Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 1149–1150. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1219–1220.

LETTERS TO THE EDITOR

Spectroscopic and Electrochemical Properties of Palladium(II) and Platinum(II) 2-(2-Pyridyl)thiophenide Complexes with 4,4'-Bipyridyl

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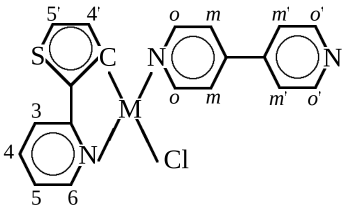
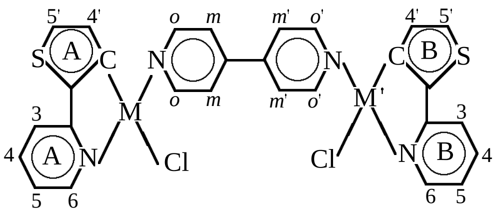
Received May 4, 2000

The specific photophysical and electrochemical properties of cyclometalated platinum(II) and palladium(II) complexes, such as the formation of long-lived electronically excited states and the tendency to reversible one-electron electrochemical reduction reactions, predetermine increased attention to synthesis of their coordinately unsaturated compounds which could be used as structural units in creating molecularly organized systems with directed charge and energy phototransfer [1].

In the present work we obtained and characterized by means of ^{1}H NMR and electronic spectroscopy, as well as by cyclic volammetry, coordinately unsaturated complexes Pt(tpy)Cl(bpy)] (**I**) and [(Pd(tpy)Cl(bpy)] (**II**) and binuclear systems on their basis [Cl(tpy)Pt(μ-bpy)Pd(tpy)Cl] (**III**) and [(Pt(tpy)Cl)$_2$(μ-bpy)] (**IV**), where tpy is the deprotonated form of 2-(2-pyridyl)thiophene and bpy is 4,4'-bipyridyl.



[M(tpy)Cl(bpy)]



[M(tpy)Cl(bpy)M'(tpy)Cl]

The synthesized complexes are stable both in the solid state and in solutions (DMF, CH_2Cl_2, CH_3CN). The ^{1}H NMR spectra of the complexes show that the substitution the chloride ligand in $[Pt(tpy)Cl_2]^-$ and $[M(tpy)(\mu\text{-}Cl)]_2$ [M = Pt(II), Pd(II)] by bipyridyl or [Pt(tpy)Cl(bpy)] stereoselectively provide *trans-N,N* isomers. This conclusion is supported by a strong shielding of the $H^{4'}$ protons of the tpy ligand, whose coordination-induced chemical shifts under the anisotropic effect of the bipyridyl ligand are –0.72, –0.79, –0.71, –0.82 ppm for compounds **I**–**IV**, respectively. As with the Pt(II) and Pd(II) 2-(2-pyridyl)thiophenide complexes studied in [2–4], the optical and electrochemical properties of compounds **I**–**IV** are mostly dependent on the metal-centered character (d_M) of the highest occupied molecular orbitals and the ligand-centered character (π^*_{tpy}, π^*_{bpy}) of the lowest unoccupied molecular orbitals. This predetermines the presence of low-energy d–π^* and π–π^* optical transitions in the electronic absorption and luminescence spectra of the complexes, as well as the metal-centered nature of their oxidation and the ligand-centered nature of their electrochemical reduction. The optical and electrochemical properties of binuclear systems **III** and **IV** are, in essence, a superposition of the properties of mononuclear components **I** and **II**, implying a weak interaction between the {Pt(tpy)}–{Pd(tpy)} and {Pt(tpy)}–{Pt(tpy)} metal-complex fragments linked by a bridging bipyridyl ligand.

***trans-N,N*-Chloro[2-(2-pyridyl)thiophen-3-ide]-(4,4'-bipyridyl)platinum(II) (I)** was obtained by the procedure described in [5]. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 6.41 ($H^{4'}$, $^3J_{HPt}$ 20), 7.00 (H^5), 7.38 ($H^{5'}$), 7.5–7.6 (3H), 7.64 ($2H_m$), 7.74 (H^4), 8.82 ($2H_{o'}$), 9.14 ($2H_o$, $^3J_{HPt}$ 47), 9.46 (H^6, $^3J_{HPt}$ 38). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 310(21.7), 337 (17.4), 430 (3.2). Luminescent characteristics (DMF, 298 K), shortwave maximum, $\nu_{max} \times 10^{-3}$, cm^{-1} (lifetime τ, μs; quantum yield *F*): 17.73 (18; 0.15). Electrochemical parameters (CH_3CN, reference Fc/Fc^+), V: $E_{1/2}$ –1.87, –2.25, –2.55; E_p (*v* 100 mV/s) 0.60.

