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LETTERS TO THE EDITOR

Synthesis and Properties of Pd(II) and Pt(II) Cyanide Complexes with Cyclometalating Ligands Derived from 2-Phenylpyridine and 2-(2-Thienyl)pyridine

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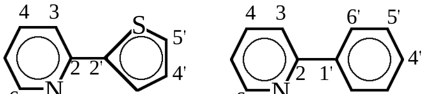
The fact that platinum complexes with cyclometalating ligands have long-lived electronically excited states and undergo reversible electron-transfer processes allows such compounds to be considered as prospective components of artificial molecularly organized systems with directed charge and energy phototransfer [1]. In this connection of particular attention are coordinately unsaturated complexes capable of combining into molecularly organized system via "complex as ligand"–"complex as metal" interactions [2].

It the present work we obtained and characterized by ^{1}H and ^{13}C NMR, IR, and electronic spectroscopy, as well as cyclic voltammetry, coordinately unsaturated cyclometalated complexes with ambident cyanide ligands: $[N(C_4H_9)_4][M(C^{\wedge}N)(CN)_2]$ [M = Pt(II) and Pd(II), $(C^{\wedge}N)^-$ = deprotonated 2-(2-thienyl)pyridine and 2-phenylpyridine].



The compounds were prepared by a general procedure involving stirring at room temperature for ~30 min saturated aqueous solutions of complexes $[M(C^{\wedge}N)En]Cl$ [M = Pt(II), Pd(II); En = ethylenediamine] [3] with excess (1 : 10) KCN, treatment of the reaction mixture with a saturated solution of $[N(C_4H_9)_4]Cl$ in CH_2Cl_2, and precipitation of the products from the methylene chloride solution with diethyl ether. Analysis of the resulting mononuclear cyclometalated Pt(II) and Pd(II) complexes with cyanide ligands (yield >85%) showed that they require no additional purification and are stable both in the solid state and in solutions (CH_2Cl_2, CH_3CN, CH_3OH, $(CH_3)_2SO$, DMF).

Complexes $[N(C_4H_9)_4][M(C^{\wedge}N)(CN)_2]$ have close C≡N vibration frequencies ($\Delta\nu$ 2–4 cm^{-1}) and coordination-induced chemical shifts (CIS = $\delta_{comp} - \delta_{lig}$) of the $H^{3'}$ and $H^{4'}$ protons of the cyclometalating ligands (ΔCIS 0.01–0.07 ppm). At the same time, the deshieliding of the H^6 protons in going from Pt(II) to Pd(II) (ΔCIS 0.27–0.38 ppm) points to a weaker donor–acceptor interaction of palladium with the pyridine moiety of the $(C^{\wedge}N)^-$ ligands.

The optical and electrochemical properties of the complexes in terms of the localized MOs model are determined by the metal-centered character of their HOMO ($d_{Pt/Pd}$) and the ligand-centered character of their LUMO ($\pi^*_{(C^{\wedge}N)}$). The destabilization of the $\pi^*_{(C^{\wedge}N)}$ orbitals because of the weaker donor–acceptor interaction between the metal and the pyridine moiety of the cyclometalating ligand in Pd(II) compared with Pt(II) complexes results in a cathodic shift of the half-wave potential ($\Delta E_{1/2}$ 130–150 mV) of ligand-centered electrochemical reduction of palladium complexes and to a short-wave shift [$\Delta\nu$ $(2–3)\times 10^3$ cm^{-1}] of their low-energy d–π^* charge-transfer transitions.

Tetrabutylammonium dicyano[2-(2-pyridyl)-thiophen-3-ido]platinate(II). Yield 86%. IR spectrum, ν(CN), cm^{-1}: 2115, 2126. ^{1}H NMR spectrum (CD_3OD), δ, ppm (J, Hz): 9.01 (H^6, $^3J_{HH}$ 5.9, $^4J_{HH}$ 1.2, $^3J_{HPt}$ 34), 7.91 (H^4, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.8), 7.47 (H^3, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.3), 7.45 ($H^{4'}$, $^3J_{HH}$ 5.2), 7.30 ($H^{3'}$, $^3J_{HH}$ 5.2, $^3J_{HPt}$ 20). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm (J, Hz): 164.2 (C^2), 163.2 ($C^{3'}$), 153.5 (C^6, $^2J_{CPt}$ 31), 145.9 ($C^{2'}$), 137.1 ($C^{4'}$, $^2J_{CPt}$ 126), 129.2 ($C^{5'}$, $^3J_{CPt}$ 62), 122.4 (C^5, $^3J_{CPt}$ 26), 118.9 (C^3, $^3J_{CPt}$ 26), 116.9 (CN), 145.4 (CN). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon\times 10^{-3}$): 299 (12.5), 330 (9.2), 398 (3.1), 532 pl (0.02), 550 (0.01). Luminescent characteristics: short-wave maximum, λ_{max}, nm [lifetime, τ,

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μs; quantum yield Φ (temperature *T*, K)]: 553 [19; 0.28 (77)]; 558 [19; 0.31 (298)]. Electrochemical parameters: $E_{1/2}$, V; E_p, V (*v* 100 mV/s): –2.36; 2.03.

