Russian Journal of General Chemistry, Vol. 74, No. 7, 2004, pp. 993–995. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 7, 2004, pp. 1076–1079.

Synthesis of Ruthenium(II) Tris(2,2'-bipyridine) Complexes

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Received October 28, 2003

Abstract—A procedure for preparing Ru(II) tris(2,2'-bipyridine) complexes containing one functionalized bipyridine ligand was developed.

Ruthenium complexes with organic ligands exhibit interesting photochemical and electrochemical properties [1]. In addition, complexes $[RuL_3]^{2+}$ (where L is 2,2'-bipyridine, 1,10-phenanthroline, 2,2'-biquinoline, etc.) are highly thermally and chemically stabile.

These complexes can be used in photochemsitry, photophysics, electrochemistry, and chemi- and electroluminescence. In 1976, Seddon E.A. and Seddon K.R. [1] found that these Ru complexes catalyze photoinduced water decomposition on exposure to visible light. There are two main problems in their practical application. The first is development of a suitable polymeric support for these complexes. Various polymers, including polymethacrylates, polyurethanes, polyamides, polyamines, polybenzimidazoles, etc.m can be used for this purpose [2–4]. Recently we studied an inorganic polymeric SiO_2 matrix as support for Ru complexes. This matrix was prepared by the sol–gel procedure involving hydrolysis of tetraalkoxysilanes with subsequent polycondensation of the hydrolysis products [5].

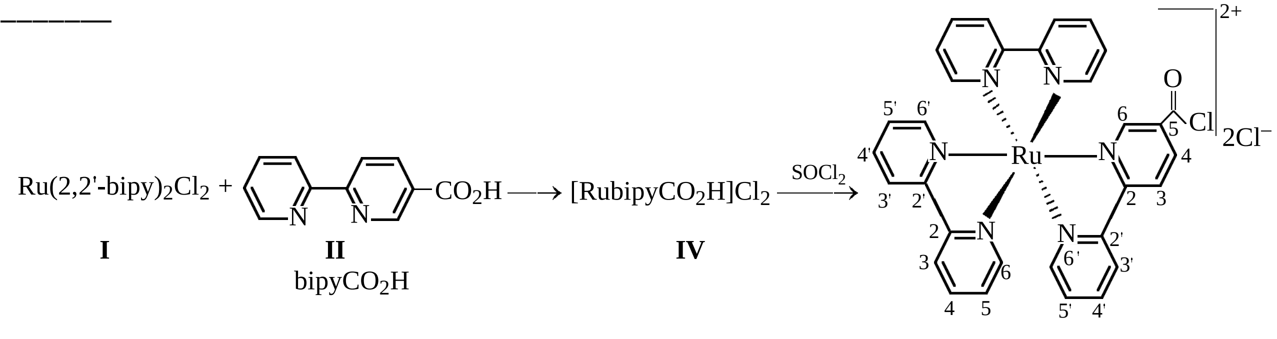
The second problem is introduction of $[RuL_3]^{2+}$ into the polymeric matrix. This can be done by several methods. The simplest procedure is reaction of functionalized polymeric matrix with the reactive groups of ruthenium(II) complexes. The aim of this work was to prepare functionalized 2,2'-bipyridine (bipy) ligands and their ruthenium(II) complexes. We also studied some chemical reactions directly with ruthenium complexes.

Di(2,2'-bipyridine)ruthenium dichloride (**I**) prepared from ruthenium(III) chloride [6, 7] was used as the precursor. The initial organic ligands were 2,2-bipyridine-4-carboxylic acid (**II**) and its methyl ester (**III**). The acid can be readily prepared by sulfonation of 2,2'-bipyridine, followed by substitution of the sulfo group with nitrile. Base hydrolysis of the resulting nitrile gives acid **II** in 20–40% yield based on 2,2'-bipyridine [8, 9].

Reaction of di(2,2'-bipyridine)ruthenium chloride **I** with acid **II**, performed by the procedure for preparing mixed ligand ruthenium(II) complexes [10, 11], gives tris(2,2'-bipyridine)ruthenium complex **IV**. The third ligand of this complex contains the carboxy group. Chloride **V** was obtained by treatment of complex **IV** with excess thionyl chloride by the procedure for preparing ruthenium complexes with 2-(2-pyridyl)-quinoline-4-carboxylic acid chloride [12].