***trans-N,N*-Chloro[2-(2-pyridyl)thiophen-3-ide]-(4,4'-bipyridyl)palladium(II) (II).** To a saturated solution of 0.4 mmol of 4,4'-bipyridyl in CH_2Cl_2 we added 0.1 mmol of $[Pd(tpy)(\mu\text{-}Cl)]_2$ [6], and the mixture was stirred for 5 days under reflux. After cooling to room temperature, the mixture was washed with saturated aqueous HNO_3 (2 × 10 ml, pH 2) and evaporated to dryness in a vacuum at 50°C. The residue was washed with ether and dried in a vacuum. Yield 35%. ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 6.34 ($H^{4'}$), 7.03 (H^5), 7.3–7.8 (6H), 8.83 ($2H_{o'}$), 9.07 ($2H_o$), 9.26 (H^6). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$): 305 (17.9), 370 (3.9). Luminescent characteristics (DMF, 77 K), $\nu_{max} \times 10^{-3}$, cm^{-1} (τ, μs; *F*): 18.66 (290; 0.13). Electrochemical parameters (DMF, reference Fc/Fc^+), V: E_p (*v* 100 mV/s): –1.80, –2.15, 0.93.

(μ-4,4'-Bipyridyl)[*trans-N,N*-chloro(2-(2-piridyl)-thiophen-3-ide)platinum(II)][*trans-N,N*-[*cis-N,N*-chloro(2-(2-pyridyl)thiophen-3-ide)palladium(II)] (III). To a saturated solution of 0.05 mmol of [Pt(tpy)Cl(bpy)] in CH_2Cl_2 we added 0.1 mmol of $[Pd(tpy)(\mu\text{-}Cl)]_2$, and the mixture was stirred for 2 days under reflux. The precipitate that formed was filtered off, washed with ether, and recrystallized from CH_2Cl_2. The yellow crystals were washed with ether and dried in a vacuum. Yield 23 %. ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 6.41 ($H^{4'A}$, $^3J_{HPt}$ 20), 6.31 ($H^{4'B}$), 6.98 (H^{5A}), 7.05 (H^{5B}), 7.1–8.2 (10H), 8.99 ($2H_{o'}$), 9.19 ($2H_o$), 9.27 (H^{6B}), 9.45 (H^{6A}, $^3J_{HPt}$ 40). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$): 335 (17.7), 355 (17.6), 395 (6.2), 430 (2.4). Luminescent characteristics (DMF, 298 K), $\nu_{max} \times 10^{-3}$ cm^{-1} (τ, μs; *F*): 17.76 (3; 0.4). Electrochemical parameters (DMF, reference Fc/Fc^+), V: $E_{1/2}$ –1.76, –2.09; E_p (*v* 100 mV/s): 0.73, 0.87.

(μ-4,4'-Bipyridyl)bis[*trans-N,N*-chloro(2-(2-pyridyl)thiophen-3-ide)platinum(II)] (IV). A saturated solution of 0.1 mmol of $[Pt(tpy)(\mu\text{-}Cl)]_2$ [7] and 0.2 mmol of 4,4'-bipyridyl in CH_2Cl_2 was stirred for 5 days at room temperature, filtered, and treated with ether. The yellowish-orange precipitate that formed was dissolved in a minimum of CH_2Cl_2, and the solution was subjected to chromatography on Al_2O_3 with acetone as eluent. The solution of the second chromatographic band was evaporated to dryness in a vacuum, and the residue was washed with ether and dried in a vacuum. Yield 45%. ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 6.40 ($2H^{4'}$, $^3J_{HPt}$ 20), 7.00 ($2H^5$), 7.37 ($2H^{5'}$), 7.5–7.6 ($2H^3$), 7.66 ($4H_m$), 7.74 ($2H^4$), 9.14 ($4H_o$, $^3J_{HPt}$ 45), 9.47 ($2H^6$, $^3J_{HPt}$ 40). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$): 312 (42.2), 337 (39.6), 420 (7.4). Luminescent characteristics (DMF, 298 K), $\nu_{max} \times 10^{-3}$, cm^{-1} (τ, μs; *F*): 17.86 (14; 0.1). Electrochemical parameters (DMF, reference Fc/Fc^+), V: $E_{1/2}$ –1.85, –2.14, –2.43; E_p (*v* 100 mV/s) 0.58.

The techniques of spectroscopic and electrochemical investigations were described in [3].

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research and the *Obshchaya i tekhnicheskaya khimiya* Interinstitution Scientific and Technical Program (project nos. 97-03-32272 and P-70).

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