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Supramolecular Assemblies with Honeycomb Structures by π-π Stacking of Octahedral Metal Complexes of 1,12-Diazaperylene

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Homoleptic Ni^{II} and Fe^{II} complexes of the "large-surface" phenanthroline-type ligand 1,12-diazaperylene (dap), $[Ni(dap)_3](BF_4)_2$ (**1**) and $[Fe(dap)_3](PF_6)_2$ (**2**), respectively, were synthesized. In the crystal structure the complex cation $[M(dap)_3]^{2+}$ (M = Ni, Fe) exhibits C_3 symmetry and interacts with three other cations by π-π stacking. It forms a new metalla-supramolecular assembly with a honeycomb structure containing nanochannels running parallel to the crystallographic *c* axis. Aggregation by π-π stacking between metal complexes of "large-surface" ligands should give new perspectives for inorganic supramolecular chemistry.

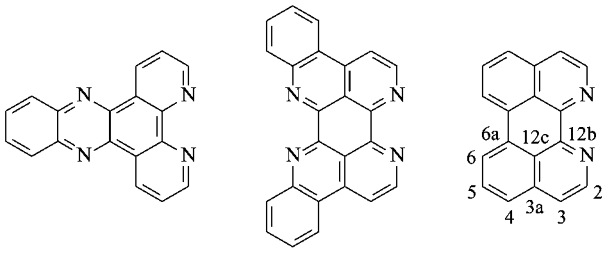
Introduction

The design and construction of nanoporous supramolecular systems has recently become one of the most active research subjects in modern coordination chemistry.[1] It is well known that weak intermolecular noncovalent interactions such as hydrogen bonds[2] and aromatic π-π stacking interactions[3] play important roles in supramolecular systems. The understanding and utilization of all noncovalent interactions, including π-π stacking, is of fundamental importance for the further development of inorganic supramolecular chemistry and the tuning and prediction of crystal structures.[3c]

In particular, π-π stacking interactions have been reported to exist between metal complexes with aromatic nitrogen-containing ligands, such as bipyridine- and 1,10-phenanthroline-based ligands.

Aggregation by π-π stacking becomes increasingly favorable with an increasing number of arene rings connected to the aromatic nitrogen-containing ligands. Dipyrido[3,2-*a*:2′,3′-*c*]phenazine[4] (dppz), eilatin[5] (eil), and 1,12-diazaperylene[6] (dap) (Scheme 1) are such ligands with increased π-surfaces (called "large-surface" ligands[7]).

In the planar dichloro(dipyridophenazine)platinum(II) complex $[PtCl_2(dppz)]$, both ligand-ligand and platinum-platinum π-π interactions lead to aggregation of this complex in the crystal, forming two infinite stacks with an interplanar distance of about 3.45 Å between the dipyridophenazine moieties.[8] The octahedral mono(eilatin) Ru^{II} and Os^{II} complexes $[M(L–L)_2(eil)]^{2+}$ (M = Ru, Os; L–L = bipyridyl-type ligands) dimerize by π-π stacking between the eilatin moieties in the solid state and in solution.[9] In all solid-state structures a well-defined discrete dimer is observed, in which the eilatin surfaces are about 3.4 Å apart, a typical distance for systems held by π-π stacking interactions.[3c,10]



dppz eil dap

Scheme 1. "Large-surface" phenanthroline-type ligands.

Homoleptic octahedral complexes with three "large-surface" phenanthroline-type ligands are rare[11] because the steric requirements for coordination at the metal center are greater than those of the parent 1,10-phenanthroline. However, such complexes provide the opportunity for optimal π-π interactions by three "large surface" ligands. They are potential rigid building blocks for the self-assembly into well-defined supramolecular architectures mediated by effective π-π interactions.

