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Os(dppe)(dppe monoxide)(CO)Cl_2 as an active intermediate in the synthesis of strongly luminescent divalent osmium complexes

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Abstract

Reaction of K_2OsCl_6 with 1,2-bis(diphenylphosphino)ethane (dppe) in 1:2 ratio afforded the osmium(II) Os(dppe)(dppeO)(CO)Cl_2 complex (where dppeO = 1,2-bis(diphenylphosphino)ethane monoxide) with the molecular structure confirmed by X-ray investigations. The Os(dppe)(dppeO)(CO)Cl_2 intermediate can be simply converted to $\mathrm{Os(dppe)(N\cap N)(CO)Cl^+ \cdots PF_6^-}$ species in reaction with $\mathrm{N\cap N}$ chelating diimines like 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline or 3,4,7,8-tetramethyl-1,10-phenanthroline. The obtained mixed $\mathrm{Os(P\cap P)(N\cap N)(CO)Cl^+ \cdots PF_6^-}$ complexes feature strong (with ϕ_{em} up to 0.57) long lived (with τ_{em} up to 25.2 μs) MLCT emission.

Keywords: Osmium complexes; X-ray crystallography; ^{31}P NMR spectroscopy; UV–Vis absorption and emission spectra

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Divalent osmium complexes $\mathrm{Os(N\cap N)_3^{2+}}$ with diimine ligands $\mathrm{N\cap N}$ such as 2,2′-bipyridine, 1,10-phenanthroline and their derivatives in general exhibit low emission quantum yields when compared to their $\mathrm{Ru(N\cap N)_3^{2+}}$ counterpart [1]. Typically, the emission bands of $\mathrm{Os(N\cap N)_3^{2+}}$ are deeply red-shifted from their Ru(II) analogs and occur in the far-red or near-infrared part of the UV–Vis radiation region. This is mainly due to the fact that Os(II) is more easily oxidized than Ru(II). It leads to decreasing the energy of excited metal-to-ligand charge-transfer states and consequently, in agreement with the energy gap law, enhances the non-radiative decay of the excited state. Replacing of one of the $\mathrm{N\cap N}$ ligand in $\mathrm{Os(N\cap N)_3^{2+}}$ ions by strong π-acid molecules like bidentate phosphines $\mathrm{P\cap P}$ [2,3] usually results in $\mathrm{Os(P\cap P)(N\cap N)_2^{2+}}$ complexes with the blue-shifted, from 750–850 to 600–650 nm, emission. The mixed ligand systems exhibit consequently much more pronounced emissive properties because of appropriate changes (increase and decrease, respectively) in the radiative k_f and non-radiative rate k_{nr} constants.

$\mathrm{Os(P\cap P)(N\cap N)_2^{2+}}$ complexes can be easily afforded [4] from K_2OsCl_6 according to the following approach. In the first step, $\mathrm{Os(N\cap N)_2Cl_2}$ is synthesized by the reaction of K_2OsCl_6 with twofold excess of $\mathrm{N\cap N}$ ligand in refluxing DMF followed by reduction of sodium dithionate in water solution. The obtained $\mathrm{Os(N\cap N)_2Cl_2}$ intermediate reacts further with $\mathrm{P\cap P}$ reactant in refluxing glycerol (or 2,2′-ethoxyethanol/glycerol mixtures). Finally, crude $\mathrm{Os(P\cap P)(N\cap N)_2Cl_2}$ is converted to appropriate (usually PF_6^-) salts by metathesis in aqueous solutions. One could expect that the changing reaction sequence in the above described procedure will lead (via $\mathrm{Os(P\cap P)_2Cl_2}$ intermediates) to $\mathrm{Os(P\cap P)_2(N\cap N)^{2+}}$ derivatives with still better (as compared to $\mathrm{Os(P\cap P)(N\cap N)_2^{2+}}$ species) emissive properties. In fact, similar approach was recently applied by Carlson and co-workers [5]. Somewhat surprisingly, however, instead of the expected $\mathrm{Os(P\cap P)_2(N\cap N)^{2+} \cdots (PF_6^-)_2}$ species, the final, emissive products with the general formula of $\mathrm{Os(P\cap P)(N\cap N)(CO)Cl^+ \cdots PF_6^-}$ have been obtained.

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Molecular structures of the synthesized complexes have been confirmed by means of X-ray investigations. Noteworthy, the newly prepared complexes exhibit unusual luminescence properties – the extremely high emission quantum yields (up to 0.75) and lifetimes distinctly longer (up to 30 μs) than that expected for typical MLCT emission.

The authors of the above cited paper have chosen to focus their attention on the physicochemical properties and crystallography of the synthesized $\mathrm{Os(P \cap P)(N \cap N)(CO)Cl^{+} \cdots PF_6^{-}}$ species without reporting more detailed investigations of the reaction mechanism. Because, of lack of any data concerning the chemical nature of the intermediate products obtained in the first reaction step, we have performed isolation and characterization of this product. Moreover, taking also into account the fact that the synthetic procedure described in [5] leads to very bright and tunable emitters (distinctly better than $\mathrm{Os(P \cap P)(N \cap N)_2^{2+}}$ complexes), we have decided to perform syntheses of some $\mathrm{Os(P \cap P)(N \cap N)(CO)Cl^{+} \cdots PF_6^{-}}$ species and check briefly their photo-physical properties as well. Here, we report the results of our investigations.

