Self-Assembly of Multinuclear Sandwich Silver(I) Complexes by Cooperation of Hexakis(aza heteroaryl)benzene Ligands, Argentophilic Interactions, and Fluoride Inclusion

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ABSTRACT: Self-assembly of AgOTf and AgF with the hexatopic ligands hexakis(pyridin-2-yl)benzene (2) and 2,4,6-tris(pyridin-2-yl)-1,3,5-tris(quinolin-2-yl)benzene (3) affords the discrete sandwich-shaped complexes [Ag4F(2)3](OTf)4, [AgF(3)2]−(OTf)2, and [AgF(2)2](OTf)4. The solid-state structures of the complexes were characterized by single-crystal X-ray diffraction analysis, which revealed that the fluoride anion is coordinated in the center of the Ag4-square or Ag5-pentagon units which are positioned between two molecules of the hexakis(azaheteroaryl)-benzene. The generation of complexes is dictated by a unique cooperation of ligand coordination, argentophilicity, and fluoride anion inclusion. All three complexes adopt highly symmetrical structures in solution, as evidenced by appearance of one set of proton resonances for the two ligands arranged face to face.

INTRODUCTION

Self-organization of organic molecules, playing the role of ligands, by metal coordination to generate supramolecular architectures of different shapes and sizes is an intensely attractive field in supramolecular chemistry. In the context of ligand design, pyridine derivatives exhibit high stability and tolerance to fluctuating redox environments and have been ubiquitously employed for the construction of metallosupramolecular entities, as well as in crucial catalytic transformations, as RuIII(2-phenylpyridinate)2 and [RuII(2,2′-bipyridin)2]24 complexes are known to be efficient photoredox systems. Examples of multinuclear Ag(I) discrete complexes and coordination polymers with pyridyl ligands have been reported, owing to the excellent affinity of Ag(I) ions for N-donor ligands and their highly flexible coordination geometry, which can vary from linear to trigonal, tetrahedral, square-planar, trigonal pyramidal, T-shaped, and octahedral. In addition, adjacent metal centers in multinuclear Ag(I) complexes may form argentophilic closed-shell interactions, which significantly influence a supramolecular topology and photophysical characteristics of the complexes, such as luminescence.

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1. Kandaiah et al. 18 Multinuclear Ag(I)-pyridyl complexes have found potential applications as photoactive materials.

2. For instance, a dinuclear Ag(I) complex containing tris(2-pyridyl)phosphine ligands shows blue thermally activated fluorescence, while a disilver(I) compound with a terpyridine ligand efficiently catalyzes the aziridination of olefins. Two dipyridylquinoline-type ligands coordinated to two Ag(I) ions by using three nitrogen atoms of each ligand to form discrete boxlike dimers with promising redox and luminescent properties. Interestingly enough, the reaction of hexakis(2-pyridyl)[3]radialene with AgBF4 resulted in the formation of a hexapodal metallosupramolecular assembly of the M6L2 type with an encapsulated fluoride anion.

Molecules based on the hexaarylbenzene core containing multiple donor sites appear to be attractive in the development of new coordination building blocks due to their unique propeller-shaped topology. Recently, we have reported a microwave-promoted synthesis of hexaheteroarylbenzenes based on a multiple iterative C–H activation protocol and preliminary results of their complexation with Ru(II), Pd(II), and Pt(II) atoms to give only dinuclear complexes. Thus, a new easy access to hexaarylbenzene ligands offers options for novel metal-driven self-assembled architectures, such as thiazole-containing hexaarylbenzenes, which were utilized in...
complexation with Ag(I) and Pt(II) ions to assemble molecular rotors. The Shionoya group designed a tris-monodentate hexaarylbenzene-type ligand with three alternately attached 3-pyridyl and p-tolyl groups, which was used in the preparation of capsule-shaped and cage-shaped complexes via self-assembly of four ligand molecules and four or six Ag(I) ions. Lee and co-workers reported monomeric dinuclear Cu(I) and Cu(II) complexes with hexakis(2-pyridyl)benzene...
derivatives, which exhibited the fluxional motion of two copper ions. However, the chemistry of Ag(I) coordination complexes based on hexakis(heteroaryl)benzene ligands with six N-donor sites is still unexplored.

