

Synthesis and crystal structure of a wheel-shaped supramolecular coordination complex

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Abstract. Supramolecular coordination complex (SCC) possessing spatially arranged three anthraquinone dimers in a slipped-cofacial orientation was achieved by the treatment of $\text{Re}_2(\text{CO})_{10}$, 2-hydroxymethylanthraquinone and tritopic N-donor *via fac*- $\text{Re}(\text{CO})_3$ -directed one pot approach. The off-set π -stacking and $\text{C}\equiv\text{O}\cdots\text{H}$ bonding interactions stabilize the ring structure.

Keywords. Rhenium; molecular ring; anthraquinone; non-covalent interactions; supramolecules; X-ray structure.

1. Introduction

The metal-directed self-assembly methods and crystal X-ray crystallography have been collectively providing supramolecular coordination complexes from aesthetically pleasing small to unimaginably big molecular architectures.¹ The crystallographic analysis has become the most powerful analytical technique for the elucidation of the structure of the final product. The details of the structural parameters and the non-covalent interactions existing in the supramolecular coordination complexes (SCCs) provide motivation to create interesting and potential new molecules as well as mimics of naturally existing molecules.

A variety of metal-directed synthetic methods have been applied to design and synthesize distorted cycles and platonic solid shaped metallacycles e.g., rectangles, prisms and octahedron; modulating the size and properties of the final structure by changing either the organic building unit or metal cores.² No attention has been paid to achieve wheel-shaped structures possessing spatially arranged π -dimers in a cyclic manner. However, owing to the poor-directionality of the π - π interactions, the construction of non-covalently bound π -stacked dimers is challenging.³ Moreover, a cyclic arrangement of close lying, non-covalently linked chromophores is an important feature of the photosynthetic antenna and reaction centre proteins where a slipped-cofacial orientation (SCO) of *bacteriochlorophyll-a*

dimers in the light harvesting complexes (LHCs) plays a crucial role in photosynthetic bacteria.³ Keeping these under consideration, efforts are still being expanded on the design and synthesis of macrocyclic ring-like functional assemblies possessing non-covalently linked π -stacked dimers of porphyrin or other chromophores using metal-directed strategy. In this paper we report a one-step synthesis and crystal structure of a wheel-shaped supramolecule possessing cyclic arrangement of slipped-cofacial dimers of anthraquinone units.

2. Experimental

2.1 General experimental methods

$\text{Re}_2(\text{CO})_{10}$, 2-hydroxymethylanthraquinone (H-mAq) and 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (tpt) were purchased from commercial sources and used as received. Toluene was purified by conventional procedures and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer. ^1H NMR spectra for **1** and the bulk product were recorded on a Bruker AMX-400 FT-NMR spectrometer. ICPMS was recorded on a Perkin-Elmer ICP Mass Spectrometer. X-ray data for complex **1** was collected using an OXFORD XCALIBUR-S CCD single crystal X-ray diffractometer. The structure was solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 program.¹⁰ The absorption corrections were done by multiscan (SHELXTL program package), and all the data was corrected for Lorentz, polarization effects.

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2.2 Synthesis of hexanuclear complex 1

A mixture of $\text{Re}_2(\text{CO})_{10}$ (98.4 mg, 0.15 mol), tpt (32 mg, 0.10 mmol), and H-mAq (71.5 mg, 0.30 mmol) in toluene (15 mL) was placed in a Teflon inliner which was placed in a stainless steel autoclave. The autoclave was placed in an oven maintained at 150°C for 25 h and then cooled to room temperature. Good quality single crystals of **1** were separated from the resulting product and washed with pet-ether. Yield: 68.1 mg. FTIR ($\text{KBr}/\text{cm}^{-1}$): 2023 ($\text{C}\equiv\text{O}$), 2018 ($\text{C}\equiv\text{O}$), 1809 ($\text{C}=\text{O}$), 1674 ($\text{C}=\text{O}$). ^1H NMR (d_6 -DMSO): δ 8.95 (12 H, d, $^3J_{\text{H,H}} = 6$ Hz, H^{a} , tpt), 8.64 (12 H, d, $^3J_{\text{H,H}} = 6$ Hz, H^{b} , tpt), 8.22–8.19 (12 H, m, $\text{H}^{8,5}$, -mAq), 8.18 (6 H, s, H^1 , -mAq), 7.94–7.91 (12 H, m, $\text{H}^{7,6}$, -mAq), 7.85 (6 H, d, H^3 , -mAq), 5.6 (6H, t, -OH, mAq), 4.7 (12 H, d, $^2J_{\text{H,H}} = 6$ Hz, $-\text{CH}_2-$, -mAq).

