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Luminescent complexes on a scaffold of P_2N_2 -ligands: design of materials for analytical and biomedical applications

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Abstract: A variety of gold(I) and copper(I) complexes based on heterocyclic phosphine platform has been obtained. Due to the presence of exocyclic chromophoric pyridyl groups in the ligands complexes demonstrate noticeable phosphorescence. Cyclic nature of the phosphine ligands is responsible for supramolecular host-behavior of the complexes. Unique structure of complexes on a scaffold of the cyclic PNNP ligands favors the stimuli-induced structural reorganizations followed by stimuli-responsive luminescence. This, in turn, makes the complexes versatile building blocks for bottom-up design of smart nanomaterials for analytical and biomedical applications.

Keywords: colloid stabilization; copper(I) complexes; cyclic aminomethylphosphines; gold(I) complexes; ICPC-22; sensors for biothiols; “stimuli responsive” luminescence; thermochromism; vapochromism.

Introduction

The luminescence as a nature phenomenon was known from the ancient times. However only within the last half of a century design of artificial luminescent species attracted considerable attention of chemist working in organic, organometallic, coordination and inorganic chemistry. The growth of the interest was mainly explained by extensive development of various emitting devices interacting in everyday life of the people [1, 2]. The other not so obvious reason is the application of luminescent compounds as sensors for temperature, pH or presence of specific chemical substances measurements for analytical and contrasting agents for microscopy for biomedical purposes [2]. In that last case the so-called “stimuli responsive” properties of emitting species are of crucial importance. Complexes of transition metals seems to be the most suitable compounds for creating OLED and luminescent sensors due to the relatively high PLOs, long life-time and sensitivity to changes in the local environment of their phosphorescence [3–8]. The phosphorescence of transition metal complexes depends not only on nature of metal but in great extend on ligands due to the involvement into electronic transitions of orbitals centered on d metal and ligand as well [6–8].

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Scheme 1: Synthesis of di- and tetranuclear copper(I) complexes based on P-pyridyl phospholanes.

Among the ligands effectively used for creating luminescent complexes of transition metals phosphino-pyridines play a special role. That kind of ligands contains two coordination centers of different nature: soft donor phosphorus atom of phosphino group and hard donor nitrogen of pyridine suitable for stabilization various mono-, poly- and heteropolynuclear species. At the same time π^* antibonding orbitals centered on pyridine are actively participating in the formation of excited states providing effective luminescence. For instance mono-, bi- and tetranuclear complexes of d^{10} -group transition metals with phosphinopyridines and relative hybriide ligands demonstrate not only effective emission in wide range of spectra, but also “stimuli responsive” luminescence finding expression in termo-, vapo- and solvochromism [9–12].

For instance, recently we describe a number of di- and tetranuclear copper(I) complexes based on P-pyridyl phospholanes (Scheme 1) with very promising luminescent properties [13].

Chemistry of cyclic aminomethylphosphines was initiated at the end of the 1970s years of the last century, when the main type of that ligands was obtained, namely 1,5-diaza-3,7-diphosphacyclooctanes [14, 15] (Scheme 1). The first representatives were described nearly simultaneously by groups of Prof. Arbuzov in Russia [14] and Märkl [15] in Germany. The structure was unambiguously established in 1982 by X-ray data [16]. Since that date the Mannich-type condensations between primary phosphines, formaldehyde, and amines had been regarded as a powerful tool for the synthesis of 1,5-diaza-3,7-diphosphacyclooctanes [17]. The coordination chemistry of 1,5-diaza-3,7-diphosphacyclooctanes containing two phosphorus and two nitrogen atoms incorporated into the 8-membered cyclic scaffold and other similar heterocyclic systems with P-CH₂-N intracyclic fragments were the theme of the recent paper [18]. Incorporation of phosphorus atoms into the cyclic backbone lead to the few sequences: the mobility of phosphorus lone pairs (P LP) is strictly limited by the cycle; turning P LP to each other in order to form chelate complexes lead to the simultaneous movement of phosphorus atoms to each other; the properties of chelate complexes will depend on conformational behavior of heterocyclic ligand on metal matrix; other atoms incorporated into the exocyclic substituents are forced to be in close proximity to the central ion of chelate complexes. The present paper is focused on the ligands containing pyridyl groups on endocyclic phosphorus atoms, design of their P,N-complexes with gold(I) and copper(I) with “stimuli responsive” luminescence and some aspects of their application as sensors for analytical and biomedical purposes.