Taking into account our previous work on the complexation of a hexakis(pyridin-2-yl)benzene ligand (2) with selected transition metals, we envisioned that hexakis(azaheteroaryl)-benzene-type ligands could interact with Ag(I) ions so as to minimize electrostatic repulsion between positively charged metal centers. Herein we describe, on the basis of a unique cooperation of ligands hexakis(pyridin-2-yl)benzene (2) and 2,4,6-tris(pyridin-2-yl)-1,3,5-tris(quinolin-2-yl)benzene (3) with fluoride anion inclusion and argentophilic interactions, the synthesis and complete characterization of three novel unexpected multinuclear Ag(I)-polypyridyl cationic complexes: [Ag₄F(2)₂]³⁺, [Ag₄F(3)₂]³⁺, and [Ag₅F(2)₂]⁴⁺.

■ RESULTS AND DISCUSSION

Hexakis(azaheteroaryl)benzene ligands 2 and 3 were readily synthesized from coupling reactions of 2-phenylpyridine (1a) and 1,3,5-tris(pyridin-2-yl)benzene (1b) with 2-bromopyridine or 2-bromoquinoline via Ru(II)-catalyzed multiple C−H functionalization under microwave conditions in water (Scheme 1).

To investigate the coordination properties of the synthesized propeller-like ligands with Ag(I) ions, the ligand 2 was first treated with 3 equiv of AgOTf in MeOH at room temperature in the dark for 12 h. A white solid, isolated by MeOH/Et₂O precipitation, was a mixture of products according to ¹H NMR analysis in a deuterated acetone solution. However, after slow evaporation of acetone a few crystals were formed and were suitable for X-ray analysis. We were able to elucidate the stoichiometry of the complex from diffraction data, which was additionally confirmed by elemental analysis. To our surprise, the crystallized compound contained four Ag(I) ions in the sandwich-type cationic [Ag₄F(2)₂]³⁺ complex with two pyridyl ligands 2 arranged facetoface, and a fluoride anion coordinated in the middle of the square formed by Ag(I) ions (Figure 1).

The six pyridyl nitrogen atoms of both ligands 2 in [Ag₄F(2)₂]³⁺ interact with the highly positively charged [Ag₄F]³⁺ nucleus of the complex. Similarly, Lu et al. reported Ag₁₂ metallocage structures with trapped nitrate anions as a result of self-assembly of AgNO₃ with tetratopic 1,2,4,5-tetrakis(benzoimidazolylmethyl)benzene ligands. At this stage, the source of the fluoride anions remains unknown, but we speculate that they were present as an impurity in AgOTf and thus actively participated in the thermodynamically favorable self-assembly process. This hypothesis could actually explain the initially observed formation of the crystalline complex [Ag₄F(2)₂](OTf)₃ in a small amount. After the complex stoichiometry was revealed ([Ag⁺]/[2]/[F⁻] ratio 4/2/1), the ligand 2 was mixed with 1.5 equiv of AgOTf and 0.5 equiv of AgF, giving the pure complex [Ag₄F(2)₂](OTf)₃ in 78% isolated yield. The solution structure of the complex was revealed by ¹H NMR spectroscopy and ESI-HRMS measurements (m/z 509.0100, 837.9912, 1824.9325: [Ag₄F(2)₂]³⁺, [Ag₄F(3)₂]³⁺, and [Ag₅F(2)₂](OTf)₃⁺, respectively).