2.3 Crystal diffraction data

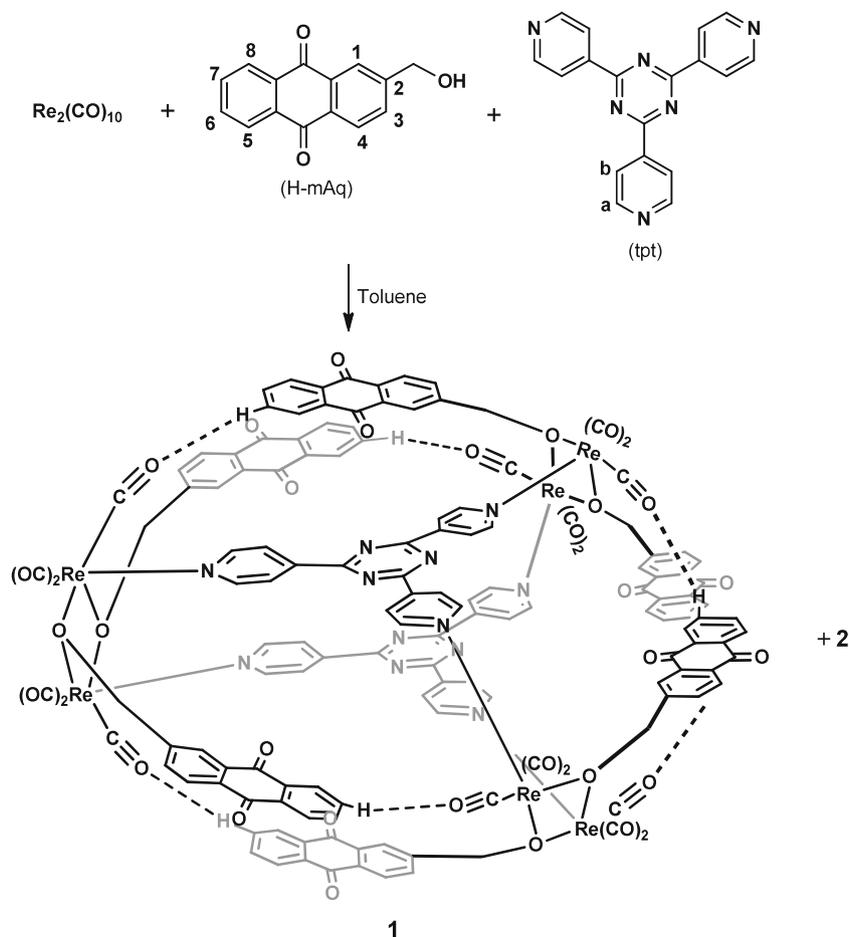
$\text{C}_{144}\text{H}_{78}\text{N}_{12}\text{O}_{37}\text{Re}_6$, $M = 3685.45$, hexagonal, $a = 24.1039(6)$, $b = 24.1039(6)$, $c = 13.1545(3)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$, $V = 6618.8(3)$ Å³, $T = 183(2)$ K,

space group $P6_32_2$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 5.552$ mm⁻¹, 36038 reflections measured, 4214 unique ($R_{\text{int}} = 0.0926$) which were used in all calculations. GOF on F^2 : 0.650. $R^{\text{a}} [I > 2\sigma(I)]: 0.0364$. R_w^{b} (all data): 0.0837. The final $wR(F_2)$ was 0.1057 (all data).

3. Results and discussion

3.1 Characterization

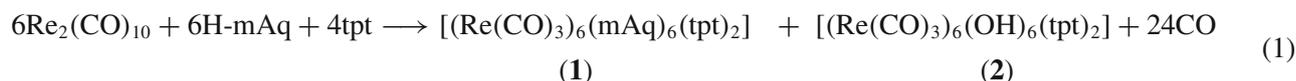
A combination of $\text{Re}_2(\text{CO})_{10}$, 2-hydroxymethyl-9,10-anthraquinone (H-mAq) and 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (tpt) in toluene under solvothermal conditions leads to a mixture of products as brown crystals and light-brown powder (scheme 1 and eq. 1). Few bigger crystals out of the bulk product were hand-picked under a microscope and used for structural analysis. The crystalline product $[(\text{Re}(\text{CO})_3)_6(\text{mAq})_6(\text{tpt})_2]$ (**1**) and powder $[(\text{Re}(\text{CO})_3)_6(\text{OH})_6(\text{tpt})_2]$ (**2**) are air- and moisture-stable and poorly soluble in most of the organic solvents. The FT-IR spectrum of **1** exhibits strong bands at 2023, 2018, and 1809 cm⁻¹,



