SUPPORTING INFORMATION

Heteroleptic $[Os(H)(CO)(N^\wedge N)(tpp)_2]^+$ and $[Os(Cl)(CO)(N^\wedge N)(tpp)_2]^+$ complexes – comparative studies of their luminescence properties

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Experimental details

Materials

Solvent used in FT-IR absorption or UV-vis absorption and emission studies, dichloromethane - CH_2Cl_2, acetonitrile - ACN, methanol - MeOH, and ethanol - EtOH, were of spectroscopic grade purchased from Aldrich.

The α-diimine - N^N and triphenylphosphine - tpp ligands, potassium hexafluorophosphate - KPF_6 and trimethylamine N-oxide - $(CH_3)_3NO$ were purchased from Lancaster, Sigma-Aldrich or Alfa Aesar companies. These commercially available reagents were used without further purification. All other reagents and solvents used in the syntheses were of analytical grade and were used without further purification. Potassium hexachloroosmate(IV) – K_2OsCl_6 (Strem Chemical Company), has been used for preparation of not commercially available $OsCl_2(CO)_2(tpp)_2$. This intermediate, prepared according to literature procedure[1] has been used in syntheses of $[Os(Cl)(CO)(N^\wedge N)(tpp)_2]^+$ and $[Os(H)(CO)(N^\wedge N)(tpp)_2]^+$ chelates. The synthesized complexes were obtained in the form of PF_6^- salts. All performed reactions were carried out under anaerobic conditions in an inert argon atmosphere.

Synthetic procedures

The chloride $[Os(Cl)(CO)(N^\wedge N)(tpp)_2]PF_6$ complexes were synthesized following the procedure published in literature.[2] In a typical experiment a mixture of 0.38 mmol of the given N^N ligand, 0.18 mmol of $OsCl_2(CO)_2(tpp)_2$ (0.15 g), and 0.75 mmol of $(CH_3)_3NO$ were heated in 20 ml of ethylene glycol monomethyl ether under reflux for about 2 h. Then an excess of KPF_6 was added to the hot solution and orange-yellow precipitate was formed. After cooling the precipitate was filtered, dried and then purified by means of column chromatography applying first silica gel and CH_3CN/toluene 1:2 solution as eluent and then using of activated basic alumina and CH_2Cl_2 as eluent. The yellow to an orange-yellow crystalline products exhibiting strong luminescence were obtained in 40-55% yields.

The hydride $[Os(H)(CO)(N^\wedge N)(tpp)_2]PF_6$ complexes were prepared by reacting an equimolar amount of $OsCl_2(CO)_2(tpp)_2$ with appropriate N^N ligand. In a typical reaction 0.24 mmol (~0.2 g) of $OsCl_2(CO)_2(tpp)_2$ and 0.24 mmol of α-diimine were heated at reflux for 3-4 h in 15-30 ml of diethylene glycol monoethyl ether. Next an excess of KPF_6 in water solution was added to the reaction mixture and precipitate was formed, then filtered and dried. The obtained strongly luminescent products were initially separated by means of column chromatography using activated basic alumina and CH_2Cl_2 as eluent and then finally purified applying silica gel and CH_3CN/toluene 1:3 or 1:4 mixtures as eluent. The final products were obtained with the yields of 20-40%.

Spectroscopic data used for identification of the synthesized compounds are collected in the Table S1.

X-ray diffraction measurements

Data processing and internal scaling were carried out with SAINT V8.35A (Bruker AXS Inc., 2015). Structures were solved by direct methods and Fourier techniques SHELXS and refined using the SHELXL programs.[3] All, except the coordinating H^- ligand which was located on the difference maps, hydrogen atoms, were calculated in geometrical positions and refined as “riding” atoms with isotropic thermal parameters based upon the corresponding bonding carbon atom [$U(H) = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl group hydrogens)].

In the structure of the $[Os(H)(CO)(bpy)(tpp)_2]PF_6$ crystal two independent complex molecules are present. In one of them the positional disorder of CO and H^- ligands is observed with site occupancy factors (s.o.f.) equal to 0.56 and 0.44 and in the second molecule the positional disorder of one phenyl in one of the tpp ligands is observed.

In the structure of the $[Os(Cl)(CO)(bpy)(tpp)_2]PF_6$ crystal the positional disorder of CO and Cl^- ligands is observed with site occupancy factors (s.o.f.) equal to 0.55 and 0.45 as well as the disorder of toluene molecule.