The ¹H NMR spectrum of [Ag₄F(2)₂](OTf)₃ in acetone-d₆ shows only one set of four signals corresponding to pyridyl groups of both coordinated ligands 2 in the same environment. The pyridyl H-3, H-4, and H-5 proton signals are expectedly shifted downfield in comparison to the free ligand 2, as a result of a loss in electron density upon coordination to Ag(I) ions (Figure 3a,b). In contrast, the resonance of the H-6 proton, which is in closest proximity to the metal binding site, remained unchanged. It can be seen from the solid-state structure of the complex that the two ligands 2 arranged face to face are rotated with respect to each other so that the pyridine ring of one ligand molecule is oriented toward the region between two pyridine rings of another ligand molecule (Figure 1). Thus, all pyridine rings are approximately parallel and the H-6 protons are pointing close to the shielding cones caused by the motion of the π electrons in pyridine rings (Figure S45).
Presumably, the H-6 proton resonance experiences a downfield shift due to the electron-withdrawing effect of the Ag(I) ion which cancels out with the upfield shift attributed to an anisotropy effect of the pyridyl groups, and consequently it remains unchanged.

The importance of fluoride anions for the successful generation of the supramolecular structure was additionally illustrated by reactions of ligand 2 with 2 equiv of AgPF6 or AgSbF6, which led to mixtures of products. On the other hand, the combination of AgPF6 or AgSbF6 with AgF in a 3:1 molar ratio again yielded the pure complexes [Ag4F(2)2](PF6)3 and [Ag4F(2)2](SbF6)3, as confirmed by comparison of their 1H NMR spectra with that resulting from the [Ag4F(2)2](OTf)3 complex. It is worth mentioning that the reaction of ligand 2 with 2 equiv of AgF solely furnished a mixture of products, indicating that the presence of weakly coordinating counterions, such as TfO−, SbF6−, and PF6−, is not negligible in the self-assembly process.

The isostructural tetranuclear complex [Ag4F(3)2](OTf)3 but with the hybrid quinolinyl-pyridyl ligand 3 was prepared and isolated in 71% yield by reacting 3 (1 equiv), AgOTf (1.5 equiv), and AgF (0.5 equiv). Its solid-state structure was unambiguously determined by X-ray analysis revealing a symmetric sandwich-type complex analogous to [Ag4F(2)2](OTf)3 (Figure 2).

An MS-ESI analysis provided the nature of ions characteristic of the complex [Ag4F(3)2](OTf)3 present in solution, which were verified by comparison of the isotopic patterns between observed and simulated peaks (Supporting Information). The major peaks correspond to [Ag4F(3)2]5+, [Ag4F(3)2](OTf)25−, and [Ag4F(3)2](OTf)2− species, indicating the presence of a multinuclear structure also in solution. While the solid-state structure of [Ag4F(3)2](OTf)3 indicates two slightly different pyridine and quinoline environments (Figure 2), a highly symmetric structure in acetone-d6 solution was evidenced by 1H NMR spectroscopy, which displayed only...
one set of resonances for pyridyl and quinolinyl groups in both coordinated ligands 3. Variable-temperature 1HN M R measurements (240 → 300 K) of the complex [Ag4F(3)2]−(OTf)3 in acetone-d6 showed no signal doubling or line broadening (Figure S4). These observations suggest a dynamic process in solution, which, however, cannot be suppressed by cooling to only 240 K.

We speculated that more than four Ag(I) ions could coordinate to the ligand 2 by simply changing the [2]/[Ag+]/[F−] ratio. Indeed, when the ligand 2 was treated with 2 equiv of AgOTf and 1 equiv of AgF, in addition to the proton signals for ligand 2 incorporated in the complex [Ag4F(2)2](OTf)3, another set of signals appeared in a symmetrical pattern (Figure 3c). All four new pyridyl signals are shifted downfield by 0.15−0.27 ppm relative to resonances of the ligand 2 in the complex [Ag4F(2)2](OTf)3. This indicated a decrease in electron density upon coordination of the nitrogen lone pair to the silver metal center and suggested a highly positively charged species. After the amounts of silver salts were changed to 2.5 equiv of AgOTf and 0.5 equiv of AgF, the pure complex [Ag5F(2)2](OTf)4 was isolated by MeOH/Et2O precipitation in 86% yield.