Scheme 1. Multicomponent assembly of metallomacroring **1**.

characteristic of *fac*-Re(CO)₃ moiety in an asymmetric environment.⁴ The absorption band at 1674 cm⁻¹ is attributed to the stretching vibrations of C=O bond of the anthraquinone fragments (figure S2).⁵ The ¹HNMR spectrum of **1** dissolved in *d*₆-DMSO by heating shows a pair of doublets (8.95, 8.64 ppm)

for the pyridyl protons of the tpt units. No significant chemical shifts were observed for the protons of anthraquinone unit in **1** as compared to anthraquinone protons of the free ligand which indicated towards the poor stability of complex **1** in solution (figure S3 in ESI[†]).



However, the ¹HNMR spectrum of the powder sample shows two types of resonance patterns; one of the patterns match exactly with that of the crystalline product (1), while the other indicates the formation of a hydroxyl-bridged trigonal prism (2) (figure S3). The observation of the molecular ion peak at 2371.87 m/Z for (2) in the ICPMS spectrum confirmed the presence of 2 (figure S4). Several attempts to procure pure 1 by varying the concentration of starting materials and reaction conditions were fruitless. The complete separation of 1 from the bulk was extremely difficult due to the poor solubility and tininess of the crystals. Based on the integration ratios of the ¹HNMR resonances, the yield of complex 1 was estimated to be above 30%. Therefore, it can be proposed that the bulk product consists of a mixture of 1 and 2.

3.2 X-ray crystal structure

Compound 1 crystallizes in a chiral space group *P*6₃2₂ and adopts a spoked-wheel structure (figure 1). The ring

in 1 is composed of alternatively arranged three rigid modules of anthraquinone dimers (mAq)₂ and three ((CO)₃Re-(μ₂-O)₂-Re(CO)₃) units having a diameter of about 2.2 nm including the van der Waals radii. The two tpt units act as spokes to support the ring structure. Several intramolecular non-covalent interactions such as C-H···O≡C and π-π stacking stabilize the ring framework. The slipped-cofacial head-to-head orientation, planarity and tilted angle favours the strong electrostatic self-complementary π-π interactions of electron rich arene portions to electron poor quinone portions of Aq units in (mAq)₂ dimer units in 1 (figure 1). The distance between the two anthraquinone moieties in a anthraquinone dimer is in the range of 3.6 to 3.8 Å (figure 2). Complex 1 has three anthraquinone dimer sets and the distance between the two mAq duplexes is *ca.* 7.27 Å. The hydrogen atom of the sixth carbon of anthraquinone unit bridges to a nearby carbonyl unit (C-H···O≡C (D = 3.11 Å, d = 2.32 Å, θ = 143°)) in a concerted fashion to complete the ring structure (figure 2).⁶ Examples of metal-based trigonal-prisms were reported

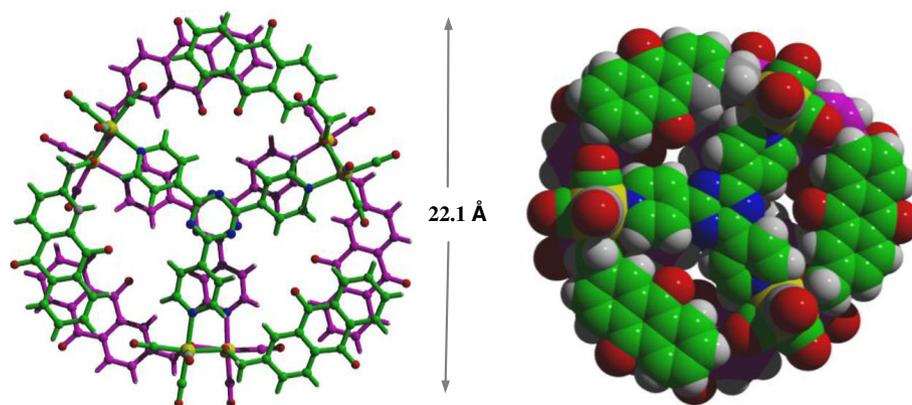


Figure 1. Structure of **1** (ball and stick and space-filling representations, Green = rose = C, white = H, blue = N, red = O, yellow = Re).

