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3D Au–Ag heterometallic supramolecular cage: Triplet capture by heavy atom effect

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ABSTRACT

The synthesis of a new 3D metallo-cage is obtained by means of the self-assembly reaction between the gold derivative [(triphos)(AuC_6F_4py)$_3$] (triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane) and AgOTf in a 2:3 ratio. Several spectroscopic and spectrofluorimetric techniques and mass spectrometry have been used for the characterization of the supramolecule. MM calculations have been also important in order to optimize the geometry of the structure and postulate its ability to act as host in molecular recognition processes by means of its empty inner cavity. Changes on the emission spectra of the guest molecules naphthalene, methylsalicylate and 8-hydroxyquinoline showed the establishment of interactions between these molecules and the cage. A 1:2 cage:naphthalene adduct has been obtained while a 2:3 ratio has been observed for methylsalicylate and 8-hydroxyquinoline.

Interestingly, the large number of metal atoms of the host has been observed to induce intersystem crossing of the organic molecules. Emission spectra at 77 K together with lifetime measurements are a definitive proof for the assignment of the triplet origin for the observed guest luminescence when trapped by the host.

1. Introduction

The multimetal array controlled by predesigned multidentate ligands has received increasing attention with respect to supramolecular architecture. This strategy has opened ways to create and modulate novel functions that have not previously been achieved by the ligands or the metal ions only [1]. Although there are numerous examples of metal-mediated self-assembly of bi-dimensional complexes, the construction of three-dimensional metallo-supramolecules is scarce since they are frequently an intriguing class of compounds which are notoriously difficult to synthesize [2].

It is interesting to note that the assembly of three-dimensional compounds using metal coordination presents additional challenging and interesting applications in the area of chemical nanosciences, being used as supramolecular containers, reaction vessels, chemical sensors, gas absorption, molecular separation, catalysis and ion channel models for biological cells [3–5]. The construction of these structures involves the organization of metal centers by edge-bridging or face-capping ligands [6]. The use of metalloligands present some advantages with respect to the organics, such as: the introduction of new functionality (e.g. chirality, spectroscopic character); flexible geometric control, which could avoid complex modification of the organic ligand structure; the ability to assemble many components into a discrete entity [7]. Moreover, metallosupramolecular cage complexes are of particular interest because of the combination of architecturally sophisticated structures arising from the assembly process, and the possibility of host–guest chemistry associated with their central cavities [8]. In order to include guest molecules, different types of molecular cages have been built by careful design of ditopic and/or tritopic ligands that coordinate to metal ions [9,10]. Based on gold(I) complexes, some examples are described, such as metallocryptands [11–13], but to the best of our knowledge, no one heterometallic gold-containing three-dimensional cage has been described so far.

In the last years, there has been an increasing interest in the development of arene-based phosphors as possible new emitting materials for organic light-emitting diodes (OLEDs) with predictable emission colors [14,15]. A strategy to sensitize the T_1 triplet-state emission of arenes relies on their complexation with trinuclear d^{10} complexes, which act as heavy-atom inducers in the resulting binary π-acid–base sandwich adducts that assemble into extended columnar stacks of alternating fluorinated and nonfluorinated molecules [14–17].

With all this in mind, in this work, we have designed and synthesized a new heterometallic three-dimensional cage by using a tripodal gold(I) metalloligand recently described by us [18]. Due

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to our expertise on the luminescence of gold complexes [11,19–22], we have explored the optical properties of this cage in order to use it as a luminescent chemosensor by using its empty inner cavity in molecular recognition processes. Moreover, the electrowithdrawing groups and the high number of metal atoms, makes it a very interesting candidate to act as host in molecular recognition processes. Luminescent sensors offer better sensitivity, specificity, and real-time monitoring with fast response time over other chemosensors [23–25] and this is a good way to study the potential applications of these molecules hardly synthesized in the laboratories. Finally, the high number of heavy metal atoms and the presence of fluoride atoms in the obtained structure made this supramolecule a good candidate to explore its capabilities to produce π-acid–base sandwich adducts and promote the population of the triplet state of arene molecules giving to phosphorescence emission as observed in trinuclear d^{10} complexes.