The structure of the complex [Ag5F(2)2](OTf)4 was determined by X-ray crystallography and revealed that the pentagonal unit of Ag(I) ions with a centrally included fluoride anion is coordinated to both ligands 2 in a symmetrical sandwich-shaped structure (Figure 4). This is consistent with the four proton signals of the coordinated ligand 2 indicating a highly symmetrical structure also in solution (Figure 3d). It is worth noting that, while four Ag(I) ions are retained in the pentanuclear complex via coordination to both polydentate ligand molecules and a fluoride anion, the fifth Ag(I) ion has interactions with only pyridyl nitrogens.

To investigate the formation of different complexes, reactions of ligand 2, 0.5 equiv of AgF, and 1.5−2.5 equiv of AgOTf were performed, and crude reaction mixtures were analyzed by 1H NMR spectroscopy (Figure 5). When the total amount of Ag(I) ions (from AgF and AgOTf) surpassed 2 equiv relative to the ligand 2, the molar portion of the complex [Ag5F(2)2](OTf)4 in the reaction mixture started to decrease, and simultaneously the amount of the product with five coordinated Ag(I) ions started to increase. Once the molar ratio [Ag(I)]/[2] reached 2.6 (2.1 equiv of AgOTf and 0.5 equiv of AgF), the complex [Ag5F(2)2](OTf)4 was formed as the sole product regardless of the additional amount of AgOTf.

The aforementioned results indicate that the self-assembly process can be regulated by a subtle choice of [Ag(I)]/[2] ratio and more importantly imply a possible structure interconversion (Figure 6). Indeed, the complex [Ag5F(2)2](OTf)4 can be easily formed from a methanolic solution of [Ag4F(2)2](OTf)3 by adding a 1.5-fold excess of AgOTf, and it was isolated by MeOH/Et2O precipitation in 61% yield. On the other hand, if the pentanuclear complex [Ag5F(2)2](OTf)4 was treated with water for 0.5 h at room temperature, the tetranuclear complex [Ag4F(2)2](OTf)3 was isolated in 72% yield. As evidenced by the X-ray structure of [Ag5F(2)2](OTf)4, one Ag(I) ion is not coordinated to the fluoride anion, and thus it can more easily dissociate from the complex due to the relatively weak Ag−N bond. The MS-ESI spectrum of...
3.2036(9) Å, respectively, and are shorter than the sum of van der Waals radii (3.44 Å). This indicates strong argentic interactions, while the Ag1...Ag2 distance is 3.5703(6) Å and is longer than the sum of van der Waals radii, which means that there is no argentic interaction. The F− anion in the center of the complex is coordinated to four silver atoms with Ag1−F and Ag2−F distances of 2.351(3) and 2.413(3) Å, respectively. On the other hand, F− is 2.961 Å from the benzene rings, thus indicating an anion−π interaction.

**Structural Analysis of AgF(2)2(OTf)4.** The complex crystallizes in the monoclinic P21/n space group. The complex has the same sandwichlike shape as AgF(2)2(OTf)3 and AgF(3)(3)2(OTf)3 but with five silver ions in an almost pentagonal orientation coordinated by two ligands. The pyridine rings deviate from the benzene ring from 68.1(2) to 89.6(6)°. The Ag2, Ag3, and Ag4 silver ions are coordinated by three pyridine nitrogen atoms and a fluoride anion (r4 = 0.80) and Ag1 is coordinated by two pyridine nitrogen atoms and an F− anion while Ag5 is coordinated only by three pyridine nitrogen atoms (Ag5−F1 = 2.724(9) Å). Distances for Ag−N bonds are in the range from 2.201(9) to 2.714(11) Å. The distances for Ag−Ag are 2.9388(14)−3.0845(16) Å and are shorter than sum of van der Waals radii (3.44 Å), indicating strong argentic interactions. The F− in the center of the complex is coordinated on four silver atoms with Ag−F distances of 2.397(7)−2.575(7) Å. The distances between F− and benzene rings (2.971 and 2.980 Å) indicate anion−π interactions.