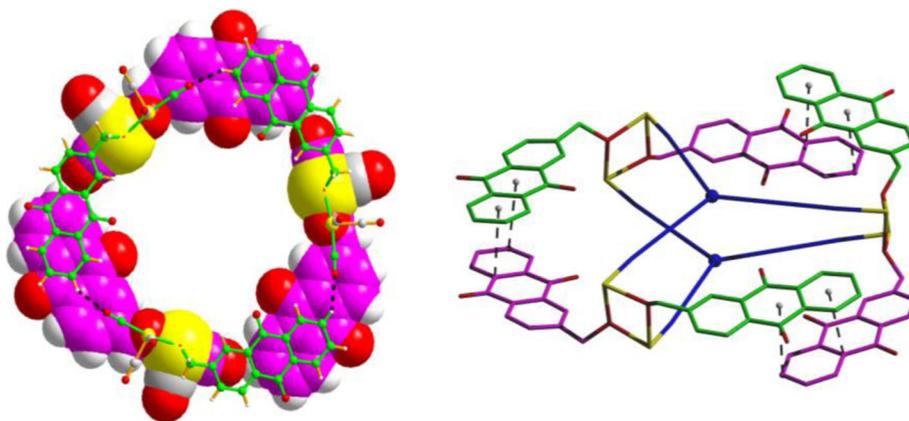


Figure 2. Left: space-filling and ball and stick view of **1** showing intramolecular H-bonds (two tpt units are omitted). Right: stick view of **1** showing dimeric unit (two tpt units are shown as blue sticks, H atoms and carbonyl groups are omitted for clarity).

previously by us and others.⁴ To the best of our knowledge, this is the first report on SCC with more than one slipped-cofacially arranged organic dimers in a cyclic manner.^{1,4}

Interestingly, the tpt units are found to be twisted in the trigonal prismatic framework of SCC **1**. The cofacial pyridyl subunits are out of the plane of the triazine rings by an angle of 21.5° and are not perfectly eclipsed; inducing chirality to **1** (triazines, dihedral angle = 0° , d (centroid \cdots centroid distance) = 3.4 \AA ; pyridines, tilted angle = 21.5° , dihedral angle = 2.3° , $d = 3.4\text{--}3.5 \text{ \AA}$) (figure 3). A variety of tpt based metalloprisms having the eclipsed pyridyl units are known to be achiral.⁴ The degree of deviation from the trigonal prismatic geometry is measured by the Bailar Twist Angles which is 18.29° for all the three pyridyl dimers.⁷ A very few

chiral self-assembled metalloprisms are known in the literature.⁸

Another feature of complex **1** is its packing arrangement. It extends as 2D hexagonal layered structure along the *ab* direction, stabilized by intermolecular C–H \cdots O interactions between anthraquinone units (C–H \cdots O=C, $D = 3.37 \text{ \AA}$, $d = 2.46 \text{ \AA}$, $\theta = 165.7^\circ$). Each anthraquinone in the ring interacts with anthraquinone units of the two neighbouring rings; hence, overall each macrocyclic ring interacts with six others (figure 4). A similar type of self-assembled H-bonded trimer of anthraquinone molecules was observed on a Cu(111) surface.⁹ In addition, the sheets are stacked in an ABAB layered pattern along the *c*-axis, resulting in 3D supramolecular network through extensive intermolecular $\pi \cdots \pi$ stacking interactions.

