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Ruthenium−Oxygen Coordination-Driven Self-Assembly of a Ru^{II}_8 Incomplete Prism: Synthesis, Structure, and Shape-Selective Molecular Recognition Study[†]

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Coordination-driven self-assembly of 1,3,5-benzenetricarboxylate (tma; **1**) and oxalato-bridged *p*-cymeneruthenium(II) building block $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-cymene})_2](O_3SCF_3)_2$ (**2**) affords an unusual octanuclear incomplete prism $[Ru_8(\eta^6\text{-}p\text{-cymene})_8(tma)_2(\mu\text{-}\eta^4\text{-}C_2O_4)_2(OMe)_4](O_3SCF_3)_2$ (**3**), which exhibits a remarkable shape-selective binding affinity for neutral phenolic compounds via hydrogen-bonding interactions (*p*-cymene = *p*-$^iPrC_6H_4Me$). Such a binding was confirmed by single-crystal X-ray diffraction analysis using 1,3,5-trihydroxybenzene as an analyte.

Coordination-driven self-assembly of supramolecular architectures of defined shapes, sizes, and functionality has witnessed rapid growth in the past few years because of their structural diversity as well as their potential applications in host−guest chemistry, catalysis, molecular recognition, etc.[1] The basic principle of directed self-assembly resides in the proper design of information-encoded building blocks that fulfill the requirements for selective molecular recognition in a self-assembly event.[2,3] In recent time, organometallic half-sandwich complexes are being used as potential building blocks by Bruno et al. and others for the construction of interesting finite supramolecular systems because of their stable coordination geometry and several interesting properties.[4] Such organometallic units have so far been focused mostly on the use of rigid nitrogen-based neutral organic linkers to construct discrete architectures.[2,3] However, anionic oxygen-based donors, in particular carboxylates, have not been used much presumably because of their flexible nature.[5] Unlike sp^2-hybridized nitrogen donors, which maintain their directionality during the self-assembly process, carboxylate-based anionic oxygen donors are not restricted in their directionality and generally result in polymers rather than discrete architectures.

Shape-selective molecular recognition of target guests by an artificial synthetic receptor has attracted much attention with the view of better understanding the recognition phenomena in nature.[6] Among various noncovalent interactions influencing a receptor for the recognition of a target guest molecule, hydrogen bonding has gained special attention in the frontier field of host−guest chemistry.[7−9] To explore the use of carboxylate instead of widely used rigid nitrogen

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[†] This work is dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday.

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Scheme 1. Schematic Presentation of the Selective Formation of Octanuclear Open Cage **3** and the Expected Molecular Prism **3′**

donors in combination with a ruthenium(II) half-sandwich building block (**2**), herein we report the synthesis, the characterization of an unusual octanuclear incomplete prism [Ru$_8$(η^6-*p*-cymene)$_8$(tma)$_2$(μ-η^4-C$_2$O$_4$)$_2$(OMe)$_4$](OTf)$_2$ (**3**), and its binding efficiency toward shape-selective aromatic hydroxy compounds.

The incomplete prism (**3**) was assembled from 1,3,5-benzenetricorboxylate (**1**) as a tritopic planar donor with half-sandwich organometallic complex [Ru$_2$(μ-η^4-C$_2$O$_4$)(MeOH)$_2$(η^6-*p*-cymene)$_2$](O$_3$SCF$_3$)$_2$ (**2**) as a ditopic "clip"-type acceptor (Scheme 1).

One can expect the formation of a hexanuclear neutral trigonal prism **3′** upon the 3:2 self-assembly of **2** and **1** (Scheme 1). Quantitative formation of the octanuclear incomplete cage **3** is quite surprising. The addition of a methanolic solution of **2** (300 mg, 0.3 mmol) into a methanolic slurry of **1** (60 mg, 0.2 mmol) yielded a clear yellow solution after 24 h of stirring. The mixture was dried and extracted with dichloromethane. The extract was concentrated, and the product was precipitated out as an orange solid with 86% (250.0 mg) isolated yield by trituration with cold diethyl ether. Complex **3** is soluble in common organic solvents like (CH$_3$)$_2$CO, CH$_3$CN, CH$_3$OH, and CH$_2$Cl$_2$ and sparingly soluble in CHCl$_3$ and H$_2$O. IR, ^{1}H NMR, and electrospray ionization mass spectral analyses of the macrocycle **3** were consistent with the octanuclear structure (Supporting Information, SI).