**CONCLUSIONS**

In summary, we have demonstrated that hexakis(heteroaryl)benzenes 2 and 3, bearing six radially extended nitrogen-coordinating groups, can serve as polynuclear ligands (L) for the construction of multinuclear silver(I) sandwich-shaped complexes of the types AgFL2 and AgFL3. Generation of the complexes [AgF(2)2(OTf)]n, [AgF(3)(3)2(OTf)]n, and [AgF(2)2(OTf)]4 is initiated by a unique cooperation of ligand molecules, argentic interactions, and fluoride anion coordination in a self-assembled manner. The tetranuclear and pentanuclear complexes consist of Ag4 and Ag5, planar units with a centrally coordinated fluoride anion, located between two polynuclear ligand molecules pointing all six of their nitrogen atoms toward the AgF or AgF plane. The reactions of ligands with AgX (X = OTf, PF6, SbF6) or AgF solely led to mixtures of products, indicating that the selective formation of the complexes is dictated by an appropriate choice of [L]/[Ag+]/[F−] ratio and noncoordinating counterion. To the best of our knowledge, we have presented here the first examples of coordination complexes containing a highly positively charged [AgF]+ or [AgF]4+ nucleus between two hexa(heteroaryl)benzene ligands. Interconversion between tetrasilver(I) and pentasilver(I) compounds was also demonstrated. The selectively prepared cationic species [AgF(2)2]+3, [AgF(3)(3)]+3, and [AgF(2)2]+4 offer a potential for catalytic applications that are currently being evaluated.

**EXPERIMENTAL SECTION**

**General Methods.** All reagents were commercial grade and were used without further purification. The ligands 2 and 3 were prepared as previously reported by our group.25 NMR spectra were recorded with a Bruker Avance III 500 MHz spectrometer. The 1^H and 13^C NMR chemical shifts are reported in parts per million (ppm) relative to the central line of the acetone-d6 signal (2.05 ppm for 1^H and 29.8
ppm for $^{13}$C. The $^{19}$F NMR chemical shifts are reported relative to the signal of trifluoromethylen benzene (−63.22 ppm). IR spectra were obtained with a Bruker ALPHA FT-IR spectrophotometer. High-resolution mass spectra were recorded with a Thermo Fisher Q-Exactive instrument, while mass spectra were recorded with a Micromass Waters Q-TOF Premier instrument. Elemental analyses (C, H, N) were performed with a PerkinElmer 2400 Series II CHNS/O Analyzer.

$\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{]. A screw-capped scintillation vial was loaded with ligand 2 (28 mg, 0.05 mmol), AgOTf (19.5 mg, 0.075 mmol), and AgF (3.4 mg, 0.025 mmol). The mixture was dissolved in 1 mL of MeOH and stirred in the dark at room temperature for 12 h. After that time Et$_2$O (2 mL) was added to precipitate the product, which was filtered off, washed with H$_2$O (1 mL) and Et$_2$O (2 × 1 mL), and dried to obtain the pure complex $\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{]}. (38 mg, 0.0195 mmol, 78% yield) as a white solid. Mp: >300 °C dec. $^{1}$H NMR (500 MHz, acetone- $^d$-O): $\delta$ 8.14 (d, $\delta$ = 5.1 Hz, 1H), 7.78 (td, $\delta$ = 7.6, 1.6 Hz, 1H), 7.74 (dd, $\delta$ = 7.7, 1.3 Hz, 1H), 7.21 (dd, $\delta$ = 7.4, 5.0, 1.5 Hz, 1H). $^{13}$C NMR (126 MHz, acetone- $d_6$): $\delta$ 156.5, 149.8, 140.8, 138.1, 127.3, 123.4. $^{19}$F NMR (471 MHz, acetone- $d_6$): $\delta$ −72.5 (d, $\delta$$_{J\text{F}}$ = 708.2 Hz, PF$_6$ $^\text{−}$), −316.0 (F $^\text{−}$). IR (ATR): 1593, 1466, 1404, 875, 836, 807, 754 cm$^{-1}$. Anal. Calcd for C$_{72}$H$_{48}$Ag$_4$F$_{19}$N$_{12}$S$_3$: C, 38.61; H, 2.16; N, 8.39. Found: C, 38.61; H, 2.10; N, 8.44.