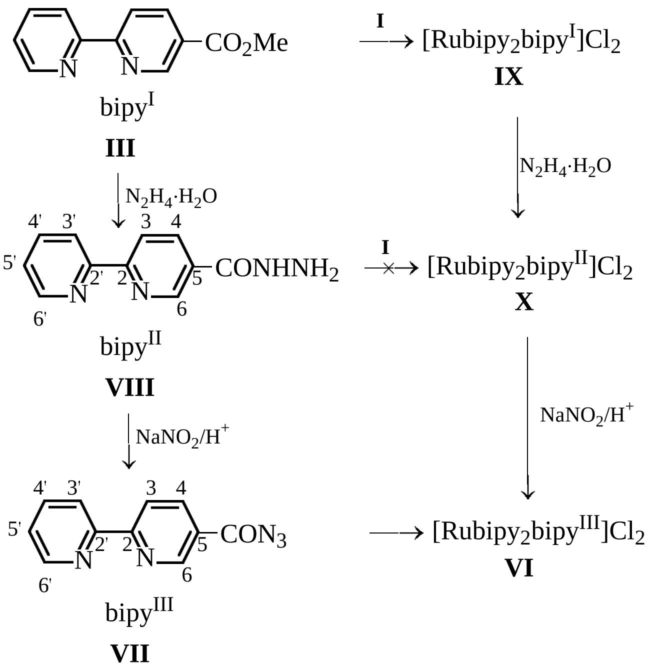
The composition and chemical structure of acid **IV** were confirmed by elemental analysis and ^1H and ^{13}C NMR spectroscopy.

Chloride **V** readily reacts with the amino groups of



I **II** bipyCO_2H **IV** **V**

the polymer in the presence of bases or propylene oxide to form the corresponding amides. Purification of chloride **V** is difficult, since tris(2,2'-bipyridine)ruthenium(II) complexes are soluble only in polar, mainly hydroxyl-containing solvents (water, methanol, ethanol) and less soluble in DMSO. To simplify the purification procedure, we prepared Ru(II) complex **VI** containing 2,2'-bipyridine-4-carboxylic acid azide **VII**.



It is known [13] that azide group readily undergoes nucleophilic substitution. Acyl azides can be used as acylating agents, since they readily react with strong nucleophilic agents (e.g., amines) [14]. At the same time, ruthenium complex **VI** containing acyl azide group is fairly stable in an aqueous-methanolic solution and can be purified, as other ruthenium complexes **IV**, **IX**, and **X**, by reprecipitation from a methanolic solution with ether or by chromatography on aluminum oxide. Ruthenium complex **X** containing hydrazide of 2,2'-bipyridine-4-carboxylic acid cannot be prepared by direct reaction of hydrazide **VIII** with di(2,2'-bipyridine)ruthenium dichloride **I**. The reaction yields a mixture of products owing to competitive coordination of the NH_2 fragment of the hydrazide group and the nitrogen atom of 2,2'-bipyridine to Ru(II).

Ruthenium complexes **IV**, **VI**, **IX**, and **X** are stable compounds with the color from orange to brick-red. Azide **VI** decomposes above 150°C. The other complexes are stable at least up to 300°C. The structure of these complexes was confirmed by elemental analysis and ^1H and ^{13}C NMR spectroscopy.

The H^6, $H^{6'}$, H^3, and $H^{3'}$ signals in the ^1H NMR spectra of complexes **IV**, **VI**, **IX**, and **X** are substantially shifted as compared 2,2'-bipyridine [15] owing to the diamagnetic anizotropic effect of the aromatic ring of the neighboring ligand. The number of signals in the ^{13}C NMR spectra of these complexes is different, which is apparently due to overlap of some signals.

Thus, a series of previously unknown tris(2,2'-bipyridine)ruthenium complexes **IV**, **VI**, **IX**, and **X** were prepared. The third ligand in these complexes is functionalized. At present, we study the photophysical and electrochemical properties of these compounds.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ on a Bruker DPX-300 spectrometer (300 MHz) using TMS as internal reference.