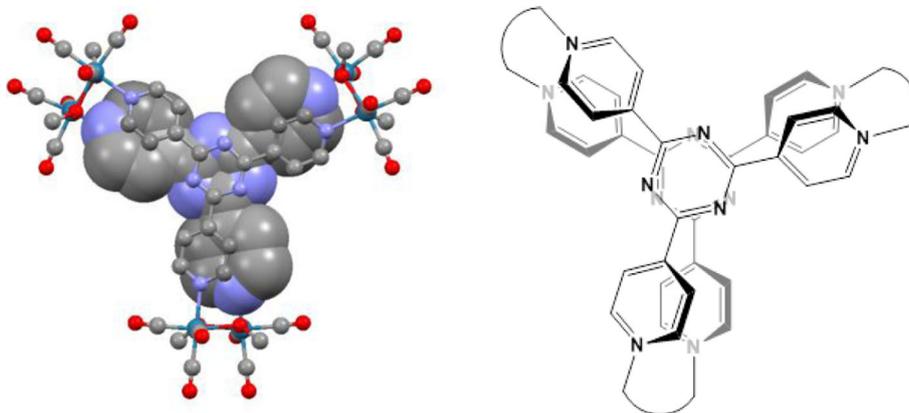


Figure 3. The Bailar Twist between the two tpt frameworks in the macrocycle **1**. All the three staggered pyridyl units show equal twist of 18.29° . The Aq dimers and hydrogens have been removed for clarity.

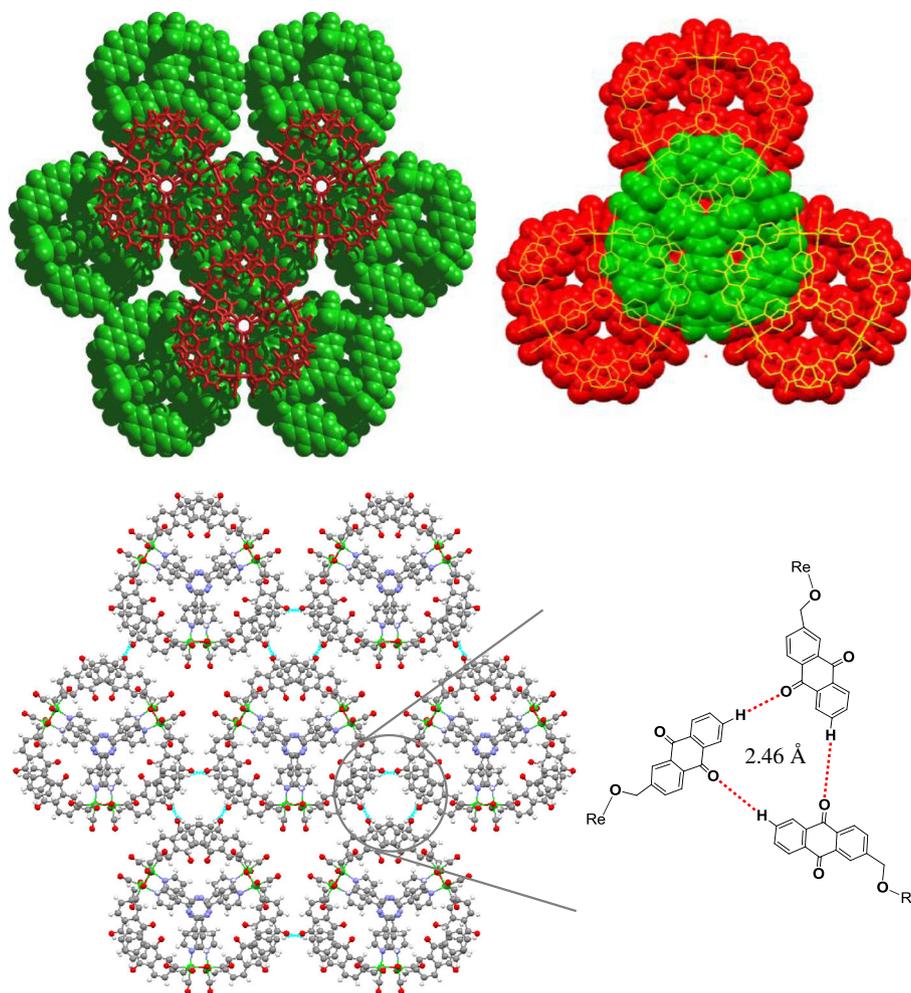


Figure 4. Top: space-filling and ball and stick view of portion of layers of molecules of **1**. Down: one layer containing six SCCs showing H-bonding interactions.

4. Conclusion

These findings proffer a one-step design strategy to achieve nanocyclic ring structure consisting of organic chromophores positioned as slipped-cofacial dimers. We believe this metal-directed building principle would provide a new direction to assemble wheel-shaped supramolecules with photoactive units. Current research in our laboratory is directed to replace anthraquinone unit by porphyrin and other light harvesting units in similar systems as complex **1**.

Supplementary Information

The electronic supplementary information can be seen at www.ias.ac.in/chemsci.

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