ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 10, pp. 2272–2273. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.V. Ivanova, K.P. Balashov, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 10, pp. 1749–1750.

**LETTERS
TO THE EDITOR**

Cyclometallated Rh(III) Complexes Based on 4,6-Diphenylpyrimidine, with Ethylenediamine, *ortho*-Phenanthroline and 2,2'-Bipyridyl

E. V. Ivanova and K. P. Balashov

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

Received June 18, 2009

DOI: 10.1134/S1070363209100284

The specificity of the electronic structure of complexes of cyclometalled platinum group metals with heterocyclic ligands characterized by long-lived excited electronic state and reversible nature of the process of electroreduction determines their promising application as components of optoelectronic devices [1, 2]. It was shown earlier [3] that cyclometalled Pt(II) and Pd(II) complexes with 4,6-diphenylpyrimidine form a metal system with a spatial transfer of photoexcitation energy between the peripheral and bridging components in their structure.

In this work we obtained and characterized by ^{1}H NMR, IR, electron absorption and emission spectroscopy, and voltammetry the complexes of the type [Rh(Hdphpm)$_2$(N^N)]ClO$_4$ [Hdphpm is monodeprotonated form of 4,6-diphenylpyrimidine, (N^N)-chelating ligands: ethylenediamine (En), *ortho*-phenanthroline (phen) and 2,2'-bipyridyl (bpy)].

These complexes are stable both in solid state and in solution in (CH$_3$)$_2$CHOH, CH$_3$CN, (CH$_3$)$_2$SO. In the ^{1}H NMR spectra of these complexes the proton resonances are observed of both two magnetically equivalent cyclometallating ligands Hdphpm-, and chelating ligands (En, Bpy, Phen). The upfield shift of the proton resonance of metallated phenyl ring of Hphpm$^-$ in the *ortho*-position to the metal [Δδ 1.2 and –0.9 ppm] as compared with the non coordunated ligand indicates the *cis*-configuration of the metallated phenyl rings of two 4,6-diphenylpyrimidine ligands in the inner sphere of the complexes, resulting in the anisotropic action of the circular current of one metallated ring on the chemical shift of protons of another ring [4]. IR spectrum of [Rh(Hdphpm)$_2$En]ClO$_4$ is characterized by a low-frequency shift of (C=N) stretching vibra-tions of the pyrimidine part of cyclometallated ligand, and by typical [5,6] change of in-plane bending (C–H) vibrations as a result of metallation of the phenyl rings.

The UV spectrum of [Rh(Hdphpm)$_2$ (N^N)]ClO$_4$ complexes in the region of ($\lambda < 330$ nm) is characterized besides the intraligand adsorption bands by the presence of specific long-wave absorption band ($\lambda =$ 390–410 nm) and vibration-structured phosphorescence (λ = 463–487 nm) as a result of the spin-allowed and spin-restricted optical transition between the orbitals localized on the metal complex fragment of (Rh(Hdphpm)$_2$). The availability in the compositions of [Rh(Hdphpm)$_2$phen]ClO$_4$ and [Rh(Hdphpm)$_2$bpy] ClO$_4$ of two cyclometallated and one chelating heterocyclic ligands determines the presence of three ligand-centered one-electron waves of reduction of the complexes as a result of electron transfer on the unoccupied π* orbitals of each ligand Substitution of heterocyclic bpy and phen by aliphatic En leads to the existence of two [Rh(Hdphpm)$_2$En]ClO$_4$ reduction waves as a result of the electron transfer on the π* orbitals of two cyclometallating ligands.

4,6-Diphenylpyrimidine was obtained along the procedure in [7]. The Rh(III) complexes were obtained according to the general methodology that included the formation of [Rh(Hdphpm)$_2$(μ-Cl)]2 precipitate by refluxing 1 equivalent of RhCl$_3$·3H$_2$O with 8 equivalents of 4,6-diphenylpyrimidine in 2-methoxyetanol followed by the substitution of chloride ligands by ethylenediamine, 1,10-phenanthroline or 2,2'-bipyridyl by the reaction of the suspension in methanol of bridging Rh(III) chloride complex with the chelating liands. Precipitation of the complexes from the methanol solution was performed by adding $NaClO_4$ to the reaction mixture. The resulting precipitate containing complex was filtered, washed with cold methanol, then with ether, and dried in air.