2,2'-Bipyridine-5-carboxylic acid hydrazide VIII. A mixture of methyl ester **III** (1.0 g) [8], 100% hydrazine hydrate (1 ml), and methanol (20 ml) was refluxed for 4 h. The solution was evaporated under reduced pressure of a water-jet pump. The residue was recrystallized from methanol. A colorless crystalline substance was obtained in 80% yield (820 mg). The purity was confirmed by TLC; mp 194–195°C. ^1H NMR [$(CD_3)_2SO$], δ, ppm: 4.60 s (2H, NH_2), 7.58 m ($H^{5'}$), 7.88 m ($H^{4'}$), 8.32 dd (H^4, J_1 8, J_2 1.5 Hz), 8.43 m (H^3, $H^{3'}$), 8.73 d ($H^{6'}$, *J* 5 Hz), 9.07 d (H^6, *J* 1.5 Hz), 10.03 s (1H, NH). ^{13}C NMR [$(CD_3)_2SO$], δ_C, ppm: 120.7 ($C^{5'}$), 121.80 ($C^{3'}$), 125.50 (C^3), 129.70 (C^5), 136.80 (C^4), 138.20 ($C^{4'}$), 148.70 ($C^{6'}$), 150.20 (C^6), 155.20 ($C^{2'}$), 157.90 (C^2), 164.90 (CO). Found, %: C 61.60; H 4.72; N 25.87. $C_{11}H_{10}N_4O$. Calculated, %: C 61.68, H 4.70; N 26.05.

2,2'-Bipyridine-5-carboxylic acid azide VII. A solution of $NaNO_3$ (0.2 g) in water (5 ml) was added in a single portion to a solution of hydrazide **VIII** (0.6 g) in water (20 ml), acidified with concentrated hydrochloric acid (0.5 ml) and cooled to 0°C. In 5 min, the reaction mixture was neutralized with excess sodium acetate solution and cooled to 0°C. The mixture was allowed to stand for 1 h. Then the product was filtered off. 0.58 g (92%) of colorless crystalline compound **VII** was obtained. The purity was confirmed by TLC; mp 144–145°C (dec.). ^1H NMR ($CDCl_3$), δ, ppm: 7.38 m ($H^{5'}$), 7.87 m ($H^{4'}$), 8.41 dd (H^4, J_1 8, J_2 1.5 Hz), 8.51 d ($H^{3'}$, *J* 8 Hz), 8.57 d (H^3, *J* 1.5 Hz), 8.765 d ($H^{6'}$, *J* 5 Hz), 9.27 (H^6, *J* 1.5 Hz). ^{13}C NMR ($CDCl_3$), δ_C, ppm: 121.10 (C^3), 122.30 ($C^{3'}$), 125.05 ($C^{5'}$), 126.45 (C^5), 137.30 (C^4), 138.20 ($C^{4'}$), 149.80 (C^6), 150.70 ($C^{6'}$), 155.05 ($C^{2'}$), 161.00 (C^2), 171.60 (CO). Found, %: C 58.25; H 3.25; N 30.82. $C_{11}H_7N_5O$. Calculated, %: C 58.67, H 3.13; N 31.10.

Mixed-ligand Ru(II) complexes I, VI, and IX. A suspension of di(2,2'bipyridine)ruthenium dichloride **I** (260 mg) in a mixture of water (40 ml) with methanol (20 ml) was refluxed for 2 h. Functionalized 2,2'-bipyridine **II**, **III**, or **VII** (1.05 equiv) was added. The resulting suspension was refluxed for 0.2–1 h to complete conversion of complex **I** (TLC on Al_2O_3). The solution was evaporated to dryness under reduced pressure of a water-jet pump. The residue was dissolved in methanol (1 ml) and reprecipitated with absolute diethyl ether (20 ml). The complex was purified additionally on aluminum oxide by elution with a methanol–methylene chloride mixture with the gradient from 1 : 50 to 1 : 10 for complexes **VI** and **IX** and from 1 : 10 to 1 : 4 for complex **IV**.