2. Experimental

All manipulations were performed under prepurified N_2 using standard Schlenk techniques. All solvents were distilled from appropriate drying agents. Infrared spectra were recorded on an FT-IR 520 Nicolet spectrophotometer. $^{31}P\{^1H\}$ NMR (δ(85% H_3PO_4) = 0.0 ppm), and ^1H NMR (δ(TMS) = 0.0 ppm) spectra were obtained on a Bruker DXR 250 and Varian Mercury 400 spectrometers. Elemental analyses of C, H, N and S were carried out at the Institut de Bio-Orgànica in Barcelona. Absorption spectra were recorded on a Cary 100 Bio UV-spectrophotometer and fluorescence emission spectra on a Horiba–Jobin–Yvon SPEX Nanolog-TM spectrofluorimeter at 298 and 77 K. Triplet decay times were measured with a laser flash photolysis LK60 Applied Photophysics system collecting the emission decay at 450 nm after laser pulse excitation at 266 nm with samples cooled at 77 K using a Dewar holder with N_2(l). ESI mass spectra were recorded on a Bruker APEX IV Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer with a 7.05 T magnet and an Apollo electrospray (ESI) ion source equipped with an off-axis 70° spray needle. Molecular modeling and calculations were done with MM+ molecular mechanics method included in the software package SPARTAN'04 V1.0.0.

Commercial reagents $AgCF_3SO_3$ (Aldrich) and triphos (Strem) were used as received. Compound [$(AuCl)_3$(triphos)] was prepared and isolated as solid from [AuCl(tht)] [26] solution by adding the appropriate amount of the corresponding triphosphane. [(triphos)$(AuC_6F_4py)_3$] was synthesized according to the literature [18].

2.1. Synthesis of {[(triphos)$(AuC_6F_4py)_3]_2Ag_3$}$(OTf)_3$

A methanol solution (3 ml) of $AgCF_3SO_3$ (15 mg, 0.06 mmol) was added to a dichloromethane (30 ml) solution of [(triphos)$(AuC_6F_4py)_3$] (75 mg, 0.04 mmol). A yellow suspension was observed after 30 min of stirring at room temperature. The solution was concentrated to 10 ml and a white solid was obtained after addition of 10 ml of diethylether. The solid was filtered and washed with diethylether giving to 75 mg of the corresponding product (85% yield).

^{31}P NMR (CD_3NO_2): δ 22.4. ^1H NMR (CD_3NO_2): δ 8.81 (d, J(H–H) = 6.7 Hz, 12H, $H_{\alpha py}$), 7.87–7.40 (m, 72H, Ph+$H_{\beta py}$). 3.72 (s, br, 12H, CH_2-P), 1.29 (s, 6H, CH_3-C). ^{19}F NMR (CD_3NO_2): −79.9 (9F, OTf^-), −116.2 (m, 12F, F_X-C-py), −146.3 (m, 12F, F_A–C–Au). IR (KBr, cm^{-1}): 1437, 947, 832 (C_6F_4), 1616, 1447, (py), 1282, 1254, 1153, 1029, 637, 517 (OTf), 1452, 1419, 1100 (triphos). ESI-FTICR (CH_3NO_2, m/z): 2130.0 ([M−2OTf^-]$^{2+}$, Calc.: 2130.0), 2002.1 ([(triphos)$(AuC_6F_4py)_3$+Ag^+]$^+$ and [M−3OTf−Ag^+]$^{2+}$, Calc.: 2002.1), 1963.1 ([M−Ag^+−C_6F_4py−2OTf^-]$^{2+}$, Calc.: 1963.1), 1894.2 ([(triphos)$(AuC_6F_4py)_3$+H^+]$^+$, Calc.: 1894.2), 1834.6 ([M−2Ag^+−C_6F_4py−3OTf^-]$^{2+}$, Calc.:1834.6), 1796.1 ([M−2Ag^+−2C_6F_4py−2OTf^-]$^{2+}$, Calc.: 1796.1), 1751.6 ([M−Ag^+−C_6F_4py−AuC_6F_4py−2OTf^-]$^{2+}$, Calc.: 1751.6), 1667.7 ([(triphos)$(AuC_6F_4py)_3$−C_6F_4py]$^+$ and [(triphos)$(AuC_6F_4py)_3$−C_6F_4py]$_2^{2+}$, Calc.: 1667.7), 1623.1 ([M−2Ag^+−C_6F_4py−AuC_6F_4py−3OTf^-]$^{2+}$, Calc.: 1623.2), 1579.1 ([(triphos)$(AuC_6F_4py)_3$−AuC_6F_4py+Ag^+]$^+$, Calc.: 1579.1), 1370.4 ([M−3OTf^-]$^{3+}$, Calc.: 1370.4), 1259.1 ([M−Ag^+−C_6F_4py−3OTf^-]$^{3+}$, Calc.: 1259.2), 1244.2 ([(triphos)$(AuC_6F_4py)_3$−AuC_6F_4py−C_6F_4py]$^+$, Calc.: 1244.2), 1183.4 ([(triphos)$(AuC_6F_4py)_3$+3 Ag^++OTf^-]$^{2+}$, Calc.: 1183.4), 1168.0 ([(triphos)$(AuC_6F_4py)_3$+2Ag^++C_6F_4py+H^+]$^{2+}$, Calc.: 1168.0), 1147.8 ([M−2Ag^+−2C_6F_4py−3OTf^-]$^{3+}$, Calc.: 1147.8), 1054.5 ([(triphos)$(AuC_6F_4py)_3$+2Ag^+]$^{2+}$, Calc.: 1054.5), 1101.6 ([(triphos)$(AuC_6F_4py)_3$+Ag^++H^+]$^{2+}$, Calc.: 1001.6). *Anal.* Calc.: C, 40.81; H, 2.44; N, 1.86; S, 1.89. Found: C, 40.85; H, 2.47; N, 1.89; S, 1.91%.