Background

Even at the first paper describing X-ray data of the chelate complex of 1,5-diaza-3,7-diphosphacyclooctane was mentioned that obtained metal containing bicyclic structure has a boat-chair conformation and

intracyclic N-atom of the boat fragment is situated in close proximity to the metal-center, but does not interact with it directly [19]. However, only in 2006 in pioneered work of DuBois and co-workers it was demonstrated that intracyclic nitrogen atoms could serve as proton relays in catalysts of hydrogen synthesis via electrolysis based on Ni(II)-complexes making these artificial systems a mimetic of natural hydrogenases [20–23].

Introduction of functionalized o-pyridyl substituent to the phosphorus atom provides a novel route for hydrogen delivery to the transition metal or its activation on the central ion. Both abilities have been demonstrated recently by the nickel(II) complexes of 1,5-diR-3,7-di(2-pyridyl)-1,3-diaza-3,7-diphosphacyclooctanes (Scheme 2) [24–26].

At the moment that complexes are the best catalyst working in pure organic solvents (acetonitrile). TOFs calculated for the novel catalysts, are much higher than those for similar complexes with phenyl substituents on phosphorus atoms [24, 25]. Moreover, it has been shown that corresponding complexes deposited on Vulcan XC-72 (C) function as both the cathode and anode catalysts in polymer electrolyte membrane fuel cell (PEMFC). In a PEMFC using $Ni(P_2^{Py}N_2^{p-Tol})/C$ at the anode and Pt/C at the cathode the power density is shown to reach 14.66 mW cm^{-2} , which is the highest power density of the none-noble organometallic analogs [27].

However, the obtained recently nickel(II) complexes with the other type of ligands with P_2N_2 scaffold containing pyridyl moieties separated from phosphorus atoms by ethylene bridged (Scheme 3) did not demonstrate any activity in electrochemical hydrogen evolution due to the formation of inactive P,N-chelates in solutions.

Scheme 2: Synthesis of 1,5-diR-3,7-di(2-pyridyl)-1,3-diaza-3,7-diphosphacyclooctanes and their nickel(II) complexes.

Scheme 3: Synthesis of 1,5-diR-3,7-di(2(2-pyridyl)ethyl)-1,3-diaza-3,7-diphosphacyclooctanes and their nickel(II) complexes.

Design of “stimuli-responsive” luminescent gold complexes

Introduction of exocyclic chromophoric pyridyl groups containing low antibonding molecular orbitals into the 1,5-diaza-3,7-diphosphacyclooctane (L¹) backbone opens an opportunity for the design of novel luminescent compounds.

Indeed, binuclear gold P,P-complexes (L¹(AuCl)₂) are readily formed by simple ligand exchange reaction (Scheme 4). Heterocyclic ligands save crown conformation of free ligands, so that both gold containing fragments are situated on the one side of the cycle [28]. X-ray data of the complexes established that in all cases heterocyclic bridging ligand possesses “crown” conformation in good accordance with that previously predicted by variable-temperature 1D and 2D NMR and DFT investigations of complexes based on P₂N₂ scaffolds [29–31].

Digold complexes demonstrate luminescence due to the metal-to-ligand transitions between highest occupied (HOMO) centered on metal and lowest unoccupied molecular orbitals (LUMO) centered on pyridyl group [28].