$\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{]}. A screw-capped scintillation vial was loaded with ligand 2 (28 mg, 0.05 mmol), AgOTf (26 mg, 0.075 mmol), and AgF (3.4 mg, 0.025 mmol). The mixture was dissolved in 1 mL of MeOH and stirred in the dark at room temperature for 12 h. After that time Et$_2$O (2 mL) was added to precipitate the product, which was filtered off, washed with H$_2$O (1 mL) and Et$_2$O (2 × 1 mL), and dried to obtain the pure complex $\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{].} (40 mg, 0.018 mmol, 86% yield) as a white solid. Mp: >300 °C dec. $^{1}$H NMR (500 MHz, acetone- $^d$-O): $\delta$ 8.14 (d, $\delta$ = 5.1 Hz, 1H), 7.78 (td, $\delta$ = 7.6, 1.6 Hz, 1H), 7.74 (dd, $\delta$ = 7.7, 1.3 Hz, 1H), 7.21 (ddd, $\delta$ = 7.4, 5.0, 1.5 Hz, 1H). $^{13}$C NMR (126 MHz, acetone- $d_6$): $\delta$ 156.5, 149.8, 140.8, 138.1, 127.3, 123.4. $^{19}$F NMR (471 MHz, acetone- $d_6$): $\delta$ −72.5 (d, $\delta$$_{J\text{F}}$ = 708.2 Hz, PF$_6$ $^\text{−}$), −316.0 (F $^\text{−}$). IR (ATR): 1593, 1466, 1404, 875, 836, 807, 754 cm$^{-1}$. Anal. Calcd for C$_{72}$H$_{48}$Ag$_4$F$_{19}$N$_{12}$S$_3$: C, 38.61; H, 2.16; N, 8.39. Found: C, 38.61; H, 2.10; N, 8.44.

X-ray Crystallographic Studies. Crystal data for complexes $\text{[Ag}_5\text{F}_2\text{]}\text{(OTf)}_3\text{], [Ag}_3\text{F}_3\text{]}\text{(OTf)}_3\text{]·3H}_2\text{O and [Ag}_4\text{F}_2\text{(OTf)}_3\text{]·2H}_2\text{O and C}_5\text{H}_4\text{O}_2}$ were collected at 150 K on an Agilent Technologies SuperNova Dual diffractometer using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were processed using CrysalisPro. $^3$ Structures were solved with the ShelXT$^4$ structure solution program using intrinsic phasing and refined by a full-matrix least-squares procedure based on $^2$F$^2$ with ShelXL$^5$ implemented in the Olex$^2$ program suite.$^4$ All non-hydrogen atoms were readily located and refined anisotropically unless otherwise noted. Hydrogen atoms were initially located in the difference Fourier maps and were subsequently included in the model at geometrically calculated positions and refined by using a riding model unless otherwise noted. For $\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{]}$, the complex cation was readily located and refined; however, only a few atoms of the counterions were located, having very large anisotropic displacement parameters, and were in further steps of the refinement removed from the model. The scattering contributions of the disordered counterions were removed with a solvent mask procedure implemented in Olex$^2$. The contribution correction was not included in the reported molecular weight and density. Although the crystals were of low quality and the data were of sufficient quality to determine the structure of $\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{]}$, they were of limited quality and the data were of sufficient quality to determine the structure of $\text{[Ag}_4\text{F}_2\text{(OTf)}_3\text{]}$.
the molecular and crystal structure. Details of the crystal, data collection, and refinement parameters as well as selected bond distances and angles are given in Tables S1–S4 in the Supporting Information. The CCDC reference numbers are 1971156–1971158.

**ASSOCIATED CONTENT**

1. Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03664.

Experimental procedures, tables of crystallographic details, NMR spectra, and MS spectra (PDF)

Accession Codes
CCDC 1971156–1971158 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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**DEDICATION**

This paper is dedicated to Professor Marijan Kočevar, University of Ljubljana, on the occasion of his 70th birthday.

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