Recently Chouai et al. synthesized the Ru^{II} complex of 1,12-diazaperylene, $[Ru(dap)_3](PF_6)_2$.[11a] In the crystal structure the asymmetric unit of $[Ru(dap)_3](PF_6)_2$ contains two $[Ru(dap)_3]^{2+}$ cations which exhibit large distortions

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from the expected D_3 symmetry. π-π Interactions are observed between two dap ligands between both complex cations of the asymmetric unit. The distance between the two approximately parallel planes that separate the two dap ligands is 3.42 Å. No other π-π interactions are observed. To utilize the π-π interaction opportunities of all three "large surface" ligands of an octahedral metal complex in order to form a supramolecular assembly, a symmetrically octahedral complex is probably necessary.

It is well known that complexes of first row transition metals can show more regular geometries than those of second row transition metals. To investigate the π-π interaction opportunities of first row transition octahedral metal complexes with "large surface" ligands, we synthesized the dap complexes of Ni^{II} and Fe^{II}, $[Ni(dap)_3](BF_4)_2$ (**1**) and $[Fe(dap)_3](PF_6)_2$ (**2**), respectively. In the solid state, **1** and **2** form honeycomb structures built by π-π stacking.

Results and Discussion

Homoleptic 1,12-diazaperylene complexes of Ni^{II} and Fe^{II} are best prepared under microwave heating. **1** was synthesized by the reaction of $Ni(BF_4)_2·6H_2O$ with dap in ethanol and **2** by the reaction of $Fe(NH_4)_2(SO_4)_2·6H_2O$ with dap in water and subsequent addition of NH_4PF_6.

Crystals suitable for the X-ray structure determinations were obtained by slow evaporation of a solution of **1** in acetone and by diffusion of ethanol into a solution of **2** in a solvent mixture of acetone, acetonitrile, and chloroform.

In the crystal structure, the complex cation $[Ni(dap)_3]^{2+}$ of **1** exhibits C_3 symmetry. Figure 1 shows the structure of the cation along the threefold axis which coincides with the crystallographic *c* axis. The asymmetric unit of $[Ni(dap)_3](BF_4)_2$ (**1**) contains one third of $[Ni(dap)_3]^{2+}$ and also one third of one $B(1)F_4^-$ anion. One of the fluorine atoms of $B(1)F_4^-$ is partially disordered. $[Ni(dap)_3]^{2+}$ and $B(1)F_4^-$ are located alternately along the crystallographic *c* axis.

The bond lengths of Ni–N1 [2.105(2) Å], Ni–N2 [2.109(2) Å] and the bite angle of N1–Ni–N2 [78.54(8)°] are similar to the corresponding values of $[Ni(phen)_3]^{2+}$.[12] The diazaperylene ligand is coplanar to within 0.1617(36) Å. The dap ligands are almost perpendicular to each other, with a dihedral angle of 87.36 °.

Each complex cation $[Ni(dap)_3]^{2+}$ interacts with three other cations by π-π stacking, using all three dap ligands (see Figure 2, a). It forms a honeycomb structure containing channels running parallel to the crystallographic *c* axis (see Figure 2, b). If the van der Waals radii of the atoms are taken into account the resulting channels are approximately 9.60 Å in diameter. The channels contain the second anion, $B(2)F_4^-$, which shows a strong degree of disorder.

The $[Fe(dap)_3](PF_6)_2$ (**2**) compound is isostructural with **1**. The resulting channels in the honeycomb structure of **1** are 0.15 Å greater in diameter (ca. 9.75 Å). The Fe–N bond lengths amount to 1.9826(19) Å and 1.9779(18) Å. The N1–Fe–N2 bite angle is 81.71(7)°. These data are similar to the corresponding values of $[Fe(phen)_3]^{2+}$.[13]

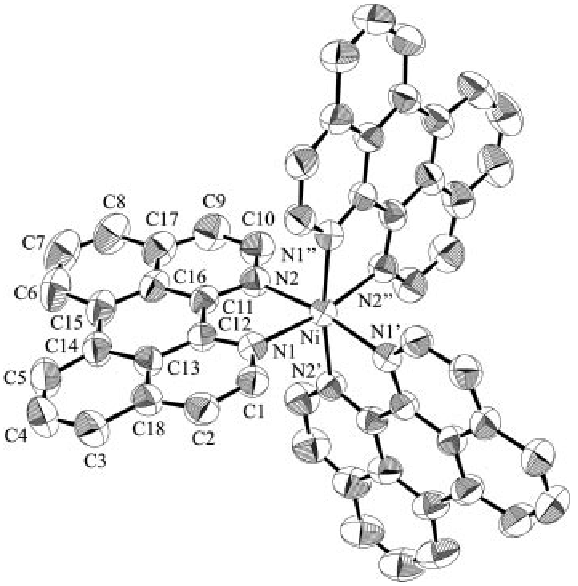

Figure 1. Structure of $[Ni(dap)_3]^{2+}$ in **1** with 50% ellipsoids. Hydrogen atoms have been omitted for clarity.