The emission characteristics of the complexes depends on the exocyclic substituents on nitrogen atoms, but also on the solvate molecules in crystals due to the formation of pseudo polymorphs [28]. Solid state interconversion of pseudo polymorphs in the presence of solvent vapors is responsible for the vapochromism of the complexes (Fig. 1). The shift of emission wave length (35 nm) is enough for detecting the presence of solvent vapors. Moreover, it has been shown that weak bonded solvent can be replaced by stronger bonded one or some other molecules containing methylammonium groups [32].

So, the molecule of the complexes could be regarded as a supramolecular host (Fig. 2). Nucleophilic binding site of the host derives from some kind of intramolecular cavity which is formed by AuCl moieties and both substituents on exocyclic nitrogen atoms situated on one side of heterocycle. The four axial hydrogens of endocyclic P-CH₂-N fragments pre-organized on the other side of the heterocycle form the electrophilic binding site of the host. DFT calculations explain the significant shift of emission wave length under the binding of specific guests *via* the electrophilic site by the rotation of pyridyl substituents along P-C bond [32].

In order to make the obtained gold complexes more attractive for biomedical applications the water solubility and stability under irradiation of the luminescent species should be increased. The stabilization of gold complexes in hydrophilic core-shell colloids using reprecipitation-encapsulation technique is one of the ways of solving the problem. Nanosized cores of the colloids were synthesized through the solvent mediated aggregation of (L¹(AuCl)₂) in aqueous organic solutions. To avoid the dissociation of the (L¹(AuCl)₂) complex the specific synthetic conditions (excess of NaCl) and hydrophilic shell deposition were utilized. The electrostatic and specific interactions at a core/shell interface lead to the adsorption of polyethylenimine onto (L¹(AuCl)₂)-based cores (Fig. 3). Luminescence of the colloids is stable for week (Fig. 4) due to restricted degradation of the complex and high positive exterior charge of the colloids [33].

Scheme 4: Synthesis of binuclear gold P,P-complexes of 1,5-diR-3,7-di(2-pyridyl)-1,3-diaza-3,7-diphosphacyclooctanes.

Fig. 1: Crystal phase luminescence (top) and X-ray structure (bottom) of the pseudo polymorphs of $L^1(AuCl)_2$: (a) crystallized from dichloromethane; (b) crystallized from acetone; (c) crystallized from a mixed solvent system (dichloromethane/acetone = 20/1).

Fig. 2: Schematic presentation of formation of supramolecular host-guest associates and corresponding changes in the emission spectra.

It has been shown that obtained colloid luminescent systems are stable in water in the presence of sodium dihydrogen phosphate, physiological salt solution and bovine serum albumin (BSA). So, nano-sized colloids seem to be a promising basis for creation a novel sensors working in cells.

The sensing properties of the colloids towards thiols and biothiols results from a stripping of Au^+ ions from $(L^1(AuCl)_2)$ -based cores by SH groups, which, in turn, quenches the colloids luminescence. Figure 4 illustrates that the fluorescent response of the colloids on L-cysteine as biorelevant representative of thiols enables to recognize it in the buffer solutions with the detection limits about 1 μM . Quenching of the luminescence

Fig. 3: Structure of branched polyethyleimine (PEI), scheme of reprecipitation-encapsulation technique of the colloid synthesis and TEM images of the dried colloid species.

Fig. 4: The quenching of $(AuCl)_2L$ complex represented as I/I_0 versus concentration of L-cysteine (I_0 is the initial emission intensity, I -values are measured in aqueous solutions of L-cysteine) along with schematic presentation of degradation of $(AuCl)_2L$ complex by biothiols as the origin of the quenching.

derives from partial degradation of the colloids mediated by the complex formation of the gold ions with L-cysteine (Fig. 4). The selective recognition of L-cysteine and glutathione versus methionine and thiocholine by luminescent response of $PEI-(L^1(AuCl)_2)$ highlights the synthesized colloids as promising for bioanalytical purposes.