A significant blue shift ($\Delta\nu_{C=O}$ = 59.5 cm^{-1}) of the symmetrical stretching frequency ($\nu_{C=O}$) corresponding to a carboxylate carbonyl group of **3** compared to the starting material **1** indicated coordination of the carboxylate oxygen to ruthenium(II) (Figure S1 in the SI). In the ^{1}H NMR spectrum of the reaction mixture (Figure S2 in the SI), the appearance of two peaks with an intensity ratio of 1:2 for the protons corresponding to the aromatic ring of tma in the product ruled out the formation of **3′**.

Finally, the formation of an incomplete prism **3** (Figure 1) was unambiguously determined by single-crystal X-ray diffraction (XRD) analysis. XRD-quality crystals were obtained by slow vapor diffusion of diethyl ether into a saturated tetrahydrofuran solution of **3** over 1 week at ambient temperature. The complex crystallized in a triclinic system with space group $P\bar{1}$. Structure analysis revealed a typical bonding connectivity of tma with ruthenium metal centers. Two carboxylate groups of tma are coordinated to two ruthenium metal centers (Ru3 and Ru4) of two different dimetallic acceptors (**2**) via one of the carboxylate oxygen atoms (Figure 1). The other ends of the dimetallic acceptors (**2**) are coordinated to two carboxylate groups of the second tma to form virtually a tetrametallic bipillared subarchitecture where the two capped tma groups are mutually 180° eclipsed (Figure 1). Interestingly, two oxygen atoms of the remaining carboxylate group of each capped tma bind to two η^6-cymene-bound ruthenium centers (Ru1 and Ru2), which are bridged by two μ_2-methoxides, forming an overall octametallic dicationic incomplete prismatic structure **3**.

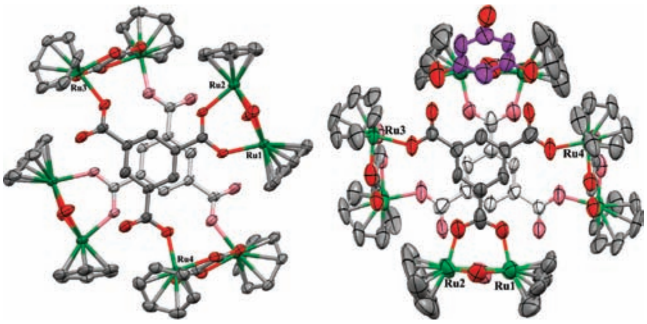

Figure 1. ORTEP presentation of the structures of **3** (left) and [**3**⊃**2THB**] (right). Methyl and isopropyl groups as well as hydrogen atoms are omitted for clarity. Color codes: green, Ru; red, O; gray/violet, C. The ellipsoids are drawn at 50% probability.

The four ruthenium centers (Ru1−Ru4) coordinated to one tma are almost coplanar (torsion angle = 7.9°) to form a tetranuclear rhomboidal surface with arm lengths of 3.3 Å (Ru1−Ru2), 7.7 Å (Ru2−Ru3), 11.0 Å (Ru3−Ru4), and 7.9 Å (Ru4−Ru1). The whole molecule consists of two such planes, and these two tetranuclear planar surfaces are almost parallel to each other and are hinged by two parallel dimetallic acceptors (**2**) to form a sandwich-type incomplete cage (Figure 1). Each ruthenium(II) maintains a half-sandwich piano-stool coordination geometry with η^6-cymene and three oxygen atoms. The Ru−Ru distance in the dimetallic pillar **2** is 5.5 Å, while the centroids of two capped tma are separated by a distance of 3.7 Å.

One of the major challenges in the field of host−guest chemistry is the selective recognition of target guest molecules.[10,11] Though complex **3** is not a closed cage, it looks like a trigonal prism with a triangular floor and roof occupied by two planar tma building blocks. We anticipated that **3** may bind organic guests through hydrogen-bonding interactions with the noncoordinated carboxylate oxygen atoms. Guest binding of **3** was initially studied using UV−vis spectroscopy. The electronic absorption spectrum (Figure S5 in the SI) of **3** showed two intense bands with absorption maxima at 265 and 320 nm along with a shoulder band with an absorption maximum at 405 nm in methanol. The intense peaks at 265 and 320 nm are assigned to $\pi \rightarrow \pi^*$ and metal-to-ligand charge-transfer transitions, respectively.[4] The shoulder band near 405 nm might be due to the weak d−d transition. Surprisingly, the initial absorption intensity of **3** enhanced significantly upon titration with an increasing concentration of 1,3,5-trihydroxybenzene (THB) in methanol (Figure 2) and thereby indicated host−guest complexation. The binding ratio of **3** with the guest (THB) was calculated by stoichiometry plot analysis, and it was calculated to be close to 1:2