The π-π stacking between two dap ligands of two $[Ni(dap)_3]^{2+}$ moieties in **1** are shown in Figure 3. The distance between the two approximately parallel planes that separate the 1,12-diazaperylene ligands is 3.341 Å (**2**: 3.456 Å). Only one arene ring of each dap is involved in π-π stacking. They interact in an offset or parallel-displaced mode.[3c] The centroid-centroid distance is 3.663 Å (**2**: 3.633 Å) and the displacement angle is 24.2° (**2**: 17.96°).

To the best of our knowledge, supramolecular assemblies with honeycomb structures were not, until now, built by π-π stacking of a metal complex.

In addition to the single-crystal X-ray structure analysis, high resolution transmission electron microscopy (HRTEM) was performed on samples of **2** to further characterize the structure of the compound. Unfortunately, the crystals of **2** were very sensitive to electron-beam-induced damage, even at low temperature (–180 °C).

The nickel(II) complex was found to be paramagnetic, with a value of 2.77 ± 0.02 B.M., as expected for a typical d^8 system. The ^1H NMR spectrum of complex **2** in $[D_6]$-acetone exhibits five signals, consistent with the expected D_3 symmetry of $[Fe(dap)_3]^{2+}$ in solution.

The absorption spectra for complexes **1**, **2**, and dap are illustrated in Figure 4. The free dap resembles perylene, showing a strong well-resolved π-π* transition at 442 nm. This same transition is evident in the Ni^{II} and Fe^{II} complexes, but is shifted to a longer wavelength by 36 and 41 nm, respectively. Moreover, the spectrum of the Fe^{II} complex **2** shows the expected MLCT transition at 684 nm. This value is the lowest-energy absorption for a tris(diimin)-iron(II) complex that has been observed. As already observed for the phenanthroline Fe^{II} complex[14] **2** shows no phosphorescence or CT emission even if cooled to 10 K.

Cyclic voltammetry experiments in CH_3CN revealed that the Fe^{II} complex **2** and the reference complex $[Fe(phen)_3]$-