Tetrabutylammonium dicyano[(2-pyridyl)-phenyl-2-ido]platinate(II). Yield 89%. IR spectrum, ν(CN), cm^{-1}: 2113, 2123. ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 9.40 (H^6, $^3J_{HH}$ 5.8, $^3J_{HPt}$ 31), 8.06 ($H^{3'}$, $^3J_{HH}$ 7.3, $^3J_{HPt}$ 49), 7.87 (H^4, $^3J_{HH}$ 5.8, $^3J_{HH}$ 7.4), 7.75 (H^3, $^3J_{HH}$ 5.8), 7.55 ($H^{6'}$, $^3J_{HH}$ 7.3), 7.15 (H^5, $^3J_{HH}$ 5.8, $^3J_{HH}$ 7.4), 7.12 ($H^{4'}$, $^3J_{HH}$ 7.3), 7.08 ($H^{5'}$, $^3J_{HH}$ 7.3). ^3C NMR spectrum (CD_2Cl_2), δ_C, ppm (*J*, Hz): 168.2 (C^2, $^2J_{CPt}$ 72), 158.2 ($C^{2'}$, J_{CPt} 804), 153.2 (C^6, $^2J_{CPt}$ 34), 147.1 ($C^{1'}$, $^2J_{CPt}$ 23), 138.8 (C^4, $^4J_{CPt}$ 4), 138.7 ($C^{3'}$, $^2J_{CPt}$ 102), 130.4 ($C^{4'}$, $^3J_{CPt}$ 56), 123.8 ($C^{5'}$, $^4J_{CPt}$ 4), 123.4 (C^5, $^3J_{CPt}$ 29), 123.0 ($C^{6'}$, $^3J_{CPt}$ 28), 118.7 (C^3, $^3J_{CPt}$ 30), 115.7 (CN), 145.5 (CN). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$): 325 (5.6), 340 (4.0), 380 pl (1.7), 443 (0.03), 475 (0.02). Luminescent characteristics: λ_{max}, nm [τ, μs; Φ (*T*, K)]: 475 [22; 0.75; (77)], 481 [1; 0.02 (298)]. Electrochemical parameters: $E_{1/2}$, V; E_p, V (*v* 100 mV/s): –2.36; 2.01.

Tetrabutylammonium dicyano[2-(2-pyridyl)-thiophen-3-ido]palladate(II). Yield 94%. IR spectrum, ν(CN), cm^{-1}: 2118, 2126. ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 8.74 (H^6, $^3J_{HH}$ 6.0), 7.88 (H^4, $^3J_{HH}$ 7.6, 6.6), 7.42 ($H^{4'}$, $^3J_{HH}$ 5.2), 7.38 (H^3, $^3J_{HH}$ 8.0), 7.18 (H^5, $H^{3'}$). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$): 296 (8.1), 370 (5.0). Luminescent characteristics: λ_{max}, nm [τ, μs; Φ (*T*, K)]: 534 [360; 0.2 (77)]. Electrochemical parameters: $E_{1/2}$, V; E_p, V (*v* 100 mV/s): – 2.49; 2.23.

Tetrabutylammonium dicyano[(2-pyridyl)-phenyl-2-ido]palladate(II). Yield 92%. IR spectrum, ν(CN), cm^{-1}: 2115, 2122. ^1H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 8.99 (H^6, $^3J_{HH}$ 5.6, $^4J_{HH}$ 1.5), 7.97 ($H^{3'}$, H^4), 7.82 (H^3, $^3J_{HH}$ 7.6), 7.64 ($H^{6'}$, $^3J_{HH}$ 7.3), 7.38 (H^5, ^{3}JHH 7.1, 5.5, $^4J_{HH}$ 1.5), 7.05 ($H^{4'}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.6), 7.04 ($H^{5'}$, $^3J_{HH}$ 7.3). Electronic absorption spectrum, λ_{max}, nm ($\varepsilon \times 10^{-3}$): 314 (7.0), 342 sh 5.0). Luminescent characterisitics: λ_{max}, nm [τ, μs; Φ (*T*, K)]: 460 [320; 0.4 (77)]. Electrochemical parameters: $E_{1/2}$, V; E_p, V (*v* 100 mV/s): –2.51; 2.23.

The ^1H, ^{13}C, IR (KBr), and electronic absorption spectra (DMF) were obtained at 298 K on Bruker AC-200F, Perkin–Elmer FT-IR-1725X, and SF-121 instruments, respectively. Luminescent measurements were performed on a KSVU-1 device with an LGI-21 laser photoexcitation (λ_{exc} 337 nm) for frozen (77 K) and liquid (298 K) solutions in toluene–DMF, 1:1. The cyclic voltammograms were taken at 298 K in DMF in the presence of a 0.1 M $[N(C_4H_9)_4]ClO_4$ solution on an SVA-1B device against a ferrocenium/ferrocene redox system.

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