Crystal data for $[Os(H)(CO)(bpy)(tpp)_2]PF_6$:

$C_{47}H_{39}N4OOsP_2 \cdot PF_6 \cdot C_7H_8$, *M* = 1136.54, translucent orange block, 0.381×0.154×0.115 mm, triclinic, space group *P*1, *a* = 14.6490(7), *b* = 14.7296(7), *c* = 23.268(1) Å, *α* = 103.447(1), *β* = 96.362(2), *γ* = 91.092(2)°, *V* = 4847.8(4) Å^3, *Z* = 4, D_c = 1.557 g/cm^3, F_{000} = 2270, D8 VENTURE DUO, Mo*Kα* radiation, *λ* = 0.71073 Å, *T* = 100(2) K, $2\vartheta_{max}$ = 61.3°, 275859 reflections collected, 26649 unique (R_{int} = 0.037). Final *GooF* = 1.29, *R* = 0.044, *wR* = 0.086, *R* indices based on 23274 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1268 parameters, 0 restraints. Lp and absorption corrections applied, μ = 2.794 mm^{-1}.

Crystal data for $[Os(Cl)(CO)(bpy)(tpp)_2]PF_6$:

$C_{47}H_{38}N_2OClOsP_2 \cdot PF_6 \cdot 0.5C_7H_8$, *M* = 1125.42, translucent intense yellow needle, 0.506×0.073×0.069 mm, tetragonal, space group $P4_2/n$, *V* = 9760(1) Å^3, *Z* = 8, D_c = 1.532 g/cm^3, F_{000} = 4472, D8 VENTURE DUO, Mo*Kα* radiation, *a* = 28.557(2), *c* = 11.9682(9) Å, *λ* = 0.71073 Å, *T* = 100(2)K, $2\vartheta_{max}$ = 49.4°, 71795 reflections collected, 8145 unique (R_{int} = 0.080). Final *GooF* = 1.11, *R* = 0.049, *wR* = 0.084, *R* indices based on 6572 reflections with with $I > 2\sigma(I)$ (refinement on F^2), 599 parameters, 14 restraints. Lp and absorption corrections applied, μ = 2.827 mm^{-1}.

Instrumentation and procedures

FT-IR, ^{31}P and ^{1}H NMR spectra were acquired using Shimadzu IRAffinity-1 and VARIAN 400-MR spectrometers, respectively. UV-vis absorption spectra were measured using Shimadzu UV 3100 spectrometer, whereas corrected steady-state luminescence spectra and emission decays by means of Gilden Photonics FluoroSense and FluoroSense-P fluorimeters. In the case of emission studies, the investigated CH_2Cl_2 solutions were carefully deaerated by the prolonged saturation with preliminary purified and dried argon.

As a quantum yield standard, a solution of quinine sulphate in 0.1 N H_2SO_4 (ϕ_{ref} = 0.51)[4] was used. The obtained emission quantum yields ϕ_{em} were measured with the estimated 10% accuracy. Emission spectra were fitted by

Table S1 Summary of the spectroscopic data used for identification of the investigated $[Os(H)(CO)(N^\wedge N)(tpp)_2]^+$ and $[Os(Cl)(CO)(N^\wedge N)(tpp)_2]^+$ complexes. Position of ν_{CO} and ν_{Os-H} band in FT-IR spectra recorded in CH_2Cl_2 solutions. Positions of ^{31}P NMR (*vs* 85% H_3PO_4) and ^{1}H NMR (*vs* TMS) signals in DMSO-d_6 solutions.