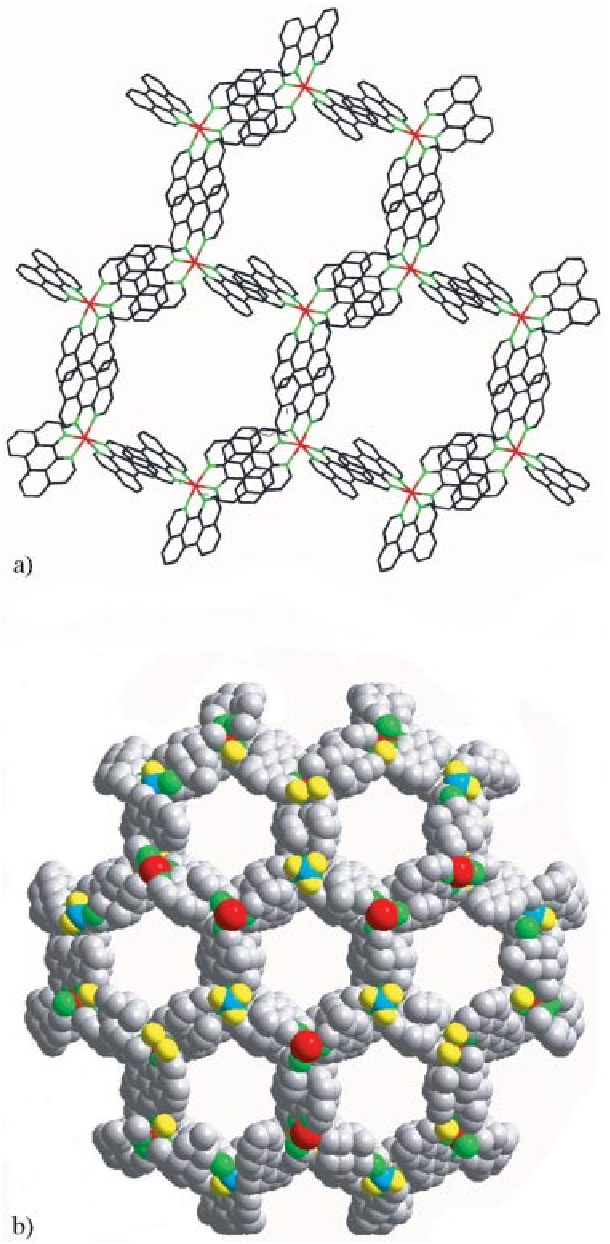

Figure 2. (a) Aggregation by π-π stacking between $[Ni(dap)_3]^{2+}$ moieties in $[Ni(dap)_3](BF_4)_2$ (**1**), viewed along the crystallographic *c* axis. Hydrogen atoms have been omitted for clarity. (b) Honeycomb structural motif in **1** (view down c) as a space-filling representation. $[Ni(dap)_3]^{2+}$ and one $B(1)F_4^-$ ion form parallel nanosized channels, which run along the crystallographic *c* axis and are filled with the second disordered $B(2)F_4^-$ counterion (omitted for clarity). Red: Ni, pink: B, yellow: F, green: N, grey: C.

$(PF_6)_2$ are oxidized at +0,69 V (rev., vs. Fc/Fc^+). These metal-centered oxidations indicate that the iron d orbitals are not influenced by complexation with dap as compared with that of phen. The reduction processes for the Fe^{II} complex **2**, as well as the Ni^{II} complex **1**, occur at the same potential (–1.08 V, irr.), probably because reduction is ligand-centered. The Ni^{II} complex **1** is oxidized at 1.34 V (irr.) and $[Ni(phen)_3](BF_4)_2$ at 1.58 V (irr.).

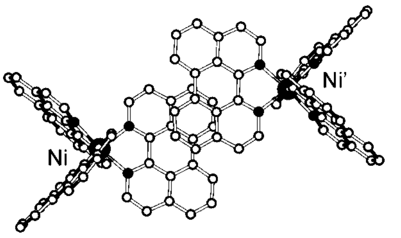

Figure 3. Aggregation by π-π stacking between two dap ligands of two $[Ni(dap)_3]^{2+}$ moieties in **1**. Hydrogen atoms have been omitted for clarity.

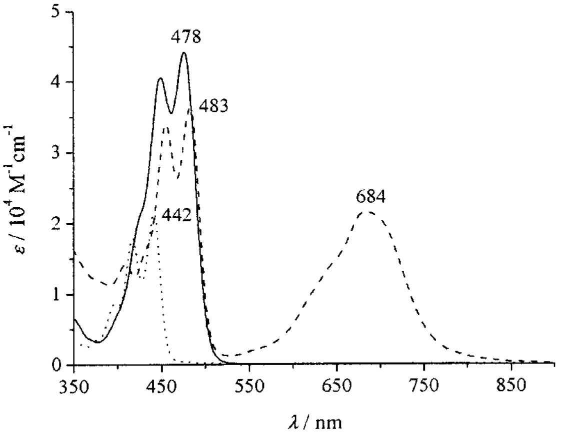

Figure 4. Absorption spectra of the complexes **1** (——) and **2** (– – – –), and of dap (······), recorded in acetonitrile ($c = 10^{-5}$ mol/L).

Conclusions

In conclusion, we have shown that homoleptic octahedral metal complexes of 1,12-diazaperylene are able to form supramolecular assemblies with honeycomb structures by π-π stacking when the complex cation, $[M(dap)_3]^{2+}$ (M = Ni, Fe), adopts a C_3 symmetry and the anions are BF_4^- or PF_6^-. Further studies with other metal complexes of 1,12-diazaperylene and derivatives of dap using π-π stacking for self-assembly are in progress. Aggregation by π-π stacking between metal complexes of "large surface ligands" should give new perspectives for the development of inorganic supramolecular chemistry.