The interaction of 3,7-bis(pyridine-2-yl) – 1,5-diaza-3,7-diphosphacyclooctanes with one equivalent of the $Au(tht)Cl$ (tht is tetrahydrothiophene) led to the precipitation of the brightly yellowish powder of the $[L_2Au_2]Cl_2$ (Scheme 5). The emission of $[L_2Au_2]Cl_2$ is manifested by wide band of low intensity with the maximum wavelength at ca. 550 nm under the excitation at 350 nm [34].

The cation $[L_2Au_2]^{2+}$ pairing with anionic hexarhenium cluster complexes ($[Re_6S_8(OH)_6]^{4-}$ and $[Re_6S_8(CN)_6]^{4-}$) is the reason for formation of supramolecular heterometallic assemblies with the cluster-centered luminescence which is enhanced under the ion-pairing of $[L_2Au_2]^{2+}$ with $[Re_6S_8(CN)_6]^{4-}$. The enhancement derives from the energy transfer, where $[L_2Au_2]^{2+}$ is a donor and $[Re_6S_8(CN)_6]^{4-}$ is an acceptor. The heterometallic $[L_2Au_2][Re_6S_8(CN)_6]$ colloids in aqueous solutions exhibit the pronounced luminescence response to acidification in the range of pH 6.0–5.5 [33]. That result is of special importance since the luminescent hexarhenium clusters have been shown to be the effective reagents for cellular imaging applications [34].

Scheme 5: Synthesis of the charged binuclear gold P,P-complexes of 1,5-diR-3,7-di(2-pyridyl)-1,3-diaza-3,7-diphosphacyclooctanes.

Scheme 6: Synthesis of tetranuclear gold(I) complexes of P,N-containing cyclophanes.

The first representatives of rather unusual P,N-containing cyclophanes with two 1,5-diaza-3,7-diphosphacyclooctane (L^2) rings incorporated into the macrocyclic core and exocyclic pyridyl-containing substituents on phosphorus atoms [35], as well as their tetranuclear gold(I) complexes $L^2(\text{AuCl})_4$ [36] have been obtained (Scheme 6). The complexation leads to a change in ligand conformations so that the diazadiphosphacyclooctane fragments of the complexes adopt twist-chair conformations, and two of the four gold(I) ions are located over and under the partially collapsed macrocyclic cavity. The complexes demonstrate moderate solid state green emission [36].

Design of “stimuli-responsive” luminescent copper complexes

The gold complexes could be regarded as the basis for luminescent sensors for bio- and medical applications, but they are too expensive for creation of light emitter devices. So, corresponding copper complexes should be regarded as candidates for both application directions. Copper complex occasionally became the first one of diazadiphosphacyclooctane coordination compounds, which was studied by the X-ray analysis [19].

Scheme 7: Synthesis of binuclear copper(I) P,P-complexes of 1,5-diR-3,7-di(2-pyridyl)-1,3-diaza-3,7-diphosphacyclooctanes.

Number of new binuclear copper(I) complexes of pyridyl containing 1,5-diaza-3,7-diphosphacyclooctanes (L^1) with bis-P,P-chelate ($L^1_2Cu_2I_2$) and unusual P,P-bridged ($L^1_2(CuI)_2$) coordination modes of heterocyclic ligands were obtained (Scheme 7). The 1,5-diaza-3,7-diphosphacyclooctane, containing aryl substituents at nitrogen atoms forms bis-P,P-chelate mononuclear as well as metalacyclic binuclear complexes with P,P-bridged coordination mode of a ligand, whereas the benzyl substituted ligands give the expected P,P-chelate complexes only [37]. Reasons for the differences in coordination modes have been found in the ligands geometry, where configuration of nitrogen atoms changed from planar to tetrahedral. However, no luminescence was mentioned so far.

In order to make a basis for copper based emitters the coordination chemistry of 1,5-diaza-3,7-diphosphacyclooctanes (L^3) with 2-(2-pyridylethyl) substituents on phosphorus atoms has been investigated. In that case pyridyl group can interact with metal ion directly.