Complex type	Ligand N^N	ν_{CO}, ν_{Os-H} /cm^{-1}	^{31}P NMR /ppm	^{1}H NMR [a] /ppm
$[Os(H)(CO)(N^\wedge N)(tpp)_2]^+$	tmphen	1925 2039	19.45	9.07 (s, 1H), 8.14 (m, 2H), 7.62 (s, 1H), 7.27-7.34 (m, 6H), 7.17-7.26 (m, 12H), 7.08-7.16 (m, 12H), 2.64 (s, 3H), 2.56 (s, 3H), 2.37 (s, 3H), 1.75 (s, 3H), −12.35 (t, 1H)
	47dmphen	1929 2041	18.44	9.33 (d, 1H), 8.08 (s, 2H), 8.02 (d, 1H), 7.51 (d, 1H), 7.25-7.33 (m, 6H), 7.15-7.23 (m, 12H), 7.04-7.12 (m, 12H), 6.83 (d, 1H), 2.77 (s, 3H), 2.71 (s, 3H), −12.20 (t, 1H)
	56dmphen	1929 2041	18.61	9.36 (d, 1H), 8.56 (d, 1H), 8.48 (d, 1H), 8.10 (d, 1H), 7.61 (dd, 1H), 7.27-7.36 (m, 6H), 7.13-7.26 (m, 12H), 7.00-7.11 (m, 12H), 6.98 (dd, 1H), 2.66 (s, 3H), 2.65 (s, 3H), −12.01 (t, 1H)
	phen	1931 2041	18.55	9.45 (d, 1H), 8.49 (d, 1H,), 8.40 (d, 1H), 8.19 (d, 1H), 7.98-8.01 (m, 2H), 7.66 (dd, 1H), 7.27-7.34 (m, 6H), 7.17-7.24 (m, 12H), 7.05-7.12 (m, 12H), 7.02 (dd, 1H), −12.07 (t, 1H)
	dpphen	1931 2035	17.98	9.56 (d, 1H), 8.31 (d, 1H), 7.86 (d, 1H), 7.80 (d, 1H), 7.61-7.67 (m, 6 H), 7.52 (dd, 2H), 7.48 (dd, 2H), 7.31-7.37 (m, 6 H), 7.23-7.29 (m, 13H), 7.15-7.21 (m, 12H), 7.00 (d, 1H), −11.92
	dtbbpy	1927 2051	18.04	8.76 (d, 1H), 8.16 (d, 1H), 8.14 (d, 1H), 7.50 (d, 1H), 7.35-7.39 (m, 6H), 7.27-7.32 (m, 12H), 7.16-7.22 (m, 13H), 6.53 (dd, 1H), 1.28 (s, 18H), −12.34 (t, 1H)
	bpy [b]	1929 2043	18.11	9.95 (d, 1H), 8.24 (m, 2H), 7.86 (t, 1H), 7.77 (t, 1H), 7.69 (d, 1H), 7.35-7.40 (m, 6H), 7.28-7.34 (m, 12H), 7.17-7.25 (m, 13H), 6.56 (m, 1H), −12.28 (t, 1H)
$[Os(Cl)(CO)(N^\wedge N)(tpp)_2]^+$	tmphen	1942	−1.37	8.37 (d, 1H), 8.26 (d, 1H), 8.13 (s, 1H), 7.71 (s, 1H), 7.26-7.38 (m, 6H), 7.12-7.25 (m, 12H), 6.98-7.10 (m, 12H), 2.77 (s, 3H), 2.65 (s, 3H), 2.06 (s, 3H), 1.96 (s, 3H)
	47dmphen	1942	−1.64	8.45 (d, 1H), 8.36 (d, 1H), 8.25 (d, 1H), 8.10 (d, 1H), 7.38 (d, 1H), 7.28-7.37 (m, 6H), 7.14-7.27 (m, 12H), 6.95-7.12 (m, 12H), 6.92 (d, 1H), 2.89 (s, 3H), 2.77 (s, 3H)
	56dmphen	1942	−1.42	8.79 (d, 1H), 8.57 (d, 1H), 8.44 (d, 1H), 8.21 (d, 1H), 7.51 (dd, 1H), 7.27-7.37 (m, 6H), 7.15-7.26 (m, 12H), 6.98-7.11 (m, 13H), 2.78 (s, 3H), 2.71 (s, 3H)
	phen	1946	−1.40	8.61 (d, 1H), 8.47 (d, 1H), 8.25 (d, 1H), 8.20 (m, 2H), 8.07 (d, 1H), 7.47 (dd, 1H), 7.17-7.27 (m, 6H), 7.07-7.16 (m, 12 H), 6.87-6.96 (m, 12H), 7.00 (dd, 1H)
	dpphen	1944	−1.45	8.59 (d, 1H), 8.21 (d, 1H), 8.09 (d, 1H), 7.98 (d, 1H), 7.60-7.72 (m, 6 H), 7.57 (dd, 2H), 7.49 (d, 1H), 7.43 (dd, 2H), 7.32-7.39 (m, 6H), 7.20-7.27 (m, 12H), 7.15 (d, 1H), 7.04-7.12 (m, 11H), 6.97 (d, 1H)
	dtbbpy	1942	−1.25	8.42 (d, 1H), 8.26 (d, 1H), 8.03 (d, 1H), 7.48 (d, 1H), 7.34-7.40 (m, 6 H), 7.23-7.30 (m, 12H), 7.14-7.21 (m, 12H), 7.10 (dd, 1H), 6.63 (dd, 1H), 1.34 (s, 9H), 1.26 (s, 9H)
	bpy [c]	1944	−1.70	8.51 (d, 1H), 8.34 (d, 1H), 8.25 (d, 1H), 8.06 (t, 1H), 7.81 (d, 1H), 7.70 (t, 1H), 7.33-7.41 (m, 6H), 7.25-7.32 (m, 12H), 7.17-7.24 (m, 12H), 7.14 (t, 1H), 6.69 (t, 1H)