Bis[(4-phenyl-3-ido)(6-phenylpyrimidino)]etylenediaminorhodium(III) perchlorate [Rh(Hdphpm)$_2$En]·ClO$_4$. Yield 65%. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 9.23 s (2H), 8.53 d ($^3J_{HH}$ 1.1; 2H), 8.41 d ($^3J_{HH}$ 7.5; 4H), 8.09 d.d ($^3J_{HH}$ 7.8, $^4J_{HH}$ 1.3; 2H), 7.67 m (6H), 7.05 d.d.d ($^3J_{HH}$ 7.8, 7.4; $^4J_{HH}$ 1.2; 2H), 6.95 d.d.d ($^3J_{HH}$ 7.3, 7.4, $^4J_{HH}$ 1.14; 2H), 6.48 d ($^3J_{HH}$ 7.7; 2H), 3.49 d ($^3J_{HH}$ 9.2; 2H), 3.03 m (2H), 2.88 d ($^3J_{HH}$ 9.1; 2H), 2.77 d ($^3J_{HH}$ 4.3; 2H). Parameters of the IR spectrum (KBr), ν, cm^{-1}: 693 and 747 (C_6H_5), 740 (C^6 H^4), 1585 (C=N). The electron absorption spectra (CH_3CN), $\lambda_{max.}$, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 278 (15), 324 (10.1), 410 (3.2). Parameters of phosphorescence [77 K, $CHON(CH_3)_2$: $CH_3C_6H_5$, 1:1], $\lambda_{max.}$, nm (τ, ms): 487, 505, 559 (13). Reduction voltammogram [(CHON $(CH_3)_2$, relatively to the Fc^+/Fc redox system], V: $E_{1/2}$ –1.90, –2.10

Bis[(4-phenyl-3-ido)(6-phenylpyrimidine)](1,10-phenanthroline)rhodium(III) perchlorate [Rh (Hdphpm)$_2$phen]ClO$_4$. Yield 67%. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 8.73 d.d ($^3J_{HH}$ 8.3, $^4J_{HH}$ 1.5; 2H), 8.49 d ($^3J_{HH}$ 1.1; 2H), 8.38 d.d ($^3J_{HH}$ 4.9, $^4J_{HH}$ 1.4; 2H), 8.24 s (2H), 8.04 s (2H), 8.24 d.d ($^3J_{HH}$ 7.8, $^4J_{HH}$ 1.4; 4H), 8.18 d.d ($^3J_{HH}$ 8.2, $^4J_{HH}$ 1.5; 2H), 7.86 d.d ($^3J_{HH}$ 4.9, 8.3; 2H), 7.56 m (6H), 7.26 d.d.d ($^3J_{HH}$ 7.7, 7.4; $^4J_{HH}$ 1.4; 2H), 7.17 d.d.d ($^3J_{HH}$ 7.6, 7.4; $^4J_{HH}$ 1.4; 2H), 6.72 d ($^3J_{HH}$ 7.4; 2H). The electron absorption spectra (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 222 (54.9), 272 (66.2), 330 (31.3), 393 (10.5). Parameters of phosphorescence [77 K, CHON $(CH_3)_2$: $CH_3C_6H_5$, 1:1], $\lambda_{max.}$, nm, (τ, ms): 463, 494, 524 (14). Reduction voltammogram [($CHON(CH_3)_2$, relatively to the Fc^+/Fc redox system], V: $E_{1/2}$ –1.68, –1.94, E_{peak} –2.16.