Experimental Section

General: All reactions were carried out in dry solvents under an argon atmosphere. 1,12-Diazaperylene was prepared according to a known procedure.[6] Reference complexes $[Ni(phen)_3](BF_4)_2$ and $[Fe(phen)_3](PF_6)_2$ were synthesized following the methods described for complexes **1** and **2**, respectively. NMR spectra were recorded using an Avance 300 spectrometer. IR spectra were recorded with a Thermo Nicolet NEXUS FTIR instrument. UV/Vis measurements were carried out with an Analytik Jena Specord S 100 spectrophotometer using sealed quartz cuvettes. The ESI spectra were recorded using a Micromass Q-TOF$_{micro}$ mass spectrometer in positive electrospray mode. Elemental analyses (C, H, N) were performed with an Elementar Vario EL elemental analyzer. For phosphorescence emission measurements, the samples were provided as solids on quartz substrates. The samples were cooled to 10 K with a helium cryostat (Optistat CF, Oxford Instruments, Wiesbaden, Germany). For excitation, 2 mJ pulses from an optical parametric oscillator (VisIR 2/120, GWU, Erfstadt, Germany), which was pumped at 355 nm with a Q-switched Nd-YAG laser (SL 400, GWU), were used. The samples were excited in the ligand π-π* band at 440 nm. Electrochemical measurements were performed with a BAS 100B system using a platinum working and auxiliary electrode, and a Ag/$AgNO_3$ reference electrode. The experiments were conducted using degassed MeCN solutions using 0.1 M [nBu$_4$N$^+$][PF$_6^-$] as the supporting electrolyte, and the Ferrocene/Ferrocinium (Fc/Fc$^+$) couple as a reference. Magnetic studies were performed at room temp. on a vibration sample magnetometer V.S.M. 3001.

[Ni(dap)$_3$](BF$_4$)$_2$ (1): A suspension of 1,12-diazaperylene (228.9 mg, 0.9 mmol) in ethanol (3 mL) was added to a solution of Ni(BF$_4$)$_2$·H$_2$O (102.1 mg, 0.3 mmol) in ethanol (4 mL). The mixture was heated in a CEM-Discover microwave oven for 15 min (temp.: 85 °C, pressure: 17 bar). After cooling the mixture the precipitate was filtered. Dichloromethane (10 mL) and diethyl ether (100 mL) were added to the crude product, the solid was filtered and dried under vacuum to yield an orange powder (245 mg, 0.25 mmol, 82%). M.p. > 360 °C. IR (KBr): $\tilde{\nu}$ = 1051 (s, B–F) cm^{-1}. UV/Vis (CH$_3$CN): λ_{max} (ε) = 478 (42700), 451 (39400), 426 (20300) sh, 352 (6400) sh nm. ESI(HR)-MS: m/z calcd. for [M – 2BF$_4$]$^{2+}$ ([C$_{54}$H$_{30}$NiN$_6$]$^{2+}$) 410.0942, found 410.0915. C$_{54}$H$_{30}$B$_2$F$_8$N$_6$Ni (995.17): C 65.17, H 3.04, N 8.44; found C 64,92, H 3.10, N 8.37.