$[Rubipy_2bipyCO_2H]Cl_2$ IV, yield 65%. ^{1}H NMR $[(CD_3)_2SO]$, δ, ppm: 8.85 m (6H), 8.33 dd (H^4, bipy · CO_2, J_1 8, J_2 1.5 Hz), 8.17 m (5H), 8.02 (H^6, bipy · CO_2, J 8 Hz), 7.74 m (5H), 7.54 m (5H). ^{13}C NMR $[(CD_3)_2SO]$, δ_C, ppm: 124.80, 125.50, 125.60, 128.50, 128.80, 138.40, 138.70, 140.50, 151.90, 152.00, 152.15, 156.60, 157.20, 157.30, 164.20. Found, %: C 51.25; H 3.30; N 11.28. $C_{31}H_{28}Cl_2N_6O_4Ru$. Calculated, %: C 51.67; H 3.36; N 11.66.

$[Rubipy_2bipy^I]Cl_2$ IX, yield 75%. ^{1}H NMR $[(CD_3)_2SO]$, δ, ppm: 8.98 m (6H), 8.52 dd (H^4, $bipy^I$, J_1 8, J_2 1.5 Hz), 8.19 m (5H), 7.97 d (H^6, $bipy^I$, J 1.5 Hz), 7.80 m (5H), 7.55 m (5H) (3H, OCH_3). ^{13}C NMR $[(CD_3)_2SO]$, δ_C, ppm: 163.95, 160.80, 157.55, 157.40, 157.25, 157.20, 156.45, 152.65, 152.35, 152.20, 152.05, 151.80, 129.70, 129.40, 128.95, 128.85, 128.80, 128.75, 126.85, 125.75, 125.55, 125.50, 53.80. Found, %: C 52.11; H 3.37; N 11.03. $C_{32}H_{30}Cl_2N_6O_4Ru$. Calculated, %: C 52.32; H 3.57; N 11.44.

$[Rubipy_2bipy^{III}]Cl_2$ VI, yield 35%. ^{1}H NMR $[(CD_3)_2SO]$, δ, ppm: 8.82 m (6H), 8.32 dd (H^4, $bipy^{III}$, J_1 8, J_2 1.5 Hz), 8.16 m (5H), 8.01 d (H^6, $bipy^{III}$, J 1.5 Hz), 7.75 m (5H), 7.53 m (5H). ^{13}C NMR $[(CD_3)_2SO]$, δ_C, ppm: 121.00, 122.20, 125.30, 125.80, 126.20, 128.75, 128.85, 136.65, 138.20, 138.70, 138.90, 143.30, 149.30, 151.05, 151.60, 151.75, 151.85, 151.95, 157.40, 157.45, 157.55, 158.45. Found, %: C 49.62; H 3.03; N 16.57. $C_{31}H_{27}Cl_2N_9 \cdot O_3Ru$. Calculated, %: C 49.94; H 3.11; N 16.91.

Transformations **IX** → **X** → **VI** involving the complexes containing ester, hydrazide, and acyl azide group, were performed by the procedure similar to those for preparing initial lignads **II**, **VII**, and **VIII**. The reaction progress was monitored by TLC. The reaction mixture was evaporated to dryness under reduced pressure of a water-jet pump. The target products were obtained by chromatographic separation of the residue on aluminum oxide.

$[Rubipy_2bipy^{II}]Cl_2$ X, eluent methanol–methylene chloride with gradient from 1 : 20 to 1 : 5, yield 52%. ^{1}H NMR $[(CD_3)_2SO]$, δ, ppm: 8.83 m (6H), 8.32 d.d (H^4, $bipy^{III}$, J_1 8, J_2 1.5 Hz), 8.17 m (5H), 7.15 (H^6, $bipy^{III}$, J 1.5 Hz), 7.74 m (5H), 7.54 m (5H). ^{13}C NMR $[(CD_3)_2SO]$, δ_C, ppm: 164.10, 157.40, 157.20, 156.65, 152.15, 152.00, 151.90, 140.50, 138.75, 138.40, 128.80, 125.50, 125.45, 124.70. Found, %: C 50.43; H 3.38; N 14.98. $C_{32}H_{30}Cl_2N_8O_3Ru$. Calculated, %: C 50.69; H 3.57; N 15.25.

ACKNOWLEDGMENTS

The authors are grateful to S.N. Smirnov for recording the ^{1}H and ^{13}C NMR spectra.

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