Bis[(4-phenyl-3-ido)(6-phenylpyrimidine)](2,2'-bipyridyl)rhodium(III) perchlorate [Rh(Hdphpm)$_2$bpy]·ClO$_4$. Yield 65%. ^{1}H NMR spectrum (CD_3CN), δ, ppm (*J*, Hz): 8.52 d ($^3J_{HH}$ 8.2; 2H), 8.49 d ($^3J_{HH}$ 1.0; 2H), 8.24 d.d ($^3J_{HH}$ 7.8, $^4J_{HH}$ 1.5; 4H), 8.21 s (2H), 8.20 d.d ($^3J_{HH}$ 7.7; 2H), 8.17 d.d.d ($^3J_{HH}$ 8.0, 7.8, $^4J_{HH}$ 1.5; 2H), 8.05 d ($^3J_{HH}$ 4.8; 2H), 7.59 m (6H), 7.54 d.d.d ($^3J_{HH}$ 5.0, 8.0, $^4J_{HH}$ 1.5; 2H), 7.22 d.d.d ($^3J_{HH}$ 7.6, 7.4; $^4J_{HH}$ 1.3; 2H), 7.12 d.d.d ($^3J_{HH}$ 7.6, 7.4; $^4J_{HH}$ 1.3; 2H), 6.62 d ($^3J_{HH}$ 7.7; 2H). Electron absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}) nm: 279 (30.1), 297 sh (26.4), 309 (25.7), 331 (19.2), 395 (6.4). Parameters of phosphorescence [77 K, ($CHON(CH_3)_2$: $CH_3C_6H_5$, 1:1), $\lambda_{max.}$, nm, (τ, ms)]: 464, 494, 524 (14). Reduction voltammogram [$CHON(CH_3)_2$, relatively to the Fc^+/Fc redox system], V: $E_{1/2}$ –1.69, –1.92, E_{peak} –2.10.

The ^{1}H NMR spectra were registered on a JNM-ECX400A instrument at 293 K in CD_3CN. Electron absorption spectra were taken on a SF-2000 spectrophotometer from CH_3CN solutions. IR spectra were recorded from KBr pellets on a Prestige-21 Shimadzu IR spectrometer. Luminescent studies were conducted on KSVU-1 setup with a pulse laser photoexcitation (LGI-21, l 337 nm, τ 10 ns) at 77 K from glassy matrices $(CH_3)_2CHOH$: $CH_3C_6H_5$ (1:1) [8]. Voltammograms were registered on EAC-1B setup at 293 K in a three-electrode cell with the separated space of working (Pt), auxiliary (C) and reference (Ag) electrodes in the presence of 0.1 M $[N(C_4H_9)_4]BF_4$ from solutions in $CHON(CH_3)_2$ [9]. Potentials are given relatively to the redox system ferrocenyl-ferrocene (Fc^+/Fc).

REFERENCES

1. Zhou, G-J., Wang, X-Z., Wong, W-Y., Yu, X-M., Kwok, H-S., and Lin, Z., *J. Organomet. Chem*., 2007, vol. 692, no. 16, p. 3461.
2. Kim, S-Y., Kim, J-H., Ha, Y., Lee, S-H., Seo, J-H., and Kim, Y-K., *Current Appl. Phys*., 2007, vol. 7, no. 4, p. 380.
3. Ivanova, E.V., Puzyk, M.V., and Balashev, K.P., *Optika i Spektr*., 2009, vol. 106, no. 3, p. 409.
4. Steel, P.J., *J. Organometal. Chem*., 1991, vol. 408, no. 3, p. 395.
5. Caygill, G.B. and Steel, P.J., *J. Organomet. Chem*., 1987, vol. 7, no. 1, p.115.
6. Caygill, G.B., Hartsorn, R.M., and Steel, P.J., *J. Organomet. Chem*., 1990, vol. 382, no. 3, p. 455.
7. Brederick, H., Gompper, R., and Morlock, G., *Chem. Ber*., 1957, vol. 90, p. 942.
8. Vasil'ev, V.V., Balashev, K.P., and Shagisultanova, G.A., *Opt. i Spektr.,* 1983, vol. 54, no. 5, p. 876.
9. Kotlyar, V.S. and Balashev, K.P., *Elektrokhimiya*, 1996, vol. 32, no. 11, p. 1358.