Indeed, it has been shown that reaction of two equivalents of copper iodide lead to the butterfly-shaped binuclear complexes ($L^3Cu_2I_2$) with the unusual P,N-chelate and P,P-bridged coordination mode of the heterocyclic ligand (Scheme 8). Complexes display emission in green range of spectra at 536 and 509 nm, with lifetimes in a microsecond domain and quantum yields of luminescence in solid state up to 38 %. Our DFT computations show that the participating FMOs at the optimized triplet-state structures of complexes are very similar to the corresponding orbitals at the ground state geometry. Thus, the emission bands can be

Scheme 8: Synthesis of binuclear copper(I) complexes of 1,5-diR-3,7-di(2-(2-pyridylethyl))-1,3-diaza-3,7-diphosphacyclooctanes.

Scheme 9: Synthesis of hexanuclear copper(I) complexes of 1,5-diR-3,7-di(2-pyridyl)ethyl-1,3-diaza-3,7-diphosphacyclooctanes.

interpreted as being of $3(X+M)LCT$ character. Thermochromic effects found for the phosphorescence in solutions are ascribed to rigidochromism [38].

We demonstrated above the preferable P,P-chelate [37, 38] and rather rear P,P-bridge and P,N-chelate [28, 34, 36–38] coordination modes of 1,5-diaza-3,7-diphosphacyclooctanes containing pyridyl and pyridylethyl substituents on phosphorus atoms in the mono- and dinuclear gold(I) [28, 34, 36] and copper(I) [37, 38] complexes. Unexpectedly reaction of ligand (L^3 R = Ph, p-Tol) with copper(I) iodide in the 1:3 ligand-to-metal ratio in acetonitrile immediately led to the precipitation of white powders of hexanuclear copper clusters ($L^3_2(Cu_3I_3)_2$) in nearly quantitative yield (Scheme 9). Two Cu_3I_3 units of the obtained complexes are assembled on the scaffold of heterocyclic polyfunctional ligands. Each of the Cu_3I_3 metal-halide cores can be formally regarded as consisting of two parts: metal-halide core with a “butterfly-like” shape with two copper(I) ions bound by μ^2 -iodine ions; this core is connected via μ^3 -iodide with another copper(I) ion coordinated by two μ -phosphorus atoms of two ligands. It should be mentioned that Cu_3I_3 units are quite rare. Most of the known polynuclear copper complexes possess Cu_2I_2 and Cu_4I_4 subunits [39].

The crystalline samples of complexes display an unusual brightly white emission. The white emission is observed due to the presence of the two broad bands in the emission spectra with the maxima at 465 and 615 nm (Fig. 5). Quantum chemical computations show that the high-energy band has $3(M+X)LCT$ origin, whereas the low-energy band is interpreted as 3CC. The origin of the emission is phosphorescence with lifetimes in the microsecond domain. The PLQY of the white-emissive complexes are about 20 % [40].

Fig. 5: White emission of ($L^3_2(Cu_3I_3)_2$) complexes with corresponding emission spectra and color diagrams.

Temperature dependence of luminescence properties was studied. Emission spectra were measured at temperatures varying in the range of 83–373 K. The increase of the temperature led to the decrease of total emission intensity and affected chromaticity coordinates due to the intensity redistribution between blue and red emission bands of compound. So, novel hexanuclear complexes could be used for design not only of light emitting devices but also as of molecular thermometers [40].

Conclusions

Complexes of gold(I) and copper(I) on heterocyclic phosphine platform demonstrate noticeable phosphorescence due to the presence of exocyclic chromophoric pyridyl groups in the ligands. Stimuli-responsive luminescence of complexes on a scaffold of the cyclic PNNP ligands is a result of the stimuli-induced structural reorganizations.

So, cyclic aminomethylphosphines containing chromophoric pyridyl fragment as a part of exocyclic substituent on phosphorus atoms could be regarded as a promising scaffold for design of luminescent complexes sensing on supramolecular principles and further development of innovative stimuli-responsive materials for analytical and biomedical applications.

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