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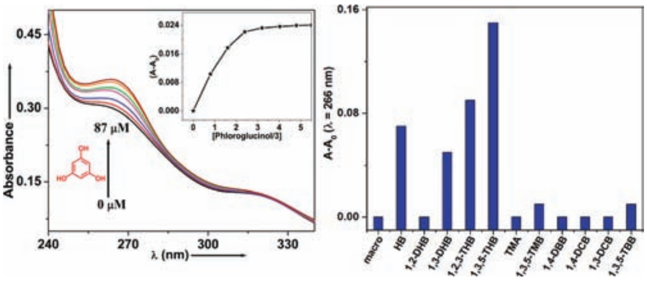

Figure 2. Absorption spectral (left) changes of **3** (6.5×10^{-6} M) upon the addition of THB [$(0-87) \times 10^{-6}$ M] in methanol at 25 °C. Plots of the absorbance change vs [THB] at 266 nm (left inset) and the change in absorbance (right) upon titration with various guests (see the SI for abbreviations).

(Figure 2, inset). A considerably high association constant ($K_a = 6.2 \times 10^2$ M^{-1}), as calculated from slope and intercept of the plot obtained using the Benesi–Hilderbrand equation, indicated strong binding interaction in the adduct [**3**⊃**2THB**] (Figure S9 in the SI). Analysis of the UV–vis spectrometric titration of **3** with a series of small aromatics displayed selective recognition toward meta-directed dihydroxy aromatics (Figure 2). Moreover, the association constant (K_a) of **3** with 1,3-dihydroxybenzene was measured to be 3.2×10^2 M^{-1}, while it was almost zero with 1,2-dihydroxybenzene.

The solution-state ^{1}H NMR spectrum of a mixture (Figure S3 in the SI) of **3** and 2 equiv of THB in CD_3CN at room temperature revealed that the peak corresponding to the OH protons of THB is largely downfield-shifted ($\Delta\delta \approx 3$ ppm) and the peak corresponding to the aromatic protons of THB is considerably upfield shifted ($\Delta\delta \approx 0.4$ ppm) compared to the free THB (Figure S4 in the SI). In addition to this, significant shifts of the peaks corresponding to the aromatic protons (Figure S3 in the SI) of complex **3** in this mixture primarily implied the formation of an adduct between **3** and THB in solution. Moreover, relative intensity ratios of the peaks in the ^{1}H NMR spectrum qualitatively indicated the formation of [**3**⊃**2THB**]. Finally, the binding nature of complex **3** with THB was unambiguously determined by single-crystal XRD analysis. The solid-state structure of [**3**⊃**2THB**] (Figure 1) revealed that two –OH groups of the guest molecule are involved in hydrogen bonding with the noncoordinated carboxylate oxygen atoms of the capped tma and the remaining hydroxyl group of the guest molecule forms hydrogen bonding with the counteranion. The solid-state packing diagram of [**3**⊃**2THB**] (Figure S8 in the SI) showed that the intermolecular porous channels are occupied by THB and $CF_3SO_3^-$ through hydrogen bonding.

The zero association constant of 1,2-dihydroxybenzene toward **3** can be attributed to the intramolecular hydrogen bonding in the analyte, which inhibits further interaction with the carboxylate oxygen atoms of tma. Moreover, the positional mismatch of the hydroxyl groups in 1,2-dihydroxybenzene with respect to the noncoordinated oxygen atoms in the capped tma of the macrocycle **3** could be a reason. Interestingly, UV–vis spectrometric titration analysis showed that complex **3** has a binding affinity toward phenol (HB) comparable to that of THB. Structural simplicity, presumably, allows access of HB to form hydrogen bonding with a noncoordinated carboxylate oxygen atom of the capped tma.

In conclusion, we report here the synthesis and characterization of an unusual octanuclear ruthenium(II)-based open cage derived from an anionic tritopic carboxylate donor (**1**) in combination with an organometallic half-sandwich precursor (**2**). Although oxygen-donor ligands are not well suited for the design of ruthenium(II) organometallic discrete molecular architectures because of the flexible nature of the donor site, the formation of **3** represents an interesting example of a Ru–O bond-directed discrete supramolecule of the ruthenium(II) precursor **2**. Complex **3** exhibits remarkable shape-selective molecular recognition toward aromatic hydroxy compounds through hydrogen-bonding interaction, which was confirmed by single-crystal XRD analysis. The use of carboxylates instead of widely used nitrogen donors in combination with organometallic half-sandwich ruthenium(II) precursors may generate a wide variety of complex architectures for a study of the molecular recognition of selective organic compounds. Studies are underway to establish the full scope of this methodology.

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Supporting Information Available: Crystallographic information of **3** and [**3**⊃**2THB**] in CIF format, experimental details, IR, NMR, and UV–vis spectra, and solid-state packing diagrams of **3** and [**3**⊃**2THB**]. This material is available free of charge via the Internet at http://pubs.acs.org.