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LETTERS TO THE EDITOR

Mixed-Ligand Cyclometalated Pd(II) and Au(III) Complexes Based on 2-Benzylpyridine

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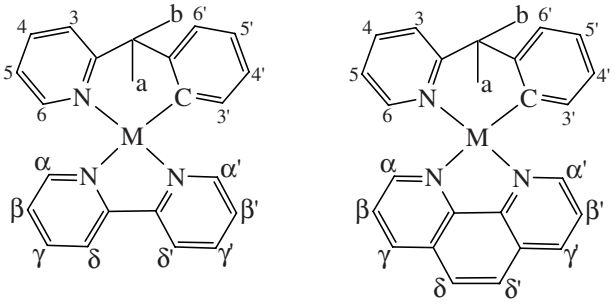
Progress in the chemistry of electronically excited metal complexes is largely connected with searching for new complexes characterized by long-lived excited states and reversible photo- and electro-induced charge transfer [1]. Cyclometalated complexes of platinum metals form a promising type of such complexes [2–4].

Proceeding with our research into Pd(II) and Au (III) complexes with 2-phenylpyridine [4, 5], in this work we synthesized mixed-ligand cyclometalated complexes based on the deprotonated form of 2-benzylpyridine (benzpy) with 2,2'-bipyridyl (bpy) and 1,10-phenantroline (phen) (see scheme) and identified the products by ^{1}H NMR, electronic absorption and emission spectroscopy, and cyclic voltammetry.



The obtained complexes are stable in the solid state and in solutions (acetonitrile, DMSO, DMF). The ^{1}H NMR data show that both cyclometalated and chelating ligands are present in the inner sphere of the complexes and that the six-membered metal-complex fragment {M(benzpy)} has a *boat*-type configuration [6–8] and does not undergo fast inversion at room temperature.

The electronic absorption spectra of these complexes, like the spectra of cyclometalated complexes based on 2-phenylpyridine [4, 5], characteristically show bathochromically shifted of intraligand bands and by the appearance of a new band in the region of 330–370 nm, assigned to a charge-transfer transition.

The reduction voltammograms of the Pd(II) complexes contain a reversible one-electron wave whose half-wave potential is almost independent of the nature of the chelating ligand ($E_{1/2}$ –1.71 V), that allows us to assign it to the electron transfer on π* orbitals preferentially localized on the {Pd(benzpy)} fragment. The irreversible reduction waves of the Au(III) complexes were assigned to the electron transfer on metal *d** orbitals, which results in formation of highly reactive Au(II) complexes undergoing subsequent fast reaction.

The vibrationally structured low-temperature luminescence spectra of the $[Pd(benzpy)bpy]^+$, $[Pd(benzpy)phen]^+$, and $[Au(benzpy)phen]^+$ complexes are similar to each other, which, along with the lifetime [τ 10^{-4}–10^{-3} s] and the characteristic vibration frequency of 1400 cm^{-1}, points to an intraligand nature of the lowest excited state localized on the {Pd(benzpy)} fragment of the complexes.

The complexes were synthesized by a common procedure including 30-min stirring preliminarily synthesized $[Pd(benzpy)(\mu\text{-}Cl)]_2$ [6] or $[Au(benzpy)Cl_2]$ [7] with 2 equiv of $AgNO_3$ in an acetonitrile solution, filtering off the AgCl precipitate, and adding 1 equiv of chelating ligand to the filtrate. After 1-h stirring at

50°C the resulting yellow precipitates of the complexes were filtered off, washed with CH_3CN and ether, and dried in air. Yields 60–70 %.

[(2-Benzyl-3-ido)pyridine](2,2'-bipyridyl) palladium(II) nitrate [Pd(benzpy)bpy]NO_3. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): {Pd(benzpy)} –8.66 d (H^6, $^3J_{HH}$ 2.9), 8.19 d (H^3, $^3J_{HH}$ 2.9), 8.04 d.d (H^4, $^3J_{HH}$ 7.3, 8.0), 7.75 d ($H^{6'}$, $^3J_{HH}$ 8.0), 7.50 t (H^5, $^3J_{HH}$ 6.5), 7.40 d ($H^{3'}$, $^3J_{HH}$ 7.3), 7.17 m ($H^{4'}$), 7.10 m ($H^{5'}$), 4.94 d (H^{α}, $^3J_{HH}$ 13.1), 4.23 d (H^{β}, $^3J_{HH}$ 15.3); {Pd(bpy)} –8.75 d ($2H^{\alpha,\alpha'}$, $^3J_{HH}$ 5.8), 8.46 d ($2H^{\delta,\delta'}$, $^3J_{HH}$ 8.0), 8.28 d.d ($2H^{\gamma,\gamma'}$ 7.3, 7.9), 7.69 d.d ($2H^{\beta,\beta'}$ 4.4, 7.2). Electronic absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} cm^{-1}): 235 (60.98), 305 (25.2), 320 (23.5), 350 sh (3.1). Phosphorescence parameters (77 K, DMF : toluene, 1 : 1) λ_{max}, nm (τ, μs): 453, 484, 515, 570 (330). Reduction voltammogram (DMF, reference Fc^+/Fc), V: $E_{1/2}$ –1.70.