[Fe(dap)$_3$](PF$_6$)$_2$ (2): A suspension of 1,12-diazaperylene (255 mg, 1 mmol) and Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O (98.04 mg, 0.25 mmol) in water (8 mL) was heated in a CEM-Discover microwave oven for 10 min (temp.: 120 °C, pressure: 15 bar). After cooling the solution, NH$_4$PF$_6$ (122.3 mg, 0.75 mmol) was added to precipitate **2**. The raw product was filtered and dissolved in acetone (25 mL). The desired product was precipitated by addition of diethyl ether (100 mL), filtered, and dried under vacuum to yield a dark green powder (270 mg, 0.24 mmol, 97%). M.p. > 360 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.83 (dd, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 0.6 Hz, 2 H, 6-H), 8.09 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, 4-H), 8.01 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, 5-H] 7.87 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, 3-H), 7.60 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, 2-H) ppm. ^{13}C NMR (300 MHz, [D$_6$]acetone): δ = 159.2 (C12b), 148.1 (C2), 138.2 (C3a), 135.3 (C5), 131.4 (C6a), 129.9 (C4), 127.6 (C3), 127.3 (C12c), 127.1 (C6) ppm. IR (KBr): $\tilde{\nu}$ = 838 (s, P–F), 558 (m, P–F) cm^{-1}. UV/Vis(CH$_3$CN): λ_{max} (ε) = 684 (21900), 483 (36700), 456 (34400), 433 (16500) sh, 410 (14500), 346 (16900) nm. ESI(HR)-MS: m/z calcd. for [M – 2PF$_6$]$^{2+}$ ([C$_{54}$H$_{30}$FeN$_6$]$^{2+}$) 409.0940, found 409.0908. C$_{54}$H$_{30}$F$_{12}$FeN$_6$P$_2$ (1108.65): C 58.50, H 2.73, N 7.58; found C 58.27, H 2.80, N 7.50.

Crystallographic Data: Data were collected with a STOE IPDS-2 diffractometer at 210(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Spherical absorption corrections were applied. Structure solution by direct methods (SHELXS-97)[15] and full-matrix refinement against F^2 (SHELXL-97).[16] Non-hydrogen atoms were refined with anisotropic temperature factors.

CCDC-290982 (for **1**) and -290981 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1: C$_{54}$H$_{30}$B$_2$F$_8$NiN$_6$, 995.16 g·mol^{-1}, orange prism 0.62 × 0.31 × 0.14 mm, trigonal, $P\bar{3}$, a = b = 18.126(3), c = 11.1481(13) Å, V = 3171.9(7) Å^3, Z = 2, F(000) = 930, ρ_{calc} = 0.961 g·cm^{-3}, μ(Mo-K_α) = 0.35 mm^{-1}, 26875 reflections measured (2Θ_{max} = 50.0°), of which 3728 were unique (R_{int} = 0.0482). 253 parameters, wR_2 = 0.1355, S = 0.974 (all data), R_1 [2806 data with $I > 2\sigma(I)$] = 0.0463, max./min. residual electron density: 0.259/–0.185 e·A^{-3}. Either of the tetrafluorborate anions, B(1)F$_4^-$, are located on the threefold axis, of which the F atoms are disordered over a mixture of full and partial occupancy sites. The second BF$_4^-$ counterion, B(2)F$_4^-$, is accommodated inside the channel. Because of its strong disordered positions, a suitable refinement model could not be found. Therefore this ion was disregarded by the SQUEEZE instruction of the program PLATON[17] and not accounted for in the final refinement cycles.

2: C$_{54}$H$_{30}$F$_{12}$FeN$_6$P$_2$, 1108.63 g·mol^{-1}, green prism 0.6 × 0.35 × 0.32 mm, trigonal, $P\bar{3}$, a = b = 18.3658(14), c = 11.5512(8) Å, V = 3374.2(4) Å^3, Z = 2, F(000) = 1120, ρ_{calc} = 1.091 g·cm^{-3}, μ(Mo-K_α) = 0.34 mm^{-1}, 21742 reflections measured (2Θ_{max} = 50.0°), of which 3956 were unique (R_{int} = 0.0555). 206 parameters, wR_2 = 0.1258, S = 0.898 (all data), R_1 [2801 data with $I > 2\sigma(I)$] = 0.0448, max./min. residual electron density: 0.255/–0.214 e·A^{-3}. The first PF$_6^-$ counterion, P(1)F$_6^-$, could be found with certainty from the Fourier map, located on the threefold axis. The second counterion, P(2)F$_6^-$, as well as solvent molecules, fill the channels. The extremely diffuse electron density indicates severely disordered occupancies. Because it was not possible to assign atoms, the observed structure factors were corrected by subtracting the electron density in this region using the SQUEEZE instruction of PLATON.

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