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LETTERS TO THE EDITOR

Cyclometallated Complexes of Pt(IV) 2-(*p*-Tolyl)pyridine and 1-Phenylpyrazole

E. A. Katlenok and K. P. Balashev

Herzen Russian State Pedagogical University, nab. reki Moiki 48, St. Petersburg, 191186 Russia
e-mail:balashevk@mail.ru

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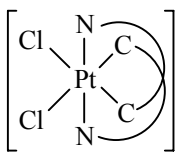
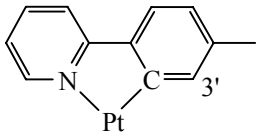
Cyclometallated complexes of platinum group metals with long excited state lifetime are widely applied in optoelectronic and sensor devices development, and as photocatalysts [1, 2].

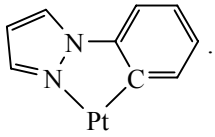
The optical and electrochemical properties of cyclometallated Pt(IV) complexes have been less studied as compared with those of Pt(II) and Ir(III) complexes. Here, we report on $[Pt(C\hat{}N)_2Cl_2]$ complexes [$(C\hat{}N)^-$ are deprotonated 2-(*p*-tolyl) pyridine (ptpy) or 1-phenylpyrazole (ppz)].



{Pt(C^N)} =



{Pt(ptpy)}



{Pt(ppz)}

The ^1H NMR and IR data confirmed the *cis*-structure of Pt(IV) octahedral complexes. The signals of two magnetically equivalent metallated ligands were observed in the ^1H NMR spectra of the complexes. Owing to mutual anisotropic action of circular currents of tolyl and phenyl fragments, the $H^{3'}$ signals were shifted upfield (δ of 1.60–1.54 ppm) as compared with the spectra of the free ligands Hptpy and Hppz. Formation of {Pt(C^N)} cycles led to the low-frequency shift of the C=N stretching band by 7 cm^{-1} and to the typical [3] change of bending bands of the S–N bond of the tolyl and phenyl ligand fragment due to deprotonation.

The absorption spectra of the complexes contained spin-allowed electronic transitions of two types: intraligand π–π* band in the range of 230–290 nm (almost coinciding with Hptpy and Hppz spectra) and the π*–*d* ligand–metal charge transfer bands (weaker) in the range of 300–360 nm.

The two-electron irreversible reduction of Pt(IV) complexes to those of Pt(II) at the potentials –1.68 to –1.91 V confirmed [4, 5] the localization of the lowest unoccupied molecular orbital at the predominantly metal-centered *d**-orbital. Oxidation potentials of the complexes were out of the range of CH_3CN (solvent) stability.

Photoexcitation of the $[Pt(ptpy)_2Cl_2]$ complex in the liquid and frozen solutions led to the vibration-structured (ν = 1400 cm^{-1}) long-lived (50–320 μs) intraligand π–π* phosphorescence in the range of 454–600 nm. Similar phosphorescence of $[Pt(ppz)_2Cl_2]$ (ν = 1400 cm^{-1}, τ = 30 μs) in the range of 420–550 nm was only observed in the frozen solution. Quenching of the phosphorescence of the $[Pt(ppz)_2Cl_2]$ complex in the liquid solution was assigned to the thermally activated population of π–π* excited states subjected to radiationless deactivation [6].

Thus, in contrast to the lowest unoccupied molecular orbital of similar Ir(III) and Rh(III) complexes (localized at the π* orbital of the cyclometallated ligand [7, 8]), the lowest unoccupied molecular orbital in the Pt(IV) complexes was metal-centered, which resulted in the change of the electronic transition nature and thus in the hypsochromic shift of long-wavelength absorption band, as well as in the anode shift of the complex reduction potential.

The complexes were prepared via the usual procedure including the preparation of Pt(Hptpy)(ptpy)Cl and [Pt(Hppz)(ppz)Cl] [5] and their oxidation by hydrogen peroxide at 80°C [9] to obtain white precipitates of Pt(IV) complexes with yield of 50–60%.

Dichlorobis[2-(*n*-tolyl-3-ido)pyridine]platinum. ^{1}H NMR spectrum ($CDCl_3$), δ , ppm (*J*, Hz): 9.67 d.d (2H, $^3J_{HH}$ 5.7, $^3J_{HPt}$ 25), 8.40 d (2H, $^3J_{HH}$ 7.5), 8.34 d.d (2H, $^3J_{HH}$ 8.0, 7.3), 7.83 d (2H, $^3J_{HH}$ 7.9), 7.75 t (2H, $^3J_{HH}$ 6.0), 6.97 d (2H, $^3J_{HH}$ 7.9), 5.69 d (2H$^{3'}$, $^3J_{HPt}$ 33), 2.04 s (6H). IR spectrum (KBr), cm^{-1}: 1609 ν(C=N); 866, 824 δ(C–H). Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (ε×10^3, L mol^{-1} cm^{-1}): 233 (34.8), 266 (29.0), 275 sh (27), 298 sh (12), 313 (16.5), 328 sh (19), 340 (19.1). Phosphorescence spectrum (CH_2Cl_2, 293 K), λ_{max}, nm (τ, μs): 458, 489, 522 sh, 558 sh (50). Phosphorescence spectrum ($CH_3OC_2H_2OH$–C_2H_5OH, 77 K), λ_{max}, nm (τ, μs): 454, 487, 515, 554 sh, 600 sh (320). Reduction voltammogram (CH_3CN), E_p, V: –1.68.

Dichlorobis[1-(phenyl-3-ido)pyrazole]platinum. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.17 d (2H, $^3J_{HH}$ 2.9), 8.45 d (2H, $^3J_{HH}$ 2.1), 7.89 d (2H, $^3J_{HH}$ 7.9), 7.19 t (2H, $^3J_{HH}$ 7.6), 7.14 d (2H, $^3J_{HH}$ 2.6, 2.5), 6.89 d (2H, $^3J_{HH}$ 7.9, 7.5), 5.95 d (2H$^{3'}$, $^3J_{HH}$ 7.8, $^3J_{HPt}$ 36). IR spectrum (KBr), cm^{-1}: 1595 ν(C=N); 755 δ(C–H). Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm (ε×10^3, L mol^{-1} cm^{-1}): 237 (27.4), 250 sh (26), 278 sh (12), 310 (4.8), 340 sh (19.1). Phosphorescence spectrum ($CH_3OC_2H_2OH$–C_2H_5OH, 77 K), λ_{max}, nm (τ, μs): 420, 447, 476, 507 sh, 550 sh (30). Reduction voltammogram (CH_3CN), E_p, V: –1.91.

^{1}H NMR ($CDCl_3$) and IR spectra were recorded with JNM-ECX400A and Shimadzu IR Prestige-21 spectrometers of the Collective Use Center at the Department of Chemistry, Herzen Russian State Pedagogical University. Electronic absorption and luminescence spectra were registered with SF-2000 and Flyuorat-02 Panorama spectrometers in CH_2Cl_2. Low-temperature (77 K) luminescence spectra were recorded in 2-methoxyethanol–ethanol (1 : 1) mixture with Flyuorat-02 Panorama spectrometer. Oxidation voltammograms of the complexes were obtained at 293 K in three-electrode cell with separated spaces of working (GC), auxiliary (Pt), and reference (Ag) electrodes in the presence of 0.1 M $[N(C_4H_9)_4]PF_6$ in CH_3CN. The potentials are given in relation to the ferrocenium/ferrocene redox system at potential scanning rate of 100 mV s^{-1}.

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