In the first step, K_2OsCl_6 was refluxed in deoxygenated DMF with 2.05 equivalents of 1,2-bis(diphenylphosphino)ethane (dppe) for 30 min similarly as it was done in [5]. The resulting solution was then precipitated into water with $Na_2S_2O_4$ dissolved at 0 °C. The white precipitate was filtered, dried and purified by means of column chromatography applying neutral activated alumina and CH_2Cl_2/CH_3OH (200:1) as eluent followed by crystallization from hexane/CH_2Cl_2 mixtures.

The resulting crystals were suitable for X-ray diffractometry measurements. All measurements of crystal were performed on a KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystal was positioned at 65 mm from the CCD camera. Thousand eight hundred (1800) frames were measured at 0.5° intervals with a counting time of 14 s. The data were corrected for Lorentz and polarization effects. Numeric analytical correction for absorption was applied [6]. Data reduction and analysis were carried out with the Oxford Diffraction programs [6,7]. The structure was solved by direct methods [8] and refined using SHELX [9]. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_0^2 > 2\sigma(F_0^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. All hydrogen atoms were located geometrically and their position and temperature factors were not refined. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in [10].

Structure refinement details: data/parameters = 11963/578; goodness-of-fit $(F^2) = 1.276$; final $R_1 = 0.0505$; wR_2 $(I > 2\sigma_I) = 0.0876$. Crystal data: $C_{107}H_{98}Cl_6O_4Os_2P_8$; $FW = 2288.78$; monoclinic P2(1)/c space group; $a, b, c =$ 11.8182(2), 37.6431(9) and 11.0651(2) Å; $\alpha, \beta, \gamma = 90.0°$, 91.379(2)° and 90.0°; $V = 4921.15(17)$ Å^3. Elementary cell contains the osmium chelate and CH_2Cl_2 molecules in 2:1 ratio.

The results of the X-ray analysis point to expected octahedral structure of the synthesized complex. As it is schematically shown in Fig. 1, the osmium atom is coordinated by three co-planar phosphor atoms; two of them from the bidentate dppe and one from the monodentate (2-(diphenyl-phosphinoyl)-ethyl)-di-phenyl-phosphane (dppeO) ligands. The remaining positions is somewhat distorted (by the steric requirements of the phosphorous ligands) octahedral central metal coordination sphere are occupied by two Cl^- and CO ligands. One of the Cl^- ions is equatorially located within the plane determined by the coordinated phosphor nuclei, whereas the second Cl^- ion and CO molecule ligands occupy the remaining free perpendicular position.

Unexpected presence of dppeO molecule in the complex structure clearly indicates partial oxidation of dppe reactant occurring in course of the applied synthetic procedure. Most probably, the oxidation takes place already in DMF solution because the presence of the strong reducing agent $Na_2S_2O_4$ makes it hardly possible during the complex isolation phase. One can speculate that the oxidation mechanism involves parallel Cl^- ions and electron transfer between $OsCl_4$ core and dppe reactant with formation of (2-(diphenyl-phosphinoyl)-ethyl)-diphenyl-dichlor-λ^5-phosphane (dppeCl_2) followed by further hydrolysis of dppeCl_2 to dppeO. Obviously, the CO ligand present in Os(dppe)(dppeO)(CO)Cl_2 complex must also be formed, by destruction of $HCON(CH_3)_2$ molecule, during refluxing of K_2OsCl_6 and dppe mixture in DMF solutions. Thus, the mechanism of Os(dppe)(dppeO)(CO)Cl_2 complex formation seems to be quite complicated and further, more detailed studies are required to explain it in more detail. Despite the complex character of the investigated reaction, the final product Os(dppe)(dppeO)(CO)Cl_2 is formed with quite high (ca. 75%) yields.

Apart from the X-ray investigations, the chemical nature of the obtained Os(dppe)(dppeO)(CO)Cl_2 product

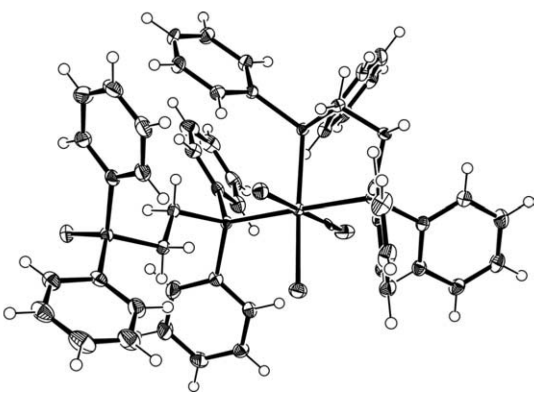

Fig. 1. ORTEP drawing (50% probability ellipsoids) of the molecular structure of Os(dppe)(dppeO)(CO)Cl_2 complex.