[(2-Benzyl-3-ido)pyridine](1,10-phenanthroline) palladium(II) nitrate [Pd(benzpy)phen]NO_3. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): {Pd (benzpy)} –8.62 d (H^6, $^3J_{HH}$ 5.1), 8.08 t.d (H^4, $^3J_{HH}$ 8.0, $^3J_{HH}$ 1.5), 7.79 d ($2H^{3,6'}$, $^3J_{HH}$ 8.0), 7.56 m (H^3), 7.17 m ($3H^{3',4',5'}$), 4.98 d (H^{α}, $^3J_{HH}$ 14.5), 4.29 d (H^{β}, $^3J_{HH}$ 14.5); {Pd(phen)} –9.05 d ($H^{\alpha'}$, $^3J_{HH}$ 4.4), 8.94 d (H^{α}, $^3J_{HH}$ 5.1), 8.83 d ($2H^{\gamma,\gamma'}$, $^3J_{HH}$ 8.0), 8.24 s ($2H^{\delta,\delta}$), 8.02 d.d ($H^{\beta'}$, $^3J_{HH}$ 6.5, 8.7), 8.00 d.d (H^{β}, $^3J_{HH}$ 6.5, 8.7). Electronic absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} cm^{-1}): 230 (55.4), 270 (51.9), 300 sh (20.7), 340 sh (9.1). Phosphorescence parameters (77 K, DMF:toluene, 1:1) λ_{max}, nm (τ, μs): 452, 483, 520, 553 (3400). Reduction voltammogram (DMF, reference Fc^+/Fc), V: $E_{1/2}$ –1.71.

[(2-Benzyl-3-ido)pyridine](2,2'-bipyridyl)gold(III) nitrate [Au(benzpy)bpy]$(NO_3)_2$. ^{1}HNMR spectrum (CD_3CN), δ, ppm (*J*, Hz): {Au(benzpy)} –8.51 d (H^6, $^3J_{HH}$ 5.9), 8.46 d ($H^{3'}$, $^3J_{HH}$ 7.3), 8.20 d ($H^{6'}$, $^3J_{HH}$ 8.0), 7.93 t (H^4, $^3J_{HH}$ 6.5), 7.58 d (H^3, $^3J_{HH}$ 8.0), 7.45 m ($2H^{4',5'}$), 7.37 m (H^5), 5.06 d (H^{α}, $^3J_{HH}$ 15.3), 4.54 d (H^{β}, $^3J_{HH}$ 15.3); {Pd(bpy)} –9.10 d ($2H^{\alpha,\alpha'}$, $^3J_{HH}$ 5.8), 8.97 d ($2H^{\delta,\delta'}$, $^3J_{HH}$ 8.0), 8.71 d.d ($2H^{\gamma,\gamma'}$ 7.3, 8.0), 8.12 d.d ($2H^{\beta,\beta'}$ 6.5, 7.3). Electronic absorption spectrum (CH_3OH), λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} cm^{-1}): 280 (18.0), 330 (6.6). Reduction voltammogram (DMF, reference Fc^+/Fc), V: E_p –0.69.

[(2-Benzyl-3-ido)pyridine](1,10-phenantroline)-gold(III) nitrate [Pd(benzpy)bpy]$(NO_3)_2$. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): {Au(benzpy)} –9.29 d (H^6, $^3J_{HH}$ 5.8), 9.22 d (H^3, $^3J_{HH}$ 8.0), 8.97 m (H^4), 8.51 t (H^5, $^3J_{HH}$ 6.5), 8.24 d ($H^{6'}$, $^3J_{HH}$ 8.0), 7.99 m ($H^{5'}$), 7.73 d ($H^{3'}$, $^3J_{HH}$ 8.0), 7.47 m ($H^{4'}$), 5.09 d (H^{α}, $^3J_{HH}$ 16.7), 4.60 d (H^{β}, $^3J_{HH}$ 15.3); {Au(phen)} –9.29 d ($2H^{\alpha,\alpha'}$, $^3J_{HH}$ 5.8), 8.53 s ($2H^{\delta,\delta'}$), 8.40 m ($2H^{\gamma,\gamma'}$), 7.47 m ($2H^{\beta,\beta'}$). Electronic absorption spectrum (CH_3OH), λ_{max}, nm ($\varepsilon \times 10^{-3}$, mol^{-1} cm^{-1}): 270 (55.4), 280 (41.9), 320 (12.4), 370 (4.6). Phosphorescence parameters (77 K, DMF : toluene, 1 : 1) λ_{max}, nm (τ, μs): 452, 480, 510 (86). Reduction voltammogram (DMF, reference Fc^+/Fc), V: E_p –0.73.

The ^{1}HNMR spectra were taken on a Bruker AC-200F spectrometer. The electronic absorption spectra were obtained on an SF-2001 spectrophotometer at 293 K. The luminescence parameters at 77 K were determined on a KSVU-1 device with a laser (LGI-21) photoexcitation [9]. The reduction voltammograms were obtained at 293 K on an SVA-1B device in a three-electrode cell with separated compartments for the working (Pt), auxiliary (Pt), and reference (Ag) electrodes [10].

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