partially overlapped with the quasireversible oxidation wave of manganese. This wave is observed during a slow potential scan (10—20 mV s^{-1}) or in alternating-current voltammetric measurements providing better resolution. In the complexes, Mn^{II} is most likely oxidized to Mn^{III}. The formal potential of this process is 10—20 mV higher than the oxidation potential of Ru^{II} in the corresponding complex (see Table 1). This fact suggests that intracomplex oxidation of Mn^{II} occurs slowly in the case of photogeneration of Ru^{III}. Hence, the complexes under study cannot be considered as promising models for artificial photosynthesis.

Experimental

All reactions were carried out with the use of anhydrous solvents. Complexes $[\mathbf{1}]\cdot Cl_2$ [5] and **2—4** [5] and the ligands 1,10-phenanthroline-5,6-dione[10] and 3,3′-dicarboxy-2,2′-bipyridyl[11] were prepared according to known procedures. The ^1H NMR spectra were measured on a Bruker AMX-400 instrument (400.13 MHz). The ESI mass spectra were recorded on a Finnigan LCQ instrument in MeCN. Cyclic voltammograms were measured on an Autolab potentiostat (Eco Chemie BV) using a three-electrode scheme, a platinum working microelectrode, and an aqueous Ag/AgCl/3 *M* KCl solution reference electrode (E° = 0.211 V at 20 °C). A 0.1 *M* Bu_4NPF_6 solution was used as the supporting electrolyte. Acetonitrile (HPLC grade) was dried over molecular sieves. To remove dissolved oxygen, the solution was purged with argon. The optical absorption spectra were recorded at ~20 °C on a Perkin—Elmer Lambda 900 UV/VIS/NIR spectrophotometer.

(μ-1,10-Phenanthroline-5,6-dione)[bis(bipyridyl)ruthenium(II)][dichlorodihydratomanganese(II)] dichloride (5). Complex **2** (100 mg, 0.14 mmol) and $MnCl_2\cdot 4H_2O$ (28 mg, 0.14 mmol) were dissolved in ethanol (15 mL). The resulting solution was stirred at ~20 °C for 2 h during which the color of the solution changed from bright-red to red-violet. The reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was dissolved in ethanol, and an excess of Et_2O was added. The crimson precipitate that formed was filtered off and dried. The yield was 81 mg (64%). Found (%): C, 45.98; H, 2.86. $C_{32}H_{26}Cl_4MnN_6O_4Ru$. Calculated (%): C, 44.88; H, 3.06. MS, *m/z*: 785 $[M - 2\,Cl]^+$, 712 $[M - 2\,Cl - 2\,HCl]^+$, 624 $[M - Mn(H_2O)_2Cl_2 - 2\,Cl]^+$.

(μ-3,3´-Dicarboxy-2,2´-bipyridyl)[bis(bipyridyl)ruthenium(II)][dichlorodihydratomanganese(II)] dichloride (6). The analogous reaction of complex **3** (100 mg, 0.15 mmol) with $MnCl_2 \cdot 4H_2O$ (31 mg, 0.15 mmol) in ethanol afforded a dark-red crystalline compound in a yield of 76 mg (62%). MS, *m/z*: 817 $[M]^+$, 745 $[M - 2 HCl]^+$, 656 $[M - Mn(H_2O)_2Cl_2]^+$.

Bis(μ-pyrazolyl)[bis(bipyridyl)ruthenium(II)][dichlorodihydratomanganese(II)] dichloride (7). The analogous reaction of complex **4** (100 mg, 0.18 mmol) with $MnCl_2 \cdot 4H_2O$ (37 mg, 0.18 mmol) in ethanol afforded a violet-red crystalline compound in a yield of 108 mg (86%). MS, *m/z*: 729 $[M + H_2O]^+$, 639 $[M - 2 HCl]^+$, 550 $[M - Mn(H_2O)_2Cl_2]^+$.

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