[a] Singlet signal from the phosphorus nuclei of tpp ligand. Additional, two time less intensive septet signals at −144.2 ppm have been recorded for all the complexes under study

[b] DFT calculations: ν_{CO} = 1935 cm^{-1} and ν_{Os-H} = 2094 cm^{-1}

[c] DFT calculations: ν_{CO} = 1953 cm^{-1}

means of a least-square method using OriginPro 9.0 software (Origin Lab Corp.) with user-defined functions. The experimental decay curves were analysed by the single-curve method using the reference convolution based on the Marquardt algorithm[5] with the χ^2 test and the distribution of residuals serving as the main criteria in the evaluation of fit quality. In all cases studied the emission decay was mono-exponential on the observation scale. Emission lifetime τ_{em} values, characterizing the recorded mono-exponential decays were measured with the temporal resolution of *ca*. 0.01 μs.

Theoretical calculation

Calculations on the electronic ground states of the investigated complexes were carried out by using B3LYP density functional theory.[6] A "double-ζ " quality basis set consisting of the Hay and Wadt[7] effective core potentials (LANL2DZ) was employed for the Os atom and 3-21G+ basis for the H, C, N, P, and Cl atoms. A relativistic effective core potential (ECP) replaced the inner core electrons of Os, leaving the outer core ($5s^25p^6$) electrons and the $5d^66s^2$ valence electrons.

The ground and the lowest triplet state geometries of the $[Os(H)(CO)(bpy)(tpp)_2]^+$ and $[Os(Cl)(CO)(bpy)(tpp)_2]^+$ complexes were optimized by using density functional theory (DFT) with the B3LYP hybrid functional starting from their respective crystal structures. Geometry optimizations were carried out to the standard convergence criteria: a maximum element of the gradient of less than 0.025 eV/Å, a RMS of gradient element of less than 0.015 eV/Å). Gas-phase geometries were obtained by a full optimization at the B3LYP level for each stationary structure in the ground S_0 and the lowest triplet T_1 electronic states. The vibrational frequency calculations were also performed for both optimized structures to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues.

Vertical electronic transitions from the minima of the S_0 or T_1 potential energy surfaces have been performed for both optimized structures within the TD-DFT calculations[8] using the B3LYP functional. All the computations were carried out by using Gaussian 03 software[9] supported by GaussView 5.0.

Notes and references

1 A. Woźna, A. Kapturkiewicz and G. Angulo, *Inorg. Chem. Commun.*, 2013, **27**, 138-141.

2 B. L. Foley, C. A. Smith and N. C. Thomas, *Inorg. Chim. Acta*, 1988, **150**, 163.

3 G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112-122.

4 R. A. Velapoldi, in: National Bureau of Standards Special Publication 378, Accuracy in Spectrophotometry and Luminescence Measurements. Proc. Conf. NBS, Gaithersburg, MD, **1972**, p. 231.

5 D. W. Marquardt, J. Soc. Ind. Appl. Math., 1963, **11**, 431-441.

6 J-F. Guillemole, V. Barone, L. Joubert and C. Adamo, *J. Phys. Chem. A*, 2002, **106**, 11354-11360.

7 P.J. Hay and W.R. Wadt, *J. Chem. Phys*., 1985, **82**, 299-312.

8 M.E. Casida, C. Jamorski, K.C. Casida and D.R. Salahub, *J. Chem. Phys*., 1998, **108**, 4439-4444.

9 Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.