3. Results and discussion

3.1. Synthesis and characterization

The Au/Ag heterometallic cage was built by self-assembly reaction between the metalloligand [(triphos)$(AuC_6F_4py)_3$] (recently described by us) [18] and AgOTf in 2:3 ratio (Scheme 1). The reaction was followed by ^{31}P NMR which indicated that the reaction was completed after 30 min of stirring. At this point, it is interesting to note that although the self-assembly reaction has been successful and occurs in one step, the clear drawback is the experimental procedure for the obtention of the gold metalloligand precursor. This synthesis involves different organic and organometallic procedures that are sometimes hard to manage and, in some cases, gives the product in very low yields.

Analytical and spectroscopic data agree with the proposed structure. The ^1H NMR spectrum shows that H_α and H_β protons of the pyridine units are shifted 0.11 ppm upfield upon coordination to the silver metal atoms. A slightly upfield shift is also observed in ^{31}P NMR (0.4 ppm) since changes in the structure occur far from the vicinity of the phosphorus atoms. The ^{19}F NMR spectrum shows two multiplets that agree with the existence of two types of non-equivalent fluorine atoms corresponding to the C_6F_4py aromatic units and a third ^{19}F signal is present at −79.9 ppm due to the triflate anions. Moreover, IR spectroscopy indicates the presence of coordinated pyridine (ν(C=N): 1616 cm^{-1}), together with that of C_6F_4py, OTf^- and triphos units. Particularly interesting is the mass spectrometry characterization. As it is shown in Fig. 1 and detailed in Section 2, this technique allowed the unambiguous identification of the targeted Au/Ag cage.

Electrospray mass spectra of a nitromethane solution of the heterometallic cage were recorded under typical ionization conditions and show the trinuclear tripodal unit coordinated to two Ag^+ ions and a triflate anion as the heaviest visible aggregate at m/z 2258.1 (see Fig. 1, above). In addition, fragments of this ion formed by subsequent losses of AgOTf, AgL (L = C_6F_4py−), and AuL, respectively, are observed in the ion series at m/z 2002.2, 1667.2, 1579.2, 1244.2 and 821.1. The fragmentation of the cage observed in solution presumably happens during the ionization process by collisions with residual solvent and nitrogen gas in the higher pressure regions of the electrospray ionization source. Tuning the electrospray parameters to achieve extremely soft ionization conditions yields a different spectrum (Fig. 1, middle and below). Now, the intact cage [$(tripod)_2Ag_3$]$^{3+}$ (tripod = (triphos)$(AuC_6F_4py)_3$) is detected with correct exact mass and isotope pattern both as a triply charged species at m/z 1370.7 as well as a doubly charged species bearing one triflate anion at m/z 2130.5. Fragments are still visible: the fragmentation pattern is similar in the doubly